

Stochastic reduction for molecular multiphoton processes^{a)}

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Reduced equations of motion (REM) are derived for molecular multiphoton processes by constructing a small set of relevant operators corresponding to populations and coherences of the molecule "dressed" by the radiation field and adopting the Mori projection operator technique. The resulting REM contain time-dependent dephasing operators which are intimately related to our reduction scheme and whose definition and evaluation do not rely on any perturbative expansion in intramolecular interactions. These operators are expressed in terms of intramolecular dipole correlation functions which are the key quantities in the present formulation and are then evaluated using a simple model. In the limit where our physical system may be separated into a "system" and a "bath" with a weak interaction, we recover the ordinary expressions of line broadening. The present formulation provides us with a hierarchy of REM which interpolate smoothly all the way from the coherent to the incoherent driving limits and are in good quantitative agreement with the existing experimental data.

I. INTRODUCTION

Studies of molecular multiphoton processes (MMP) have undergone a great progress since the first discovery that isolated polyatomic molecules can absorb around 40 photons from a CO₂ laser and dissociate.¹⁻¹¹ The following qualitative picture^{2(e),6,10,11} has emerged out of the numerous experimental and theoretical studies: The molecular energy levels are separated into three regions. In the lowest energy range (region I), the density of molecular states is very low and the laser field is interacting with isolated molecular states (coherent driving). In this region, the laser power is required to overcome the molecular anharmonicities and the enormous isotopic selectivity of the process is determined by the detuning of the laser from the appropriate molecular states in this range. The appearance of multiphoton resonances is also accounted for in terms of the molecular level scheme of region I.

After the molecule has absorbed few quanta, the density of molecular states becomes very large and we can no longer describe the time evolution in terms of few isolated molecular states. This region is denoted region II or the quasicontinuum and its exact theoretical treatment is the subject of a current lively debate.⁶⁻¹¹ A proper description of the molecular time evolution in this range requires a quantitative understanding of the mechanisms of intramolecular energy transfer and line broadening (dephasing)¹² of highly vibrationally excited polyatomic molecules, of which very little is known at present. (We should note, however, that recent developments in overtone spectroscopy,^{13,14} coherent transients,¹⁵⁻¹⁷ and high resolution optical spectroscopy¹⁸ are currently yielding novel information regarding intramolecular line broadening.)

Finally, when the molecule acquires enough energy for dissociation, it enters region III, where, in addition to all the complications of region II, we have to incorporate also the dynamics of unimolecular decomposition.

The major theoretical problems which are underlying the current studies of molecular multiphoton processes

are as follows: (i) How much energy is absorbed by a polyatomic molecule interacting with a strong infrared laser and what is the *intermolecular* distribution of energy as a function of the molecular and laser parameters (molecular size, frequencies, anharmonicities, laser frequency, intensity, and duration)? (ii) What is the *intramolecular* energy distribution? How much time does it take for the absorbed energy to flow among the various degrees of freedom? Does the energy randomize, and at what time scales (i.e., does the molecule exhibit an ergodic behavior)?¹⁹ These questions are essential for the observation of laser-specific nonthermal effects in chemical reactions. (iii) Can we use the information extracted from studies of molecular multiphoton processes to shed light on the dynamics of unimolecular reactions and, in particular, to test the validity of the various statistical approaches which are extensively used to predict reaction rates and branching ratios?²⁰

It is clear that a complete quantum-mechanical treatment of these problems is extremely complicated and is impractical. The density of molecular states is very rapidly increasing with energy. (For SF₆, say it is 10³/cm⁻¹, 2×10⁸/cm⁻¹, and 3×10¹¹/cm⁻¹ at energies of 5000, 10 000, and 19 000 cm⁻¹, respectively.²¹) Due to the lack of structural information (i.e., potential surfaces) on highly excited polyatomic molecules, we do not know the exact nature and coupling strengths of these states even for a single polyatomic molecule. Moreover, even if we had this structural (static) information, it would have been impossible to solve for the dynamics of about 10¹⁰ states interacting with a strong laser field. On the other hand, we should bear in mind that the information which is of real interest for us is much less detailed than the knowledge of the complete molecular density matrix including the amplitudes and phases of all molecular states. In practice, we are interested only in a few molecular observables and their time evolution on a coarse grained time scale which is much longer than the molecular frequencies (i.e., 10⁻¹³-10⁻¹⁴ sec).

We thus see that a complete quantum dynamical treatment of the problem is neither feasible nor desirable.

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The conventional theories of unimolecular reactions²⁰ take the other extreme approach and assume that the dynamics of highly excited polyatomics can be treated using equilibrium statistical mechanics. The basic assumption is that, due to the enormous complexity of the problem, energy is being completely randomized among all accessible molecular states and the reaction rates are then evaluated by simply counting states (or measuring volumes in phase space). The relative success of these theories in predicting reaction rates does not, however, prove the validity of their basic assumptions, and, in fact, these were very seriously challenged¹⁹ by a variety of recent experimental²² and theoretical²³ studies.

An inevitable conclusion from the foregoing discussion is that we should adopt a *mesoscopic* level of theoretical description which is intermediate between the fully dynamical and completely statistical approaches.²⁴ The basic idea of the mesoscopic level of description is to find some few key molecular variables and to adopt a reduction scheme which will enable us to derive closed reduced equations of motion (REM) describing the approximate time evolution of these variables in the presence of the rest. Formally, this is one of the most important problems in irreversible statistical mechanics²⁵ and the transport equations are typical examples of REM. There are many methods for constructing REM, e.g., the Langevin approach,²⁶⁻²⁸ the stochastic Liouville approach,^{29a} and projection operator techniques.³⁰ In this paper, we use the Mori projection operator technique.³¹⁻³³

In Sec. II, we present the general reduction scheme which allows us to construct a closed set of equations of motion for *any* chosen set of molecular variables. In Sec. III, we construct the molecular Hamiltonian for MMP describing molecular states "dressed" by the radiation field.^{34,10} We then discuss the choice of the appropriate molecular variables and construct our most general REM [Eqs. (19)].³⁵ These equations contain driving terms and dephasing terms. The latter [the G , \bar{F} , and F terms in Eq. (19)] arise naturally from our reduction scheme, are expressed in terms of intramolecular dipole correlation functions, and their definition does not require any perturbative treatment in intramolecular interactions. This is in contrast to the common formulations of line broadening.³⁶⁻³⁸ We further compare our REM with previous derivations.^{9, 39, 40}

In Sec. IV, we discuss the early stages of the molecular driving (region I) and show how the conventional perturbative expressions for line broadening are obtained as a limiting case of our general formulation. In Sec. V, we consider the quasicontinuum region. Assuming statistical factorization, the dephasing operators now depend only on the two-time dipole correlation functions $I_{nm}(t)$ [Eq. (22a)]. By choosing an appropriate scaling for the coherences, we convert the REM to the form (54), where the driving terms do not depend on the number of states but rather merely on ratios of statistical weights (this is the statistical or the "thermodynamic" limit of the present formulation). In this limit, the relaxation operators do not depend on time and the only

molecular quantities of interest are the integrated transition dipole between levels, the ratios of statistical weights and a dephasing matrix Γ_{nm} . In Sec. VI, we provide a simple model for the intramolecular dipole correlation function $I_{nm}(t)$. We now have a complete, first principle, set of REM for MMP. In Sec. VII, we discuss and analyze the behavior of our REM under several limits of physical interest. We summarize the hierarchy of REM which provides a unified description of the molecular driving process from the fully coherent up to the totally incoherent and the dissociation region, and compare it with the available experimental information.

II. THE SYSTEMATIC REDUCTION SCHEME

We consider a large system with many degrees of freedom characterized by a Hamiltonian H and a density matrix ρ . The time evolution of ρ is given by the Liouville equation

$$\frac{d\rho}{dt} = -i[H, \rho] \equiv -iL\rho, \quad (1)$$

where L is the Liouville (tetradic) operator corresponding to H , i.e.,

$$\frac{d\rho_{ab}}{dt} = -i \sum_{cd} L_{ab, cd} \rho_{cd} \quad (2)$$

and

$$L_{ab, cd} = H_{ac} \delta_{b,d} - H_{bd}^* \delta_{ac}. \quad (3)$$

The density matrix $\rho(t)$ contains the complete information regarding the state of the molecule at time t . However, evaluation of ρ is an extremely difficult task since, due to the rapid increase in the molecular density of states with energy, ρ is a huge matrix, and L is not available even for triatomic molecules. In practice, however, much of the information contained in the molecular density matrix is redundant and we are often interested only in some projections of the molecular density matrix on few "relevant" operators whose nature is determined by the initial conditions and the type of experiments considered.

We are thus interested in deriving reduced equations of motion (REM) which will provide us with just the right amount of desired information (i.e., the projections of ρ onto a preselected set of dynamical operators). The appropriate formalism to achieve that goal is the Mori projection operator technique.^{31,32} We shall adopt here a partial time ordering version which is found to be most convenient for the present problem. The procedure goes as follows: We first have to define a set of relevant molecular operators A_{nm} whose expectation values are of interest for us. We then expand the density matrix in the form

$$\rho(t) = \sum_{nm} \sigma_{nm}(t) A_{nm} + \rho'(t), \quad (4)$$

where $\rho'(t)$ is orthogonal to the subspace spanned by A_{nm} , i.e.,

$$\langle A_{nm}^\dagger, \rho' \rangle = 0, \quad (5)$$

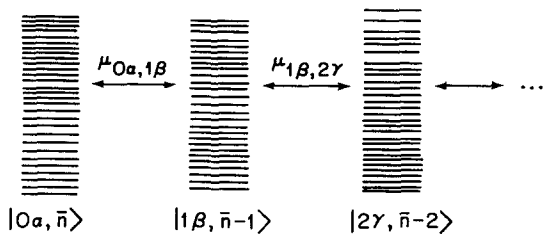


FIG. 1. Zero order molecular states "dressed" by the radiation field. $|v\alpha, \bar{n}-v\rangle$ denotes a molecular α state belonging to the v th level (with energy $\approx v\omega_0$). $|\bar{n}-v\rangle$ is the state of the radiation field having $\bar{n}-v$ photons with frequency ω_0 . μ is the Rabi frequency. Within the rotating wave approximation, we need to consider only the sequence of states $|v\alpha, \bar{n}-v\rangle$, $v = 0, 1, 2, \dots$.

and where the scalar product of two operators A and B is defined as

$$\langle A, B \rangle \equiv \text{tr}(AB). \quad (6)$$

In Eq. (4), $\sigma_{nm}(t)$ are c numbers.

We now define a Mori projection P which projects onto the subspace spanned by our relevant operators A_{nm} :

$$PB = \sum_{nm} \langle B, A_{nm}^\dagger \rangle A_{nm}. \quad (7)$$

In Eq. (7), we are assuming that the operators are orthonormal, i. e.,

$$\langle A_{nm}, A_{kl}^\dagger \rangle = \delta_{n,k} \delta_{m,l}, \quad (8)$$

since in the present work we shall adopt an orthonormal set of operators, although this is not necessary for the general reduction scheme (see Appendix A). If the initial density matrix may be expanded in terms of A_{nm} and if we are interested only in the expectation values of A_{nm} , then we need only the projection

$$P\rho(t) = \sum_{nm} \sigma_{nm}(t) A_{nm}. \quad (9)$$

Let us now define a vector \mathbf{A} whose components are the operators A_{nm} and a similar vector σ . The exact equation of motion for σ (see Appendix A) is

$$\frac{d\sigma}{dt} = -i\mathbf{K}(t)\sigma, \quad (10)$$

where $\mathbf{K}(t)$ is a tetradic operator

$$\begin{aligned} \mathbf{K}(t) &= \langle PL \exp(-iLt)P \rangle \langle P \exp(-iLt)P \rangle^{-1} \\ &= \langle L \exp(-iLt)A, A^\dagger \rangle \langle \exp(-iLt)A, A^\dagger \rangle^{-1}. \end{aligned} \quad (10a)$$

Equations (10) are our basic equations. In Sec. III, we shall define the appropriate set of operators for MMP and evaluate $\mathbf{K}(t)$.

III. REM FOR MOLECULAR MULTIPHOTON PROCESSES

We consider a polyatomic molecule initially at thermal equilibrium with temperature T . The molecule is irradiated with a monochromatic infrared laser field whose frequency is ω_0 . We further define a molecular

Rabi frequency $\Omega = \mu\epsilon$, where μ is a typical transition dipole between two molecular states and ϵ is the amplitude of the radiation field. Usually, in studies of molecular multiphoton processes, we have $\omega_0 \approx 1000 \text{ cm}^{-1}$, $kT \sim 200 \text{ cm}^{-1}$, and $\mu \leq 10 \text{ cm}^{-1}$. We thus have

$$\omega_0 \gg kT \gg \mu. \quad (11)$$

Due to the above frequency separation, we may partition the molecular states relevant for the description of the multiphoton excitation into groups (levels) where the n th level contains molecular states with energy around $n\omega_0$. (We may consider, for example, all the states with energy $n\omega_0 \pm \mu$ and which are coupled radiatively to the $n-1$ level as belonging to the n th level.) A molecular state (which is an eigenstate of the true molecular Hamiltonian) will thus be denoted by $|n\alpha\rangle$, where n denotes the level whereas α runs over all the states within the n th level. (Of course, for each n , α is running over a different set of molecular states.)

The separation of frequency scales (11) enables us further to invoke the rotating wave approximation (RWA). It is thus most convenient to consider the molecular states dressed with the radiation field.^{34,10} Denoting the number of photons initially in the radiation field by \bar{n} , then within the RWA we may consider only the following groups of states:

$$|0\alpha, \bar{n}\rangle, |1\alpha, \bar{n}-1\rangle, |2\alpha, \bar{n}-2\rangle, \dots, |n\alpha, \bar{n}-n\rangle, \dots, \quad (12)$$

where the n th group implies absorption of n quanta from the radiation field. Here, $|n\alpha, \bar{n}-n\rangle$ is a combined molecule + field state, where n denotes the molecular state and $\bar{n}-n$ is the state of the radiation field.¹⁰ We shall hereafter denote $|n\alpha, \bar{n}-n\rangle$ simply as $|n\alpha\rangle$, bearing in mind that this is a dressed state where n photons were absorbed from the radiation field. The total Hamiltonian within the rotating wave approximation is thus¹⁰

$$\begin{aligned} H &= \sum_{n\alpha} |n\alpha\rangle E_{n\alpha} \langle n\alpha| \\ &+ \epsilon \sum_{\substack{n, m=n\pm 1 \\ \alpha, \beta}} |n\alpha\rangle \mu_{\alpha\beta}^{nm} \langle m\beta| \equiv H_0 + H'. \end{aligned} \quad (13)$$

Here, $E_{n\alpha}$ is the energy of the dressed $|n\alpha\rangle$ molecular state, i. e.,

$$E_{n\alpha} = E_{n\alpha}^0 - n\omega_0, \quad (13a)$$

where $E_{n\alpha}^0$ is the energy of the "bare" $|n\alpha\rangle$ state. $\mu_{\alpha\beta}^{nm}$ is the radiative coupling between $|n\alpha\rangle$ and $|m\beta\rangle$. Within the RWA, we need consider only coupling between the neighboring levels of Eq. 12. Other coupling terms will be highly off resonant and are not expected to contribute appreciably to the time evolution.^{34,10} The level and coupling scheme of our Hamiltonian is presented in Fig. 1. The Liouville operators corresponding to H_0 and H' will be denoted by L_0 and L' , respectively.

We are now in a position to construct our set of relevant operators.³⁵ We recall that, within our general reduction scheme presented in Sec. II, we can write a closed set of exact REM for $P\rho(t)$ for any P , i. e., for any choice of relevant operators. However, if we want

$P\rho(t)$ to provide us with all the necessary information about the system, then we need that P will include all the operators required to represent $\rho(0)$, i. e., $P\rho(0) = \rho(0)P$ and also all the operators whose expectation values are of interest to us. If we add more operators than dictated by the above two requirements, it is likely that the time evolution operator $\mathbf{K}(t)$ will assume a simpler form.

The quantities which are of primary interest to us are the populations of the various levels. We thus define the following set of operators:

$$A_{nm} = \frac{1}{\sqrt{d_n}} \sum_{\alpha} |n\alpha\rangle\langle n\alpha|, \quad (14)$$

where the summation is over the states within the n th level which are strongly radiatively coupled to the $n \pm 1$ levels, d_n is the degeneracy of the n th level, the $1/\sqrt{d_n}$ factor was chosen for normalization purposes [Eq. (8)], and the population P_n of the n th level is

$$P_n = \sqrt{d_n} \sigma_{nn}. \quad (15)$$

We next define a set of operators which correspond to the time derivatives of A_{nm} , i. e., $[H, A_{nm}]$. We thus write

$$A_{nm} = \frac{1}{\gamma_{nm}} \sum_{\alpha\beta} |n\alpha\rangle \mu_{\alpha\beta}^{nm} \langle m\beta|, \quad (16)$$

with

$$\gamma_{nm}^2 = \sum_{\alpha\beta} |\mu_{\alpha\beta}^{nm}|^2, \quad m = n \pm 1. \quad (16a)$$

These operators represent *single quantum coherences*. Adopting this set of operators, we can use Eq. (10a) and Appendix A to evaluate $\mathbf{K}(t)$. The REM for σ_{nn} will be very simple since their derivatives are included as dynamical variables, but the equations for σ_{nm} will be more complicated and will require expansion of $\mathbf{K}(t)$ in powers of L' . Thus, although we can in principle write a closed

set of REM using only the operators (14) and (16) [or even only the populations (14)], since $\mathbf{K}(t)$ will be evaluated approximately, we may wish to add more variables. [We know, of course, that if we take a complete set of dynamical variables, then the equations will be first order in L' , but we anticipate that even with a much smaller set of variables we shall be able to treat L' to low order in the evaluation of $\mathbf{K}(t)$ (Eq. (10a)).]

The natural way to proceed in this direction is to define more derivative operators and include them in our set. The next group of operators will thus consist of all operators of the form

$$L^2 A_{nm} = [H, [H, A_{nm}]] = [H, A_{nm}], \quad (17)$$

which may be classified into two types: (i) $L_0 A_{nm}$ and (ii) μA_{nm} . This process may be continued generating more operators. In the present work, we shall adopt the set of operators corresponding to populations (A_{nn}) and multiquantum coherences defined as follows:

$$A_{nm} = \frac{1}{\gamma_{nm}} \sum_{\alpha\beta} \nu_{\alpha\beta}^{nm} |n\alpha\rangle\langle m\beta|, \quad (18)$$

where (taking $m > n$)

$$\nu_{\alpha\beta}^{nm} = \sum_{\gamma, \delta, \dots, \beta'} \mu_{\alpha\gamma}^{n, n+1} \mu_{\gamma, \delta, \dots}^{n+1, n+2} \mu_{\beta' \beta}^{m-1, m}, \quad (18a)$$

$$\gamma_{nm}^2 = \sum_{\alpha\beta} |\nu_{\alpha\beta}^{nm}|^2. \quad (18b)$$

(For $m < n$, we have $A_{nm} = A_{mn}^\dagger$.) When $|n - m| = 1$, the definitions (18) coincide with Eq. (16).

Using the set of relevant operators (14) and (18), we may now evaluate the operator $\mathbf{K}(t)$ [Eq. (10)]. This is done in Appendix B. The resulting REM are

$$\begin{aligned} \frac{dP_n}{dt} = & -i\Omega_{n, n+1}(\sigma_{n+1, n} - \sigma_{n, n+1}) \\ & -i\Omega_{n, n-1}(\sigma_{n-1, n} - \sigma_{n, n-1}), \end{aligned} \quad (19a)$$

$$\begin{aligned} \frac{d\sigma_{nm}}{dt} = & [-i\bar{\omega}_{nm} + G_{nm}(t)]\sigma_{nm} - i\Omega_{nm} \bar{F}_{nm}(t)(P_m/d_m - P_n/d_n) - i \sum_{\substack{i=m\pm 1 \\ i \neq n}} \Omega_{mi} F_{nm, ni}(t)\sigma_{ni}(t) \\ & - i \sum_{\substack{i=n\pm 1 \\ i \neq m}} \Omega_{ni} F_{nm, im}(t)\sigma_{im}(t), \quad |n - m| = 1, \end{aligned} \quad (19b)$$

$$\frac{d\sigma_{nm}}{dt} = [-i\bar{\omega}_{nm} + G_{nm}(t)]\sigma_{nm} - i \sum_{i=m\pm 1} \Omega_{mi} F_{nm, ni}(t)\sigma_{ni}(t) - i \sum_{i=n\pm 1} \Omega_{ni} F_{nm, im}(t)\sigma_{im}(t), \quad |n - m| > 1. \quad (19c)$$

Here, P_n [Eq. (15)] is the population of the n th level

$$\begin{aligned} \omega_{n\alpha, m\beta} &= (E_{n\alpha} - E_{m\beta})/\hbar, \\ \bar{\omega}_{nm} &= \langle L_0 \rangle_{nm, nm} \\ &= \frac{1}{\gamma_{nm}^2} \sum_{\alpha\beta} |\mu_{\alpha\beta}^{nm}|^2 \omega_{n\alpha, m\beta}, \quad |m - n| = 1, \end{aligned}$$

$$\bar{\omega}_{nm} = \bar{\omega}_{n, n+1} + \bar{\omega}_{n+1, n+2} + \dots + \bar{\omega}_{m-1, m}, \quad m > n + 1, \quad (20a)$$

$$\bar{\omega}_{mn} = -\bar{\omega}_{nm}, \quad m < n, \quad (20b)$$

$$\Omega_{nm} = \epsilon \gamma_{nm}, \quad (20c)$$

and

$$\gamma_{nm}^2 = \sum_{\alpha\beta} |\nu_{\alpha\beta}^{nm}|^2. \quad (20d)$$

G , F , and \bar{F} are dephasing operators which arise from our reduction scheme (choice of the relevant operators). They are expressed in terms of *intramolecular dipole correlation functions* which are the key quantities in the present formulation and contain all the molecular information relevant for the dynamics of MMP. The G operators represent dephasing of the coherences,

\bar{F} represent coupling of the populations and single quantum coherences, whereas the F operators couple high order coherences. G and \bar{F} are given in terms of the two-time correlation functions $I_{nm}(t)$:

$$G_{nm}(t) = \frac{d}{dt} \ln I_{nm}(t) = \frac{1}{I_{nm}} \frac{dI_{nm}(t)}{dt}, \quad (21a)$$

$$\begin{aligned} \bar{F}_{nm}(t) = & I_{nm}(t) \exp(-i\bar{\omega}_{nm}t) + [i\bar{\omega}_{nm} - G_{nm}(t)] \\ & \times \int_0^t d\tau I_{nm}(\tau) \exp(-i\bar{\omega}_{nm}\tau), \end{aligned} \quad (21b)$$

or, alternatively,

$$\begin{aligned} \bar{F}_{nm}(t) = & - \int_0^t d\tau I_{nm}(\tau) \exp(-i\bar{\omega}_{nm}\tau) \\ & \times \left[\frac{d}{dt} \ln \frac{d}{dt} \ln \int_0^t d\tau I_{nm}(\tau) \exp(-i\bar{\omega}_{nm}\tau) \right], \end{aligned} \quad (21c)$$

$$I_{nm}(t) = \tilde{I}_{nm}(t) \exp(i\bar{\omega}_{nm}t), \quad (22a)$$

$$\begin{aligned} \tilde{I}_{nm}(t) = & \frac{1}{\gamma_{nm}^2} \sum_{\alpha\beta} |\nu_{\alpha\beta}^{nm}|^2 \exp(-i\omega_{n\alpha, m\beta}t) \\ \equiv & \langle \nu_{nm}(0) \nu_{mn}(t) \rangle / \langle \nu_{nm}(0) \nu_{mn}(0) \rangle. \end{aligned} \quad (22b)$$

Here, $\nu_{mn}(t)$ is the Heizenberg operator

$$\nu_{mn}(t) = \exp(iH_0t) \nu_{mn}(0) \exp(-iH_0t). \quad (22c)$$

[By definition, $I_{nm}(0) = 1$ and physically we expect $I_{nm}(\infty) = 0$.] For subsequent use, we define also

$$\tilde{G}_{nm}(t) = \frac{1}{\tilde{I}_{nm}} \frac{d\tilde{I}_{nm}}{dt} = -i\bar{\omega}_{nm} + G_{nm}(t). \quad (21d)$$

The F operators are given in terms of three-time dipole correlation functions J , \bar{J} , and \hat{J} , defined as follows:

$$J_{abc}(\tau_1, \tau_2) = \langle \nu_{ab}(\tau_1) \nu_{ba}(0) \nu_{ac}(0) \nu_{ca}(\tau_2) \rangle, \quad (22d)$$

$$\bar{J}_{abc}(\tau_1, \tau_2) = \frac{d}{d\tau_1} J_{abc}(\tau_1, \tau_2), \quad (22e)$$

and

$$\hat{J}_{abc}(\tau_1, \tau_2) = \frac{d}{d\tau_2} J_{abc}(\tau_1, \tau_2). \quad (22f)$$

The correlation function $\langle \nu\nu\nu\nu \rangle$ implies the trace of the product of these operators. In Eqs. (22), the level a always lies between b and c .

In terms of these operators, we get the following four types of matrix elements of F :

$$(a) \quad |n-l| > |n-m|, \quad l = m \pm 1:$$

$$\begin{aligned} F_{nm, n1}^{(1)} = & \frac{\gamma_{n1}}{\gamma_{nm}\gamma_{m1}\tilde{I}_{n1}(t)} \left[-\tilde{I}_{n1}(t) + \tilde{G}_{nm}(t) \int_0^t d\tau J_{nm1}(t, \tau) \right. \\ & \left. - \int_0^t d\tau \bar{J}_{mn1}(t, \tau) \right]; \end{aligned} \quad (23a)$$

$$(b) \quad |n-l| < |n-m|, \quad l = m \pm 1:$$

$$\begin{aligned} F_{nm, n1}^{(11)} = & \frac{\gamma_{n1}}{\gamma_{nm}\gamma_{im}\tilde{I}_{n1}(t)} \left[-J_{inm}(t, t) + \tilde{G}_{nm}(t) \int_0^t d\tau J_{inm}(t, \tau) \right. \\ & \left. - \int_0^t d\tau \bar{J}_{inm}(t, \tau) \right]; \end{aligned} \quad (23b)$$

$$(c) \quad |l-m| > |n-m|, \quad l = n \pm 1:$$

$$\begin{aligned} F_{nm, im}^{(1)} = & \frac{\gamma_{im}}{\gamma_{nm}\gamma_{n1}\tilde{I}_{im}(t)} \left[\tilde{I}_{im}(t) - \tilde{G}_{nm}(t) \int_0^t d\tau J_{nim}(\tau, t) \right. \\ & \left. + \int_0^t d\tau \hat{J}_{nim}(\tau, t) \right]; \end{aligned} \quad (23c)$$

$$(d) \quad |l-m| < |n-m|, \quad l = n \pm 1:$$

$$\begin{aligned} F_{nm, im}^{(11)} = & \frac{\gamma_{im}}{\gamma_{nm}\gamma_{in}\tilde{I}_{im}(t)} \left[J_{inm}(t, t) - \tilde{G}_{nm}(t) \int_0^t d\tau J_{inm}(\tau, t) \right. \\ & \left. + \int_0^t d\tau \hat{J}_{inm}(\tau, t) \right]. \end{aligned} \quad (23d)$$

In concluding this section, we would like to point out that REM for MMP have been already postulated phenomenologically^{6,7,9} or derived^{9,33,40} by several authors. The present approach is different from the previous derivations of Hodgkinson and Briggs³⁹ and Cantrell *et al.*⁴⁰ in that we are not relying on any perturbative argument in intramolecular interactions. (In Refs. 39 and 40, the coupling between the pumped molecular mode and the rest of the molecule is treated perturbatively.) Goodman *et al.*^{9(d),9(e)} have used the idea of grouping molecular states into levels, similar to the present approach. However, they derived equations of motion for a reduced wave function rather than for a reduced density matrix. As a result, proper dephasing effects¹² are not incorporated at all in their final equations.

IV. THE PERTURBATIVE LINE-BROADENING LIMIT: WEAK COUPLING OF A SYSTEM AND A BATH

At the early stages of the molecular multiphoton excitation, the normal mode picture for the molecule is quite adequate and the anharmonicities may be treated as weak perturbations. In this limit, our REM (19) may be considerably simplified and the dephasing operators assume the well known forms from perturbative line-broadening theories.³⁶⁻³⁸ In this section, we shall analyze the behavior of the REM in the weak intramolecular interaction limit. To that purpose, we assume separation of our degrees of freedom into "system" and "bath." We further assume that only one system degree of freedom interacts directly with the radiation field. However, it is coupled to the bath by a weak perturbation V . The molecular Hamiltonian thus assumes the form

$$\begin{aligned} H = & \sum_m |m\rangle E_m \langle m| \\ & + \sum_{\alpha} |\alpha\rangle E_{\alpha} \langle \alpha| + \sum_{\substack{m, \alpha, \beta \\ \beta \neq \alpha}} |m\alpha\rangle V_{m\alpha, m\beta} \langle m\beta|. \end{aligned} \quad (24)$$

Here, m is the system quantum number whereas α comes for the collection of all bath quantum numbers. As in Eq. (13), $|m\alpha\rangle$ are molecular states "dressed" by the radiation field (m photons were absorbed at $|m\alpha\rangle$). Therefore, the intramolecular coupling cannot connect molecular states with different $|m\rangle$:

$$V_{n\alpha, m\beta} = V_{n\alpha, n\beta} \delta_{m, n}. \quad (25)$$

The radiation field is assumed to interact only with the "system" thus

$$\langle n\alpha | \mu | m\beta \rangle = \mu_{nm} \delta_{\alpha, \beta}. \quad (26)$$

In order to evaluate the dephasing terms in our REM perturbatively to lowest order in V , let us first diagonalize the molecular states to first order in V . We thus get

$$|m\beta^*\rangle = |m\beta\rangle + \sum_{\alpha \neq \beta} \frac{V_{m\beta, m\alpha}}{\omega_{\beta\alpha} + i\eta} |m\alpha\rangle, \quad (27a)$$

$$\langle n\alpha^*| = \langle n\alpha| + \sum_{\alpha \neq \beta} \langle n\beta| \frac{V_{n\beta, n\alpha}}{\omega_{\alpha\beta} - i\eta}. \quad (27b)$$

Substitution of Eq. (27) in (26) results in

$$\langle n\alpha^*| \mu |m\beta^*\rangle = \mu_{nm} \left[\delta_{\alpha, \beta} + \frac{\Delta V_{\beta\alpha}^{mn}}{\omega_{\beta\alpha} + i\eta} (1 - \delta_{\alpha\beta}) \right], \quad (28)$$

where we have defined

$$\Delta V_{\beta\alpha}^{mn} \equiv V_{m\beta, m\alpha} - V_{n\beta, n\alpha}. \quad (29)$$

Substitution of Eq. (28) in (22) results in (where for the sake of simplicity we take $\Delta V_{\alpha\alpha}^{mn} = 0$)

$$\begin{aligned} I_{nm}(t) &= \frac{1}{\gamma_{nm}^2} \sum_{\alpha\beta} |\langle n\alpha^*| \mu |m\beta^*\rangle|^2 \exp(-i\omega_{\alpha\beta}t) \\ &= |\mu_{nm}|^2 \left[\sum_{\alpha} 1 + \sum_{\alpha \neq \beta} \frac{|\Delta V_{\beta\alpha}^{mn}|^2}{\omega_{\alpha\beta}^2} \exp(-i\omega_{\alpha\beta}t) \right] \end{aligned} \quad (30a)$$

and

$$\frac{dI_{nm}}{dt} = -i |\mu_{nm}|^2 \sum_{\alpha \neq \beta} \frac{|\Delta V_{\beta\alpha}^{mn}|^2}{\omega_{\alpha\beta}} \exp(-i\omega_{\alpha\beta}t). \quad (30b)$$

From Eqs. (21a) and (30), we thus get, to second order in V ,

$$\begin{aligned} G_{nm}(t) &= \frac{1}{I_{nm}} \frac{dI_{nm}}{dt} \\ &= \frac{-i}{d} \sum_{\alpha \neq \beta} \frac{|\Delta V_{\beta\alpha}^{mn}|^2}{\omega_{\alpha\beta}} \exp(-i\omega_{\alpha\beta}t), \end{aligned} \quad (31)$$

where d is the number of relevant bath states. Since $G_{nm}(0) = 0$, Eq. (31) can be recast in the form

$$G_{nm}(t) = - \int_0^t d\tau \chi_{nm}(\tau), \quad (32)$$

where $\chi(\tau)$ is a dynamical linewidth function

$$\chi_{nm}(\tau) = \frac{1}{d} \sum_{\alpha, \beta} |\Delta V_{\beta\alpha}^{nm}|^2 \cos \omega_{\alpha\beta} \tau. \quad (32a)$$

Regarding F and \bar{F} , we recall that, to $O(\Delta V^2)$, we have

$$\nu_{ab}(\tau) = \nu_{ab}(0) \exp(i\omega_{ab}\tau), \quad (33)$$

which when substituted in Eqs. (21b) and (23) results in

$$\begin{aligned} F_{nm, n\pm 1} &= -1 + O(\Delta V^2), \quad l = m \pm 1, \\ F_{nm, l\pm 1} &= 1 + O(\Delta V^2), \quad l = n \pm 1, \\ \bar{F}_{nm} &= 1 + O(\Delta V^2). \end{aligned} \quad (34)$$

A. Ordinary line shapes

In ordinary line shape studies, the driving field is weak and is switched adiabatically. If the molecule is initially at the n th level, then the line shape predicted by our REM is the Fourier transform of the molecular coherence correlation function which is the solution of our REM for $\sigma_{nm}(t)$ with $\Omega = 0$ and $\sigma_{nm}(0) = 1$.^{29a, 33} We thus get for the absorption line shape

$$\Phi_{nm}(\omega_0) = \int_0^\infty d\tau \cos(\omega_{nm}\tau) \exp \left[- \int_0^t d\tau (t-\tau) \chi_{nm}(\tau) \right]. \quad (35)$$

B. The Markovian limit

Let us rewrite $\chi(t)$ in the form

$$\chi(t) = \chi(0) \xi(t) \quad (36)$$

and suppose $\xi(t)$ has a characteristic time scale τ_c [$\xi(0) = 1$ and $\xi(\infty) = 0$]. When

$$\tau_c \ll \chi(0)^{-1}, \Omega^{-1}, \quad (37)$$

we are in the *Markovian limit*^{29, 32, 33} whereby, on a coarse-grained time scale [$\chi(0)^2 \tau_c \gg t \gg \tau_c$], we can write

$$G_{nm}(t) - G_{nm}(\infty) = - \int_0^\infty d\tau \chi(\tau). \quad (38)$$

We note that the ordinary line shape (35) assumes a Lorentzian form in the Markovian limit with a width of $\int_0^\infty d\tau \chi(\tau)$. This is the familiar expression from the theory of line broadening.³⁶

C. Limitations of the perturbative approach

Equations (32) and (34) [or (38)], when substituted into Eq. (19), give us the final form of the REM in the weak intramolecular coupling limit. We note that the bath does not affect the driving terms and $F = \bar{F} = 1$. Furthermore, in this case, the system mode is being pumped by the radiation field and the bath merely causes a dephasing via χ but does not induce any relaxation of population (T_1) in the system (all energy absorbed from the field remains in the pumped mode). This arises since in our dressed picture the bath cannot couple states which belong to different levels [Eq. (25)] and in the perturbative limit each level is associated with a definite state of the system. We could take account for T_1 within a perturbative approach by adding more variables (each level could be split into several groups with the same total energy but with different energy in the pumped mode). This will result in a large increase in the number of variables.^{39, 40} However, we do not expect a perturbative treatment in intramolecular interactions to hold in the quasicontinuum and in the present work we have chosen a basis set ($|n\alpha\rangle$) of the true molecular states. In Sec. V, we shall develop simple expressions for the REM which make use of the complexity of the quasicontinuum without invoking any perturbation in intramolecular interactions.

The usage of a zero order (harmonic or local-mode)^{41, 42, 14} basis set with intramolecular couplings may be advantageous provided we can get along with few states (say, when only one state in each level is carrying oscillator strength to the previous level). In such a case, we can, in the Markovian limit, attribute a width of $2\pi |V|^2 W_f$ to the various levels (where W_f is the density of final molecular states), and this provides a very convenient framework for the description of molecular radiative phenomena.^{43, 10} This is the case in ordinary optical line shape and transient experiments in electronically excited states of polyatomic molecules where

it is possible to find a well defined "doorway state."⁴³ Another type of related experiments where such a zero order basis set was proven useful is the novel gas-phase CH stretch overtone spectroscopy in benzene done by Bray and Berry.^{13,14} For these experiments, by adopting a local mode picture, we may again consider a single (local mode) doorway state and perform a dynamical line shape analysis by considering its coupling to the rest of the modes.¹⁴ This is not the case, however, for MMP in the quasicontinuum.

V. THE QUASICONTINUUM REGION: SCALING OF THE COHERENCES AND THE STATISTICAL LIMIT

The perturbative approach in intramolecular interactions presented in Sec. IV may be valid during the first few steps of the molecular driving, but as soon as the molecule enters into the region of high density of states (the "quasicontinuum"), we do not expect this simple picture of a system and a bath with weak interactions to hold. However, other assumptions may be invoked which make use of the complexity of the quasicontinuum and which greatly simplify Eqs. (19). In this section, we shall introduce systematically these simplifying assumptions. We proceed in three steps. In Sec. VA, we introduce the *factorization* assumption (random phase approximation) which enables us to express all the dephasing operators in our REM in terms of the two-time correlation functions $I_{nm}(t)$ [Eq. (22a)]. In Sec. VB, we introduce the *Markovian* assumption (separation of time scales) which converts the relaxation operators into a time independent form. Finally, in Sec. VC, we introduce a *scaling* of the coherences and bring the REM into a very simple form [Eqs. (54)] which depends merely on integrated Rabi frequencies $\bar{\Omega}_{nm}$, dephasing terms Γ_{nm} , and ratios of statistical weights for the levels.

A. The factorization assumption

We assume that the distribution of μ among the various molecular levels is random so that the three-time correlation functions J_{abc} [Eq. (22d)] [and consequently also \bar{J} and \hat{J} of Eqs. (22e) and (22f), respectively] may be factorized as follows:

$$\langle \nu_{ab}(\tau_1) \nu_{ba}(0) \nu_{ac}(0) \nu_{ca}(\tau_2) \rangle \cong \frac{\langle \nu_{ab}(\tau_1) \nu_{ba}(0) \rangle \langle \nu_{ac}(0) \nu_{ca}(\tau_2) \rangle}{d_a} \quad (39)$$

Here the level a lies between b and c and approximation (39) implies that the correlations among a levels due to their interaction with c and those due to their interactions with b are uncorrelated. Utilizing this assumption, we get, for F [Eqs. (23)],

$$F_{nm,ni}^{(1)} = -1, \quad (40a)$$

$$F_{nm,ni}^{(11)} = -\frac{\bar{I}_{im}(t)}{d_i} + \frac{\bar{G}_{nm}(t) - \bar{G}_{ni}(t)}{d_i} \int_0^t d\tau \bar{I}_{im}(\tau), \quad (40b)$$

$$F_{nm,im}^{(1)} = 1, \quad (40c)$$

$$F_{nm,im}^{(11)} = \frac{\bar{I}_{ni}(t)}{d_i} - \frac{\bar{G}_{nm}(t) - \bar{G}_{im}(t)}{d_i} \int_0^t d\tau \bar{I}_{ni}(\tau). \quad (40d)$$

In summary, using the factorization assumption (39),

we now have a complete formulation of MMP, where the only molecular quantities necessary to express the various relaxation operators \bar{F} , G , and F are the two-time dipole correlation functions $I_{nm}(t)$ [Eqs. (22)].

B. The Markovian limit

Further simplification of our REM may be achieved if we make use of the fact that correlation functions have usually complicated behavior at short times and tend to decay exponentially at long times.²⁹ For the sake of illustration, we may consider the form

$$I_{nm}(t) = \exp\left\{-\frac{\Gamma}{a}[\exp(-at) - 1 + at]\right\}. \quad (41)$$

This is the well known correlation function from the theory of Brownian motion.^{29,44,45} Using this correlation function, the dephasing matrix [Eq. (21a)] assumes the form

$$G_{nm}(t) = -\Gamma[1 - \exp(-at)]. \quad (42)$$

Here, a^{-1} is a characteristic correlation time of the bath. If a^{-1} is short compared to the other time scales in the problem (the Markovian limit)

$$a \gg \Omega, \Gamma, \quad (43)$$

then we have asymptotically

$$I_{nm}(t) \cong \exp(-\Gamma_{nm}t) \quad (44)$$

and on the relevant time scale of our REM, we get, using Eq. (44),

$$G_{nm} = -\Gamma_{nm}. \quad (45a)$$

The assumption (43) is reasonable for MMP if a is say of the order of magnitude of molecular frequencies. In Sec. VI, we shall work out a microscopic expression for $I_{nm}(t)$ which will be much more complicated than the stochastic correlation function (41) but will enable us to justify the asymptotic form (44). Making use of Eq. (44) and of the factorization assumption (39), we may also simplify the expressions for F , resulting in

$$\bar{F}_{nm} = 1, \quad (45b)$$

$$F_{nm,ni}^{(1)} = -1, \quad (45c)$$

$$F_{nm,ni}^{(11)} = \frac{-1}{d_i} \theta_{ni}^n, \quad (45d)$$

$$F_{nm,im}^{(1)} = 1, \quad (45e)$$

$$F_{nm,im}^{(11)} = \frac{1}{d_i} \theta_{ni}^m. \quad (45f)$$

Here,

$$\theta_{ab}^c \equiv \frac{\Gamma_{ac} - \Gamma_{bc} + i\bar{\omega}_{ab}}{\Gamma_{ab} + i\bar{\omega}_{ab}}. \quad (46)$$

If

$$\Gamma_{ac} = \bar{\Gamma}_a + \bar{\Gamma}_c, \quad (47)$$

then θ_{ab}^c is independent of c , i. e.,

$$\theta_{ab}^c = \frac{\bar{\Gamma}_a - \bar{\Gamma}_b + i\bar{\omega}_{ab}}{\bar{\Gamma}_a + \bar{\Gamma}_b + i\bar{\omega}_{ab}}, \quad (46a)$$

and if $\Gamma_{ac} = \Gamma|a - c|$ of if $\bar{\omega}_{ab} \gg \Gamma$, then

$$\theta_{ab}^c = 1. \tag{46b}$$

In conclusion, in the Markovian limit, the REM are characterized by a time-independent evolution operator defined in terms of Eq. (45).

C. Scaling of the coherences—The statistical Markov limit

In order to get a better insight regarding the dependence of our REM on the various molecular parameters, it may be advantageous to scale our coherence variables as

$$\sigma'_{ab} = \eta_{ab} \sigma_{ab}, \tag{48}$$

where η_{ab} are scaling coefficients to be determined later. This scaling will affect our definition of the coherences but will not change, of course, the quantities which are of experimental interest for MMP, i.e., the populations P_n . Using this scaling, our REM for the coherences (19b) and (19c) remain in the same form with the replacement of F and \bar{F} by

$$F'_{ab,cd} = F_{ab,cd} \frac{\eta_{ab}}{\eta_{cd}}, \tag{49a}$$

$$\bar{F}'_{ab} = \eta_{ab} \bar{F}_{ab}. \tag{49b}$$

The equation for the populations (19a) will now be written as

$$\begin{aligned} \frac{dP_n}{dt} = & -i\Omega_{n,n+1} \hat{F}'_{n,n+1} (\sigma_{n+1,n} - \sigma_{n,n+1}) \\ & - i\Omega_{n,n-1} \hat{F}'_{n,n-1} (\sigma_{n-1,n} - \sigma_{n,n-1}), \end{aligned} \tag{50}$$

where

$$\frac{dP_n}{dt} = -i\bar{\Omega}_{n,n+1} (\sigma'_{n+1,n} - \sigma'_{n,n+1}) - i\bar{\Omega}_{n,n-1} (\sigma'_{n-1,n} - \sigma'_{n,n-1}), \tag{54a}$$

$$\frac{d\sigma'_{n,n+1}}{dt} = (-i\bar{\omega}_{n,n+1} - \Gamma_{n,n+1}) \sigma'_{n,n+1} - i\bar{\Omega}_{n,n+1} \left(P_{n+1} \sqrt{\frac{d_n}{d_{n+1}}} - P_n \sqrt{\frac{d_{n+1}}{d_n}} \right) + i\bar{\Omega}_{n+1,n+2} \sigma'_{n,n+2} - i\bar{\Omega}_{n,n-1} \sigma'_{n-1,n+1}, \tag{54b}$$

$$\begin{aligned} d\sigma'_{nm}/dt = & (-i\bar{\omega}_{nm} - \Gamma_{nm}) \sigma'_{nm} + i\bar{\Omega}_{m,m+1} \sigma'_{n,m+1} + i\bar{\Omega}_{m,m-1} \theta_{m,m-1}^n (d_m/d_{m-1})^{1/2} \sigma'_{n,m-1} \\ & - i\bar{\Omega}_{n,n+1} \theta_{n,n+1}^m (d_n/d_{n+1})^{1/2} \sigma'_{n+1,m} - i\bar{\Omega}_{n,n-1} \sigma'_{n-1,m}, \quad m > n + 1. \end{aligned} \tag{54c}$$

In Eq. (54c), we have taken $m > n + 1$. The REM for $\sigma'_{nm} (m < n - 1)$ and for $\sigma'_{n+1,n}$ are simply the complex conjugates of Eqs. (54c) and (54b), respectively. θ_{ab}^c in Eq. (54c) is given by Eq. (46) or by the approximate forms (46a) or (46b).

It is reasonable to assume that, for large molecules where only few degrees of freedom are coupled with the radiation field, $\bar{\Omega}_{nm}$ will be roughly independent of the number of states involved in the dephasing (d_n and d_m). This is expected since any quantity of the form

$$\sum_{\alpha\beta} \frac{1}{d_n} |\langle n\alpha | \mu | m\beta \rangle|^2 = |\mu_{nm}|^2 \tag{55a}$$

or

$$\sum_{\alpha\beta} \frac{1}{d_m} |\langle n\alpha | \mu | m\beta \rangle|^2 = |\mu_{nm}|^2 \tag{55b}$$

$$\hat{F}'_{ab} = \frac{1}{\eta_{ab}}. \tag{50a}$$

Let us choose

$$\eta_{ab} = (d_a d_{a+1}^2 d_{a+2}^2 \cdots d_{b-1}^2 d_b)^\alpha, \tag{51}$$

where α is a scaling exponent to be determined. The product $d_a d_{a+1}^2 \cdots d_{b-1}^2 d_b$ is the statistical weight of σ_{ab} (the number of pathways to go from level a to level b).

We thus get

$$F'_{nm,ni} = - \frac{1}{(d_i d_m)^\alpha}, \tag{52a}$$

$$F'_{nm,ni} = - \frac{1}{d_i} \theta_{ni}^n (d_i d_m)^\alpha, \tag{52b}$$

$$F'_{nm,im} = \frac{1}{(d_m d_i)^\alpha}, \tag{52c}$$

$$F'_{nm,im} = \frac{1}{d_i} \theta_{ni}^n (d_n d_i)^\alpha, \tag{52d}$$

$$\bar{F}'_{nm} = (d_n d_m)^\alpha, \tag{52e}$$

$$\hat{F}'_{nm} = \frac{1}{(d_n d_m)^\alpha}. \tag{52f}$$

We are now in a position to discuss the behavior of the REM in the statistical limit of a large molecule where only few degrees of freedom are coupled to the radiation field. To that end, let us define

$$\Omega_{nm}^2 \equiv \bar{\Omega}_{nm}^2 \sqrt{d_n d_m} \tag{53}$$

and choose the scaling exponent $\alpha = 1/4$. Our REM thus assume the form

is independent on the addition of degrees of freedom which do not couple with μ . The dipole sum rule (55a) implies $\Omega_{nm}^2 \propto d_n$ and Eq. (55b) implies $\Omega_{nm}^2 \propto d_m$. It is thus fair to assume that Ω_{nm}^2 scales as $\sqrt{d_n d_m}$, which implies that $\bar{\Omega}_{nm}$ is independent of d_n and d_m .

To summarize, in the statistical Markovian limit, our REM assume the form (54) and depend on the following molecular quantities:

- (i) $\bar{\Omega}_{nm}$ which are *effective Rabi frequencies* for the various transitions and are roughly independent of molecular size;
- (ii) dephasing terms Γ_{nm} ;
- (iii) *ratios* of statistical weights of the various levels d_n/d_m .

VI. A MODEL FOR THE INTRAMOLECULAR DIPOLE CORRELATION FUNCTIONS

In the preceding sections, we have developed a complete theory for MMP. Invoking the factorization assumption (which is very reasonable in the quasicontinuum), we were able to express all the dephasing operators appearing in our REM (F , \bar{F} , and G) in terms of the two-time intramolecular dipole correlation functions $I_{nm}(t)$ [Eqs. (19) with (20)–(22) and (40)].

In this section, we shall develop a simple microscopic model for $I_{nm}(t)$ which will enable us to relate the dephasing times (and the whole dynamics of MMP) to real molecular parameters (size, frequencies, anharmonicities, masses, etc.). We start with the molecular Hamiltonian

$$H_M = \sum_{\nu} H_{0\nu}(q_{\nu}) + H', \quad (56)$$

where $H_{0\nu}(q_{\nu})$ is a harmonic Hamiltonian for the ν th normal mode and q_{ν} is its dimensionless coordinate. H' is the anharmonic part of the Hamiltonian and includes terms cubic and higher in q . Our expressions for the dephasing rates are given in terms of the true molecular states. We thus need a way for obtaining a reasonable approximation for these states. In fact, since the dephasing is essentially a spreading process of a wave packet of molecular states on the energy shell, we need to have a "mean field" Hamiltonian which will describe correctly the motion only on the energy shell. The simplest way to achieve that is to expand H' to linear order in q_{ν} , i. e.,

$$H' = \sum_{\nu} F_{\nu}(\mathbf{q})q_{\nu}, \quad (57)$$

and to replace each $F_{\nu}(\mathbf{q})$ by its microcanonical average at energy E , i. e.,

$$\Delta_{\nu}(E) \equiv \langle F_{\nu} \rangle_E = \frac{\text{tr} F_{\nu} \delta(E - H)}{\text{tr} \delta(E - H)}. \quad (58)$$

We thus get

$$H(E) = \sum_{\nu} H_{0\nu}(q_{\nu}) + \sum_{\nu} \Delta_{\nu}(E)q_{\nu}. \quad (59)$$

(Note that Δ_{ν} and q_{ν} are dimensionless.) We have thus established a simple picture of a collection of harmonic oscillators whose equilibrium position is being shifted as a function of the molecular energy. At $E = 0$, $\langle q_{\nu} \rangle = 0$ and we recover the normal mode Hamiltonian. $\Delta_{\nu}(E)$ are related to the anharmonicities to lowest order as

$$\Delta_{\nu}(E) = \sum_{\nu'} \alpha_{\nu\nu'} \langle q_{\nu'}^2 \rangle_E, \quad (60)$$

where $\alpha_{\nu\nu'}$ are cubic anharmonicities and $\langle q_{\nu'}^2 \rangle_E$ is the microcanonical mean square displacement of the ν' th mode.

Let us consider now the following *microcanonical* correlation function:

$$I_{nm}(E, t) = \frac{1}{\gamma_{nm}^2 W(E)} \sum_{\alpha, \beta} |\mu_{nm}^{\alpha\beta}|^2 \times \exp(-i\omega_{n\alpha, m\beta} t) \delta(E_{n\alpha} - E), \quad (61)$$

where $W(E)$ is the density of molecular states at energy E . In terms of this correlation function, we have

$$I_{nm}(t) = I_{nm}(\bar{E}_n, t), \quad (61a)$$

where \bar{E}_n is the mean energy of the n th level. We further assume that the dipole operator is coupled only with one normal mode (ν_s)

$$\mu = \bar{\mu}q_s. \quad (62)$$

The quantity that may be easily evaluated is, however, the *canonical* correlation function^{46–49}

$$\hat{I}_{nm}(\beta, t) = \frac{1}{Q(\beta)} \int_0^{\infty} dE I_{nm}(E, t) W(E) \exp(-\beta E), \quad (63)$$

where $Q(\beta)$ is the partition function

$$Q(\beta) = \int_0^{\infty} dE W(E) \exp(-\beta E). \quad (64)$$

$I_{nm}(E, t)$ may then be evaluated by the inverse Laplace transform^{49, 50}

$$I_{nm}(E, t) = \frac{\int_{\lambda-i\infty}^{\lambda+i\infty} d\beta \exp(\beta E) Q(\beta) \hat{I}_{nm}(\beta, t)}{\int_{\lambda-i\infty}^{\lambda+i\infty} d\beta \exp(\beta E) Q(\beta)}. \quad (65)$$

The anharmonicity of q_s and $\Delta_s(E)$ has a special role in determining $\bar{\omega}_{nm}$ (the mean frequencies of the transitions); however, for the dephasing, it contributes just as any other mode. For the sake of simplicity, we shall assume $\Delta_s = 0$. (Incorporating Δ_s will not affect substantially our final expressions.) We then get^{46–49}

$$\hat{I}_{nm}(\beta, t) = \exp[-S(\beta)] \exp[S_+(\beta, t) + S_-(\beta, t)], \quad (66)$$

where

$$S_+(\beta, t) = \sum_{\nu} \frac{1}{2} |\Delta_{\nu}^{(nm)}|^2 (\bar{n}_{\nu} + 1) \exp(i\omega_{\nu} t), \quad (66a)$$

$$S_-(\beta, t) = \sum_{\nu} \frac{1}{2} |\Delta_{\nu}^{(nm)}|^2 \bar{n}_{\nu} \exp(-i\omega_{\nu} t), \quad (66b)$$

and

$$S(\beta) = S_+(\beta, 0) + S_-(\beta, 0) = \sum_{\nu} \frac{1}{2} |\Delta_{\nu}^{(nm)}|^2 (2\bar{n}_{\nu} + 1). \quad (66c)$$

Here,

$$\Delta_{\nu}^{(nm)} = \Delta_{\nu}(E_n) - \Delta_{\nu}(E_m) \quad (67)$$

and \bar{n}_{ν} is the mean occupation number of the ν th oscillator at temperature $\beta^{-1} = kT$, i. e.,

$$\bar{n}_{\nu} = [\exp(\beta \hbar \omega_{\nu}) - 1]^{-1}. \quad (68)$$

Evaluation of the inverse Laplace transform (65) should now be made in order to evaluate $I_{nm}(E, t)$. We recall that, under quite general conditions,^{49, 50} the inversion may be achieved by using the saddle point method. This results in the simple relation

$$I(E, t) \cong \hat{I}(\beta^*, t), \quad (69)$$

where β^* is the saddle point obtained from the solution of

$$\sum_{\nu} \bar{n}_{\nu}(\beta^*) \hbar \omega_{\nu} = E. \quad (70)$$

Using this result, we get

$$I(E, t) = \exp[-S(\beta^*)] \exp[S_+(\beta^*, t) + S_-(\beta^*, t)]. \quad (71)$$

The exact equation (61) satisfies $I_{nm}(t) = I_{mn}^*$. This is no longer the case due to our use of the saddle point; we thus take

$$I_{nm}(t) = I_{nm} \left(\frac{\bar{E}_n + \bar{E}_m}{2}, t \right). \quad (71a)$$

Substituting Eqs. (71) in (21a), we get

$$\begin{aligned} G_{nm}(t) &= \frac{1}{I_{nm}} \frac{dI_{nm}}{dt} = S'_+(\beta^*, t) + S'_-(\beta^*, t) \\ &= S'(\beta^*, 0) - \int_0^t d\tau \chi(\tau), \end{aligned} \quad (72)$$

where

$$\chi(\tau) = \chi'(\tau) + i\chi''(\tau), \quad (73)$$

$$\chi'(\tau) = \sum_\nu \frac{|\Delta_\nu^{nm}|^2}{2} \omega_\nu^2 (2\bar{n}_\nu + 1) \cos \omega_\nu \tau, \quad (74a)$$

$$\chi''(\tau) = \sum_\nu \frac{|\Delta_\nu^{nm}|^2}{2} \omega_\nu^2 \sin \omega_\nu \tau, \quad (74b)$$

$$S'(\beta^*, 0) = i \sum_\nu \frac{|\Delta_\nu^{nm}|^2}{2} (2\bar{n}_\nu + 1) \omega_\nu, \quad (74c)$$

and the dephasing rate Γ_{nm} in the Markovian limit (37) and (38) assumes the form³³

$$\Gamma_{nm} = \frac{1}{2} \int_0^\infty d\tau \sum_\nu |\Delta_\nu^{nm}|^2 (2\bar{n}_\nu + 1) \omega_\nu^2 \cos \omega_\nu \tau, \quad (75)$$

which corresponds to a Lorentzian line profile.

Let us now have a rough estimate of Γ_{nm} . The integral (75) in the high temperature limit is over a wave packet whose frequency width is the spread in molecular frequencies, which is of the same magnitude as the molecular frequencies. We thus have

$$\Delta_\nu^{nm}(E) \sim \frac{\alpha}{2} \frac{\omega_0}{\langle \omega \rangle} \quad (76a)$$

and

$$\Gamma_{nm} \sim \frac{1}{2} |\Delta|^2 (2\bar{n} + 1) \frac{\langle \omega \rangle^2}{\langle \omega \rangle} = \frac{1}{2} \left(\frac{\alpha}{2} \right)^2 (2\bar{n} + 1) \omega_0. \quad (76b)$$

Here, $\langle \omega \rangle$ is a typical molecular frequency, ω_0 is the laser frequency, and \bar{n} is the total number of absorbed quanta. α is a dimensionless cubic anharmonicity and is typically $\alpha \sim 10^{-1} - 10^{-2}$.

Taking the typical values $\bar{n} = 40$ and $\omega_0 = 1000 \text{ cm}^{-1}$, we get $\Gamma_{nm} = 1 \text{ cm}^{-1}$ assuming $\alpha = 10^{-2}$ and $\Gamma_{nm} = 100 \text{ cm}^{-1}$ assuming $\alpha = 10^{-1}$. These are very reasonable values for MMP (see Discussion, Sec. VII B). From these estimates, we can also verify the validity of the Markovian assumption leading to Eq. (75) as the relation $\Gamma \ll \tau_c^{-1} \sim \langle \omega \rangle$ is equivalent to Eq. (37).

VII. DISCUSSION

Our general REM [Eqs. (19)] provide a unified description for MMP which is valid for weak and strong driving fields and interpolate continuously all the way from the coherent to the totally incoherent limits of the molecular driving. They may be thus used to describe

the evolution of a polyatomic molecule starting in region I up to the dissociation. The different nature of the driving in the various regions is reflected in the form of the relaxation operators G , \bar{F} , and F , which change continuously with the degree of excitation. In this section, we shall summarize the basic assumptions and results of our REM (19) and analyze their limiting behavior.

A. Dephasing and reduction

Within the present formulation, the dephasing is a direct consequence of our *reduced description* of the molecular dynamics in terms of few variables.¹² The dephasing terms in our REM are $G(t)$, $F(t)$, and $\bar{F}(t)$, and they are expressed in terms of microscopic intramolecular dipole correlation functions. They are independent of the dipole strength but rather depend merely on the *functional form* of the dipole operator. *No perturbative arguments regarding intramolecular interactions are required in order to give a precise definition of these terms.* Thus, intramolecular interactions are rigorously treated by using the true molecular basis set.

If we set $\Omega = 0$ in Eqs. (19), we can solve for $\sigma_{nm}(t)$:

$$\sigma_{nm}(t) = \exp(-i\bar{\omega}_{nm}t) I_{nm}(t) \sigma_{nm}(0). \quad (77)$$

$\sigma_{nm}(t)$ is then equal to the exact intramolecular dipole correlation function for the nm transition $I_{nm}(t)$ (as it should!).

Suppose the molecule is initially at the n th level and we adiabatically switch on a weak radiation field. Within linear response theory,²⁹ Eq. (77) will predict a line shape which is the Fourier transform of the dipole correlation function, i. e.,

$$\Phi(\omega_0) = \text{Re} \int_0^\infty d\tau \exp(-i\bar{\omega}_{nm}\tau) I_{nm}(\tau). \quad (78)$$

In the absence of reduction (each level contains only one state), then $G(t) = 0$ and $F(t) = \bar{F}(t) = 1$, there is no dephasing, and we recover the ordinary limit of coherent driving. This is the situation at the early stages of the molecular multiphoton excitation (region I) where intramolecular broadening is unimportant.

Finally, we note that, due to our adoption of a basis set of true molecular states, all the anharmonicities are properly (nonperturbatively) incorporated in our REM. As a result, no relaxation of population (T_1 type) terms need to be considered. The T_1 terms which appear in the perturbative approaches couple different zero-order states and allow for energy exchange between the system and the bath. In the present formulation, they are buried in the dephasing operators. The equivalence of T_1 and T_2 depending on the choice of a basis set was discussed recently for intra- and intermolecular interactions.^{12,51}

B. The reduction hierarchy—Continuous transition from coherent to incoherent driving

We shall now summarize the assumptions and results for the various stages of our hierarchy of REM.

Let us note first that the level of theoretical descrip-

tion may be easily varied within the present formulation by changing the number of relevant operators. (For any number of operators, we can construct a closed set of equations; an appropriate choice of the operators will however lead to simple REM.) The attempts^{9,39,40} to provide a phenomenological description for MMP in terms of $N^2 \times N^2$ generalized Bloch equations (for an N level system) are intimately related to the picture of a system and a bath which are *weakly* interacting (since N^2 is the size of a complete set of system operators). From the present approach, however, it is clear that the number N^2 does not play any special role. A complete description of the molecular density matrix requires much more than N^2 operators, but in practice we may construct a convenient set of REM whereby the number of variables is significantly smaller than N^2 , e.g., it may turn out that only single quantum coherences are sufficient for a complete simple description of the molecular evolution all the way up to dissociation, and that we could ignore the effects of multiquantum coherences.

1. The coherent driving

At the early stages of the molecular excitation (region "I"), there is no reduction and consequently no dephasing ($G_{nm} = 0$ and $F = \bar{F} = 1$). This is the limit of coherent driving. The only molecular information which enters into our REM (19) is the level spacings $\bar{\omega}_{nm}$ and the transition dipole Ω_{nm} .

2. The statistical non-Markovian region

After the absorption of a few quanta, the molecule is pumped into the quasicontinuum where the effects of dephasing start to play a role. The most general REM (19) includes the relaxation operators G , \bar{F} , and F [Eqs. (21) and (23)] which in turn are expressed in terms of two-time and three-time dipole correlation functions I and J [Eqs. (22)]. However, it is plausible that the factorization assumption (39) will hold very early so that finally we end up with Eqs. (19), (21), and (40), where all relevant molecular information is contained in the two-time correlation functions $I_{nm}(t)$. Knowing $I_{nm}(t)$ thus enables us to follow the dynamics of the MMP. Equations (71) provide us with microscopic expressions for $I_{nm}(t)$.

3. The statistical Markov limit

At high degrees of excitation, we expect $I_{nm}(t)$ to have a characteristic time scale which is of the order of the molecular frequencies (71). This is much shorter than any other time scale in the problem. We thus have a separation of time scales in our REM (the Markov limit). Taking $I_{nm}(t)$ to behave exponentially at long times (which is the usual behavior of typical correlation functions),²⁹ we obtain a simple form for our REM (19) where all relaxation and driving terms are time independent [Eqs. (45)]. When the number of effectively radiatively coupled states becomes very large, we may scale the coherences and transform our REM to the form (54), which is the "thermodynamic limit" of the present theory. In this limit, each transition is char-

acterized by a frequency $\bar{\omega}_{nm}$, integrated Rabi frequency $\bar{\Omega}_{nm}$ (which is roughly independent on the molecular size), and a dephasing rate Γ_{nm} . In addition, the REM (54) includes *ratios* of statistical weights (d_n/d_m) of the various levels.

4. The complete incoherent driving

If the dephasing rates Γ_{nm} are fast compared to the driving $\bar{\Omega}_{nm}$, we may invoke a steady state assumption for the coherences, solve them, and substitute back into the equations for the populations. As a result, our REM assume the form of simple rate equations corresponding to incoherent driving⁵²

$$\frac{dP_n}{dt} = \sum_m \kappa_{nm} P_m. \quad (79)$$

If we consider only single quantum coherences, we get

$$\frac{dP_n}{dt} = \sum_{m=n\pm 1} \frac{2\Gamma_{nm}\bar{\Omega}_{nm}^2}{\Gamma_{nm}^2 + \omega_{nm}^2} \left(P_m \sqrt{\frac{d_n}{d_m}} - P_n \sqrt{\frac{d_m}{d_n}} \right). \quad (80)$$

The steady state assumption for the coherences may be invoked under less restrictive assumptions than done here (i.e., not invoking the Markov limit, leaving the time dependence in F). In this case, we get rate equations for the populations with time-dependent rates.

Equation (80) satisfies a detailed balance relation

$$\kappa_{nm}/\kappa_{mn} = d_n/d_m. \quad (81)$$

Equation (81) implies that the radiation field is tending to establish a distribution of molecular states where all radiatively coupled states are equally populated. Thus, the ratio (81) is equal to the ratio of the number of effectively coupled states in each level.

Rate equations of the form (80) were used by Lyman,⁵³ Grant and co-workers,^{7(b)} and by Bloembergen and Yablonoitch⁵⁴ for the description of molecular multiphoton processes. We should bear in mind, however, that these equations are only the final stage in the reduction hierarchy described above and only perhaps at the higher energy part of the quasicontinuum are we allowed to use the simple rate equation (80).

Furthermore, in the actual calculations,⁷ it was assumed that

$$\kappa_{nm}/\kappa_{mn} = W_n/W_m, \quad (82)$$

where W is the density of molecular states. From the present derivation, it is clear that W_n/W_m should be actually d_n/d_m , i.e., the ratio of effectively radiatively coupled states which may be very different. This may crucially affect the intermolecular energy distributions and the conclusions drawn by Grant and co-workers⁷ should thus be treated with caution. Fitting of the present REM with experimental data may thus provide a clue for understanding the dynamics of highly excited polyatomic molecules, by providing us with $\bar{\Omega}_{nm}$ and $I_{nm}(t)$ as a function of the molecular degree of excitation. Unfortunately, the experimental data available at present are not sufficiently detailed to allow for an unambiguous quantitative study and this is the reason that different authors are able to fit their data using completely dif-

ferent assumptions.⁵⁵ For that reason, it is necessary to use data from other types of experiments especially regarding the intramolecular dephasing times, which will eliminate the number of unknown parameters in the REM. A great progress has been recently achieved in that direction by various techniques.¹³⁻¹⁸ The recently developed technique of multi-quantum NMR by Pines and co-workers⁵⁶ may further provide a very nice critical check of some of the *formal* aspects of the present REM since the problem is formally similar (multi-quantum transitions in a many-level system). However, the number of states involved is much smaller than in MMP and the precise Hamiltonian is known. Thus, all the necessary correlation functions may be calculated rigorously.

Turning now to the experimental data of SF₆, the absorption cross sections were fitted to experiment assuming a rate equation (80),^{6,53,55} resulting in a cross section of $\sigma \sim 2 \times 10^{-20}$ cm² at $\bar{n} = 40$. Using Eq. (80), the cross section is given by

$$\frac{\sigma I}{\hbar \omega_0} = \frac{2\bar{\Omega}_{nm}^2}{\Gamma_{nm}}, \quad (83)$$

where I is the incoming laser flux and we have taken $\bar{\omega}_{nm} = 0$. Assuming a diluted oscillator strength of $\mu \sim 0.03-0.1$ D, we get $\Gamma_{nm} \sim 15-150$ cm⁻¹, which agrees very nicely with the estimates of Sec. VI.

Furthermore, the multiphoton absorption data⁷ indicate that the effective multiphoton absorption cross section defined as $d\langle n \rangle/dI$ (where $\langle n \rangle$ is the number of quanta absorbed per molecule) is decreasing with I (and hence with the degree of excitation). This type of behavior is predicted by our REM due to the roughly linear increase of Γ_{nm} with $\langle n \rangle$ [Eq. (76b)] and the dilution of $\bar{\Omega}_{nm}$, which result in a gradual decrease of the effective absorption cross section with $\langle n \rangle$.

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APPENDIX A: THE SYSTEMATIC REDUCTION SCHEME

Suppose we choose a set of dynamical operators A_{nm} (not necessarily orthogonal). We now write the Liouville equation

$$\dot{\rho}(t) = -iL\rho(t) = -iL \exp(-iLt)\rho(0). \quad (A1)$$

We assume that $\rho(0)$ may be expanded in terms of A_{nm} , i. e.,

$$\rho(0) = \sum_{nm} \sigma_{nm}(0) A_{nm}. \quad (A2)$$

Multiplying Eq. (A1) by A_{ki}^\dagger from the left and taking a trace, we get

$$\langle A_{ki}^\dagger \dot{\rho}(t) \rangle = -i \sum_{nm} \langle A_{ki}^\dagger L \exp(-iLt) A_{nm} \rangle \sigma_{nm}(0). \quad (A3)$$

Similarly, we may write

$$\rho(t) = \exp(-iLt)\rho(0) \quad (A4)$$

in the form

$$\langle A_{ki}^\dagger \rho(t) \rangle = \sum_{nm} \langle A_{ki}^\dagger \exp(-iLt) A_{nm} \rangle \sigma_{nm}(0). \quad (A5)$$

We now define a column vector \mathbf{A} whose components are A_{nm} and three tetradic matrices

$$W_{ki, nm} = \langle A_{ki}^\dagger L \exp(-iLt) A_{nm} \rangle, \quad (A6)$$

$$V_{ki, nm} = \langle A_{ki}^\dagger \exp(-iLt) A_{nm} \rangle, \quad (A7)$$

and

$$S_{ki, nm} = \langle A_{ki}^\dagger A_{nm} \rangle. \quad (A8)$$

We further define a vector σ and another vector λ whose components are

$$\lambda_{nm} = \langle A_{nm}^\dagger \rho(t) \rangle, \quad (A9)$$

$$\lambda = \mathbf{S} \sigma. \quad (A10)$$

Equations (A3) and (A5) can be expressed in terms of the quantities defined in Eqs. (A6)-(A10):

$$\dot{\lambda} = -i\mathbf{W}\sigma(0), \quad (A11)$$

$$\lambda = \mathbf{V}\sigma(0). \quad (A12)$$

From Eqs. (A11) and (A12), we get

$$\dot{\lambda} = -i\mathbf{W}\mathbf{V}^{-1}\lambda \quad (A13)$$

or

$$\dot{\sigma} = -i\mathbf{S}^{-1}\mathbf{W}\mathbf{V}^{-1}\mathbf{S}\sigma. \quad (A14)$$

When the operators A_{nm} are orthonormal, then \mathbf{S} is the unit matrix and $\lambda = \sigma$. Equation (A13) is equivalent to Eqs. (10).

APPENDIX B: DERIVATION OF THE REM

We wish to evaluate the reduced time evolution matrix $\mathbf{K}(t) = P\mathbf{K}(t)P$ [Eq. (10)]. To that end, we separate the projection P into two new subspaces

$$P = C + D, \quad (B1)$$

where D projects onto the set of diagonal operators A_{nn} and C to the rest, i. e.,

$$CB = \sum_{n \neq m} \langle B, A_{nm}^\dagger \rangle A_{nm} \equiv \sum_{n \neq m} C_{nm} B, \quad (B2)$$

$$DB = \sum_n \langle B, A_{nn}^\dagger \rangle A_{nn} \equiv \sum_n D_{nn} B. \quad (B3)$$

Our REM require the evaluation of the four projections CKC , DKD , CKD , and DKC .

We note that by construction

$$L_0 D = 0 \quad (B4)$$

and

$$L' D = \sum_{nm} C_{nm} \gamma_{nm} = \lambda C, \quad (B5)$$

where λ is a tetradic diagonal matrix

$$\lambda_{nm, n' m'} = \delta_{nm'} \delta_{nm} \gamma_{nm}, \quad (\text{B6})$$

and γ_{nm} were defined in Eq. (16a).

From Eqs. (10a), (B4), and (B5), we get

$$\begin{aligned} DK &= \langle DL \exp(-iLt) P \rangle \langle P \exp(-iLt) P \rangle^{-1} \\ &= \langle DL' \exp(-iLt) P \rangle \langle P \exp(-iLt) P \rangle^{-1} \\ &= \lambda C \langle P \exp(-iLt) P \rangle \langle P \exp(-iLt) P \rangle^{-1} \\ &= \lambda C. \end{aligned} \quad (\text{B7})$$

Multiplying Eq. (B7) from the right by C and D , we finally get

$$DKD = 0, \quad (\text{B8})$$

$$DKC = \lambda. \quad (\text{B9})$$

The other projections (CKC , CKD) will now be evaluated to first order in L' . We write

$$\begin{aligned} \langle \exp(-iLt) L \rangle &= \langle \exp(-iL_0 t) L_0 \rangle + \langle \exp(-iL_0 t) L' \rangle \\ &- i \int_0^t d\tau \langle \exp[-iL_0(t-\tau)] L' \exp(-iL_0 \tau) L_0 \rangle. \end{aligned} \quad (\text{B10a})$$

Or, alternatively,

$$\begin{aligned} \langle \exp(-iLt) L \rangle &= \langle L_0 \exp(-iL_0 t) \rangle + \langle L' \exp(-iL_0 t) \rangle \\ &- i \int_0^t d\tau \langle L_0 \exp[-iL_0(t-\tau)] L' \exp(-iL_0 \tau) \rangle \end{aligned} \quad (\text{B10b})$$

and

$$\begin{aligned} \langle \exp(-iLt) \rangle^{-1} &= \langle \exp(-iL_0 t) \rangle^{-1} + i \langle \exp(-iL_0 t) \rangle^{-1} \\ &\times \int_0^t d\tau \langle \exp[-iL_0(t-\tau)] L' \exp(-iL_0 \tau) \rangle \langle \exp(-iL_0 t) \rangle^{-1}. \end{aligned} \quad (\text{B11})$$

In order to evaluate CKD , it is better to use the form (B10a) recalling that $DL_0 = 0$. We get

$$\begin{aligned} CKD &= C \langle \exp(-iL_0 t) L' \rangle D + i C \langle \exp(-iL_0 t) L_0 \rangle \\ &\times \langle \exp(-iL_0 t) \rangle^{-1} \int_0^t d\tau \langle \exp(-iL_0 \tau) L' \rangle D. \end{aligned} \quad (\text{B12})$$

We shall now evaluate CKC . Making use of Eq. (B10a), we get

$$\begin{aligned} (CKC) &= \langle \exp(-iL_0 t) L_0 \rangle \langle \exp(-iL_0 t) \rangle^{-1} + \langle \exp(-iL_0 t) L' \rangle \langle \exp(-iL_0 t) \rangle^{-1} - i \int_0^t d\tau \langle \exp[-iL_0(t-\tau)] L' \exp(-iL_0 \tau) L_0 \rangle \\ &\times \langle \exp(-iL_0 t) \rangle^{-1} + i \langle \exp(-iL_0 t) L_0 \rangle \langle \exp(-iL_0 t) \rangle^{-1} \int_0^t d\tau \langle \exp[-iL_0(t-\tau)] L' \exp(-iL_0 \tau) \rangle \langle \exp(-iL_0 t) \rangle^{-1}. \end{aligned} \quad (\text{B13})$$

Or, utilizing the alternative form (B10b), we get

$$\begin{aligned} CKC &= \langle L_0 \exp(-iL_0 t) \rangle \langle \exp(-iL_0 t) \rangle^{-1} + \langle L' \exp(-iL_0 t) \rangle \langle \exp(-iL_0 t) \rangle^{-1} - i \int_0^t d\tau \langle L_0 \exp[-iL_0(t-\tau)] L' \exp(-iL_0 \tau) \rangle \\ &\times \langle \exp(-iL_0 t) \rangle^{-1} + i \langle L_0 \exp(-iL_0 t) \rangle \langle \exp(-iL_0 t) \rangle^{-1} \int_0^t d\tau \langle \exp[-iL_0(t-\tau)] L' \exp(-iL_0 \tau) \rangle \langle \exp(-iL_0 t) \rangle^{-1}. \end{aligned} \quad (\text{B14})$$

The first term in Eqs. (B13) and (B14) contributes to the diagonal part $K_{nm, nm}$ whereas the other three contribute to the off diagonal couplings $K_{nm, nm \pm 1}$ and $K_{nm, n \pm 1 m}$. Equations (23b) and (23d) were evaluated using Eq. (B13) whereas Eqs. (23a) and (23c) were evaluated using Eq. (B14).

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