Comments on some reduced descriptions of coherent and incoherent dynamics of multilevel systems

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We discuss some newly developed reduced equations of motion of systems which undergo transition from coherent to incoherent dynamics, and compare these equations with the well-established Bloch equations. We show that in spite of some structural similarities, there are important differences in the behavior of their solutions.

The continuous transition from coherent to incoherent dynamics is a universal phenomenon which occurs in a variety of physical processes. To cite a few examples, we can consider the dynamics of a magnetic dipole (or a harmonic oscillator) coupled to a heat bath and driven by an external field,[1] intramolecular line broadening in molecular multiphoton absorption,[2] and reactive scattering of complex particles.[3] One can classify these processes into two categories. (a) Systems where a limited number of *degrees of freedom of interest* are coupled to a *thermal bath* (the first examples above). (b) Systems in which the concept of a thermal bath does not hold and a reduced description of the processes of interest is obtained by deriving equations of motion for a limited set of *dynamical observables*. (The intramolecular line broadening and reactions between complex particles belong to this class.)

A graphical representation of the two categories mentioned above is given in Fig. 1. Systems which belong to class (a) are represented by two levels immersed in a heat bath (dashed background) and driven by the external field (wavy arrow). The complete set of system degrees of freedom are the elements of the 2×2 density matrix. Systems which can be classified in category (b) are represented by two groups (bins) of states. Here, one does not deal with the entire density matrix of the system, but rather, considers a limited number of coarse-grained dynamical variables, e.g., the summed probability to be in bin 1 or 2.

The discussion of problems which fall into the first category is better understood theoretically as well as experimentally. Developing a theory for such processes, one distinguishes between the "bath" and the "system" degrees of freedom, and derives equations of motion for a *complete set of system operators*. One usually obtains the well-known ordinary Bloch equations (OBE).[4] In order to discuss the relevant properties of the OBE, we quote here the equations for a driven two-level system coupled to a bath [Fig. 1(a)].[1]

$$\frac{d}{dt}\Delta P = -i\Omega(\sigma_{21}-\sigma_{12}) - \Gamma_1(\Delta P - \Delta P^{(0)}), \tag{1a}$$

$$\frac{d}{dt}\sigma_{12} = i\Omega\,\Delta P - (i\omega + \Gamma_2)\,\sigma_{12}, \tag{1b}$$

$$\sigma_{21} = \sigma_{12}^{*}, \tag{1c}$$

$$\Delta P = \tfrac{1}{2}(P_1 - P_2);\quad \frac{d}{dt}(P_1 + P_2) = 0. \tag{1d}$$

Here, Ω denotes the coupling of the external driving field to the system (the Rabi frequency). Γ_1 and Γ_2 (where $\Gamma_2 > \Gamma_1$) are the T_1 and T_2 relaxation constants for the populations P_i, $i=1,2$ and the coherences σ_{12}, respectively. The conventional coherence (off-diagonal element of the density matrix) is actually $\sigma_{12}\cdot\sqrt{2}$. The scaling factor $\sqrt{2}$ was introduced for making the comparison with Eq. (9) more transparent. The detuning $\omega = \omega_{21} - \omega_L$ is the energy difference between the two level frequency ω_{21} and the frequency of the field. $\Delta P^{(0)}$ denotes half the population difference at equilibrium. For a bath at a temperature T,

$$\Delta P^{(0)} = \tfrac{1}{2}\tanh(\omega_{21}/2kT). \tag{2}$$

The OBE have the following important properties.

(i) After sufficiently long time, the system will always relax to its steady state where the time derivatives vanish. In the absence of driving ($\Omega = 0$), the steady state is

$$\Delta P = \Delta P^{(0)},\qquad \sigma_{12} = 0. \tag{3}$$

(ii) In the limit $\Gamma_2 \gg \Omega$, the OBE reduce to simple rate equations[1(b)]

$$\frac{d\Delta P}{dt} = -\left(\frac{2\Gamma_2\Omega^2}{\omega^2+\Gamma_2^2} + \Gamma_1\right)(\Delta P - \Delta\tilde{P}),$$

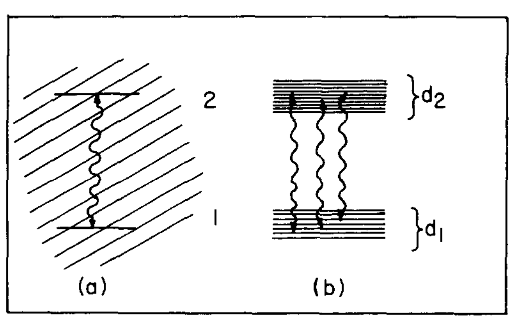

FIG. 1. A graphical illustration of the systems under discussion. (a) A two-level system coupled to a thermal bath. (b) A two bin system.

$$\Delta\tilde{P} = \Delta P^{(0)}\,\Gamma_1\Big/\left(\Gamma_1 + \frac{2\Gamma_2\Omega^2}{\omega^2+\Gamma_2^2}\right) . \tag{4}$$

(iii) The structure of the OBE guarantees that for any choice of the parameters Γ_1, Γ_2, Ω, and ω, and if at the initial time $t=0$

$$P_1 + P_2 = 1, \tag{5a}$$

$$|\Delta P| \le \tfrac{1}{2}, \tag{5b}$$

$$|\sigma_{12}|^2 \le \tfrac{1}{2}P_1P_2. \tag{5c}$$

Then the above relations hold for any later time. Thus, the solutions of the OBE are always acceptable as far as the general requirements [Eqs. (5)] on a 2×2 density matrix are concerned. This does not guarantee that the solutions describe properly the process of interest. Indeed, the OBE are justified only when the bath correlation time is much shorter than Γ_1^{-1}, Γ_2^{-1}, and Ω^{-1}. But, since the bath correlation time does not appear in the OBE themselves, there is no built-in mechanism in the OBE, which signals an improper application of the OBE. The fact that the solutions of the OBE are always "acceptable" [i.e., fulfill the requirements of Eqs. (5)] makes their application for phenomenological purposes rather popular.

With this background in mind, we shall turn our attention to the systems which fall into the category (b) mentioned above. The theoretical treatment of such systems gained recently appreciable momentum, with the derivation[2] of reduced equations of motion (REM), which govern the time evolution of the relevant dynamical observables. These equations are structurally similar to the OBE, and are sometimes referred to as the "generalized Bloch equations."[2] The main purpose of the present note is to show that, in spite of some similar features, there are important differences between the OBE and REM, which we shall demonstrate in the sequel.

We shall use a representative model system to demonstrate our claims. Consider a system whose spectrum can be subdivided into two bins, and is driven by an external interaction [Fig. 1(b)]. Let the number of states in the bins be d_1 and d_2, and let the Hamiltonian be

$$H = \sum_{\alpha=1}^{d_1} |1\alpha\rangle \epsilon_{1\alpha}\langle 1\alpha| + \sum_{\beta=1}^{d_2} |2\beta\rangle \epsilon_{2\beta}\langle 2\beta| + \sum_{\alpha\beta} (|1\alpha\rangle V_{\alpha\beta}\langle 2\beta| + |2\beta\rangle V_{\beta\alpha}\langle 1\alpha|). \tag{6}$$

In most cases, one is interested in obtaining a reduced (coarse-grained) description of the system, in terms of its slow dynamical variables. The probabilities P_i, $i=1,2$ to be in either bin form such dynamical variables

$$P_i = \mathrm{Tr}\,\rho\left[\sum_\alpha |i\alpha\rangle\langle i\alpha|\right] , \tag{7}$$

where ρ is the density matrix of the entire system. As long as the time scale τ_p which characterizes the variation of the populations is long, their evolution can be well described in terms of time-local rate equations (incoherent dynamics). When this is not the case, one may follow the newly developed methods of Ref. 2 to introduce into the description higher degree of coherent dynamics. The first stage in this systematic expansion around the incoherent description is achieved by enlarging the list of dynamical variables and including also the coarse-grained single quantum coherences σ_{12} and σ_{21}. They are defined as the expectation values of the operators.

$$S_{12} = \frac{1}{\Omega}\sum_{\alpha\beta} |1\alpha\rangle V_{\alpha\beta}\langle 2\beta|$$

and

$$S_{21} = S_{12}^\dagger , \tag{8}$$

where

$$\Omega = \left(\frac{d_1+d_2}{d_1 d_2}\right)^{1/2}\left(\sum_{\alpha\beta} |V_{\alpha\beta}|^2\right)^{1/2} . \tag{8a}$$

The coherences are characterized by a dephasing time constant $\tau_d (=\Gamma_2^{-1})$. As long as τ_p and τ_d are larger than all other time scales in the system τ_c, one can derive time local reduced equations of motion (REM) which have the following form:

$$\frac{d}{dt}\Delta P = -i\Omega(\sigma_{21}-\sigma_{12}), \tag{9a}$$

$$\frac{d}{dt}\sigma_{12} = i\Omega(\Delta P - \Delta P^{(0)}) - (i\omega + \Gamma_2)\sigma_{12}, \tag{9b}$$

where

$$\sigma_{21} = \sigma_{12}^* , \tag{9c}$$

$$\Delta P = \tfrac{1}{2}(P_1 - P_2); \quad \frac{d}{dt}(P_1+P_2) = 0, \tag{9d}$$

and

$$\Delta P^{(0)} = \frac{1}{2}\,\frac{d_1-d_2}{d_1+d_2} . \tag{10}$$

Γ_2 is again the T_2 (dephasing) time constant and ω is the mean energy difference between the bins 1 and 2.

It should be emphasized that Eq. (9a) is an *identity* which results from the definition of the coherence variables. Equation (9b) on the other hand is an approximation to the exact equation for $d\sigma_{12}/dt$. It is obtained from the exact REM by expanding its coefficients to *first order* in Ω. In this approximation, the dephasing rate Γ_2 and the mean energy difference ω are determined exclusively by the long time behavior of the correlation function

$$I(t) \equiv \sum_{\alpha\beta} |V_{\alpha\beta}|^2 \exp[i(\epsilon_{1\alpha}-\epsilon_{2\beta})t]\Big/\sum_{\alpha\beta}|V_{\alpha\beta}|^2 \cong \exp[(i\omega - \Gamma_2)t]. \tag{11}$$

Thus, Γ_2 and ω depend on the spectral range of the interaction (i.e., the frequency range of $\epsilon_{1\alpha}-\epsilon_{2\beta}$ for which $V_{\alpha\beta}$ is finite) and not on the magnitude of $V_{\alpha\beta}$. Therefore, in this approximation Γ_2 and Ω are independent parameters of the theory.

The resemblance between the REM [Eq. (9)] and the OBE [Eq. (1)] is striking. The solution of the REM

[Eq. (9)] relaxes to the steady state [Eq. (3)] after sufficiently long time [property (*i*)].

The REM, as well as the OBE contain a dephasing mechanism which arises from our loss of information in the description (i.e., reduction). When the dephasing rate is small, the time evolution is coherent whereas when it becomes large enough, the time evolution becomes incoherent. That is, in the limit $\Gamma_2 \gg \Omega$, the REM reduce to a simple rate equation [property (ii)]. Here it reads

$$\frac{d}{dt}\,\Delta P = -\,\frac{2\Gamma_2\,\Omega^2}{\omega^2+\Gamma_2^2}\,(\Delta P-\Delta P^{(0)}). \tag{12}$$

Note also that the parameters which appear in the REM can be related to the assumed slow time scales τ_P and τ_d, but τ_c does not appear in the REM. The variables in the REM, being coarse-grained quantities defined in terms of the density matrix ρ, should fulfill similar requirements to those imposed on the variables of the OBE [EQS. (5)]. In the present context, they read

$$P_1+P_2=1, \tag{13a}$$

$$|\Delta P| \le \tfrac{1}{2}, \tag{13b}$$

$$|\sigma_{12}|^2 \le \tfrac{1}{2}(d_1 d_2)^{1/2} P_1 P_2. \tag{13c}$$

The important difference between the two sets of equations is that property (iii) of the OBE *is not automatically fulfilled* by the REM [Eq. (9)]. In particular, we shall show that in order that Eq. (13b) should be observed (positive values for P_1 and P_2), the range of parameters Γ_2, Ω, and $\Delta P^{(0)}$ must be restricted severely.

In order to simplify the argument, let us take a system with two degenerate bins, that is $\omega=0$. In this case only the imaginary part of σ_{21} is of interest and let

$$S \equiv \mathrm{Im}\,\sigma_{21}.$$

The REM read now

$$\frac{d}{dt}\Delta P = 2\Omega S, \tag{14a}$$

$$\frac{d}{dt}S = -\Omega(\Delta P-\Delta P^{(0)}) - \Gamma_2 S, \tag{14b}$$

$$P_1+P_2=1. \tag{14c}$$

The initial conditions will be $\Delta P(0)=1/2$, $[P_1(0)=1]$, and $S(0)=0$. We shall also assume $d_2 \ge d_1$, which is typical of most cases of interest.

It is instructive to study the solution of Eq. (14) in the $(\Delta P, S)$ plane. Dividing Eq. (14b) by Eq. (14a) we get

$$\frac{dS}{d\Delta P} = \frac{-\Omega(\Delta P-\Delta P^{(0)})-\Gamma_2 S}{2\Omega S}. \tag{15}$$

The lines $dS=0$ and $d\Delta P=0$ are shown in Fig. 2 by dashed lines. Their intersection defines the singular solution of the equation, namely $S=0$ and $\Delta P=\Delta P^{(0)}$. This is the equilibrium point to which the solutions will approach asymptotically. The line $dS=0$ is of particular significance since in its vicinity one can solve S from Eq. (14b). Upon subsituting this solution in Eq. (14a), one obtains the rate equation (13) (with $\omega=0$).

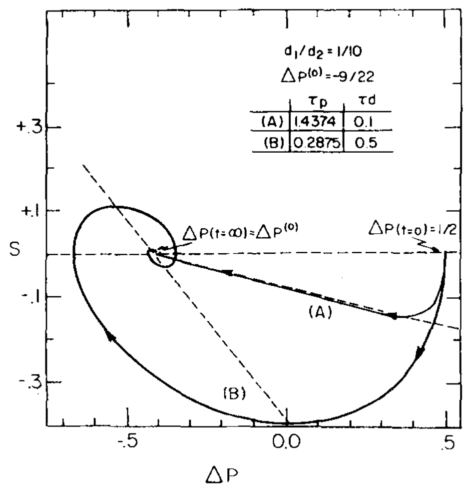

FIG. 2. Two typical solutions of the REM in the $(\Delta P, S)$ plane. The parameters for which these solutions are obtained are indicated in the figure. The arrows mark the direction of increasing time.

The solution of Eqs. (14) can be easily obtained:

$$\Delta P(t) = \Delta P^{(0)} + (\tfrac{1}{2}-\Delta P^{(0)})\,e^{-t/2\tau_d} \times\left[\cosh\left(\chi\,\frac{t}{2\tau_d}\right)+\frac{1}{\chi}\,\sinh\left(\chi\,\frac{t}{2\tau_d}\right)\right], \tag{16}$$

with

$$\tau_d = 1/\Gamma_2, \tag{17a}$$

$$\tau_p = (2\Omega^2/\Gamma_2)^{-1}, \tag{17b}$$

$$\chi = \left(1-4\,\frac{\tau_d}{\tau_p}\right)^{1/2}. \tag{17c}$$

Equation (16) is valid also when χ takes imaginary values.

Two typical solutions are shown in Fig. 2, where one sees that the condition (13b) (that $|\Delta P| \le 1/2$) is not fulfilled by the solution marked B. It can be easily shown from Eq. (16) that Eq. (13b) is satisfied only if

$$\frac{\Gamma_2^2}{2\Omega^2} \equiv \frac{\tau_p}{\tau_d} \ge \frac{4[\log(d_1/d_2)]^2}{\pi^2+[\log(d_1/d_2)]^2}. \tag{18}$$

This is the central result of this note. It proves the statement made above that the probabilities obtained from solving the REM do not necessarily behave as probabilities should. If the parameters in the REM violate the condition (18), one obtains numerical values for the probabilities which do not lie in the interval (0., 1.). This statement which was proved here analytically, for a simple case is correct for more complicated REM. Numerical results show that the probabilities attain unphysical values when the mean interaction becomes too large relative to the relevant dephasing rates.

This phenomenon limits severely the applicability of the REM [Eq. (9)] in most cases. In order to get a clearer view of the situation we shall now investigate the condition (18) in two limiting situations.

(a) $d_1 \sim d_2\,(\Delta P^{(0)} \sim 0)$. In this case, the REM [Eq. (9)] reduce to the OBE [Eq. (1)] with $\Gamma_1=0$ and $\omega=0$. In this limit, Eq. (18) does not pose any restriction on the parameters, and all the solutions of Eq. (9) are acceptable.

(b) $d_2 \gg d_1 (\Delta P^{(0)} \sim -\frac{1}{2})$. This is the case most frequently met in the application of the REM.[2,3] Here the condition (18) can be approximated by

$$\Gamma_2^2 \geq 8\Omega^2. \tag{18a}$$

Under such conditions, the solution of the REM displays the over-damped approach to equilibrium, where χ [Eq. (17c)] is real. This case is illustrated by the curve marked A in Fig. 2. The condition (18a) relaxes somewhat the strong inequality ($\Gamma_2 \gg \Omega$), which renders the simple rate Eq. (12) applicable.

When $\Omega > \Gamma$, one should question the validity of Eq. (9b), and especially the applicability of Eq. (11) as the definition of the dephasing rate. In these circumstances, the dephasing is not merely due to the coarse gained description of the spectrum, but is also affected by the mixing of states from the two bins due to the presence of the interaction. Including these effects in the REM by expanding the coefficients to *second order* in Ω modifies Eq. (9b) to read

$$\frac{d}{dt}\sigma_{12} = i\Omega(\Delta P - \Delta P^{(0)}) - (i\omega + \Gamma_2)\sigma_{12} - \frac{\Omega^2}{\omega^2 + \Gamma_2^2} \times 2i\,\mathrm{Im}[\Gamma_2 + i\omega)\sigma_{12}]. \tag{9b$'$}$$

When the bins are degenerate ($\omega = 0$) we obtain an equation which looks like Eq. (14b) with Γ_2 replaced by

$$\Gamma_2^{eff} \equiv \Gamma_2 \cdot \left[1 + 2\frac{\Omega^2}{\Gamma_2^2}\right]. \tag{19}$$

One can easily show that for all values of Γ_2 and Ω

$$(\Gamma_2^{eff})^2 > 8\Omega^2. \tag{20}$$

Hence, the modified form of the effective dephasing rate guarantees the acceptibility of the solutions of the REM.

The conclusion that should be drawn from the present study is that the mathematical structure of REM of the type presented in Eq. (9) does not automatically guarantee a physically acceptable solution for an arbitrary choice of the dephasing terms. Rather, (and in contrast with the OBE or the simple rate equations) the dephasing terms should be evaluated carefully in order to obtain a consistent description of the dephasing processes.

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