Generalized Bloch equations for decaying systems

J. Pöttinger* and K. Lendi
Institute of Physical Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland
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The well-known magnetic or optical Bloch equations are extended to the case of unstable systems such as, e.g., spontaneously decaying particles and molecules undergoing chemical reactions or decaying from excited states back to states other than those involved in resonance. The modified equations are derived from a general theory of irreversible processes where quantum Markovian master equations and the corresponding completely positive dynamical semigroups dictate the time evolution of density operators. The results are of particular importance in those situations where decay occurs level-selectively and all relaxation and decay constants are of comparable order of magnitude. The obtained generalized Bloch equations are of direct applicability to problems of time-resolved magnetic or optical resonance spectroscopy.

I. INTRODUCTION

The usefulness of Bloch equations for the description of magnetic resonance phenomena is well known,[1–4] and analogous equations are also of wide use in optical spectroscopy.[5–8] Strictly speaking, they are valid only for stable two-level systems whereas in many situations the system of interest is unstable, e.g., when particles decay spontaneously or molecules take part in chemical reactions, or when there is decay from excited states back to states other than those involved in resonance. Although some approximate approaches have been proposed from an experimental point of view,[9–11] the problem has never been solved in a satisfactory way. Theoretically, quite different methods are available for a treatment of similar problems, ranging from wave-function descriptions of closed systems[12] to quantum-statistical density-operator formalisms for open systems.[13–15] In the latter case, the main difficulty consists of finding a time evolution for the density operator such that for all times the von Neumann conditions of positivity and trace preservation are fulfilled. If this is not guaranteed very strange inconsistencies may arise.[16,17] The only tractable theory of irreversible processes which pays full attention to these difficulties is based on quantum Markovian master equations[18–24] and on an associated powerful structure theorem[23,25,26] which entirely determines the infinitesimal generator of a completely positive quantum-dynamical semigroup. We will not repeat details, merely referring the interested reader to the review articles by Gorini *et al.*,[25] by Spohn and Lebowitz,[18] and the literature cited therein.

II. THEORETICAL BACKGROUND

A. Quantum-dynamical semigroups

For an open quantum system Q coupled to a reservoir R in a Markovian approximation, there exist mathematically well-defined techniques[18,20–22] to derive an appropriate master equation for the density operator $\rho(t)$ which describes the generalized states of Q and acts on a corresponding Hilbert space $\mathscr{H}$. Since we envisage the treatment of magnetic-resonance phenomena in decaying spin systems it will be sufficient to consider finite-dimensional spaces with $\dim\mathscr{H}=N$ (N-level systems). We denote by $\mathscr{B}(\mathscr{H})$ the algebra of bounded linear operators on $\mathscr{H}$. Under the trace metric $||C||=\mathrm{Tr}(C^*C)^{1/2}$, $C\in\mathscr{B}(\mathscr{H})$, $\mathscr{B}(\mathscr{H})$ is a Banach space. Then, we introduce the subset $\mathscr{S}(\mathscr{H})\subset\mathscr{B}(\mathscr{H})$ containing all density operators $\rho=\rho^*$ with $\mathrm{Tr}\rho=1$ and $\rho\geq 0$.

If the time evolution of Q is governed by

$$\rho(t)=G(t)\rho(0)\ , \tag{1}$$

$G=\{G(t):\ t\geq 0\}$ is called a positive quantum-dynamical semigroup, if it fulfills the following requirements:

(a) $G(t)$ is linear, $t\geq 0$.

(b) $G(t)$ is positive, i.e., $\rho\geq 0$ implies

$$G(t)\rho\geq 0,\ \forall\rho\in\mathscr{S}(\mathscr{H}),\ t\geq 0\ .$$

(c) $G(t)$ preserves the trace, i.e.,

$$\mathrm{Tr}[G(t)\rho]=\mathrm{Tr}\rho=1,\ \forall\rho\in\mathscr{S}(\mathscr{H}),\ t\geq 0\ .$$

(d) $G(t)$ is strongly continuous, i.e.,

$$\lim_{t\downarrow s}||G(t)\rho-G(s)\rho||=0,\ \forall\rho\in\mathscr{S}(\mathscr{H}),\ t,s\geq 0\ .$$

(e) G is a semigroup, i.e.,

$$G(t+s)=G(t)G(s),\ t,s\geq 0\ .$$

Under these conditions it follows from the Hille-Yosida theorem[27] that one may write

$$G(t)=\exp(Lt)\ , \tag{2}$$

or a differential equation corresponding to (1),

$$\dot{\rho}(t)=L\rho(t)\ , \tag{3}$$

where the dot denotes the partial derivative with respect to time and L is the (time-independent) infinitesimal generator of the one-parameter semigroup G. Linearity, condition (a), is required because the time evolution must preserve the convexity properties of the state space.

Again, it must be emphasized that conditions (b) and (c) are indispensable for any time evolution of density operators which have to satisfy the von Neumann axioms[28] required by quantum theory, and conditions (d) and (e) formalize the mathematical existence and properties of the Markovian limit as obtained from a general master equation by a weak- or singular-coupling assumption.[18]

Of course, for any applications Eq. (3) is only useful if the detailed mathematical structure of the generator L is known and can be related to characteristics of the open quantum system such as, e.g., a Hamiltonian and various relaxation processes. In fact, L describes a rather general, mixed dynamics comprising reversible and irreversible processes. Now, Gorini, Kossakowski and Sudarshan[23] have proven the following important structural theorem.

Theorem. L is the generator of a completely positive quantum dynamical semigroup, if and only if it has the following structure (in the Schrödinger representation):

$$L\rho=-i[H,\rho]+\tfrac{1}{2}\sum_{i,j=1}^{N^2-1} a_{ij}\{[F_i,\rho F_j^*]+[F_i\rho,F_j^*]\} , \quad (4)$$

where

$$H=H^*, \quad \mathrm{Tr}(H)=0 , \quad (5)$$

$$\mathrm{Tr}(F_i)=0, \quad \mathrm{Tr}(F_iF_j^*)=\delta_{ij} , \quad i,j=1,\ldots,N^2-1 , \quad (6)$$

$$\underline{A}=\{a_{ij}\}\geq 0, \quad i,j=1,\ldots,N^2-1 . \quad (7)$$

Here, H is the Hamiltonian for the open quantum system including the energy shifts due to the interaction with the reservoir. The positive semidefiniteness of the matrix $\underline{A}$ of coefficients a_{ij} in (4) is a powerful statement on the range of admitted values of physical parameters which can be cast into a set of inequalities among them. For example, the well-known and experimentally well-established relation

$$T_{\parallel}\geq \tfrac{1}{2}T_{\perp} \quad (8)$$

for the longitudinal and transverse relaxation times in magnetic resonance (spin-$\frac{1}{2}$ systems) is a strict consequence[23] of (7).

For physically interesting situations time evolution drives the system towards a unique final destination state ρ_0,

$$\lim_{t\to\infty} G(t)\rho=\rho_0 , \quad (9)$$

for all $\rho\in\mathscr{S}(\mathscr{H})$. This class of completely positive semigroups is called "uniquely relaxing."[29]

For further general details of the dynamical semigroup aspect of irreversible processes the reader is referred to the review by Spohn and Lebowitz.[18]

As a preparation for the derivation of Bloch equations for decaying spin-$\frac{1}{2}$ systems it is first necessary to derive some general results on the time evolution of a three-level system as done in the next section.

B. Time evolution of a three-level system

We consider a three-level system with Hilbert space $\mathscr{H}=C^3$ and choose a formal spin-1 treatment.[30] As required by the structure theorem in II A, it will be necessary to explicitly construct an appropriate operator set $\{F_i \mid i=1,2,\ldots,8\}$ which in terms of

$$P_{ik}=|i\rangle\langle k| , \quad i,k=1,2,3 , \quad (10)$$

is given in Hermitian form by

$$\begin{aligned} &F_1=P_{12}+P_{21}, \quad F_5=-i(P_{13}-P_{31}) ,\\ &F_2=-i(P_{12}-P_{21}), \quad F_6=P_{23}+P_{32} ,\\ &F_3=P_{11}-P_{22}, \quad F_7=-i(P_{23}-P_{32}) ,\\ &F_4=P_{13}+P_{31}, \quad F_8=\frac{1}{\sqrt{3}}(P_{11}+P_{22}-2P_{33}) . \end{aligned} \quad (11)$$

These rules can easily be extended to N dimensions. The unit operator is $F_0=P_{11}+P_{22}+P_{33}$, and the list of algebraic relations needed for further calculations is as follows $(i,j=1,2,\ldots,8)$:

$$F_i=F_i^*, \quad \mathrm{Tr}(F_i)=0, \quad \mathrm{Tr}(F_iF_j)=2\delta_{ij} , \quad (12)$$

$$[F_i,F_j]=2i\sum_{k=1}^{8} f_{ijk}F_k , \quad (13)$$

$$\{F_i,F_j\}=\tfrac{4}{3}F_0\delta_{ij}+2\sum_{k=1}^{8} d_{ijk}F_k , \quad (14)$$

where $\{.,.\}$ denotes the anticommutator. The f_{ijk}'s are the completely antisymmetric (with respect to interchange of any pair of indices) and the d_{ijk}'s the completely symmetric structure constants of the Lie algebra of the F_i's.

The density operator ρ is conveniently decomposed into

$$\rho(t)=\tfrac{1}{3}F_0+\tfrac{1}{2}\sum_{k=1}^{8} v_k(t)F_k , \quad (15)$$

such that the components of the coherence vector for given ρ are obtained by

$$v_k(t)=\mathrm{Tr}[F_k\rho(t)] , \quad (16)$$

and the Hamiltonian may be written as

$$H=H^*=\sum_{k=1}^{8} h_kF_k , \quad (17)$$

where the h_k's are real. Choosing for $\underline{A}$ the special representation $\underline{A}=\underline{B}+\underline{C}$, where $\underline{B}$ is a real symmetric matrix with zero diagonal elements, and $\underline{C}$ is Hermitian with purely complex off-diagonal elements, and inserting (15) in (4), yields eight coupled differential equations for the coherence vector[31]

$$\mathbf{V}(t)=(v_1(t),v_2(t),\ldots,v_8(t))^T , \quad (18)$$

written in compact notation as

$$\dot{\mathbf{V}}(t)=(\underline{H}-\underline{\Gamma})[\mathbf{V}(t)-\mathbf{V}^0] . \quad (19)$$

Here, $\underline{H}$ is the Hamiltonian part, $\underline{\Gamma}=\underline{\Gamma}^{(b)}+\underline{\Gamma}^{(c)}$ the relaxation part, and $\mathbf{V}^0$ the asymptotically stationary state. The matrix elements of $\underline{H}$ and $\underline{\Gamma}$ are

$$h_{kn}=2\sum_{i=1}^{8} h_i f_{ink} , \quad (20)$$

$$\gamma_{kn}^{(b)}=4\sum_{\substack{i,m=1\\j>i}}^{8}{}' b_{ij}(f_{imn}f_{jmk}+f_{jmn}f_{imk}) , \tag{21}$$

$$\gamma_{kn}^{(c)}=4\sum_{i,m=1}^{8}\left[c_{ii}f_{imk}f_{imn}+\sum_{\substack{j=1\\j>i}}^{8}c_{ij}(f_{imk}d_{jmn}-f_{jmk}d_{imn})\right]$$
$$+b_{38}\sum_{m=1}^{8}(f_{3mn}f_{8mk}+f_{8mn}f_{3mk}) . \tag{22}$$

The prime in the summation (21) indicates that the term proportional to b_{38} has been omitted and incorporated in (22). Finally, the stationary solution $\mathbf{V}^0$ is obtained from

$$(\underline{H}-\underline{\Gamma})\mathbf{V}^0=\mathbf{Q} , \tag{23}$$

where the components $\{q_n\}$ of $\mathbf{Q}$ are given by

$$q_n=\tfrac{16}{3}\sum_{\substack{i=1\\j>i}}^{8}c_{ij}f_{ijn} . \tag{24}$$

Thus, apart from positive definiteness, the elements of the matrix $\underline{A}$ have to fulfill the condition that $(\underline{H}$-$\underline{\Gamma})$ be nonsingular in order to guarantee the existence of a unique solution for $\mathbf{V}^0$ in (23), in which case only the associated semigroup is uniquely relaxing.

III. BLOCH EQUATIONS WITH DECAY

A. Static field case

The derivation of Bloch equations including decay of the system will be formulated in such a way that, in the limit of no decay, one gets the familiar equations for a spin-$\frac{1}{2}$ system. It is instructive first to see how in this three-level version, where the third level is reserved for the decay products, ordinary Bloch equations for stable systems are obtained by just letting the third level play a dummy role. For this purpose the relevant components of the coherence vector, $v_1(t)$, $v_2(t)$ and $v_3(t)$ can directly be related to the magnetization (divided by the Bohr magneton) since, F_1, F_2 and F_3 are simply the Pauli matrices trivially complemented by a third dimension.

To keep a familiar notation we write

$$\mathbf{M}(t)=(M_x(t),M_y(t),M_z(t))^T , \tag{25}$$

where $M_x=v_1$, $M_y=v_2$, and $M_z=v_3$ is understood. Then, the appropriate elements of the matrix $\underline{A}$ in (7) and $\underline{H}$ in (5) are set equal to zero,

$$a_{ij}=0,\ \ 4\le i,j\le 8 ,$$
$$h_i=0,\ \ 4\le i\le 8 , \tag{26}$$

and the magnetization obeys the equation

$$\dot{\mathbf{M}}(t)=(\underline{H}-\underline{\Gamma})[\mathbf{M}(t)-\mathbf{M}^0] \tag{27}$$

with the explicit matrices

$$\underline{H}=2\begin{bmatrix}0 & -h_3 & h_2\\ h_3 & 0 & -h_1\\ -h_2 & h_1 & 0\end{bmatrix} , \tag{28}$$

$$\underline{\Gamma}^{(b)}=4\begin{bmatrix}0 & b_{12} & b_{13}\\ b_{12} & 0 & b_{23}\\ b_{13} & b_{23} & 0\end{bmatrix} , \tag{29}$$

$$\underline{\Gamma}^{(c)}=4\begin{bmatrix}c_{22}+c_{33} & 0 & 0\\ 0 & c_{11}+c_{33} & 0\\ 0 & 0 & c_{11}+c_{22}\end{bmatrix} , \tag{30}$$

where $\mathbf{M}^0=(M_x^0,M_y^0,M_z^0)^T$ is a solution of

$$(\underline{H}-\underline{\Gamma})\mathbf{M}^0=\mathbf{Q}=8(c_{23},-c_{13},c_{12})^T . \tag{31}$$

All these elements follow from (20), (21), (22), and (24). The Bloch equations for an anisotropic spin-$\frac{1}{2}$—system result from (27) when considering the more special case[23] $\Gamma^{(b)}=0$. Then, due to the positive-semidefinite property of the matrix $\underline{A}$ (see Appendix A), the diagonal relaxation parameters

$$\gamma_x=4(c_{22}+c_{33}) ,$$
$$\gamma_y=4(c_{11}+c_{33}) , \tag{32}$$
$$\gamma_z=4(c_{11}+c_{22}) ,$$

say, are restricted by the inequalities

$$8c_{11}=\gamma_y+\gamma_z-\gamma_x\ge 0 ,$$
$$8c_{22}=\gamma_x+\gamma_z-\gamma_y\ge 0 , \tag{33}$$
$$8c_{33}=\gamma_x+\gamma_y-\gamma_z\ge 0 ,$$

and, furthermore, in terms of a real vector $\mathbf{z}=(z_1,z_2,z_3)^T$, the off-diagonal elements or, equivalently, certain linear combinations of the asymptotically stationary magnetization components of $\mathbf{M}^0$, as obtained from (31), are connected to the inverse relaxation times through the following relations:

$$c_{12}=(c_{11}c_{22})^{1/2}z_3 ,$$
$$c_{13}=(c_{11}c_{33})^{1/2}z_2 , \tag{34}$$
$$c_{23}=(c_{22}c_{33})^{1/2}z_1 ,$$

where

$$0\le z_1^2+z_2^2+z_3^3\le 1 . \tag{35}$$

This agrees with the results of Ref. 23, where some further details may be found. We note, in particular, that for axially symmetric systems $\gamma_x=\gamma_y\equiv 1/T_\perp$ holds and, with the definition $\gamma_z\equiv 1/T_{||}$, the third of Eqs. (33) yields the relation well known in magnetic resonance,

$$T_{||}\ge\tfrac{1}{2}T_\perp . \tag{36}$$

It must be stressed that this type of useful inequality is obtained directly via the structural theorem for the generator L and, consequently, without solving differential equations, whereas working with purely phenomenologically derived master equations first requires their solution and then, from physical arguments one may deduce similar inequalities. This clearly shows a particular advantage of using completely positive dynamical semigroups.

We now return to the genuine three-level case and consider the simple model of an open system as in Fig. 1, where the upper levels $|\alpha\rangle$ $(\equiv|1\rangle)$ and $|\beta\rangle$ $(\equiv|2\rangle)$ are spin-down and spin-up states. The solid arrow Γ represents the partly irreversible transitions described by the matrix elements in (21) and (22), whereas the dotted arrow stands for the Hamiltonian evolution given by (20). H does not couple to the third level and only irreversible decay from $|\alpha\rangle$ with rate k_α and from $|\beta\rangle$ with k_β to the final state $|3\rangle$ is considered. Thus, e.g., in chemical systems a species X may undergo a first-order reaction

$$X \underset{k_\alpha,k_\beta}{\rightrightarrows} \sum_{i=1}^{m} \nu_i P_i \tag{37}$$

to m final diamagnetic products P_i with stoichiometric weights ν_i, or similarly, react with a second species Y under pseudo-first-order conditions,

$$X+Y \underset{k_\alpha,k_\beta}{\rightrightarrows} \sum_{i=1}^{m} \nu_i P_i, \quad Y \cong \text{const} . \tag{38}$$

It is therefore natural to introduce, in addition to the magnetization, as fourth observable, the normalized particle number (or concentration)

$$\begin{aligned} N(t) &= \mathrm{Tr}[(P_{11}+P_{22})\rho(t)] \\ &= \frac{1}{\sqrt{3}} \mathrm{Tr}\left[\left[\frac{2}{\sqrt{3}}F_0+F_8\right]\rho(t)\right] . \end{aligned} \tag{39}$$

It follows from this definition that $0 \le N(t) \le 1$ and $N(0)=1$. Thus, the components v_1, v_2, v_3, and v_8 of the coherence vector are the relevant quantities where v_8 is related to N by

$$N=(v_8+2/\sqrt{3})/\sqrt{3} .$$

A careful inspection of all matrix elements of Γ shows that the dynamics of these four components is decoupled from the remaining ones by choosing

$$a_{ij}=0, \quad 1 \le i \le 3 < j \le 7 \text{ and } 4 \le i \le 8 = j , \tag{40}$$

$$h_i=0, \quad 4 \le i \le 7 . \tag{41}$$

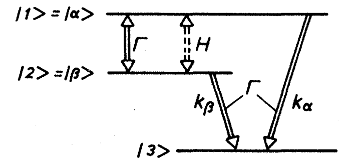

FIG. 1. Open three-level system with reversible (H) and irreversible (Γ) contributions to the infinitesimal generator of the dynamics of the coherence vector.

To adapt this still quite general choice for $\underline{A}$ to the particular model of Fig. 1, we look at the relaxation of the individual diagonal elements of the density matrix and find the relations

$$\begin{aligned} 8c_{45} &= 4(c_{44}+c_{55}) = k_\alpha , \\ 8c_{67} &= 4(c_{66}+c_{77}) = k_\beta , \end{aligned} \tag{42}$$

which force the matrix $\underline{A}$ into a block structure (see Appendix A). The final results will depend essentially upon the average and the difference of the decay rates,

$$\bar{k}=\tfrac{1}{2}(k_\alpha+k_\beta), \quad \overline{\Delta k}=\tfrac{1}{2}(k_\alpha-k_\beta) . \tag{43}$$

Again, we put

$$\begin{aligned} \mathbf{M}(t) &= (v_1(t),v_2(t),v_3(t))^T \\ &\equiv (M_x(t),M_y(t),M_z(t))^T \end{aligned}$$

and form a four-component vector

$$\mathbf{R}(t)=(M_x(t),M_y(t),M_z(t),N(t))^T , \tag{44}$$

which obeys the differential equation

$$\dot{\mathbf{R}}(t)=(\underline{H}-\underline{\Gamma})[\mathbf{R}(t)-\mathbf{R}_D^0] , \tag{45}$$

where $\mathbf{R}_D^0$ is now the asymptotically stationary coherence vector including decay, in contrast to the earlier introduced $\mathbf{M}^0$ in Eq. (31). The explicit calculations yield the 4×4 matrix

$$\underline{H}-\underline{\Gamma}=\begin{bmatrix} -(\gamma_x+\bar{k}) & -2h_3+\frac{4}{\sqrt{3}}c_{38}-4b_{12} & 2h_2-\frac{4}{\sqrt{3}}c_{28}-4b_{13} & -8c_{23} \\ 2h_3-\frac{4}{\sqrt{3}}c_{38}-4b_{12} & -(\gamma_y+\bar{k}) & -2h_1+\frac{4}{\sqrt{3}}c_{18}-4b_{23} & 8c_{13} \\ -2h_2+\frac{4}{\sqrt{3}}c_{28}-4b_{13} & 2h_1-\frac{4}{\sqrt{3}}c_{18}-4b_{23} & -(\gamma_z+\bar{k}) & -8c_{12}-\overline{\Delta k} \\ 0 & 0 & -\overline{\Delta k} & -\bar{k} \end{bmatrix} . \tag{46}$$

It may be verified by direct computation that $\mathbf{R}_D^0=0$ is the only solution to $(\underline{H}-\underline{\Gamma})\mathbf{R}_D^0=\mathbf{Q}$, where $\mathbf{Q}$ is found to be

$$\mathbf{Q}=(\tfrac{16}{3}c_{23}\,,-\tfrac{16}{3}c_{13},\tfrac{16}{3}c_{12}+\tfrac{2}{3}\overline{\Delta k},\tfrac{2}{3}\bar{k})^T . \tag{47}$$

Physically, this expresses the fact that, after complete irreversible decay to the diamagnetic products, there are neither any magnetization nor any paramagnetic particles left. Further inspection of the matrix $\underline{H}-\underline{\Gamma}$ shows that c_{18}, c_{28}, and c_{38} can be reabsorbed in the definition of h_1, h_2, and h_3 and, consequently, one may set $c_{18}=c_{28}=c_{38}=0$.

Since, for the case of no decay, the well-known Bloch equations should be obtained, one has, according to the considerations at the beginning of this section, where $\underline{\Gamma}^{(b)}$ has been put equal to zero, $b_{13}=b_{23}=b_{12}=0$. We choose the magnetic field in the z direction and put $2h_3=\omega_0$ ($h_1=h_2=0$), where ω_0 is the Larmor frequency, and parametrize, for convenience and in agreement with Eq. (31), the constants c_{12}, c_{13}, and c_{23} by $\mathbf{M}^0$, i.e., in terms of the stationary magnetic properties of the system in the absence of decay. By all foregoing reductions one arrives at the simplest nontrivial generalization of Bloch equations for decaying systems, compatible with a time evolution given by a completely positive-dynamical semigroup:

$$\begin{aligned}
\dot{M}_x(t)&=-\left[\frac{1}{T_x}+\bar{k}\right]M_x(t)-\omega_0 M_y(t)\\
&\quad+\left[\frac{M_x^0}{T_x}+\omega_0 M_y^0\right]N(t)\,,\\
\dot{M}_y(t)&=+\omega_0 M_x(t)-\left[\frac{1}{T_y}+\bar{k}\right]M_y(t)\\
&\quad+\left[\frac{M_y^0}{T_y}-\omega_0 M_x^0\right]N(t)\,,\\
\dot{M}_z(t)&=-\left[\frac{1}{T_z}+\bar{k}\right]M_z(t)+\left[\frac{M_z^0}{T_z}-\overline{\Delta k}\right]N(t)\,,\\
\dot{N}(t)&=-\overline{\Delta k}\,M_z(t)-\bar{k}N(t)\,,
\end{aligned} \tag{48}$$

where the relaxation times

$$T_i=\frac{1}{\gamma_i},\quad i=x,y,z \tag{49}$$

have been introduced. The first three equations would coincide with those proposed by Verma and Fessenden,[9] but only for first-order decay and $\overline{\Delta k}=0$. Spin-selective decay, i.e., $k_\alpha \neq k_\beta$, enters through the difference $\overline{\Delta k}$ appearing in the last two coupled equations. Qualitatively, the solution for $N(t)$ will depend on $\overline{\Delta k}$ such that $M_x(t)$ as well as $M_y(t)$ will also depend upon this quantity. The somewhat complicated general solutions, as found by standard Laplace transform, will be given in Appendix B.

B. Alternating field case

The derivation of Bloch equations with decay in presence of a static and an alternating classical field will be given, as far as possible, along the lines of Sec. III A. For the model of Fig. 1 we choose a Hamiltonian

$$H(t)=H_0+W(t)\,, \tag{50}$$

where, again, the static field is in the z direction, and in terms of the Larmor frequency ω_0, we can write

$$H_0=\frac{\omega_0}{2}F_3\,, \tag{51}$$

and the alternating field $W(t)$ may be of the form

$$W(t)=W\cos(\omega t)\,, \tag{52}$$

where, in the basis $\{|1\rangle,|2\rangle,|3\rangle\}$ (see Fig. 1) W connects only level $|1\rangle$ with level $|2\rangle$. This conforms to the conventional arrangement in magnetic resonance with the alternating field being perpendicular to the static one. The field strength ω_1 is simply given by the off-diagonal matrix element

$$\omega_1=\langle 1|W|2\rangle\,, \tag{53}$$

where W has been assumed real, and $W(t)$ may finally be written as

$$W(t)=\omega_1 F_1\cos(\omega t)\,. \tag{54}$$

As usually, for the field strengths of interest, the Bloch-Siegert shift may be neglected,[4,6,32] which means that the action of the alternating field is taken into account in the rotating-wave approximation,

$$W_-(t)=\tfrac{1}{2}\omega_1(P_{12}e^{-i\omega t}+P_{21}e^{i\omega t})\,. \tag{55}$$

As a next step, a transformation to a rotating coordinate system is performed in order to eliminate the explicit time dependence of W_-. This is achieved by introducing a special interaction representation for any operator $O\in\mathscr{B}(\mathscr{H})$, say, through

$$\hat{O}=U(t)OU^*(t)\,. \tag{56}$$

The unitary transformation $U(t)$ is generated by F_3,

$$U(t)=\exp[\tfrac{1}{2}i\omega F_3 t]\,. \tag{57}$$

By direct calculation one verifies that

$$\hat{W}_-=\tfrac{1}{2}\omega_1 F_1\,. \tag{58}$$

Again, the master equation is given by (3) and (4) with an explicitly time-dependent Hamiltonian, but constant matrix $\underline{A}$,[33] leading to a time-dependent Cauchy problem which, in general, may be difficult to solve. However, we try to obtain a time-independent problem after transformation to the rotating frame,

$$\dot{\hat{\rho}}(t)=[\hat{L}_h+\hat{L}_d(t)]\hat{\rho}(t)\,, \tag{59}$$

where

$$\hat{L}_h\hat{\rho}(t)=-i[(\hat{H}_0+\hat{W}_-),\hat{\rho}(t)]+i\frac{\omega}{2}[F_3,\hat{\rho}(t)]\,, \tag{60}$$

$$\hat{L}_d(t)\hat{\rho}(t)=\sum_{i,j=1}^{8}a_{ij}\{[\hat{F}_i(t),\hat{\rho}(t)\hat{F}_j(t)]+[\hat{F}_i(t)\hat{\rho}(t),\hat{F}_j(t)]\}\,, \tag{61}$$

by requiring that $\hat{L}_h+\hat{L}_d(t)$ be time independent. Since, obviously, $[\partial/\partial t,\hat{L}_h]=0$ is already satisfied, we are left with the condition

$$\left[\frac{\partial}{\partial t},\hat{L}_d(t)\right]=0\,. \tag{62}$$

This, again, implies certain restrictions on the matrix elements a_{ij}, as will be shown by the following considerations. First of all, from (56) it follows for the matrix elements of $\hat{\rho}$ that

$$\hat{\rho}_{ij}(t)=g_{ij}(t)\rho_{ij}(t) \ , \tag{63}$$

where we have introduced the abbreviation,

$$g_{ij}(t)=U_{ii}(t)U_{jj}^*(t) \ . \tag{64}$$

Recall that the generator F_3 is diagonal and, consequently, U is also diagonal. Next, denoting the contribution of the dissipative part to the time evolution of $\hat{\rho}$ by $\dot{\hat{\rho}}^{(d)}=\hat{L}_d\hat{\rho}$, we have

$$\dot{\hat{\rho}}_{ij}^{(d)}(t)=g_{ij}(t)\sum_{k,l=1}^{3}(L_d)_{ij}^{kl}\rho_{kl}(t) \ , \tag{65}$$

where the superoperator notation $(L_d)_{ij}^{kl}$ has been used. Equation (65) follows directly from $\hat{L}_d\hat{\rho}=U(L_d\rho)U^*$. The products of the functions $g_{ij}(t)$ have the properties

$$g_{ij}(t)g_{kl}(t)=\begin{cases}1, & i=j,k=l \ ,\\ 1, & i=l,j=k \ ,\\ G_{ijkl}(t), & \text{otherwise} \ ,\end{cases} \tag{66}$$

where $G_{ijkl}(t)$ are functions of time whose properties will not be needed further. With the help of Eqs. (63) and (66), Eq. (65) can be rewritten as

$$\dot{\hat{\rho}}_{ij}^{(d)}(t)=\sum_{k,l=1}^{3}g_{ij}(t)g_{lk}(t)(L_d)_{ij}^{kl}\hat{\rho}_{kl}(t) \ , \tag{67}$$

which is the explicit form of $\dot{\hat{\rho}}^{(d)}=\hat{L}_d\hat{\rho}$ and establishes the relation

$$[\hat{L}_d(t)]_{ij}^{kl}=g_{ij}(t)g_{lk}(t)(L_d)_{ij}^{kl} \ . \tag{68}$$

Thus, the commutator in (62) vanishes only if $g_{ij}(t)g_{lk}(t)=\text{const.}$ for all $i,j,l,k=1,2,\ldots,8$. From (66) it follows that the only nonzero elements of $\hat{L}_d$ are

$$(\hat{L}_d)_{ij}^{kl}=(L_d)_{ij}^{kl}[\delta_{ij}\delta_{kl}(1-\delta_{ik})+\delta_{ik}\delta_{jl}] \ , \tag{69}$$

where δ is the Kronecker symbol. This yields implicitly the restrictions on the a_{ij} coefficients. To get the connection with the components of the coherence vector in the rotating frame one calculates

$$\dot{\hat{v}}_k^{(d)}=\mathrm{Tr}(F_k\dot{\hat{\rho}}^{(d)}) \ . \tag{70}$$

and finds from (11) and Eq. (69) that, e.g.,

$$\dot{\hat{v}}_1^{(d)}=\mathrm{Re}(L_d)_{12}^{12}\hat{v}_1^{(d)}+\mathrm{Im}(L_d)_{12}^{12}\hat{v}_2^{(d)} \ , \tag{71}$$

$$\dot{\hat{v}}_2^{(d)}=\mathrm{Re}(L_d)_{12}^{12}\hat{v}_1^{(d)}-\mathrm{Im}(L_d)_{12}^{12}\hat{v}_2^{(d)} \ , \tag{72}$$

where Re($\cdots$) and Im($\cdots$) denote the real and imaginary parts, respectively, and analogous relations hold for the remaining components. A detailed comparison of the preceding Eqs. (71) and (72) with the general structure of (4) yields the result that the matrix $\underline{A}$ (after rearrangement) must have the following block form:

$$\underline{A}=\begin{pmatrix} c_{11} & a_{12} & 0 & \cdots & & & & \cdots & 0\\ a_{21} & c_{11} & 0 & 0 & & & & & \vdots\\ 0 & 0 & c_{33} & a_{38} & 0 & & & & \\ \vdots & 0 & a_{83} & c_{88} & 0 & 0 & & & \\ & & 0 & 0 & c_{44} & a_{45} & 0 & & \\ & & & 0 & a_{54} & c_{44} & 0 & 0 & \\ & & & & 0 & 0 & c_{66} & a_{67} \\ 0 & \cdots & & & & 0 & a_{76} & c_{66} \end{pmatrix} , \tag{73}$$

where, in agreement with the earlier notation,

$$a_{kl}=b_{kl}+ic_{kl},(b_{kl},c_{kl}\in\mathbb{R},k\neq l) \ .$$

Now, the Bloch equations can be written down by using again Eq. (45) and the matrix $\underline{H}-\underline{\Gamma}$ in (46), but taking into account the following additional requirements. Since $c_{11}=c_{22}$ in (73), we set

$$\begin{aligned}\gamma_x=\gamma_y\equiv\gamma_\perp, \quad \gamma_\perp=\frac{1}{T_\perp}\\ \gamma_z\equiv\gamma_{\|}, \quad \gamma_{\|}=\frac{1}{T_{\|}} \ ,\end{aligned} \tag{74}$$

due to (32). Equation (60) shows that the effective Hamiltonian in the rotating frame is

$$\hat{H}=H_0+\hat{W}_- -\frac{\omega}{2}F_3 \ , \tag{75}$$

and the decomposition (17) yields

$$-2h_3=\omega-\omega_0\equiv\Delta\omega, \quad 2h_1=\omega_1 \ . \tag{76}$$

In this way, one finally obtains the four coupled differential equations referring to the rotating frame,

$$\begin{aligned}\dot{\hat{M}}_x(t)&=-\left[\frac{1}{T_\perp}+\bar{k}\right]\hat{M}_x(t)+\Delta\omega\hat{M}_y(t) \ ,\\ \dot{\hat{M}}_y(t)&=-\Delta\omega\hat{M}_x(t)-\left[\frac{1}{T_\perp}+\bar{k}\right]\hat{M}_y(t)-\omega_1\hat{M}_z(t) \ ,\\ \dot{\hat{M}}_z(t)&=\omega_1\hat{M}_y(t)-\left[\frac{1}{T_{\|}}+\bar{k}\right]\hat{M}_z(t)+\left[\frac{\hat{M}_{\|}^0}{T_{\|}}-\overline{\Delta k}\right]\hat{N}(t) \ ,\\ \dot{\hat{N}}(t)&=-\overline{\Delta k}\,\hat{M}_z(t)-\bar{k}\hat{N}(t) \ ,\end{aligned} \tag{77}$$

where $\hat{M}$ and $\hat{N}$ are defined similarly as in (25) and (39). Note in comparison with the static field case (31) that here $\hat{M}_x^0=\hat{M}_y^0=0$ follows from the special block structure of $\underline{A}$ which reflects the axial symmetry of the system under consideration.

Again, $\hat{M}_{\|}^0$ characterizes the stationary magnetic properties of the system in the absence of decay and can be expressed through the a_{ij}'s [see Eq. (31)]. Since, in general, this parameter will not be separately accessible in an experiment one may take it as an adjustable quantity. The set of Eqs. (77) can be solved by standard methods, as shown in Appendix C, where also analytical solutions for the special case of resonance ($\Delta\omega=0$) are given.

If the system is not axially symmetric Eq. (77) is not applicable but one still may use Eq. (59) whose solutions, however, are extremely difficult to discuss. For an analysis of related problems we refer to Ref. 34.

IV. DISCUSSION

The generalized Bloch equations (77) for a decaying spin-$\frac{1}{2}$ system in comparison with the ordinary Bloch equations in the rotating frame

$$\dot{\hat{M}}_x(t)=-\frac{\hat{M}_x(t)}{T_\perp}+\Delta\omega\hat{M}_y(t)\ ,$$
$$\dot{\hat{M}}_y(t)=-\Delta\omega\hat{M}_x(t)-\frac{\hat{M}_y(t)}{T_\perp}-\omega_1\hat{M}_z(t)\ , \tag{78}$$
$$\dot{\hat{M}}_z(t)=\omega_1\hat{M}_y(t)-\frac{\hat{M}_z(t)-M_{\|}^0}{T_{\|}}\ ,$$

show the following marked features.

(i) The relaxation constants $T_\perp^{-1}$ and $T_{\|}^{-1}$ both are augmented by the average decay constant $\bar{k}=\frac{1}{2}(k_\alpha+k_\beta)$.

(ii) The time derivative of the z component is additionally coupled to the decaying particle density $\hat{N}(t)$ via the difference of the decay constants $\overline{\Delta k}=\frac{1}{2}(k_\alpha-k_\beta)$.

(iii) There is, of course, a fourth extra equation for the particle density governed by the average decay constant $\bar{k}$ and coupled only to the z component of the magnetization, again via the difference $\overline{\Delta k}$.

Evidently, the coupling among the equations is, in general, such that the decay of any one of the magnetization components will depend on $\overline{\Delta k}$. It is only for $k_\alpha=k_\beta$ and, consequently, $\overline{\Delta k}=0$, that Eqs. (77) would coincide with those given by Verma and Fessenden[9,35] but, of course, only in the case of first- or pseudo-first-order decay, whereas in the theory of chemically induced dynamic-spin polarization by Freed and Pedersen[36] the influence of decay has only been taken into account in the equation for $\dot{\hat{M}}_z$.

As long as the spin dynamics is fast in comparison with the decay, the magnetization has enough time to adjust itself to the values obtained from solving ordinary Bloch equations, and the influence of decay will be obtained by just multiplying every magnetization component by the decay law. Thus, the magnetization will vanish in exactly the same way as the particle number does, and no interference between the two types of dynamics will be noticed. On the other hand, for a situation where $\bar{k}$ and $\overline{\Delta k}$ are of the same order of magnitude and, at the same time, $\bar{k}$ and at least the inverse magnetic relaxation time $T_{\|}^{-1}$ is also comparable in magnitude, the deviation from the above case will be most pronounced. In particular, the spin selectivity of decay, i.e., $k_\alpha\neq k_\beta$, should easily be discovered from the solutions which depend essentially on $\overline{\Delta k}$ as seen from Appendix C. Prominent physical examples which perfectly fit these requirements will be found among certain molecular crystals at very low temperature where many different experiments have been performed in order to reveal the selectivity of population and depopulation of the triplet sublevels.[37–44] The general situation may be explained using the particular example of a naphtalene mixed crystal[37] ($C_{10}D_8$:0,2% $C_{10}H_8$) where, after uv excitation of the lowest singlet state and subsequent intersystem crossing, the three triplet sublevels are populated at appreciably different rates due to selection rules. Because of the zero-field splitting parameters D and E the energy spectrum as a function of the external static field H_0 is asymmetric such that, e.g., an ESR transition of 9.4 GHz involves only two levels. In particular, for H_0 in the z direction of the crystal,[37] there is a transition between the upper two levels for $H_0=2.28$ kG, whereas the second transition between the lower two levels is far apart ($H_0=4.41$ kG). In addition, there is decay from both levels by radiationless processes as well as by emission of phosphorescence radiation, but at different rates for each one of them. Thus, to an extremely good approximation, one deals with a decaying two-level system as shown in Fig. 1, and our treatment is well applicable. A comparison with the results of Ref. 37 yields, for this particular case, roughly a ratio $k_\alpha/k_\beta\cong 3$, implying $\bar{k}/\overline{\Delta k}\cong 2$ and, furthermore, $T_{\|}^{-1}/\bar{k}\cong 3$. It is interesting to note that $T_{\|}$ can be varied by changing the temperature or the concentration of the undeuterated component. On the other hand, $T_\perp$ processes in this and similar systems seem to be of the order of microseconds[42,45] and do not play any significant role in the above-mentioned case but only in short-time coherence experiments.

Whether similar favorable conditions can be found, e.g., in spin-selective chemical reactions of radicals or spontaneously decaying particles such as muons in liquids or solids, remains to be shown by experiment. For reacting radical systems, second-order decay processes may play a substantial role[9,36] and the present methods have to be modified in order to take into account this nonlinear type of decay law. In fact, for this purpose, the present linear master equation has to be transformed into a more general stochastic equation of the "birth and death" type[46,47] with appropriate inclusion of the spin degrees of freedom, and this will be the aim of subsequent investigations.

In conclusion, we have shown that the mathematically rigorous concept of completely positive dynamical semigroups for Markovian master equations and the corresponding time evolution of density operators allows a derivation of Bloch-type equations generalized to include spin-selective first- or pseudo-first-order decay of the spin system. The results are able to describe a complicated dynamical behavior where, in the most general case, spin dynamics and decay cannot be factorized and separated from each other. The obtained equations are the simplest possible generalization, and their derivation shows clearly that the general structure of the semigroup generator would admit even more general versions where, in principle, the time derivative of any magnetization component can be coupled to all other components and therefore, additional relaxation parameters will come into play. This may lead to a complicated multiexponential behavior of the solutions which is always difficult to resolve in practice. Whether such details will be of practical importance remains to be shown by future high-accuracy time-resolved measurements.

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APPENDIX A

A positive semidefinite Hermitian $N\times N$ matrix $\underline{A}$ ($\underline{A}\geq 0$) has the following properties,[44,48]

$$\mu_i \geq 0,\quad i=1,2,\ldots,N\ , \tag{A1}$$

where $\{\mu_i\}$ are the eigenvalues of $\underline{A}$,

$$a_{ii}\geq 0,\quad i=1,2,\ldots,N\ , \tag{A2}$$

$$\underline{\mathscr{L}}_m \geq 0,\quad m\leq N\ , \tag{A3}$$

where $\underline{\mathscr{L}}_m$ is a leading $m\times m$ submatrix of $\underline{A}$ defined by

$$\underline{\mathscr{L}}_m=\begin{bmatrix} a_{ii} & \cdots & a_{ik} & \cdots & a_{ij}\\ \vdots & & \vdots & & \vdots\\ a_{ki} & \cdots & a_{kk} & \cdots & \\ \vdots & & \vdots & & \vdots\\ a_{ji} & \cdots & & \cdots & a_{jj}\end{bmatrix},$$

$$1\leq i<k<j\leq N\ . \tag{A4}$$

From (A1) one gets the useful relation,

$$|a_{ik}|^2\leq a_{ii}a_{kk},\quad \forall i,k\ . \tag{A5}$$

For the starting considerations in Sec. II A some details are needed for the special case $N=3$ [see Eq. (26)]. The complete set of inequalities reads,

$$a_{11},a_{22},a_{33}\geq 0\ , \tag{A6}$$

$$a_{11}a_{22}+a_{11}a_{33}+a_{22}a_{33}\geq |a_{12}|^2+|a_{13}|^2+|a_{23}|^2\ , \tag{A7}$$

$$a_{11}a_{22}a_{33}+2\,\mathrm{Re}(a_{12}a_{23}a_{31})\geq |a_{12}|^2a_{33}+|a_{13}|^2a_{22}+|a_{23}|^2a_{11}\ . \tag{A8}$$

Equation (A7) follows directly from (A5), and (A8) by calculating the characteristic polynomial

$$-\det(\underline{A}-\mu\mathbb{1})=\mu^3+a\mu^2+b\mu+c=0\ . \tag{A9}$$

Since the three roots μ_1, μ_2, and μ_3 are positive and, from Vieta's root theorem,

$$\mu_1\mu_2\mu_3=-c=-\det(\underline{A})$$

holds, (A8) is obtained by expressing c in terms of the matrix elements of $\underline{A}$. Of course, in terms of a real vector

$$\mathbf{z}=(z_1,z_2,z_3)^T\ , \tag{A10}$$

one may rewrite (A7) in the form

$$|a_{12}|=(a_{11}a_{22})^{1/2}z_1\ ,\quad |a_{13}|=(a_{11}a_{33})^{1/2}z_2\ ,\quad |a_{23}|=(a_{22}a_{33})^{1/2}z_3\ , \tag{A11}$$

under the restriction,

$$z_1^2+z_2^2+z_3^2\leq 1\ . \tag{A12}$$

For the 8×8 matrix in Sec. III A, obtained after decoupling of the relevant coherence vector components [Eq. (40)], successive application of (A4), (A5), and (A8) and use of Eq. (42) yields the block structure

$$\underline{A}=\tfrac{1}{8}\begin{bmatrix} 8\underline{D} & & & & \\ & k_\alpha & ik_\alpha & & \\ & -ik_\alpha & k_\alpha & & \\ & & & k_\beta & ik_\beta\\ & & & -ik_\beta & k_\beta\end{bmatrix}. \tag{A13}$$

where the 4×4 submatrix $\underline{D}$ has been obtained by rearranging the eighth row and column,

$$\underline{D}=\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{18}\\ a_{21} & a_{22} & a_{23} & a_{28}\\ a_{31} & a_{32} & a_{33} & a_{38}\\ a_{81} & a_{82} & a_{83} & a_{88}\end{bmatrix}, \tag{A14}$$

and, of course, $\underline{D}\geq 0$. For a comparison with the further discussion in Sec. III A one should keep in mind the particular decomposition of $\underline{A}$ into $\underline{B}$ and $\underline{C}$.

APPENDIX B

The solutions to Eqs. (48) may be represented in the form

$$\begin{bmatrix} M_x(t)\\ M_y(t)\end{bmatrix}=\exp(s_1t/2s_2)\underline{F}_1(t)\begin{bmatrix} M_x(0)\\ M_y(0)\end{bmatrix}+[\exp(s_1t/s_2)\underline{F}_2(t)-\exp(s_3t/s_4)\underline{F}_3(t)]\begin{bmatrix} M_z(0)\\ N(0)\end{bmatrix},$$

$$\begin{bmatrix} M_z(t)\\ N(t)\end{bmatrix}=\exp[s_3t/s_4]\underline{F}_4(t)\begin{bmatrix} M_z(0)\\ N(0)\end{bmatrix}, \tag{B1}$$

with the four time-dependent 2×2 matrices,

$$\underline{F}_1(t)=\begin{bmatrix} 2s_2\cos(s_2t)-(T_x^{-1}-T_y^{-1})\sin(s_2t) & 4\omega_0\sin(s_2t)\\ -4\omega_0\sin(s_2t) & 2s_2\cos(s_2t)+(T_x^{-1}-T_y^{-1})\sin(s_2t)\end{bmatrix}, \tag{B2}$$

$$[\underline{F}_2(t)]_{ik}=x_{ik}s_2\cos(s_2t)+[s_1x_{ik}+y_{ik}]\sin(s_2t),\quad i,k=1,2\ , \tag{B3}$$

$$[\underline{F}_3(t)]_{ik} = x_{ik}s_4\cosh(s_4t) + [s_3x_{ik} - z_{ik}]\sinh(s_4t), \quad i,k = 1,2 \;, \tag{B4}$$

$$\underline{F}_4(t) = \begin{bmatrix} s_4\cosh(s_4t) + \frac{1}{2}T_z^{-1}\sinh(s_4t) & f\sinh(s_4t) \\ (\overline{\Delta k} - \frac{1}{2}T_z^{-1})\sinh(s_4t) & s_4\cosh(s_4t) \end{bmatrix} , \tag{B5}$$

where the following abbreviations have been used:

$$f = \overline{\Delta k} - M_z^0 T_z^{-1} \;, \tag{B6}$$

$$s_1 = -\tfrac{1}{2}(T_x^{-1} + T_y^{-1} + 2\bar{k}), \quad s_2 = +[\omega_0^2 - \tfrac{1}{4}(T_x^{-1} - T_y^{-1})^2]^{1/2} \;, \tag{B7}$$

$$s_3 = -(\tfrac{1}{2}T_z^{-1} + \bar{k}), \quad s_4 = \tfrac{1}{2}(4\overline{\Delta k}f + T_z^{-2})^{1/2} \;. \tag{B8}$$

For $i,k = 1,2$,

$$x_{ik} = [\beta_{ik}(s_3^2 - s_1^2 - s_2^2 - s_4^2)] - 2\alpha_{ik}(s_1 - s_3)/D \;, \tag{B9}$$

$$y_{ik} = (2\beta_{ik}(s_1 - s_3)[s_1^2 + s_2^2] + \alpha_{ik}[s_3^2 - s_1^2 - s_2^2 - s_4^2 + 4s_1(s_1 - s_3)])/D \;, \tag{B10}$$

$$z_{ik} = -(2\beta_{ik}(s_1 - s_3)(s_3^2 - s_4^2) + \alpha_{ik}[s_3^2 - s_1^2 - s_2^2 - s_4^2 - 4s_3(s_1 - s_3)])/D \;, \tag{B11}$$

$$D = (s_3^2 - s_1^2 - s_2^2 - s_4^2)^2 + 4(s_1 - s_3)[s_1(s_3^2 - s_4^2) - s_3(s_1^2 + s_2^2)] \;, \tag{B12}$$

$$\alpha_{11} = -\overline{\Delta k}[\omega_0 u_2 + (T_y^{-1} + \bar{k})u_1], \quad \beta_{11} = -\overline{\Delta k}\,u_1 \;, \tag{B13}$$

$$\alpha_{12} = f\alpha_{11}/\overline{\Delta k}, \quad \beta_{12} = -fu_1 \;, \tag{B14}$$

$$\alpha_{21} = \overline{\Delta k}[(T_x^{-1} + \bar{k})u_2 - \omega_0 u_1], \quad \beta_{21} = \overline{\Delta k}\,u_2 \;, \tag{B15}$$

$$\alpha_{22} = f[(T_x^{-1} + \bar{k})u_2 + \omega_0 u_1], \quad \beta_{22} = fu_2 \;, \tag{B16}$$

$$u_1 = -(M_x^0 T_x^{-1} - \omega_0 M_y^0) \;, \tag{B17}$$

$$u_2 = (M_y^0 T_y^{-1} - \omega_0 M_x^0) \;. \tag{B18}$$

APPENDIX C

In terms of the four-component vector

$$\mathbf{R}(t) = (\hat{M}_x(t), \hat{M}_y(t), \hat{M}_z(t), \hat{N}(t))^T \;, \tag{C1}$$

the Bloch equations (77) are written in compact form as

$$\dot{\mathbf{R}}(t) = \underline{\Delta}\mathbf{R}(t) \tag{C2}$$

with the matrix

$$\underline{\Delta} = \begin{bmatrix} -(T_\perp^{-1} + \bar{k}) & \Delta\omega & 0 & 0 \\ -\Delta\omega & -(T_\perp^{-1} + \bar{k}) & -\omega_1 & 0 \\ 0 & \omega_1 & -(T_\parallel^{-1} + \bar{k}) & M_\parallel^0 T_\parallel^{-1} - \overline{\Delta k} \\ 0 & 0 & -\overline{\Delta k} & -\bar{k} \end{bmatrix} . \tag{C3}$$

The solution to (C2) is most easily found by first solving the eigenvalue problem[50]

$$\underline{\Delta}\mathbf{x} = \lambda\mathbf{x} \;, \tag{C4}$$

$$\det(\underline{\Delta} - \lambda\underline{1}) = 0 \;. \tag{C5}$$

In terms of the so obtained four eigenvalues λ_i and corresponding eigenvectors $\mathbf{x}^{(i)}$ ($i = 1,2,3,4$), the general solution is constructed to be

$$\mathbf{R}(t) = \sum_{i=1}^{4} s_i e^{\lambda_i t}\mathbf{x}^{(i)} \;, \tag{C6}$$

where the four constants s_i are determined by the initial condition,

$$\mathbf{R}(0) = \sum_{i=1}^{4} s_i\mathbf{x}^{(i)} \;. \tag{C7}$$

Defining a vector $\mathbf{s} = (s_1, s_2, s_3, s_4)^T$, one can write

$$\mathbf{R}(0) = \underline{X}\mathbf{s} \;, \tag{C8}$$

where $\underline{X}$ is the matrix whose columns are the eigenvector components. For a given $\mathbf{R}(0)$, $\mathbf{s}$ is then calculated from

$$\mathbf{s} = \underline{X}^{-1}\mathbf{R}(0) \;. \tag{C9}$$

Of course, the general (4×4) problem must be solved on the machine, although lengthy analytical expressions could, in principle, be given.

We proceed to the special case of resonance,

$$\Delta\omega=0\ , \tag{C10}$$

where analytical expressions are still useful. The characteristic equation (C5) then factorizes and yields

$$\lambda_1=\gamma_\perp+\bar{k}\ , \tag{C11}$$

$$\mathbf{x}^{(1)}=(1,0,0,0)^T\ , \tag{C12}$$

where we abbreviate for convenience

$$\frac{1}{T_\perp}=\gamma_\perp,\ \ \frac{1}{T_{||}}=\gamma_{||}\ . \tag{C13}$$

The second factor is a polynomial of third degree,

$$\lambda^3+a\lambda^2+b\lambda+c=0\ , \tag{C14}$$

with the following constants,

$$a=3\bar{k}+\gamma_\perp+\gamma_{||}\ , \tag{C15}$$

$$b=3\bar{k}^2+2\bar{k}(\gamma_\perp+\gamma_{||})+\gamma_\perp\gamma_{||}+\omega_1^2-\overline{\Delta k}[\overline{\Delta k}-\gamma_{||}M_{||}^0]\ , \tag{C16}$$

$$c=\bar{k}[(\gamma_\perp+\bar{k})(\gamma_{||}+\bar{k})+\omega_1^2]-\overline{\Delta k}[\overline{\Delta k}-\gamma_{||}M_{||}^0](\gamma_\perp+\bar{k})\ . \tag{C17}$$

Equation (C14) is brought to standard form,[51]

$$y^3+py+q=0\ , \tag{C18}$$

though the substitution $y=\lambda+a/3$, yielding

$$p=b-\frac{a^3}{3}\ ,$$
$$q=\tfrac{2}{27}a^3-\tfrac{1}{3}ab+c\ , \tag{C19}$$

and the discriminant D of the cubic equation is then

$$D=(q/2)^2+(p/3)^3\ . \tag{C20}$$

Using the abbreviations

$$u=(-q/2+\sqrt{D})^{1/3}\ , \tag{C21}$$

$$v=(-q/2-\sqrt{D})^{1/3}\ , \tag{C22}$$

the roots y_i ($i=2,3,4$) of (C18) are classified as follows. For $D>0$, there are one real and two complex conjugated, for $D=0$, three real solutions, two of them coinciding with each other. Both cases are represented by

$$\begin{aligned} y_2&=u+v\ ,\\ y_3&=-\tfrac{1}{2}(u+v)+i\frac{\sqrt{3}}{2}(u-v)\ ,\\ y_4&=-\tfrac{1}{2}(u+v)-i\frac{\sqrt{3}}{2}(u-v)\ . \end{aligned} \tag{C23}$$

The third case is the so-called *casus irreducibilis* for $D<0$, providing three real, different roots of the form

$$\begin{aligned} y_2&=2(|p|/3)^{1/2}\cos(\phi/3)\ ,\\ y_3&=-2(|p|/3)^{1/2}\cos(\phi/3-\pi/3)\ ,\\ y_4&=-2(|p|/3)^{1/2}\cos(\phi/3+\pi/3)\ , \end{aligned} \tag{C24}$$

where

$$\phi=\arccos[-q/2(|p|/3)^{-3/2}]\ . \tag{C25}$$

From these solutions, the effective eigenvalues of $\underline{\Lambda}$ are found from

$$\lambda_i=y_i-a/3,\ \ i=2,3,4\ . \tag{C26}$$

Finally, the corresponding eigenvectors $\mathbf{x}^{(i)}$ are expressed in terms of the λ_i's and the quantity

$$r_i=\left[\frac{\omega_1^2}{(\overline{\Delta k})^2}\left[\frac{\lambda_i+\bar{k}}{\lambda_i+\bar{k}+\gamma_\perp}\right]^2+\left[\frac{\lambda_i+\bar{k}}{\overline{\Delta k}}\right]^2+1\right]^{-1/2}\ , \tag{C27}$$

by the final relations for the components, valid for $i=2,3,4$,

$$\begin{aligned} x_1^{(i)}&=0\ ,\\ x_2^{(i)}&=r_i\ ,\\ x_3^{(i)}&=-\frac{r_i}{\overline{\Delta k}}(\lambda_i+\bar{k})\ ,\\ x_4^{(i)}&=\frac{\omega_1 r_i}{\overline{\Delta k}}\left[\frac{\lambda_i+\bar{k}}{\lambda_i+\bar{k}+\gamma_\perp}\right]\ . \end{aligned} \tag{C28}$$

It may be added that in the case of the complex roots of (C18), oscillating transient effects will be observed similar to those discussed in the famous paper by Torrey[52] whereas real roots lead to smooth multiexponential behavior of the solutions.

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*Present address: Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland.

[1] C. P. Slichter, *Principles of Magnetic Resonance* (Springer, Berlin, 1978).

[2] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Longon, 1961).

[3] N. M. Atherton, *Electron Spin Resonance* (Wiley, New York, 1973).

[4] *Time Domain Electron Spin Resonance,* edited by L. Kevan and R. N. Schwartz (Wiley, New York, 1979).

[5] J. D. Macomber, *The Dynamics of Spectroscopic Transitions* (Wiley, New York, 1976).

[6] M. Sargent III, M. O. Scully, and W. E. Lamb, Jr., *Laser Physics* (Addison-Wesley, Reading, 1974).

[7] L. Allen and J. H. Eberly, *Optical Resonance in Two-Level Atoms* (Wiley-Interscience, New York, 1975).

[8] R. G. Brewer, in *Frontiers in Laser Spectroscopy,* edited by R.

Balian, S. Haroche, and S. Liberman (North-Holland, Amsterdam, 1977), Vol. 1.

[9]N. C. Verma and R. W. Fessenden, J. Chem. Phys. **65**, 2139 (1976).

[10]*Frontiers in Laser Spectroscopy,* Ref. 8, Vols. 1 and 2.

[11]C. B. Harris and W. G. Breiland, in *Laser and Coherence Spectroscopy,* edited by J. I. Steinfeld (Plenum, New York and London, 1978).

[12]M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964).

[13]R. Zwanzig, in *Lectures in Theoretical Physics,* edited by W. E. Brittin, B. W. Downs, and J. Downs (Wiley Interscience, New York, 1961), Vol. 3.

[14]F. Haake, in *Quantum Statistics in Optics and Solid State Physics* (Springer Tracts in Modern Physics No. 66), edited by G. Hohler (Springer, Berlin, 1973).

[15]H. Grabert, *Projection Operator Techniques in Nonequilibrium Statistical Mechanics* (Springer, Berlin, 1982).

[16]K. Lendi and M. Rothier do Amaral, Jr., Rev. Bras. Fís. **13**, 294 (1983).

[17]K. Lendi, J. Chem. Phys. **67**, 4774 (1977).

[18]H. Spohn and J. L. Lebowitz, in *Advances in Chemical Physics,* edited by S. A. Rice (Wiley, New York, 1978), Vol. 38.

[19]A. Kossakowski, Rep. Math. Phys. **3**, 247 (1972).

[20]E. B. Davies, Commun. Math. Phys. **39**, 91 (1974).

[21]E. B. Davies, Ann. Inst. Henri Poincaré **11**, 265 (1975).

[22]E. B. Davies, Math. Ann. **219**, 147 (1976).

[23]V. Gorini, A. Kossakowski, and E. C. G. Sudarshan, J. Math. Phys. **17**, 821 (1976).

[24]E. B. Davies, *Quantum Theory of Open Systems* (Academic, New York and London, 1976).

[25]V. Gorini, A. Frigerio, M. Verri, A. Kossakowski, and E. C. G. Sudarshan, Rep. Math. Phys. **13**, 149 (1978).

[26]G. Lindblad, Commun. Math. Phys. **48**, 119 (1976).

[27]E. B. Davies, *One-Parameter Semigroups* (Academic, London, 1980).

[28]U. Fano, Rev. Mod. Phys. **29**, 74 (1957).

[29]H. Spohn, Rep. Math. Phys. **10**, 189 (1976).

[30]K. T. Mahanthappa, P. M. Mathews, and J. Rau, Phys. Rev. **115**, 478 (1959).

[31]F. T. Hioe and J. H. Eberly, Phys. Rev. Lett. **47**, 838 (1981).

[32]S. Feneuille, Rep. Prog. Phys. **40**, 1257 (1977).

[33]G. Lindblad, *Non-Equilibrium Entropy and Irreversibility* (Reidel, Dordrecht, 1983).

[34]H. Tanabe, *Equations of Evolution* (Pitman, London, 1979).

[35]N. C. Verma and R. W. Fessenden, J. Chem. Phys. **58**, 2501 (1973).

[36]J. H. Freed and J. B. Pedersen, in *Advances in Magnetic Resonance,* edited by J. S. Waugh (Academic, New York, 1975).

[37]M. Schwoerer and H. Sixl, Z. Naturforsch. **24a**, 952 (1969).

[38]M. Schwoerer and H. Sixl, Chem. Phys. Lett. **2**, 14 (1968).

[39]A. Hammer, M. Schwoerer, and H. Sixl, Chem. Phys. Lett. **5**, 434 (1970).

[40]H. Sixl and M. Schwoerer, Chem. Phys. Lett. **6**, 21 (1970).

[41]H. Sixl and M. Schwoerer, Z. Naturforsch. **25a**, 1383 (1970).

[42]J. Schmidt and J. H. van der Walls, Ref. 4, p. 343.

[43]M. A. El-Sayed, in *Excited States,* edited by E. C. Lim (Academic, New York, 1974), Vol. I.

[44]H. Levanon, in *Multiple Resonance Spectroscopy,* edited by M. M. Dorio and J. H. Freed (Plenum, New York, 1979).

[45]W. G. Breiland, C. B. Harris, and A. Pines, Phys. Rev. Lett. **30**, 158 (1973).

[46]D. A. McQuarrie, J. Appl. Prob. **4**, 413 (1967).

[47]N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

[48]H. R. Schwarz, H. Rutishauser, and E. Stiefel, *Numerik symmetrischer Matrizen* (Teubner, Stuttgart, 1972).

[49]F. R. Gantmacher, *Matrizenrechnung* (VEB Deutscher, Berlin, 1958).

[50]M. Braun, *Differential Equations and Their Applications* (Springer, New York, 1978).

[51]I. N. Bronstein and K. A. Semendjajew, *Taschenbuch der Mathematik* (Harri Deutsch, Frankfurt a.M., 1962).

[52]H. C. Torrey, Phys. Rev. **76**, 1059 (1949).