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Quantum-dynamical semigroup generators for proton-spin relaxation in water

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Various aspects of a rather general treatment of proton-spin relaxation in water are discussed within the framework of quantum-dynamical semigroup theory for a four-level system coupled to a reservoir in equilibrium. In particular, the specifications of the infinitesimal generator of time evolution, either in Kossakowski or in Davies form, are worked out in detail. With the help of the Lie algebra of SU(4), the results are used to derive, under suitable simplifications, generalized Bloch equations for the static and alternating-field case. The relevant correlation functions are calculated using conventional approaches but supplemented by taking into account explicitly results from a stochastic model for formation and breaking of hydrogen bridges. A further approximate reduction of the coupled general equations to simpler ordinary Bloch equations leads to an identification of the relevant relaxation times. This approach provides a somewhat different interpretation of rotational correlation times whose numerical values are estimated over a wide temperature range.

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I. INTRODUCTION

The ordinary equation for the evolution of the density operator, which is widely used in the NMR literature to investigate spin relaxation in fluid systems, is given by the Redfield master equation [1,2], which is derived from an approximative solution of the Liouville equation for the density operator of the open quantum system S with a large time-independent interaction Hamiltonian and a comparatively small time-dependent one. The application of this or similar equations for the density operator can, of course, lead to difficulties. The basic laws of quantum mechanics require that the density operator satisfies, for all times, the von Neumann conditions of hermiticity, trace preservation, and positivity. The description of the time evolution of an N-level system with a completely positive quantum-dynamical semigroup guarantees automatically that the von Neumann conditions are fulfilled. The detailed mathematical structure of the associated generator is given by the theorem of Gorini, Kossakowski, and Sudarshan and by Lindblad [3,4]. It must be stressed that the method used to derive the structure of the Kossakowski generator is totally different from the considerations leading to Redfield's results. The underlying relation for the time evolution of the open quantum system S is now obtained by a partial trace operation acting on the state of the total system Q constituted by S and the reservoir R. The necessary conditions for the validity of the Redfield theory are replaced through the positive semidefiniteness of the relaxation matrix.

On the other hand, in a series of papers Davies showed [5–7], starting from the exact Nakajima-Zwanzig master equation, that a second more special form of the quantum-dynamical semigroup generator exists. The relationship between the Kossakowski and the Davies generator allows the determination of relaxation parameters from first principles. Especially, one is able to express in a quantum mechanically correct way the elements of the relaxation matrix and the diagonal relaxation parameters in the spectral density functions of the reservoir. Moreover, the transition from the original Kossakowski master equation to the corresponding matrix equation for the coherence vector [8] yields generalized Bloch equations in the static field case as well as in the alternating field case.

In this paper we investigate the spin relaxation in water with quantum-dynamical semigroup generators. To make the reader familiar with the basic results, the next section gives a short review of the general theory. For the four-level system of the two proton spins in an H_2O molecule the exact expansion of the diagonal relaxation parameters in terms of the correlation functions of the reservoir R will be given. To get the connection between the spectral density functions and the microscopic parameters of the reservoir an attempt is made to calculate approximately the quantum correlation functions. Finally, from the coherence vector formulation of the Kossakowski master equation, one can deduce the general Bloch equations for the fluid system of water molecules. The general Bloch equations allow the identification of the longitudinal relaxation time T_1. The expression for T_1 also depends on the characteristic times τ_{HB}, τ_f of the hydrogen bond dynamics. In the extreme narrowing case one can compare the calculated value for T_1 with conventional results.

II. GENERAL THEORY

In the following we consider an open quantum system S coupled to a reservoir R. The total system $Q=S\cup R$

does not exchange any energy with its environment. The reservoir remains in a fixed reference state P_R for all times. An example for an open quantum system is given by a spin-$\frac{1}{2}$ particle in a static, homogeneous magnetic field and a time-dependent electromagnetic field whose field modes serve as a reservoir [9]. In order to describe the time evolution of an open quantum system one needs a one-parameter family of dynamical maps $\{\Lambda_t, t \geq 0\}$, such that

$$\rho(t)=\Lambda_t\rho(0), \quad t\geq 0 , \tag{2.1}$$

where ρ is the density operator of the open quantum system S. The family of the dynamical maps Λ_t has to fulfill the conditions of a completely positive quantum-dynamical semigroup. We mention here only the important semigroup condition

$$\Lambda_{t+s}=\Lambda_t\Lambda_s, \quad t,s\geq 0 . \tag{2.2}$$

Under these conditions it follows from the Hille-Yosida theorem [10] that one may write

$$\Lambda_t=e^{Lt}, \quad t\geq 0 , \tag{2.3}$$

where L is the infinitesimal generator of the completely positive quantum-dynamical semigroup. For the differential equation corresponding to (2.1), one finds

$$\dot{\rho}(t)=L\rho(t) . \tag{2.4}$$

Gorini, Kossakowski, and Sudarshan have shown that the most general generator of a quantum-dynamical semigroup for the case of a finite-dimensional Hilbert space $\mathcal{H}_s$ can be written in final normal form as [3]

$$L\rho(t)=-i[H,\rho(t)]+\tfrac{1}{2}\sum_{i,j=1}^{N^2-1} a_{ij}\{[F_i,\rho(t)F_j^\dagger] + [F_i\rho(t),F_j^\dagger]\} , \tag{2.5}$$

where

$$H=H^\dagger, \quad \mathrm{tr}(H)=0 , \tag{2.6}$$

$$\mathrm{tr}(F_i)=0, \quad \mathrm{tr}(F_iF_j^\dagger)=\delta_{ij} , \tag{2.7}$$

$$i,j=1,\ldots,N^2-1 , \tag{2.8}$$

$$A=\{a_{ij}\}\geq 0, \quad i,j=1,\ldots,M=N^2-1 . \tag{2.9}$$

The first term of the generator L describes the pure Hamiltonian dynamics of the open N-level system, whereas the second term represents the non-Hamiltonian dynamics of S. Possible energy shifts due to the interaction with the reservoir are taken into account through the Hamiltonian H of the open quantum system S. The linear operators F_i together with the unit operator $F_0=\mathbb{1}$ form a basis in the Banach space $\mathcal{B}(\mathcal{H}_S)$. Of great importance is the positivity property (2.9) of the complex matrix A. For further features which follow from the positive semidefiniteness of the relaxation matrix A the reader is referred to the lecture notes by Alicki and Lendi [8]. A convenient representation of the operators F_i is realized by the Hermitian $(N\times N)$ matrices that constitute a basis set of the Lie algebra associated with the SU(N) group. Especially, the two following relations hold:

$$[F_i,F_k]=i\sum_{l=1}^{M} f_{ikl}F_l , \tag{2.10}$$

$$\{F_i,F_k\}=\frac{2}{N}F_0\delta_{ik}+\sum_{l=1}^{M} d_{ikl}F_l , \tag{2.11}$$

where $\{\ ,\ \}$ denotes the anticommutator. The f_{ikl}'s are the completely antisymmetric (with respect to interchange of any pair of indices) and the d_{ikl}'s the completely symmetric structure constants of the Lie algebra. In the literature the reader can find a systematic scheme for how to construct the F_i matrices for arbitrary N and a complete list of the generators and structure constants [8] for SU(N), $N=2,3,4$. To investigate the differential equation (2.4) it is appropriate to go over to the coherence-vector formulation

$$\dot{\rho}(t)=L\rho(t)\rightarrow\dot{\mathbf{v}}(t)=G\mathbf{v}(t)+\mathbf{k} . \tag{2.12}$$

The components of the coherence vector $\mathbf{v}(t)$ appear as coefficients in the expansion of the density operator in the basis $\{F_i\}_1^M$

$$\rho(t)=\frac{1}{N}F_0+\sum_{i=1}^{M} v_i(t)F_i . \tag{2.13}$$

By trace operation it follows immediately that

$$v_i(t)=\mathrm{tr}[F_i\rho(t)] . \tag{2.14}$$

According to the structure of the Kossakowski generator one can decompose the $(M\times M)$ matrix G into a matrix Q and a matrix R,

$$G=Q+R . \tag{2.15}$$

Bearing in mind the expansion

$$H=\sum_{n=1}^{M} h_nF_n, \quad h_n\in\mathbb{R} \tag{2.16}$$

for the Hamiltonian H, one gets for the matrix elements q_{sm} of Q the result

$$q_{sm}=\sum_{n=1}^{M} h_nf_{nms} . \tag{2.17}$$

In consequence of the complete antisymmetry of the structure constants f_{ikl}, the matrix Q is skew symmetric:

$$Q=-Q^T . \tag{2.18}$$

Next, we consider the following commutators:

$$[H,\rho(t)]=\sum_{i,j=1}^{M} h_iv_j(t)[F_i,F_j] , \tag{2.19}$$

$$[F_i,\rho(t)F_k]=\frac{1}{N}[F_i,F_k]+\sum_{j=1}^{M} v_j(t)[F_i,F_jF_k] , \tag{2.20}$$

$$[F_i,F_jF_k]=\frac{i}{2}\sum_{l=1}^{M} \bar{z}_{jkl}[F_i,F_l] , \tag{2.21}$$

where the complex structure constants z_{ijk} are defined by

$$z_{ijk}=f_{ijk}+id_{ijk} . \tag{2.22}$$

Together with the properties

$$i \sum_{i,k,l=1}^{M} \mathrm{Re}(a_{ik})(f_{kls}d_{ilm} - f_{ils}d_{klm}) = 0 \ , \tag{2.23}$$

$$i \sum_{i,k,l=1}^{M} \mathrm{Im}(a_{ik})(f_{ils}f_{klm} + f_{kls}f_{ilm}) = 0 \ , \tag{2.24}$$

we finally find for the elements r_{sm} of R the real forms

$$\begin{aligned} r_{sm} = -\tfrac{1}{4} \sum_{\substack{i,k,l=1 \\ (i \le k)}} & (2-\delta_{ik})\mathrm{Re}(a_{ik}) \\ & \times (f_{ils}f_{klm} + + f_{kls}f_{ilm}) \\ + \tfrac{1}{2} \sum_{\substack{i,k,l=1 \\ (i<k)}} & \mathrm{Im}(a_{ik})(f_{kls}d_{ilm} - f_{ils}d_{klm}) \ . \end{aligned} \tag{2.25}$$

The components k_s of the inhomogeneous part k of the differential equation (2.12) are given by

$$k_s = -\frac{2}{N} \sum_{\substack{i,k=1 \\ (i<k)}} \mathrm{Im}(a_{ik}) f_{iks}, \quad s = 1, \ldots, M \ , \tag{2.26}$$

where we have used the relations

$$\mathrm{Re}(a_{ik}) = \mathrm{Re}(a_{ki}), \quad \mathrm{Im}(a_{ik}) = -\mathrm{Im}(a_{ki}) \ . \tag{2.27}$$

For a detailed discussion of the differential equation (2.12) the reader is referred to the literature [8,11]. In addition to the structure theorem (2.5) of Gorini, Kossakowski, and Sudarshan, there exists a second approach to the reduced dynamics of an open quantum system, systematically investigated by Davies [5]. The fundamental equation in this context is given by the Nakajima-Zwanzig master equation. We will present it here in the integrated form

$$\rho(t) = U_t\rho(0) + \lambda^2 \int_{s=0}^{t} \int_{u=0}^{s} U_{t-s} K(\lambda, s-u) \rho(u)\, du\, ds \ . \tag{2.28}$$

A detailed derivation using the projection operator technique can be found elsewhere [12–14]. It is important to note that the Eq. (2.28) for the reduced dynamics of the open quantum system S is exact. Now a powerful theorem by Davies states which conditions the single terms in the Feynman-Dyson expansion [15] of the integral kernel $K(\lambda, s-u)$ have to be fulfilled in order that a generator D exists with the property

$$\lim_{\substack{\lambda \to 0 \\ \lambda^2 t = \tau}} \| U_{-\tau\lambda^{-2}} U^{\lambda}_{\tau\lambda^{-2}} \rho - e^{D\tau}\rho \| = 0 \ . \tag{2.29}$$

One may show then that the generator D satisfies a semigroup condition and the connection with the density operator is determined again through

$$\rho(t) = e^{Dt}\rho(0) \ . \tag{2.30}$$

An interesting fact is that one can deduce the necessary decay properties for the correlation functions of the reservoir from the Davies restrictions for the terms in the Feynman-Dyson expansion of the kernel $K(\lambda, s-u)$. The exact structure of the generator D can be found from Eq. (2.28) by rescaling the time and going over to the weak-coupling limit. This procedure yields the following result for the Davies generator D [16,17]:

$$D = D_H + D_R \ , \tag{2.31}$$

where

$$D_H = -i \sum_{\omega \in \mathrm{Sp}([H_s, .])} \sum_{i,k} s_{ik}(\omega) [A_k^{\dagger}(\omega) A_i(\omega), .] \ , \tag{2.32}$$

$$\begin{aligned} D_R = \tfrac{1}{2} \sum_{\omega \in \mathrm{Sp}([H_s, .])} \sum_{i,k} c_{ik}(\omega) (& [A_i(\omega) ., A_k^{\dagger}(\omega)] \\ & + [A_i(\omega), . A_k^{\dagger}(\omega)]) \ . \end{aligned} \tag{2.33}$$

$\mathrm{Sp}([H_S, .])$ denotes the spectrum of the Liouville–von Neumann operator $[H_S, .]$ [18]. It is the set $\{\varepsilon_m - \varepsilon_n | \varepsilon_m, \varepsilon_n \in \mathrm{Sp}(H_S)\}$ if one assumes that the Hamiltonian H_S of the open quantum system has a discrete spectrum

$$H_S = \sum_i \varepsilon_i |i\rangle\langle i| \ . \tag{2.34}$$

Furthermore the operators $A_i(\omega)$ are given by

$$A_i(\omega) = \sum_{\varepsilon_m - \varepsilon_n = \omega} P_{nn} A_i P_{mm}, \quad P_{nm} = |n\rangle\langle m| \ . \tag{2.35}$$

Recall that the operators A_i appear in the interaction Hamiltonian H_{SR},

$$H_{SR} = \sum_i A_i \otimes B_i, \quad A_i = A_i^{\dagger}, \quad B_i = B_i^{\dagger} \ , \tag{2.36}$$

which couples S to the reservoir R. The coefficients $c_{ik}(\omega)$ and $s_{ik}(\omega)$ are the Fourier—and the Hilbert—transforms of the correlation functions $h_{ik}(t)$,

$$c_{ik}(\omega) = \int_{-\infty}^{+\infty} dt\, h_{ik}(t) e^{-i\omega t} \ , \tag{2.37}$$

$$s_{ik}(\omega) = i \int_0^{\infty} dt\, h_{ik}(t) e^{-i\omega t} - \frac{i}{2} c_{ik}(\omega) \ , \tag{2.38}$$

where

$$h_{ik}(t) = \mathrm{tr}_R[P_R B_k B_i(t)] \ , \tag{2.39}$$

with

$$B_i(t) = U_{-t}^R B_i U_t^R, \quad U_t = e^{-iH_R t} \ . \tag{2.40}$$

The first term D_H of the Davies generator (2.31) yields a correction to the Hamiltonian part of the dynamics, whereas the second term D_R contains pure non-Hamiltonian contributions. A comparison of the two generators (2.5) and (2.31) allows one to express the matrix elements a_{ik} of the relaxation matrix A in the Fourier transforms $c_{ik}(\omega)$ of the reservoir correlation functions $h_{ik}(t)$. Especially for a two-level system, it is possible to identify the longitudinal and transverse relaxation times and to give their exact expansions in the Fourier transforms of the reservoir correlations [8,19].

III. OPEN QUANTUM SYSTEM

The H_2O molecule carries two hydrogen proton spins. The *gg* nucleus of the oxygen atom possesses no spin. In a static, homogeneous magnetic field $\mathbf{B}=(0,0,-B_0)$ the interaction Hamiltonian of the open quantum system of the two proton spins is given by

$$H_S=\omega_L I_{1z}+\omega_L I_{2z}+J\mathbf{I}_1\cdot\mathbf{I}_2\ , \tag{3.1}$$

where

$$\omega_L=\gamma B_0(1-\sigma)\ , \tag{3.2}$$

with the proton gyromagnetic ratio γ, the chemical shift σ, and the indirect coupling constant J of the water molecule [20–22]. The operators H_S, $I=I_1+I_2$, and $I_z=I_{1z}+I_{2z}$ satisfy the commutation relations

$$[H_S,I^2]=0,\quad [H_S,I_z]=0,\quad [I^2,I_z]=0\ . \tag{3.3}$$

Consequently, the simultaneous eigenstates are obtained from the transformation equation [23,24]

$$|j_1j_2jm\rangle=\sum_{m_1,m_2}|j_1j_2m_1m_2\rangle\langle j_1j_2m_1m_2|j_1j_2jm\rangle\ . \tag{3.4}$$

As a result one gets the following eigenstates:

$$\begin{aligned}
&\text{Singlet:}\quad |p_1\rangle=|\tfrac{1}{2}\tfrac{1}{2}00\rangle=\frac{1}{\sqrt{2}}(\alpha_1\beta_2-\beta_1\alpha_2)\\
&\text{Triplet:}\quad |p_2\rangle=|\tfrac{1}{2}\tfrac{1}{2}11\rangle=\alpha_1\alpha_2\ ,\\
&\qquad |p_3\rangle=|\tfrac{1}{2}\tfrac{1}{2}10\rangle=\frac{1}{\sqrt{2}}(\alpha_1\beta_2+\beta_1\alpha_2)\ ,\\
&\qquad |p_4\rangle=|\tfrac{1}{2}\tfrac{1}{2}1,-1\rangle=\beta_1\beta_2\ ,
\end{aligned} \tag{3.5}$$

where the particular basis in the direct product spin space of the composite system

$$\alpha_1\alpha_2,\quad \alpha_1\beta_2,\quad \beta_1\alpha_2,\quad \beta_1\beta_2 \tag{3.6}$$

is spanned by the eigenvectors of I_{1z} and I_{2z}. The representation of the interaction Hamiltonian H_S in the basis $|p_i\rangle$ yields

$$H_S=\begin{bmatrix} -\frac{3}{4}J & 0 & 0 & 0\\ 0 & \omega_L+\dfrac{J}{4} & 0 & 0\\ 0 & 0 & \dfrac{J}{4} & 0\\ 0 & 0 & 0 & -\omega_L+\dfrac{J}{4}\end{bmatrix}\ , \tag{3.7}$$

or, in spectral representation,

$$\begin{aligned}H_S=&-\tfrac{3}{4}J|p_1\rangle\langle p_1|+\left[\omega_L+\frac{J}{4}\right]|p_2\rangle\langle p_2|\\ &+\frac{J}{4}|p_3\rangle\langle p_3|+\left[-\omega_L+\frac{J}{4}\right]|p_4\rangle\langle p_4|\ .\end{aligned} \tag{3.8}$$

The complete set of eigenvalues and eigenvectors of the Liouville–von Neumann operator $[H_S,.\,]$ can be obtained from

$$[H_S,|p_i\rangle\langle p_j|\,]=(\varepsilon_i-\varepsilon_j)|p_i\rangle\langle p_j|\ , \tag{3.9}$$

where ε_i denotes an eigenvalue of H_S. Thus, the eigenvalues of the Liouville–von Neumann operator are

$$\pm 2\omega_L,\pm(\omega_L+J),\pm\omega_L,\pm(\omega_L-J),\pm J,0\ . \tag{3.10}$$

All allowed transitions are obtained from time-dependent perturbation theory using the Hamiltonian [25]

$$H(t)=-\tfrac{1}{2}\gamma B_1[(I_1^+I_2^+)e^{-i\omega t}+(I_1^-+I_2^-)e^{i\omega t}] \tag{3.11}$$

for the interaction of the two proton spins with an alternating field $\mathbf{B}_1(t)=B_1(\cos\omega t,\sin\omega t,0)$. The transition probability $W_{ba}(t)$ for a transition from a state $|a\rangle$ with energy E_a to a state $|b\rangle$ with energy E_b is given in first order by the equation

$$W_{ba}(t)=\left|\int_0^t dt' e^{it'(E_b-E_a)}\langle b|H_1(t')|a\rangle\right|^2\ . \tag{3.12}$$

As a result one gets the selection rules

$$j=1,\quad \Delta m=\pm 1 \tag{3.13}$$

for the allowed transitions, in good agreement with the experiment.

IV. RESERVOIR

We consider a system of water molecules in the liquid state. Each molecule is represented by a hard sphere. The total spins are at the centers of the identical hard spherical molecules [1,26]. The system is placed in a static, homogeneous magnetic field B_0. The transitions in the open four-level system of a molecule are induced due to the statistically modulated intra- and intermolecular dipole-dipole interaction. For the corresponding Hamiltonian one may write [22,27–29]

$$H_{SR}=\sum_{\mu=1}^{3}I_\mu\otimes B_\mu\ , \tag{4.1}$$

with

$$B_\mu=\left[\frac{6\pi}{5}\right]^{1/2}\gamma^2\sum_j\sum_{\nu=1}^{3}M_{\mu\nu}^{(j)}S_\nu^{(j)}\ . \tag{4.2}$$

The operator $\mathbf{I}$ is the total spin of the open quantum system, whereas $S^{(j)}$ is the spin operator of the reservoir molecule *j*. To study the transformation properties of the dipole-dipole interaction Hamiltonian, it is of course more convenient to use its representation in terms of irreducible second-rank tensor operators. The Hamiltonian of the reservoir is given by

$$H_R=\sum_j\frac{\mathbf{p}_j^2}{2m}+\sum_j\omega_L S_z^{(j)}+\sum_{i<j}U(\mathbf{r}_i-\mathbf{r}_j)\ . \tag{4.3}$$

Details about the structure of the interaction potential U between the molecules are available elsewhere [30,31].

We will investigate now the expansion of the matrix elements a_{ik} of the relaxation matrix A in the Fourier transforms $c_{ik}(\omega_l)$ of the reservoir correlation functions. To solve this problem one starts with the Davies generator $\tilde{D}$ for the open four-level system of the H_2O molecule

$$\tilde{D}=\tilde{D}_H+\tilde{D}_R \ , \tag{4.4}$$

where

$$\tilde{D}_H=-i\sum_{i,k=1}^{3}\sum_{l=-5}^{+5} s_{ik}(\omega_l)[A_k^\dagger(\omega_l)A_i(\omega_l),.] \ , \tag{4.5}$$

$$\tilde{D}_R=\tfrac{1}{2}\sum_{i,k=1}^{3}\sum_{l=-5}^{+5} c_{ik}(\omega_l)([A_i(\omega_l).,A_k^\dagger(\omega_1)] +[A_i(\omega_l),.A_k^\dagger(\omega_l)]) \ . \tag{4.6}$$

A comparison of (2.36) with (4.1) yields

$$A_i(\omega_l)=I_i(\omega_l)=\sum_{\varepsilon_m-\varepsilon_n=\omega_l} P_{nn}I_iP_{mm} \ . \tag{4.7}$$

Here we use the convention

$$\begin{aligned}
&\omega_0=0,\quad \omega_{\pm 3}=\omega_L \ ,\\
&\omega_{\pm 1}=\pm J,\quad \omega_{\pm 4}=\pm(\omega_L+J) \ ,\\
&\omega_{\pm 2}=\pm(\omega_L-J),\quad \omega_{\pm 5}=\pm 2\omega_L \ ,
\end{aligned} \tag{4.8}$$

for the eigenfrequencies of the Liouville–von Neumann operator $[H_S,.]$. After some calculations one finds that the only nonvanishing matrices $A_i(\omega_l)$ are

$$A_1(\omega_{\pm 3})=\tfrac{1}{2}I^{\mp},\quad A_2(\omega_{\pm 3})=\pm\frac{i}{2}I^{\mp},\quad A_3(\omega_0)=I_z \ . \tag{4.9}$$

The operators I^+,I^- denote the ordinary raising or lowering operators. The expansion of the operators $A_i(\omega_l)$ in terms of the basis $\{F_i\}_1^M$ with

$$F_i=F_i^\dagger,\quad \mathrm{tr}(F_i)=0,\quad \mathrm{tr}(F_iF_j)=\delta_{ij} \tag{4.10}$$

yields

$$A_i(\omega_l)=\sum_{\mu=1}^{15}\lambda_{il}^{\mu}F_\mu \ . \tag{4.11}$$

Consequently, one gets for the two commutators in the second term $\tilde{D}_R$ of the Davies generator (4.4) the results

$$[A_i(\omega_l),.A_k^\dagger(\omega_l)]=\sum_{\mu,\nu=1}^{15}\lambda_{il}^{\mu}\lambda_{kl}^{\nu *}[F_\mu,.F_\nu] \ , \tag{4.12}$$

$$[A_i(\omega_l).,A_k^\dagger(\omega_l)]=\sum_{\mu,\nu=1}^{15}\lambda_{il}^{\mu}\lambda_{kl}^{\nu *}[F_\mu.,F_\nu] \ . \tag{4.13}$$

Inserting (4.12) and (4.13) in $\tilde{D}_R$ and comparing (4.6) with the non-Hamiltonian part of (2.5) leads to

$$a_{\mu\nu}=\sum_{i,l=1}^{3}\sum_{l=-5}^{+5}\lambda_{il}^{\mu}\lambda_{kl}^{\nu *}c_{ik}(\omega_l) \tag{4.14}$$

for the matrix elements of the relaxation matrix A. The expansion coefficients λ_{il}^{μ} can be found from Eq. (4.11). The only nonvanishing ones are given by

$$\lambda_{13}^{6}=\lambda_{1,-3}^{6}=\lambda_{13}^{13}=\lambda_{1,-3}^{13}=\lambda_{23}^{7}=\lambda_{2,-3}^{7}=\lambda_{23}^{14}=\lambda_{2,-3}^{14}=\tfrac{1}{2} \ , \tag{4.15a}$$

$$\begin{aligned}
\lambda_{23}^{6}=\lambda_{2,-3}^{6*}=\lambda_{23}^{13}=\lambda_{2,-3}^{13*}&=-\lambda_{13}^{7}\\
&=-\lambda_{1,-3}^{7*}\\
&=-\lambda_{13}^{14}=-\lambda_{1,-3}^{14*}=\frac{i}{2} \ ,
\end{aligned} \tag{4.15b}$$

$$\lambda_{30}^{3}=-\frac{1}{\sqrt{2}},\quad \lambda_{30}^{8}=\frac{1}{\sqrt{6}},\quad \lambda_{30}^{15}=\frac{2}{\sqrt{3}} \ . \tag{4.15c}$$

This result together with the relation (4.14) allows the explicit calculation of the matrix elements $a_{\mu\nu}$. The systematic evaluation yields

$$\begin{aligned}
&a_{33}=\tfrac{1}{2}c_{33}(\omega_0),\quad a_{88}=\frac{1}{6}c_{33}(\omega_0) \ ,\\
&a_{38}=-\frac{1}{\sqrt{12}}c_{33}(\omega_0),\quad a_{8,15}=\frac{\sqrt{2}}{3}c_{33}(\omega_0) \ ,\\
&a_{3,15}=-(\tfrac{2}{3})^{1/2}c_{33}(\omega_0),\quad a_{15,15}=\tfrac{4}{3}c_{33}(\omega_0) \ ,
\end{aligned} \tag{4.16}$$

and

$$a_{66}=a_{6,13}=a_{77}=a_{7,14}=a_{13,13}=a_{14,14}=f_+-ig_- \ , \tag{4.17a}$$

$$a_{67}=a_{6,14}=-a_{7,13}=a_{13,14}=g_++if_- \ , \tag{4.17b}$$

with the abbreviations

$$f_\pm=\tfrac{1}{4}\{c_{11}(\omega_3)+c_{22}(\omega_3)\pm[c_{11}(\omega_{-3})+c_{22}(\omega_{-3})]\} \ , \tag{4.18a}$$

$$g_\pm=\tfrac{1}{4}\{c_{12}(\omega_3)-c_{21}(\omega_3)\pm[c_{12}(\omega_{-3})-c_{21}(\omega_{-3})]\} \ . \tag{4.18b}$$

The remaining matrix elements vanish. In a next step we treat the correction $\tilde{D}_H$ to the Hamiltonian part of the dynamics. By expressing the commutators in $\tilde{D}_H$ according to the relations (4.9), one finds

$$\tilde{D}_H=-i[\lambda(I_x^2+I_y^2)+\nu I_z^2+\mu I_z,.] \ , \tag{4.19}$$

where the coefficients are given by

$$\begin{aligned}
\lambda=&\tfrac{1}{4}\{s_{11}(\omega_3)+s_{22}(\omega_3)+s_{11}(\omega_{-3})+s_{22}(\omega_{-3})\}\\
&+\frac{i}{4}\{s_{12}(\omega_{-3})-s_{21}(\omega_{-3})-s_{12}(\omega_3)+s_{21}(\omega_3)\} \ ,
\end{aligned} \tag{4.20a}$$

$$\begin{aligned}
\mu=&\tfrac{1}{4}\{s_{11}(\omega_3)+s_{22}(\omega_3)-s_{11}(\omega_{-3})-s_{22}(\omega_{-3})\}\\
&-\frac{i}{4}\{s_{12}(\omega_{-3})-s_{21}(\omega_{-3})+s_{12}(\omega_3)-s_{21}(\omega_3)\} \ ,
\end{aligned} \tag{4.20b}$$

$$\nu=s_{33}(\omega_0) \ . \tag{4.20c}$$

Thus the modified Hamiltonian $\overline{H}_S$ including level shifts can be written in the form

$$\overline{H}_S = H_S + \lambda(I_x^2 + I_y^2) + \nu I_z^2 + \mu I_z \ . \tag{4.21}$$

Later on we shall show that the Hilbert transforms $s_{ik}(\omega_l)$ satisfy the properties

$$\lambda = \nu = \mathrm{Im}(\mu) = 0, \quad \mathrm{Re}(\mu) \neq 0 \tag{4.22}$$

with respect to the reservoir model under consideration. Hence one finds for the structure of the matrix $\overline{H}_S$ the final form

$$H_S = \begin{bmatrix} -\frac{3}{4}J & 0 & 0 & 0 \\ 0 & [\omega_L + \mathrm{Re}(\mu)] + \dfrac{J}{4} & 0 & 0 \\ 0 & 0 & -\dfrac{J}{4} & 0 \\ 0 & 0 & 0 & -[\omega_L + \mathrm{Re}(\mu)] + \dfrac{J}{4} \end{bmatrix} , \tag{4.23}$$

where, obviously,

$$\mathrm{tr}(\overline{H}_S) = 0 \tag{4.24}$$

in agreement with (2.6). Furthermore, the resonance frequency ω_L is shifted to

$$\overline{\omega}_L = \omega_L + \mathrm{Re}(\mu) \ . \tag{4.25}$$

Later on we shall estimate the frequency shift $\mathrm{Re}(\mu)$ of the highest and the lowest energy level. The study of the differential equations (2.12) for the components of the coherence vector indicates that the diagonal relaxation times play an important role. Especially, one needs them to identify the measured longitudinal and transverse relaxation times. Thus, we proceed to the calculation of the diagonal relaxation times in terms of the Fourier transforms $c_{ik}(\omega_l)$ of the reservoir correlation functions. We rewrite Eq. (2.25) in terms of two matrices $\Gamma^{(b)}$ and $\Gamma^{(c)}$,

$$\Gamma_{sm}^{(b)} \equiv \tfrac{1}{4} \sum_{\substack{i,k,l=1 \\ (i<k)}}^{15} 2\,\mathrm{Re}(a_{ik})\{f_{ils}f_{klm} + f_{kls}f_{ilm}\} - R_S \ , \tag{4.26a}$$

$$\begin{aligned} \Gamma_{sm}^{(c)} \equiv {} & \tfrac{1}{4} \sum_{i,l=1}^{15} 2a_{ii}\{f_{ils}f_{ilm}\} \\ & + \tfrac{1}{2} \sum_{\substack{i,k,l=1 \\ (i<k)}}^{15} \mathrm{Im}(a_{ik})\{f_{ils}d_{klm} - f_{kls}d_{ilm}\} + R_S \ , \end{aligned} \tag{4.26b}$$

where

$$\begin{aligned} R_S \equiv {} & \tfrac{1}{4} \sum_{l=1}^{15} 2\,\mathrm{Re}(a_{38})\{f_{3ls}f_{8lm} + f_{8ls}f_{3lm}\} \\ & + \tfrac{1}{4} \sum_{l=1}^{15} 2\,\mathrm{Re}(a_{3,15})\{f_{3ls}f_{15lm} + f_{15ls}f_{3lm}\} \\ & + \tfrac{1}{4} \sum_{l=1}^{15} 2\,\mathrm{Re}(a_{8,15})\{f_{8ls}f_{15lm} + f_{15ls}f_{8lm}\} \ . \end{aligned} \tag{4.26c}$$

It should be noted that the matrix $\Gamma^{(b)}$ is symmetric. Furthermore the definitions (4.26a)–(4.26c) allow one to write the matrix elements r_{sm} in the compact form

$$r_{sm} = -\{\Gamma_{sm}^{(b)} + \Gamma_{sm}^{(c)}\} \ . \tag{4.27}$$

The diagonal elements of the matrix $\Gamma^{(c)}$ given by the equation

$$\begin{aligned} \Gamma_{mm}^{(c)} = {} & \tfrac{1}{2} \sum_{i,l=1}^{15} a_{ii}(f_{ilm})^2 + \tfrac{1}{2} \sum_{\substack{i,k,I=1 \\ (i<k)}}^{15} \mathrm{Im}(a_{ik})\{f_{ilm}d_{klm} - f_{klm}d_{ilm}\} \\ & + \sum_{l=1}^{15} \{\mathrm{Re}(a_{38})f_{3lm}f_{8lm} + \mathrm{Re}(a_{3,15})f_{3lm}f_{15lm} + \mathrm{Re}(a_{8,15})f_{8lm}f_{15lm}\} \ , \end{aligned} \tag{4.28}$$

define, at the same time, the diagonal relaxation times. With the relation [8]

$$a_{ii}a_{kk} \geq |a_{ik}|^2, \quad \forall i \neq k \ , \tag{4.29}$$

it may be verified that the inequality

$$\Gamma_{ii}^{(c)} \geq 0 \tag{4.30}$$

is satisfied. From Eqs. (4.16)–(4.18) one finally gets the expressions

$$\Gamma_{11}^{(c)} = \Gamma_{22}^{(c)} = \tfrac{1}{2}\{c_{33}(\omega_0) + f_+ + f_-\} \ ,$$

$$\Gamma_{33}^{(c)} = \tfrac{1}{2}\{f_+ + f_-\} \ ,$$

$$\Gamma_{44}^{(c)} = \Gamma_{55}^{(c)} = f_+ \ ,$$

$$\Gamma_{66}^{(c)} = \Gamma_{77}^{(c)} = \tfrac{1}{2}\{c_{33}(\omega_0) + 3f_+ + f_-\} \ ,$$

$$\Gamma_{88}^{(c)}=\tfrac{1}{6}\{13f_{+}+f_{-}\}\ , \tag{4.31}$$

$$\Gamma_{99}^{(c)}=\Gamma_{10,10}^{(c)}=\tfrac{1}{2}\{c_{33}(\omega_0)+f_{+}-f_{-}\}\ ,$$

$$\Gamma_{11,11}^{(c)}=\Gamma_{12,12}^{(c)}=2c_{33}(\omega_0)+f_{+}\ ,$$

$$\Gamma_{13,13}^{(c)}=\Gamma_{14,14}^{(c)}=\tfrac{1}{2}\{c_{33}(\omega_0)+3f_{+}-f_{-}\}\ ,$$

$$\Gamma_{15,15}^{(c)}=\tfrac{2}{3}\{2f_{+}-f_{-}\}\ ,$$

for the expansions of the diagonal relaxation times in the spectral density functions.

To proceed further, we evaluate the diagonal relaxation times in the microscopic parameters of the reservoir. We follow an idea by Abragam and assume that a snapshot of the reservoir always yields a quasicrystalline structure for the microscopic distribution of the water molecules [25]. Thus the mean field that couples to the components of the total nuclear spin I is generated by the surrounding reservoir molecules in a triplet state and can be calculated with the method of Pierre Weiss [29,32]. The statistical properties of the local field will be realized through the fluctuating functions $M_{\mu\nu}^{(j)}$. To become familiar with these principal assumptions we begin with the relation

$$H_{SR,\mu}=I_{\mu}\otimes\varepsilon\sum_{j}S_{\mu}^{\prime(j)},\quad \mu=x,y,z \tag{4.32}$$

for the components of the interaction Hamiltonian (4.1) with the abbreviations

$$\varepsilon=\left[\frac{6\pi}{5}\right]^{1/2}\gamma^{2},\quad S_{\mu}^{\prime(j)}=\sum_{\nu=1}^{3}M_{\mu\nu}^{(j)}S_{\nu}^{(j)}\ . \tag{4.33}$$

On the other hand the z component of the local field is given by

$$H_{SR,z}=-\gamma I_{z}B_{l,z}\ . \tag{4.34}$$

By comparison of the two relations (4.32) and (4.34) one gets

$$\mathbf{B}_{l,z}=-\frac{\varepsilon}{\gamma}\sum_{j}\sum_{\nu=1}^{3}M_{z\nu}^{(j)}\langle S^{(j)}\rangle\mathbf{n}_{z} \tag{4.35}$$

for the local field in the z direction $[\mathbf{n}_{z}=(0,0,1)]$. The Weiss approximation consists of replacing the spin operators of the reservoir particles by their expectation values. Analogous results follow for the x and y components. Consequently, one may write the total local field in the form

$$\mathbf{B}_{l}=-\frac{\varepsilon}{\gamma}\sum_{j}\sum_{\nu=1}^{3}\left(M_{x\nu}^{(j)}\langle S^{(j)}\rangle\mathbf{n}_{x}+M_{y\nu}^{(j)}\langle S^{(j)}\rangle\mathbf{n}_{y}+M_{z\nu}^{(j)}\langle S^{(j)}\rangle\mathbf{n}_{z}\right)\ . \tag{4.36}$$

The expectation values of the bath operators $S_{\mu}^{(j)}$ can be calculated with the equation

$$\langle S_{\mu}^{(j)}\rangle=\mathrm{tr}_{S}(S_{\mu}^{(j)}\rho_{\beta})\ , \tag{4.37}$$

where the thermal equilibrium state ρ_{β} of the open quantum system is given by

$$\rho_{\beta}=Z^{-1}e^{-H_{s}/k_{B}T},\quad Z=\mathrm{tr}_{S}(e^{-H_{s}/k_{B}T})\ . \tag{4.38}$$

In the high-temperature limit one finds

$$\langle S_{\mu}^{(j)}\rangle=\tfrac{1}{4}\{\mathrm{tr}_{S}(S_{\mu}^{(j)})-\mathrm{tr}_{S}(H_{S}/k_{B}TS_{\mu}^{(j)})\}\ . \tag{4.39}$$

With the relations

$$\mathrm{tr}_{S}(H_{S}S_{x}^{(j)})=\mathrm{tr}_{S}(H_{S}S_{y}^{(j)})=0,\quad \mathrm{tr}_{S}(H_{S}S_{z}^{(j)})=2\omega_{L}\ , \tag{4.40}$$

one may introduce the following definition for the correlation functions of the fluctuating field $\mathbf{B}_{1}$:

$$h_{qq'}(t)=K\sum_{i,j}\mathrm{tr}_{R}[P_{R}M_{q3}^{(j)}(0)M_{q3}^{(i)}(t)]\ , \tag{4.41}$$

where K is an effective coupling constant. According to present knowledge the evaluation of these correlation functions is possible only under some simplifying assumptions. It has been assumed in all theoretical treatments so far that the properties of $h_{qq'}(t)$ are entirely determined by rotational and translational diffusion dynamics of the molecules. As far as the explicit time dependence is concerned we will follow this point of view without modifications. However, the weight with which these processes determine the relaxation rates is also affected by another important stochastic process, namely, the fluctuating formation and breaking of hydrogen bridges. From a purist point of view one should construct, consequently, a universal conditional probability density comprising at the same time all three stochastic processes and perform the calculation in the same way as has been done for diffusion only. On one hand this is not practicable on the basis of presently available data which, on the other hand, suggest a reasonable alternative treatment due to obviously different time scales. In a comprehensive review article [33] the lifetimes τ_{f} (H bond broken) and τ_{HB} (H bond intact) are given over a wide temperature range. We will see that these values are shorter than rotational or translational correlation times, in most cases by more than one order of magnitude. Assuming that diffusion dynamics is effective only in the absence of hydrogen bridges, these processes take place during a fraction of time, which is given by $\tau_{f}/(\tau_{f}+\tau_{\mathrm{HB}})$. This determines the effective coupling constant as

$$K=\frac{\varepsilon^{2}\tau_{f}}{\tau_{f}+\tau_{\mathrm{HB}}}\ , \tag{4.42}$$

where ε^{2} is as defined in (4.33). Note that $K=\varepsilon^{2}$ is the result in agreement with earlier approaches and valid obviously in the limit $\tau_{f}\gg\tau_{\mathrm{HB}}$ in this treatment.

For the evaluation of the correlation functions some standard calculations for a dipole-dipole interaction Hamiltonian yield the relationship between the $M_{\mu\nu}^{(j)}$ components and the spherical harmonics [29,34,35]. We omit the details but quote some intermediate results with the upper index j dropped. In terms of the abbreviations

$$\Delta=\left[\frac{24\pi}{5}\right]^{1/2}, \tag{4.43}$$

$$\begin{aligned} F^0&=\Delta r^{-3}Y_2^0(\Omega)\,,\\ F^{\pm1}&=\Delta r^{-3}Y_2^{\pm1}(\Omega)\,,\\ F^{\pm2}&=\Delta r^{-3}Y_2^{\pm2}(\Omega)\,, \end{aligned} \tag{4.44}$$

one gets the following expansion of the reservoir correlation function $f_{11}(t)$ from the Eqs. (4.1) and (4.2):

$$\begin{aligned} h_{11}(t)=K\Delta^{-2}\{&\mathrm{tr}_R[P_RF^{+1}F^{+1^*}(t)]\\ &+\mathrm{tr}_R[P_RF^{-1}F^{-1^*}(t)]\\ &-\mathrm{tr}_R[P_RF^{+1}F^{-1^*}(t)]\\ &-\mathrm{tr}_R[P_RF^{-1}F^{+1^*}(t)]\}\,. \end{aligned} \tag{4.45}$$

A complete list of all expansions of the functions $h_{ik}(t)$ will be given in Appendix A. Because there is no analytically accessible procedure to calculate the quantum correlations $\mathrm{tr}_R[P_RF^iF^{j^*}(t)]$ one assumes a classical behavior of the reservoir molecules. This assumption is based on the fact that the mean de Broglie wavelength at room temperature [36,37]

$$\lambda_B=(2Mk_BT)^{-1/2}\approx0.07\ \text{Å}\,, \tag{4.46}$$

is small compared to the intermolecular distance $d_i=3.5$ Å. Thus, it is possible to link the correlations $h_{qq'}(t)$ to the classical propagator $P(y_2,y_1,t)$ in the following manner [25,38]:

$$\begin{aligned} &\mathrm{tr}_R[P_RF^mF^{n^*}(t)]\\ &\quad=\int\int p(y_1)P(y_2,y_1,t)F^m(y_1)F^{n^*}(y_2)dy_1,dy_2\,, \end{aligned} \tag{4.47}$$

where $m,n=0,\pm1,\pm2$. $P(y_2,y_1,t)$ is given by the solution of the appropriate Fokker-Planck equation [39,40]. To treat this problem we first make some remarks concerning the rotational and translational motion of the water molecules. The rotational motion of the water molecule, influenced by a continuous bombardment from other molecules, produces a random behavior of the intramolecular dipole-dipole interaction. The translational motion of a water molecule relative to a neighboring one produces a random behavior of the intermolecular dipole-dipole interaction. Furthermore, translational and rotational motion may be investigated independently of one another; in other words, we neglect rototranslational effects. In a next step we evaluate the rotational correlation functions $h_{qq'}^R(t)$ of the bath. An extended description of the underlying method can be found elsewhere [25,41]. For this reason we present here only the basic equation

$$\mathrm{tr}_R[P_RF^mF^{n^*}(t)]=\frac{\Delta^2}{4\pi}r_0^{-6}\sum_{k=-2}^{+2}e^{-|t|/\tau_2}\delta_{km}\delta_{kn} \tag{4.48}$$

with $m,n=0,\pm1,\pm2$. Recall that τ_2 denotes the rotational correlation time while r_0 is the intramolecular distance. If use is made of Appendix A, (4.48), and (2.37), one obtains

$$\begin{aligned} &c_{qq'}^R(\omega)=0,\quad q\neq q'\,,\\ &c_{11}^R(\omega)=c_{22}^R(\omega)=\tfrac{3}{4}c_{33}^R(\omega)=\frac{K}{\pi}r_0^{-6}\frac{\tau_2}{1+(\omega\tau_2)^2} \end{aligned} \tag{4.49}$$

for the spectral density functions. According to (2.38) it follows immediately that the Hilbert transforms are given by

$$\begin{aligned} &s_{qq'}^R(\omega)=0,\quad q\neq q'\,,\\ &s_{11}^R(\omega)=s_{22}^R(\omega)=\tfrac{3}{4}s_{33}^R(\omega)=\frac{K}{2\pi}r_0^{-6}\frac{\omega\tau_2^2}{1+(\omega\tau_2)^2}\,. \end{aligned} \tag{4.50}$$

The translational diffusion can be investigated in a similar manner [1,25]. The basic result is

$$\begin{aligned} &\mathrm{tr}_R[P_RF^mF^{n^*}(t)]\\ &\quad=(-1)^{-(m+n)}\tfrac{3}{4}N\Delta^2d^{-3}\\ &\qquad\times\sum_{\hat m=-2}^{+2}\delta_{-m,\hat m}\delta_{\hat m,-n}\\ &\qquad\qquad\times\int_0^\infty[J_{3/2}(u)]^2e^{-2D|t|ud^{-3}}u^{-1}du\,, \end{aligned} \tag{4.51}$$

where N denotes the density of spins per cm^3, D is the translational diffusion coefficient, and d is the molecular diameter. The spectral density functions $c_{qq'}^T(\omega)$ are proportional to the integral

$$I_1(\omega)=\int_0^\infty du\,u[J_{3/2}(u)]^2[u^4+\omega^2\tau^2]^{-1}\,,\qquad \tau=d^2/2D\,. \tag{4.52}$$

Its solution is [42]

$$I_1(z)=p_1(z)+e^{-z}\{p_2(z)\cos(z)+p_3(z)\sin(z)\}\,, \tag{4.53}$$

where

$$\begin{aligned} p_1(z)&=-2z^{-5}+z^{-3}\,,\\ p_2(z)&=2z^{-5}+4z^{-4}+z^{-3}\,,\\ p_3(z)&=-2z^{-5}+z^{-3},\quad z=\sqrt{2|\omega|\tau}\,. \end{aligned} \tag{4.54}$$

The limit of $I_1(z)$ as $z\to0$ is $\frac{2}{15}$. Hence one finds for the Fourier transforms $c_{qq'}^T(\omega)$ the following results:

$$\begin{aligned} &c_{qq'}^T(\omega)=0,\quad q\neq q'\,,\\ &c_{11}^T(\omega)=c_{22}^T(\omega)=\tfrac{3}{4}c_{33}^T(\omega)=\tfrac{3}{2}KN(dD)^{-1}I_1(\omega)\,. \end{aligned} \tag{4.55}$$

The Hilbert transforms can be deduced from the solution of the integral

$$I_2(\omega)=\frac{\pi}{2}b^2\int_0^\infty du[J_{3/2}(u)]^2[u(u^4+\omega^2\tau^2)]^{-1}\,,\qquad b=\sqrt{|\omega|\tau}\,. \tag{4.56}$$

As a result one gets [43]

$$I_2(z)=\pi\{p_1(z)+e^{-z}[p_2(z)\cos(z)+p_3(z)\sin(z)]\}\ , \qquad (4.57)$$

where we have used the abbreviations

$$\begin{aligned} &p_1(z)=(3z^2)^{-1}-(2z^3)^{-1}-z^{-5}\ ,\\ &p_2(z)=z^{-5}-(2z^3)^{-1}\ , \qquad (4.58)\\ &p_3(z)=z^{-5}+2z^{-4}+(2z^3)^{-1},\quad z=\sqrt{2|\omega|\tau}\ . \end{aligned}$$

The limit of $I_2(z)$ as $z\rightarrow 0$ is 0. Therefore the Hilbert transforms $s_{qq'}^{T}(\omega)$ are given by

$$\begin{aligned} &s_{qq'}^{T}(\omega)=0,\quad q\neq q'\ ,\\ & \qquad (4.59)\\ &s_{11}^{T}(\omega)=s_{22}^{T}(\omega)=\tfrac{3}{4}s_{33}(\omega)=\tfrac{3}{\pi}\operatorname{sgn}(\omega)\frac{KN}{2dD}I_2(\omega)\ . \end{aligned}$$

We are now in a position to verify the relations (4.22). Bearing in mind (4.50) and (4.59) the imaginary parts of μ and λ may be omitted. Because the Hilbert transforms $s_{ii}^{R}(\omega)$ and $s_{ii}^{T}(\omega)$, $i=1,2,3$ are odd functions of ω, the real part of λ is zero, while the level shift $\mathrm{Re}(\mu)$ is determined by

$$\mathrm{Re}(\mu)=\frac{K}{2\pi}r_0^{-6}\frac{\omega_L\tau_2^2}{1+(\omega_L\tau_2)^2}+\frac{3}{\pi}\frac{KN}{2dD}I_2(\omega_L)\ . \qquad (4.60)$$

The remaining relation $\nu=s_{33}(\omega=0)=0$ follows directly from (4.50) and (4.59). An average numerical estimate using parameter values from Table I in a static field of 1 T yields for $\mathrm{Re}(\mu)$ about 10^{-2} Hz, that is much smaller than the indirect nuclear coupling $J_{HH}=7.18$ Hz and can, therefore, be neglected in the following.

Substitution of the calculated spectral density functions in (4.31) leads to the desired expressions for the diagonal relaxation times in terms of the microscopic parameters of the reservoir. We only need to focus our attention on specific values of the matrix elements $\Gamma_{44}^{(c)}$, $\Gamma_{55}^{(c)}$:

$$\Gamma_{44}^{(c)}=\Gamma_{55}^{(c)}=\frac{K}{2\pi}r_0^{-6}\frac{\tau_2}{1+(\omega_L\tau_2)^2}+\frac{3}{2}\frac{KN}{dD}I_1(\omega_L)\ . \qquad (4.61)$$

The collection of all diagonal relaxation times can be found in Appendix B. In order to find the relationship between the relaxation times $\{T_1,T_2\}$ and the $\Gamma_{ii}^{(c)}$'s one has to study the solution of the differential equation of the coherence vector. This will be done in the next section, but we anticipate here that after some faster transient behavior, the essential time decay of the diagonal density matrix elements is like $\exp(-\Gamma_{44}^{(c)}t)$ and, therefore, T_1 is given directly by the inverse of $\Gamma_{44}^{(c)}$. The final explicit formula in terms of all relevant parameters is given by

$$\Gamma_{44}^{(c)}=\frac{6\hbar^2\gamma^4\tau_f}{25d^3r_0^6(\tau_f+\tau_{\mathrm{HB}})}(5d^3+18\pi Nr_0^6)\tau_2\ , \qquad (4.62)$$

where the extreme narrowing case has been assumed and D has been replaced by

$$D^{-1}=18\tau_2/d^2\ , \qquad (4.63)$$

as follows from the Rayleigh-Stokes relations [1,25]. The temperature-dependent quantities are τ_f, τ_{HB}, and τ_2. Given the data by Bertolini *et al.* [33], one can use measured longitudinal relaxation times for a determination of the rotational correlation times τ_2. Note that from our point of view τ_2 is a "free" correlation time, that is one in absence of any interrupting effects caused by hydrogen bridges. Qualitatively, this must yield values which are longer than those obtained from the conventional theory for which τ_2 must be interpreted as an "effective" correlation time, including somehow the neglected bridge effects. A detailed evaluation and comparison is displayed in Table I on the basis of available data (including some extrapolations) for a wide temperature range. The following parameter values have been used: $d=3.5\times10^{-8}$ cm, $r_0=1.5\times10^{-8}$, cm, $N=6.67\times10^{22}$ cm^{-3}, $\hbar=1.055\times10^{-27}$ erg s, $\gamma=2.675\times10^{4}$ s^{-1} G^{-1}.

For completeness we also give values in the limit $\tau_f \gg \tau_{\mathrm{HB}}$, where one should get more or less the standard values as obtained from Redfield theory. The discrepancies are by no means surprising since the level of approximations is different in the two approaches.

V. GENERALIZED BLOCH EQUATIONS

A. Static field case

In this section we solve the coupled system of differential equations for the components of the coherence vector (2.12) in the static, homogeneous magnetic field. We start with the equation

TABLE I. Parameter values T_1 and τ's for a range of temperatures. T_1: experimental values [45]; τ_f,τ_{HB}: hydrogen bridge data [33]; τ_2: calculated from Eq. (4.62); $\tau_2^{(0)}$: values of τ_2 in the limit $\tau_f \gg \tau_{\mathrm{HB}}$; τ_c: values of τ_2 from ordinary Redfield theory [25,33].

T (°C)	T_1 (s)	τ_f (ps)	τ_{HB} (ps)	τ_2 (ps)	τ_2^0 (ps)	τ_c (ps)
10	2.39	0.329	0.683	18.70	6.08	4.29
20	3.15	0.319	0.579	12.98	4.61	3.15
25	3.6	0.313	0.536	10.97	4.04	2.73
30	4.03	0.307	0.497	9.44	3.61	2.39
40	5.0	0.298	0.431	7.11	2.91	1.87
50	6.02	0.289	0.377	5.56	2.41	1.57
75	9.09	0.272	0.278	3.23	1.6	1.0

$$q_{sm}=\sum_{n=1}^{15} h_n f_{nms}, \quad s,m=1,2,\ldots,15 \;. \tag{5.1}$$

The h_n's can be evaluated from the expansion of the matrix H_S in terms of the matrices $F_1, F_2, \ldots, F_{15}$. The result is

$$\bar{H}_S=\sum_{n=1}^{15} h_n F_n = h_3 F_3 + h_8 F_8 + h_{15} F_{15} \;, \tag{5.2}$$

where

$$h_3=-\frac{1}{\sqrt{2}}(\varpi_L+J), \quad h_8=\frac{1}{\sqrt{6}}(\varpi_L-J) \;,$$
$$h_{15}=\frac{1}{\sqrt{3}}\left[2\varpi_L-\frac{J}{2}\right] . \tag{5.3}$$

Thus with the symmetry property (2.18) one is able to determine the matrix Q. The computation of the matrix R is more complicated. The basic equation is given by the relation (2.25) with $M=15$. Note that the first term defines a symmetric matrix. The somewhat lengthy routine calculations are omitted. The results, especially the connection between the matrix elements r_{sm} and the diagonal relaxation times $\Gamma_{ii}^{(c)}$ can be found elsewhere [43]. To treat the remaining vector $\mathbf{k}$, one uses the following equation:

$$k_S=-\tfrac{1}{2}\sum_{\substack{i,k=1\\(i<k)}}^{15} \operatorname{Im}(a_{ik}) f_{iks}, \quad s=1,2,\ldots,15 \;. \tag{5.4}$$

The information (4.16)–(4.18) about the detailed structure of the relaxation matrix A yields for the components k_S the relations

$$k_S=0, \quad s\neq 3,8,15 \;,$$
$$k_3=\frac{1}{2\sqrt{2}}\operatorname{Im}(a_{67}), \quad k_8=-\frac{1}{2\sqrt{6}}\operatorname{Im}(a_{67}) \;,$$
$$k_{15}=-\frac{1}{\sqrt{3}}\operatorname{Im}(a_{67}) \;. \tag{5.5}$$

In consequence of (4.18a), (4.49), and (4.55) the components k_3, k_8, and k_{15} vanish, too. Hence, $\mathbf{k}=0$ holds for the reservoir under consideration. This agrees with the fact that in the thermal equilibrium the triplet states are nearly equally populated. For two neighboring triplet states with energies E_a, E_b, and occupation probabilities $p(E_a)$ and $p(E_b)$, one has

$$\frac{p(E_a)}{p(E_b)}=\exp\left[\frac{\varpi_L}{k_B T}\right], \quad E_a<E_b \;. \tag{5.6}$$

The ratio $\varpi_L/k_B T$ is approximately 10^{-6} at room temperature. Therefore, one may assume that $p(E_a)/p(E_b)\cong 1$. The differential equations for the components of the coherence vector are as follows. Due to a decoupling, one distinguishes six linear and homogeneous systems of first-order differential equations. Four of them involve an antisymmetric (2×2) matrix, one a symmetric (3×3) matrix, and one a (4×4) matrix of mixed symmetry. We present here only the system

$$\begin{bmatrix}\dot{v}_3\\ \dot{v}_8\\ \dot{v}_{15}\end{bmatrix}=\begin{bmatrix}-\frac{1}{2}\Gamma_{44}^{(c)} & \frac{\sqrt{3}}{2}\Gamma_{44}^{(c)} & 0\\ \frac{\sqrt{3}}{2}\Gamma_{44}^{(c)} & -\frac{13}{6}\Gamma_{44}^{(c)} & \frac{2\sqrt{2}}{3}\Gamma_{44}^{(c)}\\ 0 & \frac{2\sqrt{2}}{3}\Gamma_{44}^{(c)} & -\frac{4}{3}\Gamma_{44}^{(c)}\end{bmatrix}\begin{bmatrix}v_3\\ v_8\\ v_{15}\end{bmatrix} \tag{5.7}$$

for the diagonal density-matrix components. Since the matrix is symmetric and, therefore, diagonalizable, the solutions can be found by the simple standard eigenvalue-eigenvector method [11,44] in the form

$$\mathbf{x}(t)=c_1 e^{\lambda_1 t}\mathbf{w}^{(1)}+c_2 e^{\lambda_2 t}\mathbf{w}^{(2)}+c_3 e^{\lambda_3 t}\mathbf{w}^{(3)} \;, \tag{5.8}$$

where the eigenvalues are given by

$$\lambda_1=-3\Gamma_{44}^{(c)}, \quad \lambda_2=-\Gamma_{44}^{(c)}, \quad \lambda_3=0 \tag{5.9}$$

and

$$\mathbf{w}^{(1)}=\begin{bmatrix}\frac{\sqrt{3}}{6}\\ -\frac{5}{6}\\ \frac{\sqrt{2}}{3}\end{bmatrix}, \quad \mathbf{w}^{(2)}=\begin{bmatrix}-\frac{1}{2}\\ \frac{\sqrt{3}}{6}\\ \frac{\sqrt{6}}{3}\end{bmatrix}, \quad \mathbf{w}^{(3)}=\begin{bmatrix}\frac{\sqrt{6}}{3}\\ \frac{\sqrt{2}}{3}\\ \frac{1}{3}\end{bmatrix} . \tag{5.10}$$

The vector of solutions is defined by

$$\mathbf{x}(t)=\begin{bmatrix}v_3(t)\\ v_8(t)\\ v_{15}(t)\end{bmatrix} . \tag{5.11}$$

B. Alternating field case

In an additional alternating field $\mathbf{B}(t)=[-2B_1\cos(\omega t),0,0]$ the Hamiltonian may be written in the form

$$H_S(t)=\varpi_L I_{1z}+\varpi_L I_{2z}+J\mathbf{I}_1\cdot\mathbf{I}_2+W(t) \tag{5.12}$$

with

$$W(t)=\tfrac{1}{2}W(e^{i\omega t}+e^{-i\omega t}) \;, \tag{5.13}$$

or else

$$W(t)=-\boldsymbol{\mu}\cdot\mathbf{B}(t)=\tfrac{1}{2}\gamma B_1(I^+ + I^-)(e^{i\omega t}+e^{-i\omega t}) \;. \tag{5.14}$$

By comparison of (5.13) with (5.14), one gets

$$W=\gamma B_1(I^+ + I^-) \tag{5.15}$$

and the matrix representation

$$W(t)=\omega_1\cos(\omega t)\begin{bmatrix}0 & 0 & 0 & 0\\ 0 & 0 & \sqrt{2} & 0\\ 0 & \sqrt{2} & 0 & \sqrt{2}\\ 0 & 0 & \sqrt{2} & 0\end{bmatrix} \tag{5.16}$$

of the operator $W(t)$ with respect to the basis $|p_i\rangle$, where $\omega_1=\gamma B_1$. For the ratios (ω_1/ω_L) usually met in nuclear resonance the Bloch-Siegert shift may be neglected, which means that the action of the alternating field can be taken into account in the rotating-wave approximation [46–48]

$$W^{\mathrm{RWA}}(t)=\tfrac{1}{2}\omega_1(e^{-i\omega t}I^{+}+e^{i\omega t}I^{-}) \ . \tag{5.17}$$

The time dependence of $W^{\mathrm{RWA}}(t)$ is eliminated by transforming to a rotating coordinate system. By introducing the unitary operator

$$U(t)=\exp(i\omega t I_z) \ , \tag{5.18}$$

any operator O is transformed into

$$\hat{O}=U(t)OU^{\dagger}(t) \ . \tag{5.19}$$

By direct calculation one verifies that

$$W^{\mathrm{RWA}}=\tfrac{1}{2}\omega_1 I_x \ . \tag{5.20}$$

Furthermore, the master equation in the rotating frame is

$$\dot{\hat{\rho}}(t)=[\hat{L}_h+\hat{L}_d(t)]\hat{\rho}(t) \ , \tag{5.21}$$

where

$$\hat{L}_h=-i[(\bar{\omega}_L-\omega)I_z+J\mathbf{I}_1\cdot\mathbf{I}_2+\omega_1 I_x,.] \ , \tag{5.22}$$

$$\hat{L}_d=\tfrac{1}{2}\sum_{i,j=1}^{15} a_{ij}\{[\hat{F}_i(t),.\hat{F}_j(t)]+[\hat{F}_i(t).,\hat{F}_j(t)]\} \ . \tag{5.23}$$

Here, we assume again a constant matrix A. Now, following the standard procedure [8,19], we use the superoperator notation

$$(L_d)_{ij}^{kl}=\tfrac{1}{2}\sum_{m,n=1}^{15} a_{mn}\{\langle p_i|[F_{m'}|p_k\rangle\langle p_l|F_n]|p_j\rangle$$
$$+\langle p_i|[F_m|p_k\rangle\langle p_l|,F_n]|p_j\rangle\} \tag{5.24}$$

and the abbreviation

$$g_{ij}(t)=U_{ii}(t)U_{jj}^{\dagger}(t) \tag{5.25}$$

to get the matrix elements $\dot{\hat{\rho}}_{ij}^{(d)}(t)$ of the operator $\dot{\hat{\rho}}^{(d)}=\hat{L}_d\hat{\rho}$ in the compact form

$$\dot{\hat{\rho}}_{ij}^{(d)}(t)=g_{ij}(t)\sum_{k,l=1}^{4}(L_d)_{ij}^{kl}\rho_{kl}(t) \ . \tag{5.26}$$

In a next step we investigate the product

$$g_{ij}(t)g_{kl}(t)=U_{ii}(t)U_{jj}^{\dagger}(t)U_{kk}(t)U_{ll}^{\dagger}(t) \ . \tag{5.27}$$

Evaluation of the matrix elements of the operator U yields

$$g_{ij}(t)g_{kl}(t)=\exp[i(m_i-m_j+m_k-m_l)\omega t] \tag{5.28}$$

and therefore

$$g_{ii}(t)g_{kk}(t)=g_{ik}(t)g_{ki}(t)=1, \quad \forall(i,k) \ . \tag{5.29}$$

By utilizing (5.25), (5.29), and

$$\hat{\rho}_{ij}(t)=U_{ii}(t)U_{jj}^{\dagger}(t)\rho_{ij}(t) \ , \tag{5.30}$$

we obtain

$$g_{lk}(t)\hat{\rho}_{kl}(t)=g_{lk}(t)g_{kl}(t)\rho_{kl}(t)=\rho_{kl}(t) \ . \tag{5.31}$$

Substituting (5.31) into the right side of (5.26) gives us the new result

$$\dot{\hat{\rho}}_{ij}^{(d)}(t)=\sum_{k,l=1}^{4}[L_d(t)]_{ij}^{kl}\hat{\rho}_{kl}(t) \ . \tag{5.32}$$

Use has been made of the definition

$$[\hat{L}_d(t)]_{ij}^{kl}\equiv g_{ij}(t)g_{lk}(t)(L_d)_{ij}^{kl} \ . \tag{5.33}$$

From the structure of the Hamiltonian part $\hat{L}_h$ of the Kossakowski generator $\hat{L}$ it is obvious that the commutation relation $[\partial/\partial t,\hat{L}_h]=0$ is satisfied. Thus, we are left with the condition

$$\left[\frac{\partial}{\partial t},\hat{L}_d(t)\right]=0 \tag{5.34}$$

to reestablish the original structure of the master equation (2.5) in the rotating frame. With the help of the two equations

$$\left\langle p_i\left|\frac{\partial}{\partial t}\hat{L}_d(t)\hat{\rho}(t)\right|p_j\right\rangle=\sum_{k,l=1}^{4}\frac{\partial}{\partial t}[g_{ij}(t)g_{lk}(t)(L_d)_{ij}^{kl}\hat{\rho}_{kl}(t)] \tag{5.35}$$

and

$$\left\langle p_i\left|\hat{L}_d(t)\frac{\partial}{\partial t}\hat{\rho}(t)\right|p_j\right\rangle=\sum_{k,l=1}^{4}g_{ij}(t)g_{lk}(t)(L_d)_{ij}^{kl}\dot{\hat{\rho}}_{kl}(t) \ , \tag{5.36}$$

it follows that the commutator in (5.34) vanishes only if $g_{ij}(t)g_{lk}(t)=\mathrm{const}$ for all $i,j,k,l=1,2,3,4$. With respect to the relations (5.28) and (5.29) there exist only two possibilities for the product $g_{ij}(t)g_{lk}(t)$ to become time independent:

$$g_{ij}(t)g_{lk}(t)=\delta_{ij}\delta_{kl} \ , \tag{5.37a}$$

$$g_{ij}(t)g_{lk}(t)=\delta_{ik}\delta_{jl} \ . \tag{5.37b}$$

The combination of the two possibilities leads to the equation

$$g_{ij}(t)g_{lk}(t)=\delta_{ij}\delta_{kl}(1-\delta_{ik})+\delta_{ik}\delta_{jl} \ . \tag{5.38}$$

Consequently, one obtains for the dissipative part $\hat{L}_d$ the following result in superoperator notation:

$$(\hat{L}_d)_{ij}^{kl}=(L_d)_{ij}^{kl}[\delta_{ij}\delta_{kl}(1-\delta_{ik})+\delta_{ik}\delta_{jl}] \ . \tag{5.39}$$

To get the connection with the components of the coherence vector in the rotating frame, one needs the relation

$$\dot{v}_k=\mathrm{tr}(F_k\dot{\hat{\rho}})=\mathrm{tr}(F_k\dot{\hat{\rho}}^{(h)})+\mathrm{tr}(F_k\dot{\hat{\rho}}^{(d)})$$
$$=\dot{\hat{v}}_k^{(h)}+\dot{\hat{v}}_k^{(d)} \ , \tag{5.40}$$

where

$$\hat{\rho}(t)=\frac{1}{4}F_0+\sum_{i=1}^{15}\hat{v}_i(t)F_i \ . \tag{5.41}$$

Thus, one finally finds, on one hand

$$\hat{v}_k^{(h)} = -i \sum_{i,j,l=1}^{4} \langle p_j|F_k|p_i\rangle \{ \langle p_i|[(\varpi_L-\omega)I_z + J\mathbf{I}_1\cdot\mathbf{I}_2]|p_l\rangle\langle p_l|\hat{\rho}(t)|p_j\rangle + \langle p_i|\omega_1 I_x|p_l\rangle\langle p_l|\hat{\rho}(t)|p_j\rangle - \langle p_i|\hat{\rho}(t)|p_l\rangle\langle p_l|[(\varpi_L-\omega)I_z + J\mathbf{I}_1\cdot\mathbf{I}_2]|p_j\rangle - \langle p_i|\hat{\rho}(t)|p_l\rangle\langle p_l|\omega_1 I_x|p_j\rangle \} , \tag{5.42}$$

and, on the other hand,

$$\hat{v}_k^{(d)} = \sum_{i,j=1}^{4} \langle p_j|F_k|p_i\rangle \sum_{m,l=1}^{4} (L_d)_{ij}^{ml}[\delta_{ij}\delta_{ml}(1-\delta_{im})+\delta_{im}\delta_{jl}]\hat{\rho}_{ml}(t), \quad k=1,2,\ldots,15 \tag{5.43}$$

for the two contributions $\hat{v}_k^{(h)}$ and $\hat{v}_k^{(d)}$. Now, with the preceding equations (5.42) and (5.43) the generalized Bloch equations in the alternating field case can be written down. A detailed calculation yields two homogeneous systems of first-order differential equations. We present here only the system with the (6×6) coefficient matrix

$$\begin{bmatrix} \dot{\hat{v}}_1 \\ \dot{\hat{v}}_2 \\ \dot{\hat{v}}_4 \\ \dot{\hat{v}}_5 \\ \dot{\hat{v}}_9 \\ \dot{\hat{v}}_{10} \end{bmatrix} = \begin{bmatrix} -\Gamma_{11}^{(c)} & [(\varpi_L-\omega)+J] & 0 & \frac{\omega_1}{\sqrt{2}} & 0 & 0 \\ -[(\varpi_L-\omega)+J] & -\Gamma_{11}^{(c)} & -\frac{\omega_1}{\sqrt{2}} & 0 & 0 & 0 \\ 0 & \frac{\omega_1}{\sqrt{2}} & -\Gamma_{44}^{(c)} & J & 0 & \frac{\omega_1}{\sqrt{2}} \\ -\frac{\omega_1}{\sqrt{2}} & 0 & -J & -\Gamma_{44}^{(c)} & -\frac{\omega_1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & \frac{\omega_1}{\sqrt{2}} & -\Gamma_{11}^{(c)} & -[(\varpi_L-\omega)-J] \\ 0 & 0 & -\frac{\omega_1}{\sqrt{2}} & 0 & [(\varpi_L-\omega)-J] & -\Gamma_{11}^{(c)} \end{bmatrix} \begin{bmatrix} \hat{v}_1 \\ \hat{v}_2 \\ \hat{v}_4 \\ \hat{v}_5 \\ \hat{v}_9 \\ \hat{v}_{10} \end{bmatrix} , \tag{5.44}$$

whereas the other one will be given in Appendix C. As in the static field case the nonzero matrix elements of the coefficient matrices are composed of certain relaxation rates, the indirect coupling J, the effective resonance frequency ϖ_L, and the pair of frequencies (ω_1,ω) characterizing the alternating field. It is interesting to note that in comparison with the static field case no new diagonal relaxation times enter the matrices. Furthermore, the coefficient matrix in (5.44) is purely antisymmetric whereas the other one in (C1) is of mixed symmetry. Both systems, can be solved by the same standard method, as mentioned in Sec. V A.

VI. DISCUSSION

The application of the mathematically rigorous concept of completely positive quantum-dynamical semigroups for Markovian master equations to the problem of proton-spin relaxation in water leads to more general results than in Redfield's theory. Especially, the transformation of the Kossakowski master equation into coherence-vector form, using the Lie algebra of the special unitary group SU(4), allows the derivation of generalized Bloch-type equations for the four-level system under consideration. In particular, we have obtained two sets of homogeneous linear systems of differential equations, one for the static field case, the other for the alternating field case. If needed the corresponding eigenvalue problem must be solved on a computer. Recall that the solutions of these generalized Bloch equations fulfill the von Neumann conditions of hermiticity, trace preservation, and positivity as required by the general laws of quantum theory. This is guaranteed by the fundamental concept of complete positivity, which represents an essential distinction in comparison to Redfield's theory. It is worthwhile to note also from the preceding sections that one can study finer details concerning the relaxation processes with the new theoretical approach [8,19]. Moreover, with the Davies theorem one is able to link, in a very general manner, the matrix elements of the relaxation matrix A to the Fourier transforms $c_{ik}(\omega)$ of the correlation functions $h_{ik}(t)$ of the reservoir. Finally, to get a form of the general Bloch equations similar to that obtained from Redfield's theory, one only has to find the relations between the diagonal matrix elements $\Gamma_{ii}^{(c)}$ of the matrix $\Gamma^{(c)}$ and the a_{ik}'s of the matrix A. As a result one obtains the general Bloch equations in terms of the spectral density functions $c_{ik}(\omega)$.

Following the method of Pierre Weiss to calculate the local mean field that couples to the components of the total nuclear spin I, we have established general expressions for the quantum correlation functions $h_{ik}(t)$ of the bath. They are generated by a classical propagator. This is justified as seen by comparison of the mean de Broglie wavelength of the reservoir particles with the intermolecular distance. Using the standard procedure to find the rotational and translational contributions to the correlation functions, one finally gets the spectral density functions in terms of the microscopic parameters of the reservoir. Thus the diagonal relaxation times and, therefore, the coefficient matrices of the general Bloch equations, for example, depend on the parameters τ_{HB} and τ_f of the hydrogen bond dynamics of the reservoir. Now, the study of the differential equations for the components of the coherence vector in the static field case suggests that the relaxation rate $\Gamma_{44}^{(c)}$ can be used to interpret the measured longitudinal relaxation time τ_1. The resulting interpretation of rotational correlation times or else, by the Rayleigh-Stokes relations, of the self-diffusion constant must necessarily refer to diffusion dynamics of free water molecules in the liquid in absence of any hindering by intermolecular bonds. The latter effect is accounted for by an effective coupling constant. Disregarding the hydrogen bond influence, we have also shown that a systematic derivation of Bloch equations from quantum-dynamical semigroup concepts leads to relaxation or correlation times comparable to those obtained from conventional Redfield theory.

APPENDIX A

After some calculations, one finds the following expansions of the reservoir correlation functions $h_{ik}(t)$:

$$h_{11}(t)=\frac{K}{\Delta^2}\{\mathrm{tr}_R[P_RF^{+1}F^{+1^*}(t)]+\mathrm{tr}_R[P_RF^{-1}F^{-1^*}(t)]-\mathrm{tr}_R[P_RF^{+1}F^{-1^*}(t)]-\mathrm{tr}_R[P_RF^{-1}F^{+1^*}(t)]\}\ , \tag{A1}$$

$$h_{12}(t)=i\frac{K}{\Delta^2}\{\mathrm{tr}_R[P_RF^{+1}F^{-1^*}(t)]-\mathrm{tr}_R[P_RF^{+1}F^{+1^*}(t)]+\mathrm{tr}_R[P_RF^{-1}F^{-1^*}(t)]-\mathrm{tr}_R[P_RF^{-1}F^{+1^*}(t)]\}\ , \tag{A2}$$

$$h_{13}(t)=\frac{4}{\sqrt{6}}\frac{K}{\Delta^2}\{\mathrm{tr}_R[P_RF^{0}F^{-1^*}(t)]-\mathrm{tr}_R[P_FF^{0}F^{+1^*}(t)]\}\ , \tag{A3}$$

$$h_{21}(t)=i\frac{K}{\Delta^2}\{\mathrm{tr}_R[P_RF^{+1}F^{-1^*}(t)]+\mathrm{tr}_R[P_RF^{+1}F^{+1^*}(t)]-\mathrm{tr}_R[P_RF^{-1}F^{-1^*}(t)]-\mathrm{tr}_R[P_RF^{-1}F^{+1^*}(t)]\}\ , \tag{A4}$$

$$h_{22}(t)=\frac{K}{\Delta^2}\{\mathrm{tr}_R[P_RF^{+1}F^{-1^*}(t)]+\mathrm{tr}_R[P_RF^{+1}F^{+1^*}(t)]+\mathrm{tr}_R[P_RF^{-1}F^{-1^*}(t)]+\mathrm{tr}_R[P_RF^{-1}F^{+1^*}(t)]\}\ , \tag{A5}$$

$$h_{23}(t)=-\frac{4}{\sqrt{6}}i\frac{K}{\Delta^2}\{\mathrm{tr}_R[P_RF^{0}F^{-1^*}(t)]+\mathrm{tr}_R[P_RF^{0}F^{+1^*}(t)]\}\ , \tag{A6}$$

$$h_{31}(t)=\frac{4}{\sqrt{6}}\frac{K}{\Delta^2}\{\mathrm{tr}_R[P_R-F^{-1}F^{0^*}(t)]-\mathrm{tr}_R[P_RF^{+1}F^{0^*}(t)]\}\ , \tag{A7}$$

$$h_{32}(t)=\frac{4}{\sqrt{6}}i\frac{K}{\Delta^2}\{\mathrm{tr}_R[P_RF^{+1}F^{0^*}(t)]+\mathrm{tr}_R[P_RF^{-1}F^{0^*}(t)]\}\ , \tag{A8}$$

$$h_{33}(t)=\frac{8}{3}\frac{K}{\Delta^2}\mathrm{tr}_R[P_RF^{0}F^{0^*}(t)]\ . \tag{A9}$$

APPENDIX B

The list of the diagonal relaxation times $\Gamma_{ii}^{(c)}$ is as follows:

$$\Gamma_{11}^{(c)}=\Gamma_{22}^{(c)}=\Gamma_{99}^{(c)}=\Gamma_{10,10}^{(c)}=\frac{K}{2\pi}r_0^{-6}\tau_2\left[\frac{2}{3}+\frac{1}{2}\frac{1}{1+(\omega_L\tau_2)^2}\right]+\frac{KN}{dD}\left[\frac{2}{15}+\frac{3}{4}I_1(\omega_L)\right]\ , \tag{B1}$$

$$\Gamma_{33}^{(c)}=\frac{1}{2}\frac{K}{\pi}r_0^{-6}\frac{\tau_2}{1+(\omega_L\tau_2)^2}+\frac{3}{4}\frac{KN}{dD}I_1(\omega_L)\ , \tag{B2}$$

$$\Gamma_{44}^{(c)}=\Gamma_{55}^{(c)}=\frac{K}{\pi}r_0^{-6}\frac{\tau_2}{1+(\omega_L\tau_2)^2}+\frac{3}{2}\frac{KN}{dD}I_1(\omega_L)\ , \tag{B3}$$

$$\Gamma_{66}^{(c)}=\Gamma_{77}^{(c)}=\Gamma_{13,13}^{(c)}=\Gamma_{14,14}^{(c)}=\frac{K}{\pi}r_0^{-6}\tau_2\left[\frac{2}{3}+\frac{3}{2}\frac{1}{1+(\omega_L\tau_2)^2}\right]+\frac{KN}{dD}\left[\frac{2}{15}+\frac{g}{4}I_1(\omega_L)\right]\ , \tag{B4}$$

$$\Gamma_{88}^{(c)}=\frac{13}{6}\frac{K}{\pi}r_0^{-6}\frac{\tau_2}{1+(\omega_L\tau_2)^2}+\frac{13}{4}\frac{KN}{dD}I_1(\omega_L)\ , \tag{B5}$$

$$\Gamma^{(c)}_{11,11}=\Gamma^{(c)}_{12,12}=\frac{K}{\pi}r_0^{-6}\tau_2\left[\frac{8}{3}+\frac{1}{1+(\omega_L\tau_2)^2}\right]+\frac{KN}{dD}\left[\frac{8}{15}+\frac{3}{2}I_1(\omega_L)\right], \tag{B6}$$

$$\Gamma^{(c)}_{15,15}=\frac{4}{3}\frac{K}{\pi}r_0^{-6}\frac{\tau_2}{1+(\omega_L\tau_2)^2}+2\frac{KN}{dD}I_1(\omega_L)\,. \tag{B7}$$

APPENDIX C

The second homogeneous system of first-order differential equations in the alternating field case shows the following structure:

$$\begin{pmatrix} \dot{\hat{v}}_3 \\ \dot{\hat{v}}_6 \\ \dot{\hat{v}}_7 \\ \dot{\hat{v}}_8 \\ \dot{\hat{v}}_{11} \\ \dot{\hat{v}}_{12} \\ \dot{\hat{v}}_{13} \\ \dot{\hat{v}}_{14} \\ \dot{\hat{v}}_{15} \end{pmatrix} = \begin{bmatrix} -\frac{1}{2}\Gamma^{(c)}_{44} & 0 & -\frac{\omega_1}{\sqrt{2}} & \frac{\sqrt{3}}{2}\Gamma^{(c)}_{44} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\Gamma^{(c)}_{66} & -(\bar{\omega}_L-\omega) & 0 & 0 & \frac{\omega_1}{\sqrt{2}} & 0 & 0 & 0 \\ \frac{\omega_1}{\sqrt{2}} & (\bar{\omega}_L-\omega) & -\Gamma^{(c)}_{66} & -(\frac{3}{2})^{1/2}\omega_1 & -\frac{\omega_1}{\sqrt{2}} & 0 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2}\Gamma^{(c)}_{44} & 0 & (\frac{3}{2})^{1/2}\omega_1 & -\frac{13}{6}\Gamma^{(c)}_{44} & 0 & 0 & 0 & -(\frac{2}{3})^{1/2}\omega_1 & \frac{2\sqrt{2}}{3}\Gamma^{(c)}_{44} \\ 0 & 0 & \frac{\omega_1}{\sqrt{2}} & 0 & -\Gamma^{(c)}_{11,11} & -2(\bar{\omega}_L-\omega) & 0 & -\frac{\omega_1}{\sqrt{2}} & 0 \\ 0 & -\frac{\omega_1}{\sqrt{2}} & 0 & 0 & 2(\bar{\omega}_L-\omega) & -\Gamma^{(c)}_{11,11} & \frac{\omega_1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{\omega_1}{\sqrt{2}} & -\Gamma^{(c)}_{66} & -(\bar{\omega}_L-\omega) & 0 \\ 0 & 0 & 0 & (\frac{2}{3})^{1/2}\omega_1 & \frac{\omega_1}{\sqrt{2}} & 0 & (\bar{\omega}_L-\omega) & -\Gamma^{(c)}_{66} & -\frac{2\omega_1}{\sqrt{3}} \\ 0 & 0 & 0 & \frac{2\sqrt{2}}{3}\Gamma^{(c)}_{44} & 0 & 0 & 0 & \frac{2\omega_1}{\sqrt{3}} & -\frac{4}{3}\Gamma^{(c)}_{44} \end{bmatrix} \begin{pmatrix} \hat{v}_3 \\ \hat{v}_6 \\ \hat{v}_7 \\ \hat{v}_8 \\ \hat{v}_{11} \\ \hat{v}_{12} \\ \hat{v}_{13} \\ \hat{v}_{14} \\ \hat{v}_{15} \end{pmatrix} \tag{C1}$$

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