Master-equation approach to muonium depolarization in solids

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The theory of master equations for open systems is applied to describe the spin relaxation of muonium in solids. An equation of motion for the density matrix of muonium is derived which takes into account the interaction of the bound electron with the host. The calculated muon relaxation rates depend strongly on the applied magnetic field. The range of validity of the Markov approximation is investigated and the results are compared with those of previous theories.

I. INTRODUCTION

The positive muon is used extensively as a probe in solid-state physics and chemistry. In insulators, semiconductors, and liquids, the muon may bind an electron to form a one-electron atom which can be studied by measuring the time dependence of the muon spin polarization.

Two different paramagnetic muon states have been observed[1] in silicon, germanium, and diamond. The hyperfine spectrum of the so-called normal muonium state is analogous to that of vacuum muonium but with a reduced hyperfine frequency. The observed spectra of anomalous muonium are describable by an axially symmetric hyperfine interaction.

In the presence of an external field B the magnetic interactions of a muonium atom in its ground state are given by the Hamiltonian

$$H_{\mathrm{Mu}}=A\vec{\mathrm{S}}_\mu\cdot\vec{\mathrm{S}}_e+g_e\mu_B\vec{\mathrm{S}}_e\cdot\vec{\mathrm{B}}+g_\mu\mu_\mu\vec{\mathrm{S}}_\mu\cdot\vec{\mathrm{B}}\ . \quad (1.1)$$

The hyperfine structure constant A is found from the relativistic interaction energy (Fermi contact term) to be[2]

$$A=-\frac{8\pi}{3}g_e\mu_B g_\mu\mu_\mu\,|\,\psi_{1s}(0)\,|^2\ , \quad (1.2)$$

where $|\,\psi_{1s}(0)\,|^2$ is the electron density at the muon and where the operators for the magnetic moments of the electron and of the muon are

$$\vec{\mu}_e=-g_e\mu_B\vec{\mathrm{S}}_e\ , \quad (1.3)$$

$$\vec{\mu}_\mu=-g_\mu\mu_\mu\vec{\mathrm{S}}_\mu\ . \quad (1.4)$$

The time dependence of the muon spin polarization which is determined by the Hamiltonian (1.1) can be solved analytically.[3]

Using the notation

$$\gamma_\mu=-\frac{g_\mu\mu_\mu}{h}=13.55\ , \quad (1.5)$$

measured in MHz/kG,

$$\Gamma=\frac{g_e\mu_B-g_\mu\mu_\mu}{h}=2.82\ , \quad (1.6)$$

measured in MHz/G, and

$$\nu_0=A/h\ , \quad (1.7)$$

the eigenvalues of (1.1) are given by

$$\begin{aligned}E_1/h&=\nu_1=\nu_0/4+\Gamma B/2-\gamma_\mu B\ ,\\ E_3/h&=\nu_3=\nu_0/4-\Gamma B/2+\gamma_\mu B\ ,\\ E_{2,4}/h&=\nu_{2,4}=-\nu_0/4\pm\frac{(\nu_0^2+\Gamma^2B^2)^{1/2}}{2}\ .\end{aligned} \quad (1.8)$$

A plot of the energy levels of the Hamiltonian (1.1) in the case of germanium ($\nu_0=2361$ MHz) versus the field strength is given in Fig. 1.

The $M=\pm1$ levels diverge linearly with the field because they are eigenstates with $m_\mu=m_e=\pm\frac{1}{2}$. The two $M=0$ levels are field-dependent linear combinations of $m_\mu=-m_e=\pm\frac{1}{2}$.

In a muon-spin-rotation (μSR) experiment in a longitudinal field, i.e., where the initial μ^+ polarization is parallel to the applied field, only the transitions obeying the selection rule $\Delta M=0$ occur. The parallel component of the muon polarization is given by

$$P_\mu^{\parallel}(t)=1-\alpha+\alpha\cos\omega_{24}t\ , \quad (1.9)$$

where $\omega_{24}=2\pi(E_2-E_4)/h$ and

$$\alpha=\frac{\nu_0^2}{2\nu_0^2+2\Gamma^2B^2}\ . \quad (1.10)$$

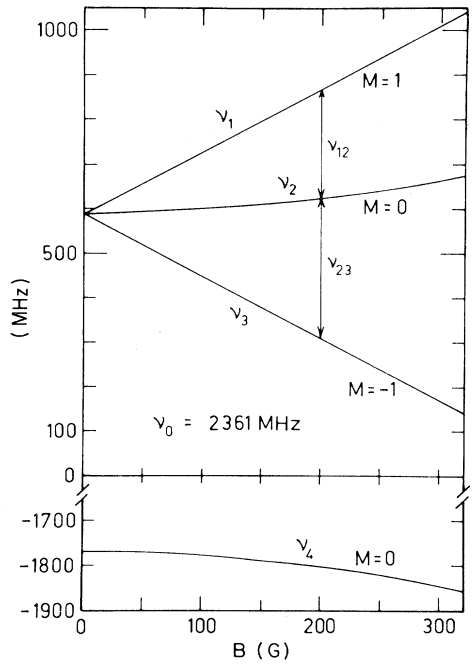

FIG. 1. Breit-Rabi diagram for muonium in Ge.

Since the present experimental resolution is lower than 500 MHz, all terms oscillating with the frequency ω_{24} are averaged to zero.[4] Thus in a longitudinal field experiment, no μSR frequency is observed, but since the ratio between the constant part and the oscillating part of the polarization depends on the field and on the hyperfine frequency ν_0, a measurement of the polarization as a function of the field yields information about ν_0.

In a transverse field, transitions with $|\Delta M|=1$ occur and one gets

$$p_\mu^\perp(t)=\tfrac{1}{2}[\cos^2\beta(\cos\omega_{21}t+\cos\omega_{43}t) +\sin^2\beta(\cos\omega_{41}t+\cos\omega_{23}t)], \quad (1.11)$$

where

$$\tan(2\beta)=\nu_0/\Gamma B, \quad (1.12)$$

and where the two frequencies ω_{41} and ω_{43} between the singlet and triplet states are (for normal muonium) too high to be detectable. The transitions $1\leftrightarrow 2$ and $2\leftrightarrow 3$, however, are in the experimentally accessible range for fields below 300 G.

Equations (1.9) and (1.11) also apply to the case of anomalous muonium if the field is along a $\langle 111\rangle$ axis of the crystal. Since the hyperfine parameters are then 1 order of magnitude smaller than for normal muonium, the corresponding frequency ω_{24} should easily be observable in small longitudinal fields and the amplitude α would strongly depend on the field.

The dependence of the transition frequencies on the field and (for anomalous muonium) on the crystal orientation has been measured in various experiments. All results are well described by Eqs. (1.9) and (1.11), and precise values of the hyperfine parameters as a function of temperature have been obtained.[5] The observed time dependence of the muon polarization, however, also shows marked depolarization effects which depend on external parameters such as temperature, doping concentration of the crystal, etc. To account for these relaxation phenomena the interactions between the muonium electron and the host must be considered. Various kinds of interactions which affect the electron spin exist in semiconductors. There is the hyperfine interaction[6] between the muonium electron and the magnetic moments of nuclei (^{29}Si,^{73}Ge). At low temperatures the exchange interaction of the electron with paramagnetic dopant atoms may be important, and at higher temperatures there are collisions with charge carriers. Furthermore, all mechanisms which lead to spin-lattice relaxation may play a role in certain temperature ranges.

A phenomenological description of the influence of a general relaxation mechanism on the muon spin polarization has been given by Yakovleva[7] by adding to the equations of motion for the polarization components a term which leads to a relaxation of the muonium electron with a rate ν. This model, which is based on the Wangsness-Bloch theory,[8] has further been applied to muonium in solids by Nosov and Yakovleva[9] and by Ivanter and Smilga.[10]

In this work a general approach to muonium depolarization is presented. It is based on the theory of master equations for an open system interacting with a reservoir. The derivations of the basic formulas of this theory are given in Sec. II. The application to muonium in solids, where the bound electron is interacting with the surroundings, is discussed within the Born approximation in Sec. III. An equation of motion for the density matrix of muonium is obtained by integrating over all degrees of freedom of the reservoir. Following Argyres and Kelley,[11] correlation functions of the reservoir are introduced which describe the dissipative behavior of the host.

In Sec. IV it is shown how the previous models for muonium relaxation can be obtained as a limiting case of our general theory. The dependence of the muon relaxation rates on the magnetic field is discussed in detail. Finally, in Sec. V the results are compared to recent μSR experiments in Ge and Si.

For definiteness, all equations have been formulated to describe the behavior of (normal) muonium in solids. They can easily be modified to account also for anomalous muonium.

II. THEORY OF MASTER EQUATIONS

A. Formal derivation

The theory of master equations has been applied[12] to investigate the dynamics of open systems (A) behaving irreversibly under the influence of their surroundings (B). As a basis for the discussion of the open system A we use a complete microscopic description of the composite system $A \oplus B$. By eliminating the coordinates of B we infer the behavior of A. The motivation for this approach is that nature frequently confronts us with coupled systems only one of which is of experimental relevance. We shall restrict ourselves in the following to the case where we have only two subsystems. A generalization to more than two subsystems is straightforward. Further, as it is our aim to obtain dissipation effects we have to choose at least one of the two subsystems macroscopically large; this is necessary in order that dissipation may occur. We call the subsystem of interest S and the other one R (reservoir). In order to derive an equation of motion for our system S we shall only make assumptions about the initial state, i.e., that S and R are initially separated and that only the macroscopic properties of the reservoir are known.

With the use of the projection-operator technique of Zwanzig[13] an exact equation for the reduced density matrix of S is established by summing over the degrees of freedom of the reservoir. The reduced density matrix then enables one to calculate all expectation values of the observables for the subsystem of interest.

In quantum statistical mechanics the states of a given system are represented by statistical operators ρ, called density matrices. The time evolution of the states is governed by the von Neumann equation

$$i\frac{d\rho(t)}{dt}=[H,\rho(t)] , \tag{2.1}$$

where $\hbar=1$. The Liouville operator L for the total system is defined by

$$LX=[H,X]=HX-XH . \tag{2.2}$$

It operates on elements X of the Liouville space which is the product space of $\mathcal{L}_S$ and $\mathcal{L}_R$. The spaces $\mathcal{L}_S$ and $\mathcal{L}_R$ are generated by the set of all Hilbert-Schmidt operators on the Hilbert space of the subsystem S and of the reservoir R, respectively.

For the Laplace transform of the density matrix ρ,

$$\tilde{\rho}(z)=\int_0^\infty dt\, e^{-zt}\rho(t) , \tag{2.3}$$

the von Neumann equation (2.1) reads

$$iz\tilde{\rho}(z)-i\rho(t=0)=L\tilde{\rho}(z) . \tag{2.4}$$

S and R are assumed to be uncorrelated initially such that the density matrix at time zero factorizes,

$$\rho(t=0)=\rho_S^0\rho_R^0 , \tag{2.5}$$

where ρ_R^0 is a stationary distribution.

The total Hamiltonian H is decomposed into

$$H=H_0+V , \tag{2.6}$$

where H_0 is the sum of the Hamiltonians of S and R, i.e.,

$$H_0=H_S+H_R , \tag{2.7}$$

and V is the interaction between S and R. We are interested in the dynamics of the reduced density matrix of S, which is obtained by summing over all degrees of freedom of R,

$$\rho_S=\mathrm{Tr}_R\rho . \tag{2.8}$$

In order to get an equation of motion for ρ_S it is convenient to define a linear operator P which acts on elements X of $\mathcal{L}$ in the following way:

$$PX=\rho_R^0\mathrm{Tr}_R X . \tag{2.9}$$

P is idempotent. Its complement is denoted by Q.

Operating with P and Q, respectively, on the von Neumann equation (2.4) one gets two coupled equations for $P\tilde{\rho}$ and $Q\tilde{\rho}$. Elimination of $Q\tilde{\rho}$ leads to

$$izP\tilde{\rho}(z)-i\rho(t=0) =PLP\tilde{\rho}(z)+PL(iz-QL)^{-1}QLP\tilde{\rho}(z) . \tag{2.10}$$

According to (2.6) and (2.7), the Liouville operator L is split into

$$L=L_S+L_R+L_V . \tag{2.11}$$

It is assumed that

$$\mathrm{Tr}_R(V\rho_R^0)=0 . \tag{2.12}$$

This condition, which assures that $PL_VP=0$, implies no restriction since it can be fulfilled in general by an appropriate redefinition of H_0 and V.

Furthermore, the relations $P(L_S+L_R)=L_SP$ and $L_RP=0$ hold. Therefore, we have

$$PLP\tilde{\rho}(z)=L_SP\tilde{\rho}_S(z) . \tag{2.13}$$

In a similar way the last term of (2.10) can be rewritten. By the use of the relations $PLQ=PL_VQ$, $QLP\rho=L_VP\rho$, and $QLQ=(L_S+L_R+QL_V)Q$, one obtains

$$iz\,P\tilde{\rho}(z)-i\rho_S^0\rho_R^0=L_SP\tilde{\rho}(z)+PL_V(iz-L_S-L_R-QL_V)^{-1}L_VP\tilde{\rho}(z) . \tag{2.14}$$

Using (2.8) and (2.9), one finally obtains the equation of motion for the reduced density matrix $\tilde{\rho}_S$ in the form

$$[iz - L_S - M(z)]\tilde{\rho}_S(z) = i\rho_S^0 , \tag{2.15}$$

where

$$M(z) = \mathrm{Tr}_R[L_V(iz - L_S - L_R - QL_V)^{-1}L_V\rho_R^0] . \tag{2.16}$$

Thus in *time space* ρ_S obeys the integro-differential equation

$$i\frac{d\rho_S(t)}{dt} = L_S\rho_S(t) + \int_0^t dt' M(t')\rho_S(t-t') , \tag{2.17}$$

with the memory kernel

$$M(t) = -i\,\mathrm{Tr}_R\{L_V \exp[-i(L_S + L_R + QL_V)t] \times L_V\rho_R^0\} . \tag{2.18}$$

These equations in conjunction with the initial condition $\rho_S(0) = \mathrm{Tr}_R\rho(0)$ determine completely the time evolution of all observables in our subsystem of interest. The first term in (2.17) describes the unperturbed motion of S, whereas the term containing $M(t)$ may be considered as a generalized collision operator, correct to all orders in V. It is clear that this term involves memory effects, i.e., the rate of change of $\rho_S(t)$ at time t depends on all earlier values of $\rho_S(t)$.

This form of equation of motion represents a convenient starting point for obtaining microscopic foundations of phenomenological equations which describe dissipation.[12] The application of the general theory to specific problems usually requires an approximate treatment of M, which can be obtained by a perturbation expansion of the exponential $\exp[-i(L_S + L_R + QL_V)t]$ occurring in (2.18) in terms of the interaction Liouvillian L_V:

$$M(z) = \mathrm{Tr}_R\left[L_V \frac{1}{iz - L_S - L_R}\sum_{n=0}^{\infty}[QL_V(iz - L_S - L_R)^{-1}]^n L_V\rho_R^0\right] . \tag{2.19}$$

However, this perturbation series makes sense only if it can be identified to be in terms of a small dimensionless parameter which is, formally, $O(L_V)/O(L_S + L_R)$. The present theory is not adequate in cases where the interaction between S and R is too strong for the expansion (2.19) to converge.

If, on the other hand, the series is in terms of a small dimensionless parameter, the use of the generalized master equation offers substantial advantages over other methods of evaluating $\rho_S(t)$, e.g., the perturbation theoretical solution of (2.1). This latter method proceeds by expanding the time-evolution operator in

$$\rho_S(t) = \mathrm{Tr}_R\{\exp[-i(L_S + L_R + L_V)t]\rho(0)\} ,$$

in terms of L_V. It is easy to see that an infinite number of terms of all orders of this elementary perturbation expansion have to be summed up in order to recover a given finite order approximation to the series (2.19).

B. Born approximation

In order to see more explicitly the nature of the equation of motion for $\rho_S(t)$, Eq. (2.17), we consider here the case of a system interacting weakly with the reservoir. In the lowest Born approximation the operator M is of order V^2 and is obtained from (2.18) by replacing $\exp[-i(L_S + L_R + QL_V)t]$ by $\exp[-i(L_S + L_R)t]$. Since we want to analyze (2.17) in terms of the separate properties of the reservoir, it is useful[11] to expand V in a complete set of operators $u_\kappa v_\kappa$, i.e.,

$$V = \sum_\kappa u_\kappa v_\kappa , \tag{2.20}$$

where u_κ and v_κ operate in the spaces of the reservoir and the system of interest, respectively. Bearing in mind that

$$\exp(-iL_0t)V = \exp(-iH_0t)V\exp(iH_0t) ,$$

we can rewrite (2.17) in the lowest Born approximation:

$$i\dot{\rho}_S(t) = L_S\rho_S(t) - i\sum_{\kappa,\lambda}\int_0^t d\tau\{c_{\kappa\lambda}(\tau)[v_\kappa, \exp(-iL_S\tau)v_\lambda\rho_S(t-\tau)] - c_{\lambda\kappa}(-\tau)[v_\kappa, \exp(-iL_S\tau)\rho_S(t-\tau)v_\lambda]\} . \tag{2.21}$$

In the last expression all reference to the reservoir has been concentrated in the quantities $c_{\kappa\lambda}(\tau)$, which are the thermodynamic correlation functions for the Heisenberg operators $u_\kappa(t) = \exp(iL_Rt)u_\kappa$ of R, defined by

$$c_{\kappa\lambda}(\tau) = \mathrm{Tr}_R[\rho_R^0 u_\kappa(\tau)u_\lambda] . \tag{2.22}$$

The Laplace transform of Eq. (2.21) is given by

$$(iz-L_S)\tilde{\rho}_S(z)=i\rho_S(0)+M(z)\tilde{\rho}_S(z)\ , \tag{2.23}$$

with

$$M(z)\tilde{\rho}_S(z)=-i\sum_{\kappa,\lambda}[v_\kappa,j^+_{\kappa\lambda}(z+iL_S)[v_\lambda,\tilde{\rho}_S(z)]+j^-_{\kappa\lambda}(z+iL_S)[v_\lambda,\tilde{\rho}_S(z)]_+]\ , \tag{2.24}$$

where $[a,b]_+=ab+ba$, and

$$j^\pm_{\kappa\lambda}(z)=\int_0^\infty d\tau e^{-z\tau}c^\pm_{\kappa\lambda}(\tau) \tag{2.25a}$$

and

$$j_{\kappa\lambda}(z)=\int_0^\infty d\tau e^{-z\tau}c_{\kappa\lambda}(\tau) \tag{2.25b}$$

are the Laplace transforms of the correlation functions

$$c^\pm_{\kappa\lambda}(\tau)=\tfrac{1}{2}[c_{\kappa\lambda}(\tau)\pm c_{\lambda\kappa}(-\tau)]=\pm c^\pm_{\lambda\kappa}(-\tau)\ . \tag{2.25c}$$

If the influence of the reservoir can be approximated by *a random field of force,* which requires that the reservoir temperature is much larger than typical system energies, the expression (2.24) considerably simplifies,[11]

$$M(z)\tilde{\rho}_S(z)=-i\sum_{\kappa,\lambda}[v_\kappa,j_{\kappa\lambda}(z+iL_S)[v_\lambda,\tilde{\rho}_S(z)]]\ . \tag{2.26}$$

Equations (2.24) and (2.26) will be further discussed in the next section. At this point we would like to indicate the differences between our approach which leads to relaxation functions involving memory effects [see Eqs. (2.21) and (2.23)] and theories which work directly with Markovian equations of motion. It can be shown that Eq. (2.21) can be approximated by a Markovian equation of motion under the assumption that the relaxation times of the system are much larger than τ_c, the relaxation time of the reservoir. The latter can mathematically be characterized by the condition that for all thermodynamic correlation functions $c_{\kappa\lambda}(\tau)$ one has

$$c_{\kappa\lambda}(\tau)=0 \quad \text{for} \quad |\tau|>\tau_c\ . \tag{2.27}$$

This implies the energy spectrum of the reservoir to be continuous, otherwise the $c_{\kappa\lambda}$'s are quasiperiodic functions of τ, as seen from (2.22).

Under these restrictions one finds that for long times ($t>\tau_c$),

$$i\dot{\rho}_S(t)=L_S\rho_S(t)-i\sum_{\kappa,\lambda}[v_\kappa,[j^+_{\kappa\lambda}(iL_S)v_\lambda,\rho_S(t)]+[j^-_{\kappa\lambda}(iL_S)v_\lambda,\rho_S(t)]_+]\ . \tag{2.28}$$

The Laplace transform of this Markovian equation of motion reads

$$\begin{aligned}&[iz-L_S-M(z)]\tilde{\rho}_S(z)=i\rho^0_S\ ,\\ &M(z)\tilde{\rho}_S(z)=-i\sum_{\kappa,\lambda}[v_\kappa,[j^+_{\kappa\lambda}(iL_S)v_\lambda,\tilde{\rho}_S(z)]\\ &\qquad\qquad+[j^-_{\kappa\lambda}(iL_S)v_\lambda,\tilde{\rho}_S(z)]_+]\ .\end{aligned} \tag{2.29}$$

If the influence of the surroundings on the subsystem can be described by a random field of force, this equation reduces to

$$M(z)\tilde{\rho}_S(z)=-i\sum_{\kappa,\lambda}[v_\kappa,[j_{\kappa\lambda}(iL_S)v_\lambda,\tilde{\rho}_S(z)]]\ , \tag{2.30}$$

which is the Markovian approximation to Eq. (2.26).

III. APPLICATION TO MUONIUM

In this section the general theory is applied to describe the behavior of the muon spin polarization in a muonium atom where the bound electron is interacting with the surroundings. With the use of the concepts and the formulas of Sec. II, an equation of motion for the density matrix of the muonium spin system alone will be obtained.

In dealing with the dynamics of the muonium spin system it is convenient to represent the observables in the basis generated by the direct product of the Pauli spin matrices τ^i and σ^i ($i=1,2,3$) of the electron and the muon, respectively, and $\tau^0=\sigma^0=\mathbb{1}$, where $\mathbb{1}$ is the identity matrix.

We denote the basis vectors by

$$f^{\alpha\beta}=\sigma^\alpha\otimes\tau^\beta\ ,\quad \alpha,\beta=0,1,2,3\ . \tag{3.1}$$

Whereas H_{Mu} or ρ are linear operators in the four-dimensional Hilbert space spanned by the states of the spin-$\frac{1}{2}$—spin-$\frac{1}{2}$ system, one considers[14] in the Liouville formalism a different space which has dimension 16. In $\mathscr{L}_S$ the quantum-mechanical operators are vectors which will be expressed in terms of the basis (3.1), and the Liouville operator L_S as well as the resolvent R are linear operators in this vector space which is spanned by the basis (3.1). For our spin problem a scalar product is naturally defined by

$$(f^{\alpha\beta},f^{\mu\nu})=\mathrm{Tr}(\sigma^{\alpha}\tau^{\beta}\sigma^{\mu}\tau^{\nu})=4\delta_{\alpha\mu}\delta_{\beta\nu}\ . \tag{3.2}$$

Thus the Hamilton operator (1.1) is given by the following vector expressed in terms of the basis (3.1):

$$H_{\mathrm{Mu}}=\frac{A}{4}f^{ii}+\frac{b_i}{2}f^{0i}+\frac{c_i}{2}f^{i0}\ , \tag{3.3a}$$

where the sum over i is implied and

$$\begin{aligned} b_i&=g_e\mu_B B_i\ ,\\ c_i&=g_\mu\mu_\mu B_i\ . \end{aligned} \tag{3.3b}$$

The action of the linear transformation L_s on the 16 basis vectors can be easily obtained. Using the commutation properties of the Pauli matrices one gets

$$\begin{aligned} L_S f^{00}&=0\ ,\\ L_S f^{0j}&=i\epsilon_{jkl}\left[\frac{A}{2}f^{lk}+b_l f^{0k}\right]\ ,\\ L_S f^{j0}&=i\epsilon_{jkl}\left[\frac{A}{2}f^{kl}+c_l f^{k0}\right]\ ,\\ L_S f^{ij}&=i\epsilon_{ijk}\frac{A}{2}(f^{0k}-f^{k0})\\ &\quad+i\epsilon_{jkl}c_l f^{kj}+i\epsilon_{jkl}b_l f^{ik}\ . \end{aligned} \tag{3.4}$$

Therefore, the transformation operator L_S can be represented by a 16×16 matrix according to

$$L_S f^{\alpha\beta}=(\underline{L}_S)_{\mu\nu/\alpha\beta}f^{\mu\nu}\ , \tag{3.5}$$

where the sum over repeated indices is implied. All operators in $\mathscr{L}_S$ can be written as linear combinations of spin operators and can therefore be represented by matrices.

The basis (3.1) is most convenient since the initial value of the reduced density matrix ρ_S^0 can be written as

$$\rho_S^0=\tfrac{1}{4}\Pi_{\alpha\beta}^0 f^{\alpha\beta}\ , \tag{3.6}$$

where the $\Pi_{\alpha\beta}^0$ are the components of the initial polarization matrix

$$\Pi_{\alpha\beta}^0=\mathrm{Tr}_S(\rho_S^0 f^{\alpha\beta})\ . \tag{3.7}$$

Further, the Laplace transform of the time-dependent polarization matrix can be expressed as

$$\Pi_{\alpha\beta}(z)=\mathrm{Tr}_S[\tilde{\rho}_S(z)f^{\alpha\beta}]=\mathrm{Tr}_S[R(z)\rho_S^0 f^{\alpha\beta}]\ , \tag{3.8}$$

where the resolvent operator $R(z)$ follows from (2.15),

$$R(z)=[z+iL_S+iM(z)]^{-1}\ , \tag{3.9}$$

and is given by the 16×16 matrix with elements

$$R(z)f^{\alpha\beta}=(\underline{R})_{\mu\nu/\alpha\beta}(z)f^{\mu\nu}\ . \tag{3.10}$$

Using (3.8) and (3.10) we finally obtain

$$\Pi_{\alpha\beta}(z)=\underline{R}_{\alpha\beta/\mu\nu}(z)\mathrm{Tr}_S(\rho_S^0 f^{\mu\nu})=\underline{R}_{\alpha\beta/\mu\nu}(z)\Pi_{\mu\nu}^0\ . \tag{3.11}$$

This equation determines the evolution of the spin system from the initial polarization if the elements of the resolvent matrix $\underline{R}$ are known.

To proceed, the interaction V between the muonium system and the reservoir has to be specified. Instead of investigating a particular microscopic interaction in which $\vec{S}_e$ couples to magnetic moments, we discuss the general features for a model where all relaxation mechanisms are approximated by a randomly fluctuating field. This field is assumed to jump randomly between two values $\pm T_\alpha$ ($\alpha=x,y,z$) with a probability per unit time equal to $(2\tau_c)^{-1}$. Such a change in the field may have its origin, e.g., in the diffusion of the muonium atom or in collisions with charge carriers, or in the flipping of localized spins due to exchange or spin-lattice relaxation.

With the use of the notation of Eq. (3.1), the interaction Hamiltonian V is thus written as

$$V=\frac{\delta_{\mathrm{ex}}}{2}T_i(t)f^{0i}\ , \tag{3.12}$$

where the T_i's are the Cartesian components of the fluctuating field representing the reservoir and δ_{ex} is the interaction strength. This particular choice of the interaction possesses many of the features of a dipolar coupling; however, it is more simple to treat. In fact, the assumption of a random field of force and the resulting form of the thermodynamic correlation functions between the bath operators considerably reduce the complexity of the formalism sketched in Sec. II.

The correlation functions for the reservoir are found to be[15]

$$\begin{aligned} c_{\kappa\lambda}(\tau)&=\frac{\delta_{\mathrm{ex}}^2}{4}\mathrm{Tr}_R[T_\kappa(\tau)T_\lambda\rho_R^0]\\ &=\frac{\delta_{\mathrm{ex}}^2}{4}\delta_{\kappa\lambda}\langle T_\kappa^2\rangle_{\mathrm{av}}e^{-|\tau|/\tau_c}\ ,\quad \kappa,\lambda=x,y,z\ . \end{aligned} \tag{3.13}$$

In the following we will assume an isotropic fluctuating field which implies

$$\langle T_x^2\rangle_{\mathrm{av}}=\langle T_y^2\rangle_{\mathrm{av}}=\langle T_z^2\rangle_{\mathrm{av}}=1\ . \tag{3.14}$$

Then with the help of (3.13) and (3.14), Eq. (2.26) can be rewritten as

$$M(z)\tilde{\rho}_S(z)=-i\sum_{\kappa}[v_\kappa,j_\kappa(z+iL_S)[v_\kappa,\tilde{\rho}_S(z)]]\ , \tag{3.15}$$

where

$$j_\kappa(z)=\int_0^\infty d\tau e^{-z\tau}c_\kappa(\tau)\ , \tag{3.16}$$

or, using our basis representation,

$$M(z)f^{\alpha\beta}=-i\sum_{\kappa=1,2,3}[f^{0\kappa},j_\kappa(z+iL_S)[f^{0\kappa},f^{\alpha\beta}]]\ . \tag{3.17}$$

Further, the action of $j_\kappa(z+iL_S)$ on a general basis vector is given by

$$j_\kappa(z+iL_S)f^{\alpha\beta}=\frac{\delta_{\rm ex}^2}{4}\left[\left[z+\frac{1}{\tau_c}\right]\underline{\mathbb{1}}+i\underline{L}_S\right]^{-1}f^{\alpha\beta}\ . \tag{3.18}$$

This leads finally to the following form of the relaxation matrix $\underline{M}(z)$,

$$\underline{M}(z)=-i\frac{\delta_{\rm ex}^2}{4}\sum_{\kappa=1,2,3}\underline{F}^{0\kappa}\left[\left[z+\frac{1}{\tau_c}\right]\underline{\mathbb{1}}+i\underline{L}_S\right]^{-1}\underline{F}^{0\kappa}\ , \tag{3.19}$$

where $\underline{F}^{0\kappa}$ and $(z+1/\tau_c)\underline{\mathbb{1}}+i\underline{L}_S$ are 16×16 matrices, whose elements are determined according to the notation introduced by Eqs. (3.5) and (3.10). Thus $\underline{F}^{0\kappa}$ is the matrix representing the action of the commutator $[\tau^\kappa,\ldots]$ on all other elements of the basis (3.1), and the elements of this matrix identify the coefficients of such an expansion on orthogonal operators. With the help of (3.9), (3.11), and (3.19), we are now able to determine the complete evolution of the muon spin polarization. This result is obtained in the Born approximation but is valid for arbitrary long correlation times τ_c.

As a consequence of the interaction of the muonium with the medium, one then expects a broadening or a splitting of the different lines corresponding to transitions between the four energy levels of the muonium spin system [Eq. (1.8)]. The characteristic features of the line shapes are determined by the two parameters of our model, $\delta_{\rm ex}$ and τ_c. Different choices can generate a variety of possible relaxation effects, which will be discussed in more detail in the next section.

An interesting case occurs when the correlation time of the reservoir becomes very small (e.g., smaller than the typical relaxation times of our spin system, which are known from experiments and are of the order of 1 μs). Then, as discussed at the end of Sec. II, the memory effects can be neglected and the Markov approximation, represented by Eq. (2.30), becomes valid.

Following the same lines leading to (3.19) one finds

$$(z+iL_S+M)\tilde{\rho}_S(z)=\rho_S^0\ , \tag{3.20}$$

where M is now frequency independent and has elements given by

$$\underline{M}=\frac{\delta_{\rm ex}^2}{4}\sum_{\kappa,\alpha,\beta}\left[\left[\frac{1}{\tau_c}\underline{\mathbb{1}}+i\underline{L}_S\right]^{-1}\right]_{\alpha\beta/0\kappa}\underline{F}^{0\kappa}\underline{F}^{\alpha\beta}\ . \tag{3.21}$$

It should be noted that this equation differs from the $z=0$ limit of Eq. (3.19). This difference can already be seen from (2.26) and (2.30).

The evaluation of $\underline{M}$ is still tedious, but we have here the advantage that $\underline{M}$, as well as $i\underline{L}_S$, are matrices with constant elements. Instead of (3.20) we can then write

$$(z+iL_{\rm eff})\tilde{\rho}_S(z)=\rho_S^0\ , \tag{3.22}$$

and a simple diagonalization of the effective Liouvillian $L_{\rm eff}$ is possible.

The spin dynamics of our system is then fully determined by the complex eigenvalues of the matrix $-i\underline{L}_{\rm eff}$, which are c numbers representing the complex frequencies governing the time evolution of the polarization components $\Pi_{\alpha\beta}(t)$:

$$\Pi_{\alpha\beta}(t)=\sum_j A_j e^{\lambda_j t}\ , \tag{3.23}$$

where the A_j's are the complex amplitudes found by decomposing the initial polarization in a linear combination of the eigenvectors. Let us here briefly consider the case of free muonium ($L_{\rm eff}=L_S$). As a consequence of the reversibility in the evolution of the total system, no dissipation will occur, and one has purely imaginary eigenvalues λ.

Now the introduction of *irreversible processes* leads in a first-order approximation to damping effects. The free muonium frequencies are unchanged if the strength of the interaction and the correlation time τ_c are small enough. Thus instead of (1.9) and (1.11) we can write

$$p_\mu^{||}(t)=\alpha e^{-\Lambda_{||}t}\ , \tag{3.24}$$

$$p_\mu^{\perp}(t)=\tfrac{1}{2}[\cos^2\beta e^{-\Lambda_{21}t}\cos(\omega_{21}t)+\sin^2\beta e^{-\Lambda_{23}t}\cos(\omega_{23}t)]\ , \tag{3.25}$$

where we have omitted the frequencies which cannot be detected experimentally, and where $\Lambda_{||}$ (Λ_{21} and Λ_{23}) are the so-called parallel (transverse) relaxation rates. A study of the dependence of these dampings on the various parameters, in particular on the field

strength assuming τ_c and δ_{ex} to be fixed, and a comparison with the results of the Ivanter-Smilga model[10] is part of the subject of the next section.

IV. RESULTS

Before presenting the results of the theory developed in the previous sections we would like to discuss other theories of muonium relaxation. Yakovleva[7] derived an equation of motion for the muonium density matrix based on the Wangsness-Bloch theory,[8] starting from the premise that, independently of its interaction with the μ^+ spin (and with the external magnetic field if present), the muonium electron becomes depolarized in the medium. In other words, the existence of a mechanism is assumed by which the electron spin flips from time to time, the average time between such events being denoted by $1/\nu$.

Various predictions of this model have been discussed by Nosov and Yakovleva.[9] Later, Ivanter and Smilga[10] generalized the model by taking into account the effects of a finite chemical lifetime of muonium.

In our formalism the assumption made by Yakovleva can be formulated simply by choosing a particular ansatz for the relaxation matrix $\underline{M}$. If one assumes that the electron interacts with the surroundings independently from its coupling with the μ^+ spin and with the external field by flipping with a mean expectation time $1/\nu$, one has

$$\begin{aligned} \underline{M}f^{00}&=\underline{M}f^{j0}=0\ , \\ \underline{M}f^{0j}&=2\nu\underline{\mathbb{1}}f^{0j}\ , \\ \underline{M}f^{ij}&=2\nu\underline{\mathbb{1}}f^{ij}\ . \end{aligned} \tag{4.1}$$

The solution of (3.20) with $\underline{M}$ given by (4.1) is still complicated but analytic results can be found in the cases of fast or very slow flipping frequency.[9,10]

Thus the model of Yakovleva and of Ivanter and Smilga is contained as a limiting case in the master-equation approach. Starting from Eq. (3.21), one can show that when τ_c becomes very short, i.e., when

$$\tau_c^{-1}\gg A,b_i,c_i\ , \tag{4.2}$$

the complexity of the relaxation matrix $\underline{M}$ considerably reduces. Assuming that

$$\left[\left[\frac{1}{\tau_c}\right]\underline{\mathbb{1}}+i\underline{L}_S\right]^{-1}\approx\tau_c\underline{\mathbb{1}}\ ,$$

one finds for $\underline{M}$ a simple diagonal matrix which becomes identical to the relaxation matrix (4.1) if one sets

$$\delta_{ex}^2\tau_c=\nu\ . \tag{4.3}$$

This result can be identified as a motional narrowing effect.[16] The electron depolarizes independently only if the rate of change $1/\tau_c$ of the fluctuating field is fast enough.

If the inequality (4.2) does not hold, the muon damping rates predicted from the master-equation approach show a marked difference from the results based on the Wangsness-Bloch theory.[9,10] This is illustrated in Figs. 2–4 which show the results of numerical solutions of Eq. (3.20) for a representative set of parameter values δ_{ex} and τ_c. The hyperfine parameters used are those referring to normal muonium in silicon ($A/h=2012$ MHz).

In Fig. 2 both the longitudinal relaxation rate $\Lambda_{||}$ and the transverse relaxation rates $\Lambda_\perp$ are plotted in units of $\delta_{ex}^2\tau_c$ versus the field strength for a value of $\tau_c=10^{-11}$ s. In this case, the inequality (4.1) still holds and the predictions of Eq. (3.20) completely agree with those obtained by Ivanter and Smilga.[10] For $\tau_c=10^{-10}$ s, however, one has $A\tau_c\sim 1$, and the calculated relaxation rates shown in Fig. 3 exhibit a different field dependence. The ratio of $\Lambda_\perp$ to $\Lambda_{||}$ is increased as compared to Fig. 2. This change is more pronounced for $\tau_c=10^{-9}$ s which is still small enough to justify the Markov approximation ($\tau_c\Lambda\ll 1$) since $\Lambda\sim 10^6$ s^{-1}. This case is shown in Fig. 4 where the value of δ_{ex} has been fixed to 3.16×10^7 s^{-1}. The parallel relaxation rate $\Lambda_{||}$ decreases from 0.5 μs^{-1} at zero field with increasing field. The relaxation rate Λ_{12} corresponding to the lower triplet precession frequency also decreases with higher field values, whereas Λ_{23} first also drops but then asymptotically reaches a constant value. The different behavior of Λ_{12} and Λ_{23} at very low fields is of no relevance since the difference of the frequencies ω_{12} and ω_{23} is smaller than Λ_{23}.

The different behavior of the relaxation rates $\Lambda_{||}$,

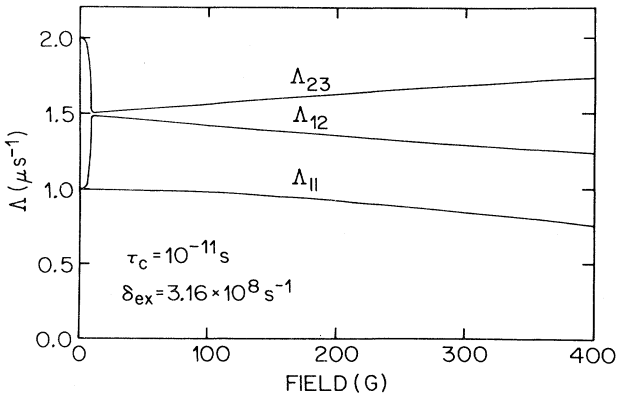

FIG. 2. Parallel ($\Lambda_{||}$) and transverse (Λ_{12} and Λ_{23}) relaxation rates vs field for parameter values $\tau_c=10^{-11}$ s and $\delta_{ex}=3.16\times 10^8$ s^{-1}. The hyperfine parameters used are those referring to normal muonium in silicon.

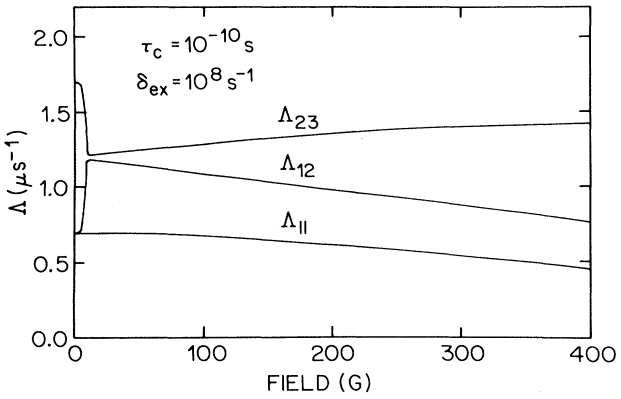

FIG. 3. Parallel and transverse relaxation rates vs field for $\tau_c = 10^{-10}$ s and $\delta_{ex} = 10^8$ s^{-1}.

$\Lambda_{\perp 1}$, and $\Lambda_{\perp 2}$ at high fields can be traced to the fact that in the Paschen-Back region the muon and electron spins are decoupled, and an interaction of the form (3.12) has no effect on the transitions $1 \leftrightarrow 2$ and $3 \leftrightarrow 4$. This can be demonstrated by the following solution of Eq. (3.20).

If the field becomes very large we can assume that the dominant part of iL_S is given by the terms $b_i = g_e \mu_B B_i$ $(i = 1,2,3)$. Then the evaluation of $[(1/\tau_c)\mathbb{1} + iL_S]^{-1}$ is straightforward; omitting all terms of order $1/b_i$ and choosing the field direction along 3 one finds

$$\left[\frac{1}{\tau_c}\mathbb{1} + i\underline{L}_S\right]^{-1}_{03,03} = \tau_c$$

and (4.4)

$$\left[\frac{1}{\tau_c}\mathbb{1} + i\underline{L}_S\right]^{-1}_{\alpha\beta,0\kappa} = 0 ,$$

$$\alpha,\beta = 0,1,2,3,\ \kappa = 1,2,3 ,$$

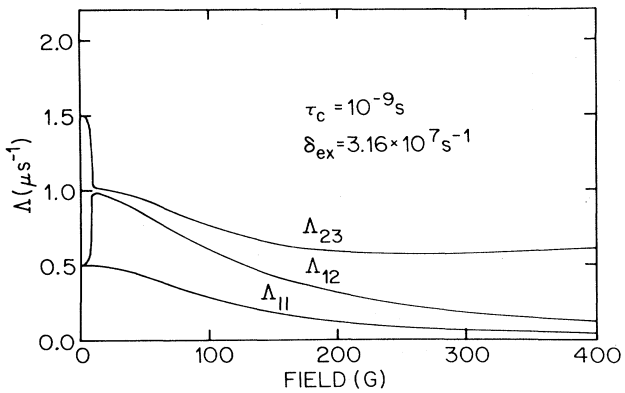

FIG. 4. Parallel and transverse relaxation rates vs field for $\tau_c = 10^{-9}$ s and $\delta_{ex} = 3.16 \times 10^7$ s^{-1}. The field dependence is more pronounced than in Figs. 2 and 3, where the correlation time was smaller than the inverse of the hyperfine frequency.

for all others α,β,κ. This allows us to simplify Eq. (3.21),

$$\underline{M} \simeq \frac{\delta_{ex}^2}{4}\tau_c \underline{F}^{03}\underline{F}^{03} , \tag{4.5}$$

i.e., the only nonvanishing terms of $\underline{M}$ are on the diagonal, and an analytical solution of Eq. (3.20) is possible leading to two undamped frequencies,

$$\begin{aligned} \omega_{12} &= i(c + A/2 - A^2/4b) , \\ \omega_{34} &= i(c - A/2 - A^2/4b) , \end{aligned} \tag{4.6}$$

and to two damped oscillations,

$$\begin{aligned} \omega_{14} &= -\Gamma + i(b + A/2 + A^2/4b) , \\ \omega_{23} &= -\Gamma + i(b - A/2 + A^2/4b) , \end{aligned} \tag{4.7}$$

where the damping term is given by $\Gamma = \delta_{ex}^2 \tau_c$. This asymptotic result is different from that obtained in the model of Ivanter and Smilga, where the exchange frequency ν is considered to be independent of all system parameters (hyperfine frequency and external field). In the latter case, even for very large applied transversal fields, no undamped frequencies are found.

As can be seen from Figs. 2–4, τ_c is a very sensitive parameter governing the characteristic dependence of the different dampings $(\Lambda_{||},\Lambda_{\perp})$ on the applied field. Thus by measuring the various muonium relaxation rates as a function of the external field, one can determine the correlation time τ_c of the reservoir.

Deviations of the results of the general theory from those of the Markov approximation are also seen in Figs. 5–7 where we have plotted some line shapes of the spectrum of our spin system. These representations seem especially interesting because of the possibility to compare them with the measured Fourier spectra.

The line shapes are obtained by evaluating the real part of the polarization components $\Pi_{\alpha\beta}(z)$ as a function of the pure imaginary frequency $z = i\omega$. As a consequence of the interaction with the medium, one then expects broadenings or splittings of the different energy levels of our two-spin system [Eq. (1.8)]. The widths of the lines give a measure of the relaxation rate of the corresponding transition. The frequency range was chosen in order to show one (ω_{12}) of the two visible lines in a μSR experiment in silicon with a transverse applied field of 100 G. In addition, in Fig. 7 the evolution of the line shape at zero frequency [referring to the nonoscillating part of $p_\mu^{||}(t)$] is shown.

As has been discussed in Sec. II, the validity of the Markov approximation is restricted to cases where the correlation time τ_c of the reservoir is suf-

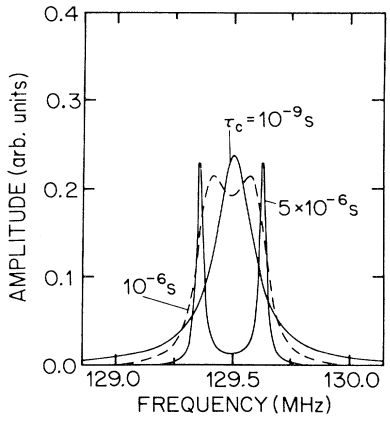

FIG. 5. Calculated line shape of the transition $1\leftrightarrow 2$ at a transverse field of 100 G for three different values of the correlation time τ_c.

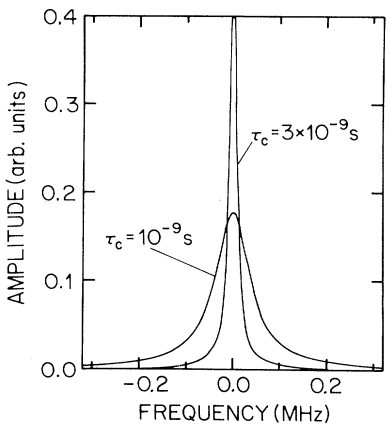

FIG. 7. Plot of the line shape at zero frequency for $\tau_c = 10^{-9}$ s and $\tau_c = 3\times10^{-9}$ s (where the maximum of the amplitude is at 0.8).

ficiently small, e.g., smaller than the measured relaxation times (~ 1 μs). This can clearly be seen by a comparison of Figs. 5 and 6. For $\tau_c \gtrsim 10^{-7}$ s, the Markov approximation gives a result which is very different from that obtained from formula (3.19). The results of the latter give for τ_c greater than 10^{-6} s a characteristic splitting of $\Delta\omega \sim \delta_{ex}$ for the frequency ω_{12} in a transverse field. In this case the dynamics of the subsystem is governed by frequencies which are much higher than the rates of change $[1/(2\tau_c)]$ of the fluctuating field produced by the reservoir. This implies the occurrence of two effective fields in which the electron spin precesses. The splitting in Fig. 5 is due to the approximation of the interaction term by Eq. (3.12) using a single value of δ_{ex}. In actual cases one has to consider a distribution of δ_{ex} values which is determined, e.g., by the average distance between the muonium and the neighboring spins. Instead of a splitting, one then observes a distribution of frequencies obtained by taking a statistical average over all δ_{ex}.

On the other hand, as shown in Fig. 7, the line shape at zero frequency is characterized by the fact that no splitting occurs, even for large τ_c ($\gtrsim 10^{-5}$ s). This means that the parallel relaxation rate disappears in the static limit, as expected.

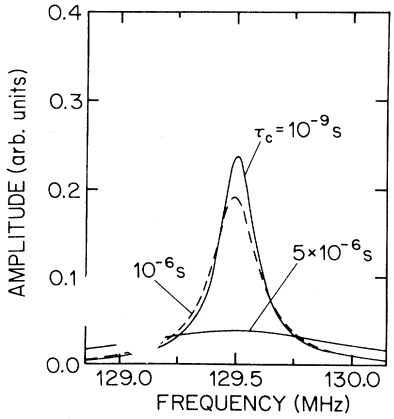

FIG. 6. Line shape calculated in the Markov approximation for three values of the correlation time τ_c. For $\tau_c = 10^{-9}$ s the line shape is the same as the corresponding one in Fig. 5. For larger values of τ_c, the Markov approximation predicts different line shapes.

V. COMPARISON TO EXPERIMENTS AND CONCLUSIONS

Recently transverse and longitudinal relaxation rates of muonium have been measured as a function of temperature in germanium[17] and silicon.[18] For high temperatures ($T > 150$ K for Si), the ratio between $\Lambda_\perp$ measured at 10 G and $\Lambda_{||}$ at 200 G decreases from about 2.0 to 1.5 with increasing temperature. For temperatures lower than 50 K, $\Lambda_{||}$ is very small, and $\Lambda_\perp$ has a typical value of some 10^6 s^{-1} depending on the doping concentration of the crystal.

The measurements have been interpreted[17] in terms of different depolarization mechanisms. At low temperatures the muonium relaxation is due to the exchange interaction with paramagnetic dopant atoms, while the strong increase of the relaxation rate at high temperatures is attributed to either a chemical reaction or a Raman process.

The existing data are too scarce to allow a systematic analysis in terms of the relaxation theory discussed in this paper. The general features, however, agree with the behavior expected from our discussion. At low temperatures the correlation times

are large ($\tau_c \gtrsim 10^{-7}$ s), and one is close to the static limit where the longitudinal relaxation rate is zero and the transverse rates are proportional to δ_{ex} due to the splitting of the frequencies (see Figs. 5 and 7).

For intermediate values of the correlation time ($10^{-11} < \tau_c < 10^{-8}$ s), one expects a characteristic field dependence of both longitudinal and transverse relaxation rates (see Figs. 2—4). With decreasing τ_c, the ratio $\Lambda_\perp/\Lambda_{||}$ decreases towards a value of 1.5 attained in the limit of complete motional narrowing. A decrease of this ratio with increasing temperature has indeed been observed.[18] We therefore suggest a measurement of the relaxation rates as a function of both the field and the temperature. This then would allow one to make a direct comparison with our model of relaxation and to extract the temperature dependence of τ_c. The qualitative agreement between the existing data and our predictions is encouraging.

In conclusion, the application of the theory of master equations for open systems to muonium in solids leads to a general description of relaxation phenomena. It has been shown that the model allows one to study depolarization effects for arbitrary correlation times going from the static limit to the limit of motional narrowing. In the latter case, the model of Ivanter and Smilga based on the Wangsness-Bloch equations is recovered. The fact that the dynamics of the spin system under consideration cannot be separated from the relaxation mechanism with the reservoir shows up in the field dependence of the relaxation rates. Therefore, an analysis of the field and temperature dependence of the relaxation rates of both normal and anomalous muonium in semiconductors with the help of the formalism presented here allows one to extract information about the intrinsic relaxation times of the host.

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