Muon Depolarization in Presence of Several Chemical Channels

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Abstract. We develop a formalism for the investigation of muon depolarization in presence of several chemical channels. We emphasize particularly the creation of chemical radicals. Relaxation effects in these radicals are discussed.

We study the depolarization and phase shifts as well as the time dependence of the precession of the muons with the help of numerical examples.

I. Introduction

With the first experiments on depolarization effects of positive muons in condensed matter it became evident that such investigations could become a tool for studies of chemical kinetics and of relaxation phenomena. Useful results have already been obtained in several experiments [1, 2] whose interpretations were based on the phenomenological theory of Ivanter and Smilga [3]. In this article we develop a formalism suitable for an investigation of chemical reaction constants for reactions of muonium into diamagnetic compounds as well as radical formations. Such processes have already been observed and analyzed by a different formalism [4]. Our formalism, however, leads us to a subtlety in muonium-radical formation which, considering the experimental possibilities at meson factories, may give us new insight into the nature of radical formations in general. The method is a modification of a procedure of Ivanter and Smilga [5] in a different context and is easily adapted for computer calculations.

In the chapter on perturbation of muonium in condensed matter we shall give a discussion on the conditions of validity of the Wangsness–Bloch equations for the description of muon depolarization of muonium in condensed matter.

II. Recapitulations about the Muonium

Let us consider the well known muonium hamiltonian with an external magnetic field B. (We use the symbol Mu for the muonium)

$$H^{\text{Mu}} = a\vec{\sigma}^{\mu}\vec{\sigma}^{e} + g_e \frac{e}{2m_e c} \vec{\sigma}^{e} \cdot \vec{B} + g_{\mu} \frac{e}{2m_{\mu}c} \vec{\sigma}^{\mu} \cdot \vec{B}. \tag{1}$$

In the following, we take for the g-factors $g_e = g_{\mu} = 2$. $\hbar\omega_0 = 4a$ is the hyperfine splitting for the Fermi contact interaction. This hamiltonian leads to a picture of
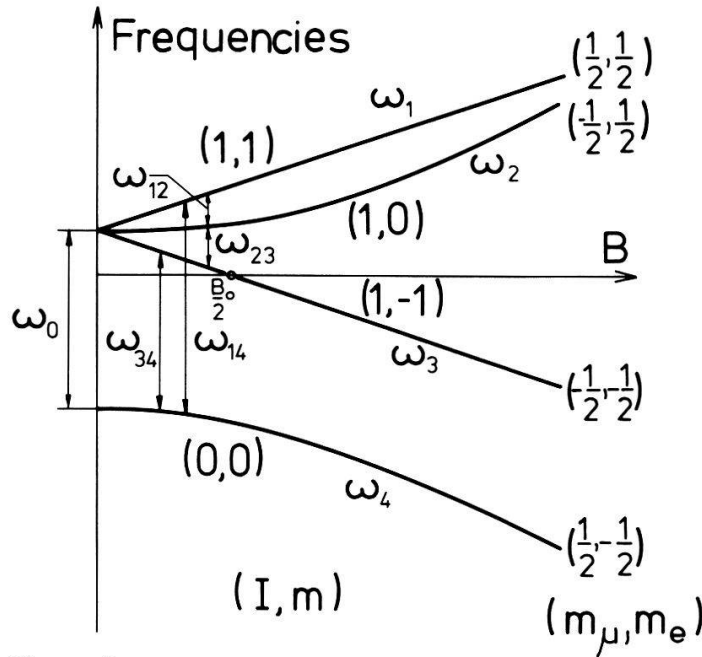
Figure 1
Hyperfine diagram for muonium. For small external magnetic field the levels are marked with the total spin and third component of the muonium. In the Paschen Back region the projections of the muon and electron spin are given. The critical field is $B_0 = 1590$ gauss. We have also indicated the transition frequencies which become essential in the following.

hyperfine structure as shown in Fig. 1. The splitting between the triplet and singlet states for vanishing external field is

$$\hbar\omega_0 = \frac{32}{3} \mu_u \mu_e \frac{1}{a_0^3} = 1.85 \cdot 10^{-5} \text{ eV}. \tag{2}$$

μ_u and μ_e are the magnetic moments of the muon and the electron. a_0 is the Bohr radius of the s-state muonium in vacuum. We shall see later that a_0 may change its value if the muonium interacts with the surrounding medium. In this paper we shall use as time unit $2/\omega_0 = 7.2 \cdot 10^{-11}$ sec.

We write the states of total spin of the muonium with two component spinors in the following form.

$$\chi_{11} = \alpha_e \alpha_\mu$$

$$\chi_{10} = c\alpha_e \beta_\mu + s\beta_e \alpha_\mu$$

$$\chi_{1-1} = \beta_e \beta_\mu \tag{3}$$

$$\chi_{00} = c\beta_e \alpha_\mu - s\alpha_e \beta_\mu.$$

The mixing coefficients s and c depend on the external magnetic field and are given by

$$s = \frac{1}{\sqrt{2}} \left[1 - \frac{x}{\sqrt{1 + x^2}} \right]^{1/2} \quad c = \frac{1}{\sqrt{2}} \left[1 + \frac{x}{\sqrt{1 + x^2}} \right]^{1/2} \tag{4}$$

where $x = B/B_0$; B_0 is the magnetic field, created by the magnetic moment of the muon at the place of the electron—$B_0 = 1590$ Gauss. For $x = 0$ we have $s = c = 1/\sqrt{2}$. In this case only the total spin of the muonium indicated in $\chi_{j,m}$ in (3) is a good quantum number of the hamiltonian (1). If $x \gg 1$, then $s \simeq 0$ and $c \simeq 1$, the muonium

is in the Paschen–Back region. In this region the μ- and e-spin are decoupled by the strong external magnetic field and the states $|\pm\frac{1}{2} \pm \frac{1}{2}\rangle$ and $|\pm\frac{1}{2}, \mp \frac{1}{2}\rangle$ are also eigenstates of H^{Mu}.

Let us now restrict on the region of low external field. The magnetic moments of the muonium in the corresponding states are then

$$\mu_{1,\pm 1} \simeq \mp \mu_e \quad \mu_{1/2 \pm 1/2,0} \simeq \frac{\mp x/2}{\sqrt{1+x^2}} \mu_e = \mp \mu_e \frac{B}{2B_0}. \tag{5}$$

For simplicity we have here neglected the interaction of the magnetic moment of the μ^+ with the external field. The energy eigenvalues of H^{Mu} for the four different states are

$$a + \mu_e B$$

$$a + \mu_e B \cdot \frac{B}{2B_0}$$

$$a - \mu_e B$$

for the triplet states and

$$-3a - \mu_e B \cdot \frac{B}{2B_0}$$

for the singlet state.

The precession in a transverse magnetic field with respect to the muon spin is therefore a superposition of the four different transition energies.

$$
\begin{aligned}
\omega_{12} &\simeq \mu_e B_\perp \left(1 - \frac{B_\perp}{2B_0}\right) & |11\rangle &\rightarrow |10\rangle \\[2mm]
\omega_{23} &\simeq \mu_e B_\perp \left(1 + \frac{B_\perp}{2B_0}\right) & |10\rangle &\rightarrow |1-1\rangle \\[2mm]
\omega_{14} &\simeq \hbar\omega_0 + \mu_e B_\perp \left(1 + \frac{B_\perp}{2B_0}\right) & |11\rangle &\rightarrow |00\rangle \\[2mm]
\omega_{34} &\simeq \hbar\omega_0 - \mu_e B_\perp \left(1 - \frac{B_\perp}{2B_0}\right) & |1-1\rangle &\rightarrow |00\rangle.
\end{aligned} \tag{6}
$$

Since the interaction between the magnetic moment of the muon and the external field has been neglected the levels 1 and 2 do not cross for formula (6). This approximation is, however, quite good for small external fields, that is $x < 1$. For small fields, the frequencies ω_{14} and ω_{34} are too big to be observed experimentally. The beat behaviour of the muon spin precession due to ω_{12} and ω_{23} has, however, been observed [6].

Let us now formulate the equation of motion of the muonium as it was first given by Nosov and Yakovleva [7]. We write the spin density operator as

$$\hat{\rho} = \tfrac{1}{4} \sum_{\lambda,\mu=0}^{3} \rho_{\lambda\mu} \sigma_\lambda^{(\mu)} \otimes \sigma_\mu^{(e)}. \tag{7}$$

$\sigma^{(\mu)}$ and $\sigma^{(e)}$ refer to the μ- and e-spin; σ_0 is the 2-component unit matrix. With this definition the electron and muon polarizations are given by

$$P_\mu^{(e)} = \rho_{0\mu} \quad P_\lambda^{(\mu)} = \rho_{\lambda 0} \qquad \lambda, \mu = 1, 2, 3. \tag{8}$$

$\rho_{\lambda\mu}$ with λ, μ both $\neq 0$ describe the correlations between the muon and electron spin due to the hyperfine interaction. The equation of motion is (units $\hbar = c = 1$)

$$\dot{\hat{\rho}} = -i[H^{\mathrm{Mu}}, \hat{\rho}]. \tag{9}$$

If we express the time in units of the inverse hyperfine-splitting energy (time unit is $2/\omega_0$) we obtain for the components of the density matrix the following set of equations.

$$\dot{\rho}_{\lambda 0} = -\epsilon_{\lambda\varkappa\nu}\rho_{\varkappa\nu} - 2\zeta x_k \epsilon_{\lambda k\alpha}\rho_{\alpha 0}$$

$$\dot{\rho}_{0\mu} = \epsilon_{\mu\lambda\alpha}\rho_{\lambda\alpha} + 2x_m \epsilon_{\mu m\alpha}\rho_{0\alpha} \tag{10}$$

$$\dot{\rho}_{\lambda\mu} = \epsilon_{\lambda\mu\nu}\rho_{\nu 0} - \epsilon_{\lambda\mu\alpha}\rho_{0\alpha} + 2x_m \epsilon_{\mu m\alpha}\rho_{\lambda\alpha} - 2\zeta x_k \epsilon_{\lambda k\alpha}\rho_{\alpha\mu}.$$

x_m are the components of the external field in units of $B_0 = 1590$ G. $\zeta = m_\mu / m_e$.

Note that the interaction of the external field with the magnetic moment of the muon is not neglected here.

III. Perturbation of Muonium in Condensed Matter

As a first possible modification of the behaviour of muonium in condensed matter we may mention the coupling of the muon or electron charge to a collective action of the charge carriers or the ionic crystal field of a solid. This coupling can lead to an effective mass of the muonium electron different from its free mass. Modification of the Coulomb law due to collective shielding effects may be very important. These effects lead to a change of size of the muonium and hence according to (2) to a drastic change of the hyperfine splitting energy. Such effects have been observed experimentally with muonium in semiconductors [6, 8]. As far as these interactions just lead to a modification of the hyperfine splitting, they only change our time scale in the equations of motions. Therefore, we do not consider any longer these effects. We have, however, to keep in mind that the frequency ω_0 must not necessarily correspond to the vacuum value and hence may be a phenomenological parameter in our theory.

Another perturbation of the muonium may be due to the coupling of the magnetic moments of charge carriers or the crystal field to the magnetic moment of the electron of the muonium. Due to its smallness we can neglect the coupling to the magnetic moment of the muon. It is, however, evident that the polarization of the muon is influenced by the perturbation of the electron over the muonium hyperfine interaction. The coupling to the magnetic moments in the medium will be a very strong relaxation mechanism e.g. in paramagnetic substances. If the paramagnetism is due to unpaired electrons these molecules will be in general very reactive with the muonium. Such chemical effects shall be discussed in the next section. In the case of paramagnetism with an even number of electrons (e.g. molecular oxygen) the main effect will probably be a quite high spin–flip frequency of the muonium electron due to interactions with the magnetic moments of the paramagnetic centers during collisions.

The interaction with the crystal field is of the form

$$\frac{\beta}{2c} \vec{\sigma}^{(e)}(\vec{v} \wedge \vec{E}), \quad \vec{E} = -\vec{\nabla}\varphi \tag{11}$$

where φ is the potential of the crystal field in a solid, v the velocity of the muonium. Since $v \ll c$ this coupling as a relativistic effect, cannot present a strong perturbation of the muonium spin motion.

In semiconductors the most important perturbation mechanism presumably consists in the muonium-electron collisions with mutual spin–flip of the electrons, that is

$$(\mu^+ e^- \downarrow) + e^- \uparrow \rightarrow (\mu^+ e^- \uparrow) + e^- \downarrow. \tag{12}$$

The frequency of such a reaction depends on the energy distribution of the free or quasifree electrons in the solid and on the energy dependence of this spin–flip cross-section. It should be clear that this relaxation mechanism in semiconductors should be temperature dependent [9].

A systematic experimental investigation of these possibilities of muonium perturbation has not been done yet. In the mean time we want to include such perturbations by means of some phenomenological relaxation parameter in the equation of motion (9). Before using them let us first state a few critical remarks.

We introduce the following operators:

H^{Mu} = hamiltonian (1) of muonium and its interaction with an external field.

H^B = hamiltonian of all surrounding particles.

V = interaction operator acting between muonium and medium. It describes one (or several) of the interactions mentioned above.

Let $\hat{\rho}^{MB}$ be the density operator of the combined system. $\hat{\rho}^M$ and $\hat{\rho}^B$ are the density operators of the muonium and the surrounding medium. We assume as initial condition that the muonium and medium are uncorrelated, that is

$$\hat{\rho}_0^{MB} = \hat{\rho}_0^M \cdot \hat{\rho}_0^B \quad \text{for } t = t_0 \ll 10^{-10} \text{ sec} \tag{13}$$

where $\hat{\rho}_0^B$ describes a thermal equilibrium state of the medium and $\hat{\rho}_0^M$ the state with polarized muon and unpolarized electron. $\hat{\rho}_0^B$ and $\hat{\rho}_0^M$ are the states, defined by the experimental set up at time $t = 0$. During the time t_0 drastic physical processes take place:

(1) Stopping of the muon to an energy of a few eV by collision processes.
(2) Capture of an electron to form muonium.

By assuming the initial conditions (13) we therefore make the following physical assumptions:

(1) The radiation damages in the medium due to the interactions which have stopped the muon are far away or have healed out already after 10^{-10} sec. That is, there are no excited local hot regions which interact with the muonium.

(2) We assume that the distortions of the medium due to the capture process dissipate away sufficiently fast. The medium around the muonium is always considered to be in thermal equilibrium. Note that the muonium after the first capture

does not have thermal velocity yet. Therefore there may be a whole strain of successive captures and ionizations.

(3) We also assume that during stopping time and capture mechanism no depolarization of the muon is taking place. The former is possible due to the small magnetic moment of the muon. The latter is true if the capture time is smaller than $1/\omega_0 \simeq 10^{-10}$ sec.

If these conditions are fulfilled we can write [10]

$$\hat{\rho}_\tau^M = e^{-iH^{Mu}\tau}Tr_B\{\hat{\rho}_0^M\hat{\rho}_0^B - \pi\tau[\overline{V}[\overline{V}, \hat{\rho}_0^M\hat{\rho}_0^B]]\}e^{iH^{Mu}\tau} \tag{14}$$

where $\hat{\rho}_0^B$ is the density operator of the canonical ensemble and $\overline{V}$ is the portion of V which is diagonal in the total energy.

If the effects of interaction of the muonium with the medium dissipate away quickly the state of the bath B does not change significantly during time τ and we can write for (14) the equation (Wangsness–Bloch equation)

$$\dot{\hat{\rho}}^M = -i[H^{Mu}, \hat{\rho}^M] - \pi Tr^B[\overline{V}[\overline{V}, \hat{\rho}_0^M\hat{\rho}_0^B]]. \tag{15}$$

If we now express the double commutator by a phenomenological relaxation parameter, we obtain the equations of Ivanter and Smilga [3]. Assuming that this relaxation acts only on the electron of the muonium we have to add to the second and third equation of the system (10) the following terms respectively

$$-\gamma\rho_{0\lambda} \quad \text{and} \quad -\gamma\rho_{\mu\lambda}. \tag{16}$$

In the spirit of the spin–flip reactions mentioned above we may interpret γ as a collision frequency.

We can give to the equation (10), with relaxation terms (16) for an external magnetic field, transverse to the initial μ-polarization, the following special form.

$$\frac{d}{dt}\begin{pmatrix} P_1^\mu + iP_2^\mu \\ P_1^e + iP_2^e \\ \rho_{13} + i\rho_{23} \\ \rho_{31} + i\rho_{32} \end{pmatrix} = i\begin{pmatrix} -2\zeta x & 0 & 1 & -1 \\ 0 & i\gamma + 2x & -1 & 1 \\ 1 & -1 & i\gamma - 2\zeta x & 0 \\ -1 & 1 & 0 & i\gamma + 2x \end{pmatrix}\begin{pmatrix} P_1^\mu + iP_2^\mu \\ P_1^e + iP_2^e \\ \rho_{13} + i\rho_{23} \\ \rho_{31} + i\rho_{32} \end{pmatrix}. \tag{17}$$

We write the formal solution as

$$P_\alpha(t) = [\exp(iA(\gamma, x)(t - t'))]_{\alpha\beta}P_\beta(t') \tag{18}$$

where A is the matrix of the system of equations (17).

IV. Chemical Effects

Apart from isotopic corrections the muonium behaves in a medium like atomic hydrogen—it is a chemical radical and has therefore a strong tendency to proceed into a chemically bound state. These influence the depolarization mechanism of the muon via the hyperfine interaction very strongly.

Let us explain this effect. The magnetic field produced by the electron at the site of the muon in muonium is according to (1) and (2)

$$\vec{B} = \frac{4\pi}{3} \beta_e g_e |\Psi(0)|^2 \langle \vec{\sigma} \rangle. \tag{19}$$

This field is responsible for the depolarization of the muon. Suppose now that the muonium is bound covalently to some molecule. This bond produces a full s-shell and hence

$$\vec{B} = \frac{4\pi}{3} \beta_e g_e (|\Psi_\uparrow(0)|^2 - |\Psi_\downarrow(0)|^2). \tag{20}$$

In a diamagnetic compound $|\Psi_\uparrow|^2 = |\Psi_\downarrow|^2$ and hence $B = 0$. In this case no hyperfine interaction acts anymore on the muon and therefore the depolarization mechanism ceases. The muon now precesses with its free Larmor frequency. The damping of this precession amplitude is determined by relaxation mechanisms which are exactly analogous to the relaxation of conventional proton spin resonance. (Apart from the μ-decay of course.) These relaxation times are very big compared to $1/\omega_0 \simeq 10^{-10}$ sec, namely 10^{-7}–10^{-5} sec and we therefore neglect them in this work. We should like to point out, however, that the measurement of such relaxation times provides a complementary tool to the method of proton spin resonance, with the advantage that no high-frequency field is needed. This has been demonstrated by a series of experiments by A. Schenck et al. [12, 13].

In this work, we also want to include the possibility of formation of chemical radical states by the muonium. In a chemical radical the electron spins are not paired off. Take as an example

$$C_6H_6 + Mu \rightarrow C_6H_6Mu^{\cdot}. \tag{21}$$

As can be seen from Figure 2 the muonium has gone into a covalent bond. One of the resonating π-orbitals becomes free, however and may now act with its magnetic moment on the moment of the muon. This hyperfine interaction is usually weaker than the interaction in muonium since the distance between the two magnetic moments in the radical is larger than the muonium radius. This implies the continuation of the muon depolarization in a radical, but with a much slower rate than in muonium.

$$a_H^{CH_2} = 47.71 g$$
$$a_2 = a_6 = 8.99$$
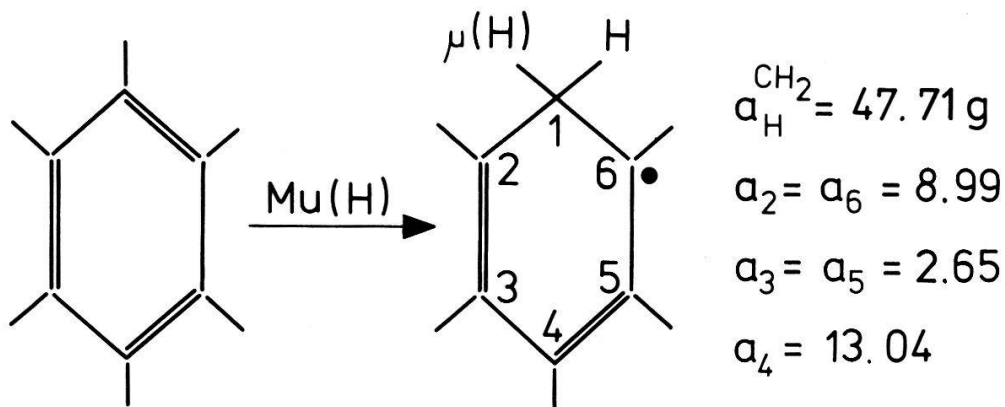$$a_3 = a_5 = 2.65$$
$$a_4 = 13.04$$

Figure 2
Illustration of the radical formation with muonium and benzene. The corresponding radical formed with atomic hydrogen is cyclohexadienyl. The hyperfine fields at the proton sites determined by ESR are also given.

We should like to point out, however, that the interaction between the muon and the unpaired electron is not necessarily only of the contact type, as in muonium. If the two particles have relative angular momentum $l = 1$ a dipole–dipole coupling may be important. Furthermore, we have to consider that this unpaired electron is not necessarily localized and hence its magnetic moment is completely smeared out over the molecule. The magnetization density in the molecule is

$$\vec{M} = -\beta_e g_e \cdot \rho \cdot \vec{S}, \quad \rho = |\Phi_e(r)|^2 \tag{22}$$

where Φ_e is the wave function of the electron. The interaction with the muon can then be written as

$$\frac{8\pi}{3} g_e \beta_e g_\mu \beta_\mu (\vec{\sigma}^{(e)} \cdot \vec{\sigma}^{(\mu)}) |\Phi_e(\vec{R})|^2 + g_e \beta_e g_\mu \beta_\mu \vec{\sigma}^{(\mu)} \cdot \vec{\nabla}_R \int \frac{\vec{\nabla} \cdot (\vec{\sigma}^{(e)} \rho(r))}{|\vec{r} - \vec{R}|} \, d^3 r. \tag{23}$$

The g-factor of the electron is usually also somewhat different from the free value.

Let us now look at the situation in our example (21). In C_6H_6 the carbon under consideration has three sp^2-hybridization σ-bonds and one π-bond. In the radical (muonic cyclohexadienyl radical) the π-bond has gone over to a fourth sp-hybridized σ-bond. The cycle of nonlocal π-bonds of C_6H_6 is therefore broken. From ESR-data [11] we know the hyperfine fields at the different protons produced by the unpaired electron. The fields are given in units of gauss in Figure 2. These numbers indicate that the unpaired electron can not be entirely localized at place 6.

These observations also give us some indications about the nature of possible relaxation mechanisms of the precession of the muon. We realize that these mechanisms must be very similar to those observed in proton spin resonance in chemical radicals. We have relaxation due to rotations and, because of interactions of the electron with possible paramagnetic centers, due to translational movements of the radical. The relaxation due to magnetic interaction of the muon with protons via the unpaired electron may also be important. The direct μ-proton interaction is weak and corresponds to a large relaxation time, since

$$T_{ep}, T_{e\mu} \ll T_{p\mu}.$$

The hyperfine interaction in muonium is given by $\omega_0 \simeq 10^{10} \text{ sec}^{-1}$. In a radical the hyperfine frequency is smaller due to the considerable spreading of the electron wave function, say $\omega_r \simeq 10^9 \text{ sec}^{-1}$. This corresponds to a hyperfine field of $B_0 \simeq 160 \text{ G}$. If the correlation time for the electron relaxation is smaller than 10^{-9} sec the interaction between unpaired electron and muon is decoupled by the rapid movement of the electron spin. In such cases there is little or even no depolarization of the muon in the radical.

Of course this radical as a highly reactive object will react with the surrounding and the muonium will finally end up again in a diamagnetic compound. Then the depolarization stops definitely as indicated above.

After all what has been said in this section, we may now have the suspicion that it could be possible to determine chemical reaction constants and lifetimes of radicals by investigating the polarization of μ^+-particles in condensed matter. Due to the possibly strong relaxations in radicals, it seems to us, however, most essential that the analysis of experimental data will be coupled with the information available from ESR. The experimental program should be chosen accordingly.

V. Muonium Depolarization in Presence of Several Chemical Reaction Channels

We assume the existence of the following four different states for the muon in a condensed medium:

0 Muonium diamagnetically bound.
1 Muonium bound in a radical.
2 Muonium free in its ground state.
3 Muonium bound diamagnetically through the radical channel. (This is not necessarily the same bound as in 0.)

We neglect the slow depolarization mechanisms in the states 0 and 3. These mechanisms correspond to the relaxations as observed in proton spin resonance and have relaxation times of order μs. In the states 1 and 2 the hyperfine interaction leads to depolarization whose strength is given by the splitting ω_0 and ω_r, with $\omega_r < \omega_0$.

The chemical rate constants for transition from one state into another are denoted by α_{21}, α_{20} and α_{13}. These constants are defined as $\tau = 1/\alpha$ where τ is the average lifetime of the muonium with respect to the corresponding chemical reaction. Due to the low concentration of the muonia we have $\tau = k[X]$, where k is the reaction constant in units 10^{10} [l/molsec] and $[X]$ the concentration of the reagent. α is therefore an experimentally variable parameter.

Suppose that the ratio β of the initial number of muonia (not yet thermalized) go directly through a hot chemical reaction into the diamagnetic state 0. The ratio ρ may proceed through a hot reaction into the radical state 1. We describe this situation with Figure 3. The chemical rate equations are obviously

$$
\begin{aligned}
\dot{N}_2 &= -(\alpha_{21} + \alpha_{20})N_2 \\
\dot{N}_0 &= \alpha_{20}N_2 \\
\dot{N}_1 &= \alpha_{21}N_2 - \alpha_{13}N_1 \\
\dot{N}_3 &= \alpha_{13}N_1
\end{aligned}
\tag{24}
$$

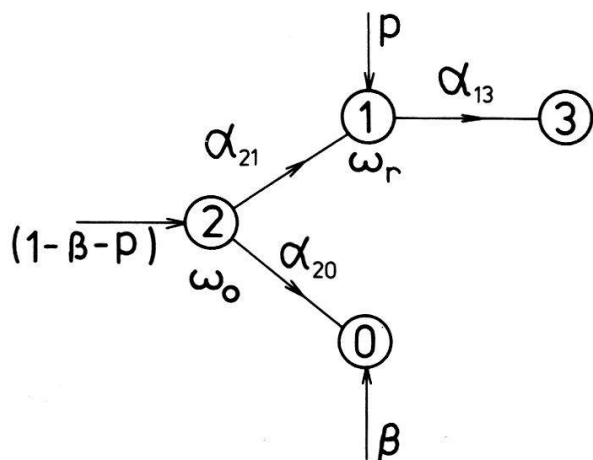with the initial conditions $N_1(0) = \rho$, $N_0(0) = \beta$ and $N_2(0) = 1 - \rho - \beta$.

Figure 3

Diagram illustrating the chemical states and the reaction channels for the muonium. 2, free muonium; 1, radical; 0, muonium diamagnetically bound; 3, muonium diamagnetically bound through radical channel. ρ and β are the ratios of muoniums which go through hot chemical reactions into state 1, resp. 0, $(1 - \rho - \beta)$ muoniums thermalize in the state of free muonium.

We have normalized the initial numbers of muons to 1 and assumed that all of them form muonium. Since the muons decay we have

$$\sum_{i=0}^{3} N_i(t) = N(t) = e^{-t/\tau_\mu} \tag{25}$$

with $\tau_\mu = 2.2 \cdot 10^{-6}$ sec being the muon lifetime.

The positron distribution of the muon decay gives the information on the polarization of the muon. The counting rate from decay asymmetry is given by

$$P_i(t) = N_i(t)\bar{P}_i(t) \qquad \text{for each state and}$$
$$P(t) = \sum_{i=0}^{3} P_i(t) \qquad \text{totally} \tag{26}$$

where $\bar{P}_i$ is the degree of polarization of a muon in state i.

Let us now fix the coordinate system. The external magnetic field points into the direction [2] and the initial muon polarization is along the [1]-axis. In this case the movement of the muon spin in the depolarization stage in the states 1 and 2 is given by the complex quantities

$$\bar{P}_2(t) = \sum_{j=1}^{4} q_{\omega_0}^{1j}(t - t')\bar{P}_2^j(t')$$
$$\bar{P}_1(t) = \sum_{j=1}^{4} q_{\omega_r}^{1j}(t - t')\bar{P}_1^j(t'). \tag{27}$$

The q^{ij} are the matrix elements of the exponential in equation (18). The second equation of (27) implies that we assume a similar depolarization mechanism in the radical stage as in the muonium. We have seen in Section IV that this is probably very rarely the case. We believe that at this point information from electron spin resonance experiments should be introduced in order to utilize this analysis in concrete cases.

For the polarizations in the different states we obtain from (24) and (26)

$$\dot{P}_0 = \alpha_{20}P_2 + \partial_t P_0|_{N_0}$$
$$\dot{P}_1 = \alpha_{21}P_2 - \alpha_{13}P_1 + \partial_t P_1|_{N_1}$$
$$\dot{P}_2 = -(\alpha_{21} + \alpha_{20})P_2 + \partial_t P_2|_{N_2}$$
$$\dot{P}_3 = \alpha_{13}P_1 + \partial_t P_3|_{N_3}. \tag{28}$$

$\partial_t P_i|_{N_i}$ contains the variation of polarization (at constant number of muons) due to depolarization mechanisms in the corresponding channels.

For free muonium we have

$$\partial_t P_2|_{N_2} = (1 - \beta - \rho)e^{-(\alpha_{21} + \alpha_{20})t}\dot{q}_{\omega_0}^{11}(t). \tag{29}$$

In the states 0 and 3 these derivatives just express the free muon precession and are therefore

$$\partial_t P_{0,3}|_{N_{0,3}} = i\omega_\mu P_{0,3}(t) \tag{30}$$

where ω_μ is the Larmor precession frequency of the muon. In the case of a muonium, bound in a chemical radical we get

$$\partial_t P_1|_{N_1} = \rho e^{-\alpha_{13}t}\dot{q}_{\omega_r}^{11}(t) + \alpha_{21} \sum_j \int_0^t e^{-\alpha_{13}(t-t')}\dot{q}_{\omega_r}^{1j}(t - t')P_2^j(t') \, dt'. \tag{31}$$

The first term in (31) represents the depolarization of muons which, after forming muonium, have entered the radical through a hot chemical reaction with a time delay smaller than 10^{-10} sec. The second term gives the depolarization for muons which lived as muonium up to time t' and then reacted with a reagent to form a radical.

Substitution of 29–31 into 28 leads to a coupled set of integro-differential equations. If we integrate these equations formally and take into consideration the initial conditions, we obtain the following coupled Volterre integral equations.

$$P_0(t) = \beta e^{i\omega_\mu t} + \alpha_{20} \int_0^t e^{i\omega_\mu(t-t')} P_2(t')\, dt'$$

$$P_1(t) = \rho e^{-\alpha_{13}t} q_{\omega_r}^{11}(t) + \alpha_{21} \int_0^t \sum_{j=1}^4 e^{-\alpha_{13}(t-t')} q_{\omega_r}^{1j}(t-t') P_2^j(t')\, dt'$$ (32)

$$P_2(t) = (1 - \beta - \rho) e^{-(\alpha_{21}+\alpha_{20})t} q_{\omega_0}^{1j}(t)$$

$$P_3(t) = \alpha_{13} \int_0^t e^{i\omega_r(t-t')} P_1(t')\, dt'.$$

We should like to add here a remark concerning the second equation of the system (32). The sum in this equation indicates that the muon and electron polarization, as well as the correlations between the two spins, are transferred from the muonium stage into the radical. This may only be true if the unpaired electron in the radical is also responsible for the binding of the muon to the radical. The situation described in our example in Section IV seems to us rather more frequent. In such cases the correlations between muon and electron spins are interrupted during the reaction. The depolarization mechanism due to the hyperfine interaction in the radical restarts with the conditions:

$$P_k^{(\mu)}(t') = P_k^\mu \qquad \text{polarization from muonium stage}$$

$$P_i^{(e)}(t') = 0$$ (33)

$$\rho_{ij}(t') = 0.$$

In this case the second equation of (32) becomes obviously

$$P_1(t) = \rho e^{-\alpha_{13}t} q_{\omega_r}^{11}(t) + \alpha_{21} \int_0^t e^{-\alpha_{13}(t-t')} q_{\omega_r}^{11}(t-t') P_2^1(t')\, dt'.$$ (34)

We now apply to the system (32) a Laplace transform and get for the transformed polarization $p_i(\sigma)$ the following set of algebraic equations.

$$p_0(\sigma) = [\beta + \alpha_{20} p_2(\sigma)] \frac{1}{\sigma - i\omega_\mu}$$

$$p_1(\sigma) = \rho \tilde{q}_{\omega_r}^{11}(\sigma + \alpha_{13}) + \alpha_{21} \sum_{j=1}^4 \tilde{q}_{\omega_r}^{1j}(\sigma + \alpha_{13}) p_2^j(\sigma)$$ (35)

$$p_2^j(\sigma) = [1 - \beta - \rho] \tilde{q}_{\omega_0}^{1j}(\sigma + \alpha_{21} + \alpha_{20})$$

$$p_3(\sigma) = \alpha_{13} p_1(\sigma) \frac{1}{\sigma - i\omega_\mu}.$$

The $\tilde{q}_{\omega_0,\omega_r}^{ij}$ is the Laplace transformation of the exponential solving matrix (18) for hyperfine splitting ω_0 resp. ω_r. The modification of the second equation due to break off of the correlations during the reaction to the radical state is obvious from (34).

Solving the system (35) leads for every $p_i(\sigma)$ to a rational function in σ. Hence the inverse Laplace transform leads to expressions like

$$P_i(t) = \sum_{j=1}^{n} A_j^{(i)} e^{\sigma_j^{(i)} t} \tag{36}$$

where σ_j are the poles and A_j the residues of the rational function. We assume that this rational function has no double poles. The roots of the denominators (highest degree appears in p_3 and is 9) and the residues can be calculated approximately on the computer. We utilized the inclusion algorithm of Henrici and Gargantini [14] as well as tests based on the criteria given by Lehmer [15].

VI. Numerical Examples and Discussion

The muonium lives only a certain time in the states 2 and 1. The corresponding reaction constants $\alpha_{21} + \alpha_{20}$ and α_{13} appear as damping constants in the exponential of (36). Hence the hyperfine frequencies in this state (Fig. 1) die out. After a long time all muons (apart from muon decay) are in state 0 and 3 where they precess with the free muon Larmor frequency. Since we neglect here the weak relaxation processes in diamagnetic compounds the precession in these states is not damped. The signal can therefore be written as

$$A_0 e^{i(\omega_\mu t + \delta_0)} + A_3 e^{i(\omega_\mu t + \delta_3)}. \tag{37}$$

This can be transformed into

$$P_{\text{res}}(t) = A e^{i(\omega_\mu t + \delta)} \tag{38}$$

with the residual polarization

$$A = [A_0^2 + A_3^2 + 2A_0 A_3 \cos(\delta_3 - \delta_0)]^{1/2} \tag{39}$$

and the phase shift

$$\delta = \text{arctg}\left\{ \frac{A_3 \sin(\delta_3 - \delta_0)}{A_0 + A_3 \cos(\delta_3 - \delta_0)} \right\} + \delta_0. \tag{40}$$

In the following we shall give numerical examples which correspond to the situation described by (34). That is, electron polarization and spin correlations of the muonium are destroyed during the chemical reaction which leads to the radical.

Figure 4a shows the time dependence of the movement of the muon spin vector for the reaction parameters given there. We see that the signal is already reasonably represented by (38) after 4 nsec. In this example the residual polarization is $A = 0.25$. The phase shift is clearly demonstrated, $\delta = -11.3°$.

In Figure 4b we give the development of the muon polarization for small times with higher resolution. The high frequencies correspond to the transitions ω_{14}, $\omega_{13} \simeq \omega_0$ in the muonium. The slower component is related to the transitions $\omega_{12} \simeq \omega_{23}$. This oscillation is also seen in Figure 4a. With the reaction constants considered here, these oscillations have to die out after 2.4 nsec. The frequencies of the radical cannot be seen in this example, since the short chemical lifetime ($\tau_{13} \simeq 0.3$ nsec)
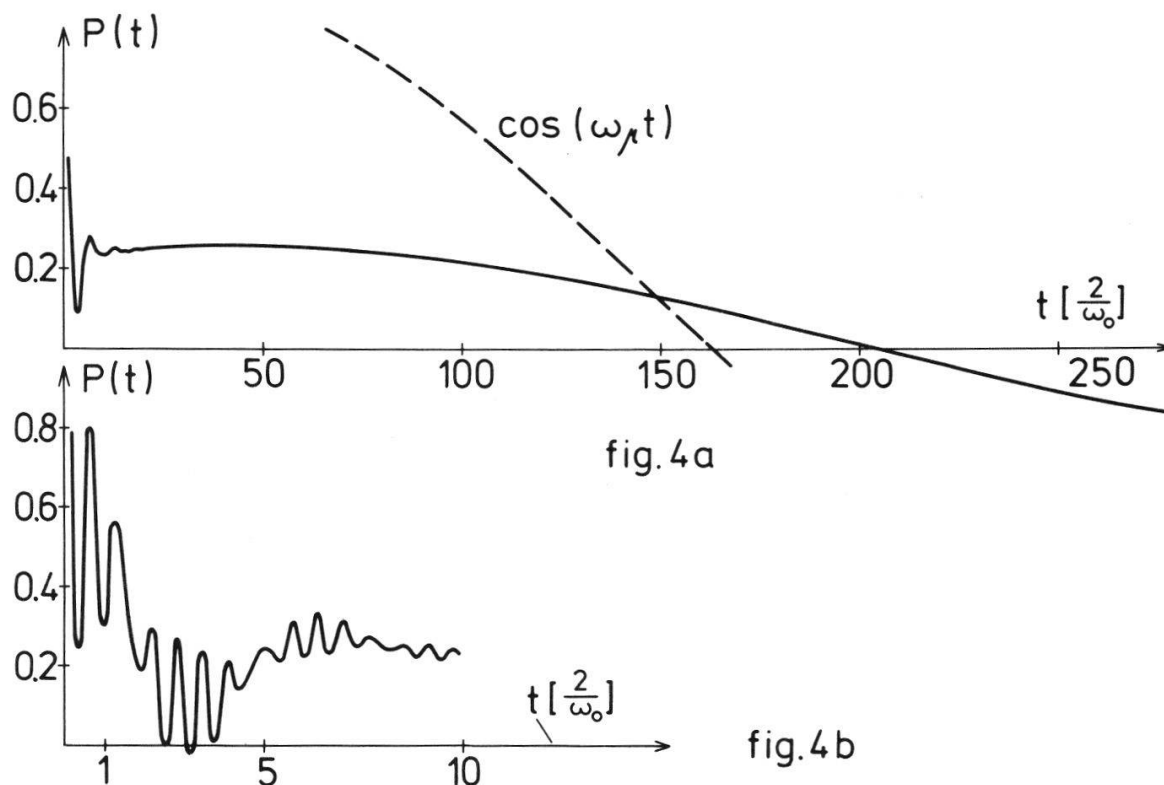
Figure 4
(a) Variation in time of the muon polarization for a situation as described in Figure 3. The time unit is $2/\omega_0 = 7.2 \cdot 10^{-11}$ sec. In this figure the high frequencies have been smoothed out for $t < 10$. The dashed curve corresponds to free muon precession. The parameters are: $B = 320$ gauss, $\beta = 0.2$, $\rho = 0$, $\nu = \nu_r = 0$ no relaxation, $\omega_r = 0.1$ (unit ω_0), $\alpha_{12} = 0.02$, $\alpha_{13} = 0.2$, $\alpha_{20} = 0.01$. The damping factor (unit $2/\omega_0$) due to the decay of the muons is not included here. (b) Parameters as in (a). Details of oscillations for small time.
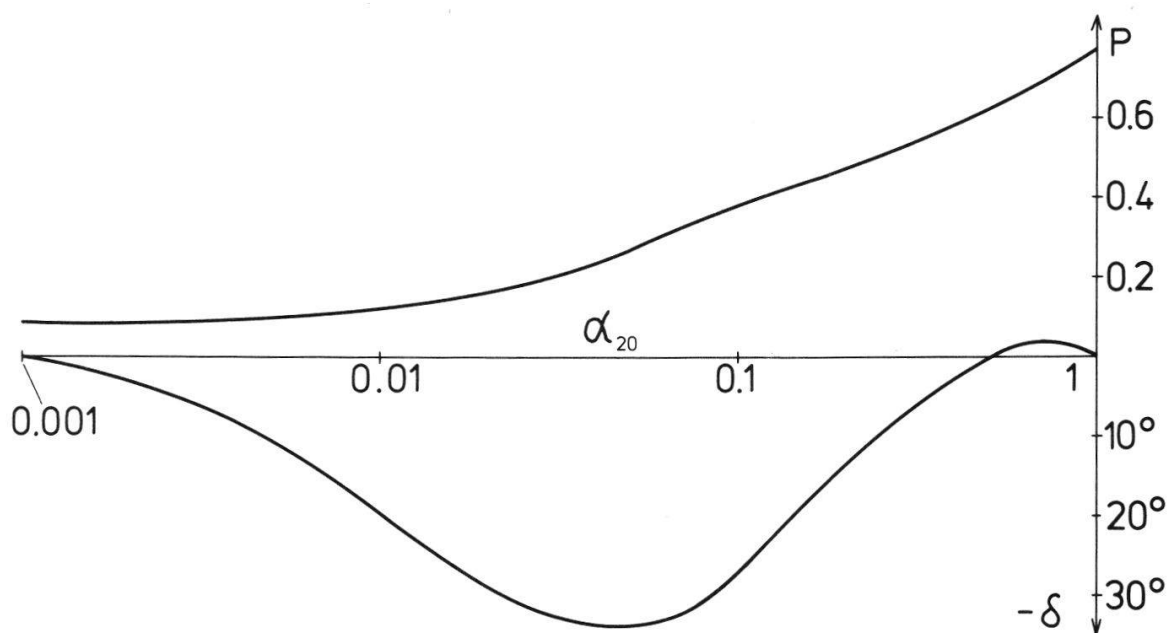

Figure 5
Muon polarization and phase shift in dependence of the chemical reaction constant α_{20}. The parameters are: $B = 320$ gauss, $\beta = 0.02$, $\rho = 0$, $\alpha_{12} = \alpha_{13} = 0.02$ (unit $2/\omega_0$), $\omega_3 = 0.2$, $\nu = \nu_r = 0$ (unit ω_0).

prevents the development of these oscillations. They distort, however, the muonium oscillations and give some contribution to the total phase shift of the final free muon precessions. If concentrations in the chemical solutions can be chosen such that the muonium and the radical live longer, the experimental observation of some of the oscillations may be feasible.

Figure 5 shows the dependence of the residual polarization and the phase shift on the chemical reaction constant $\alpha_{20} = (k[X])^{-1}$ where $[X]$ is the concentration of the reagent. For a reagent concentration of 1 mol/l and $k = 1$ the scale covers $\tau = 10^{-10}$–10^{-7} sec for the lifetime of the free muonium with respect to this chemical reaction. The soft shoulder in the region of $\alpha_{20} \simeq 0.1$ becomes more pronounced if the radical channel is absent. (See also Ref. 4.)

In Figure 6 we have drawn the dependence of the residual polarization and phase shift on the number of muonia which go through hot chemical reaction into a diamagnetic bond. It is evident that the more muons go through this channel, the smaller are the depolarization effects. Maybe it is possible to use such methods for investigation of hot chemistry.
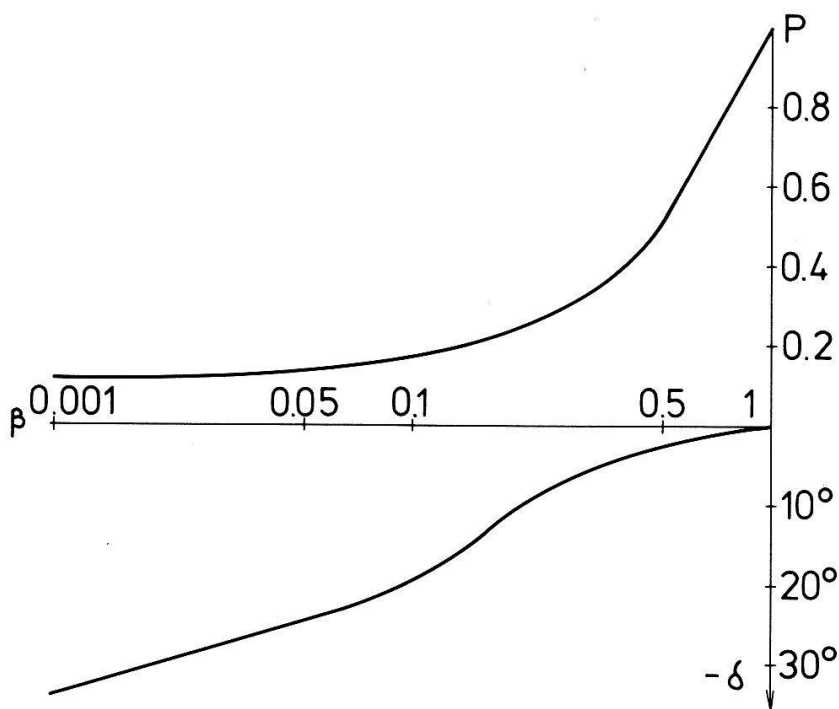

Figure 6

Muon polarization and phase shift for different values of β (ratio of muonia which go through hot chemical reaction into diamagnetic bond). The parameters are: $B = 320$ gauss, $\rho = 0$, $\nu = \nu_r = 0$, $\omega_r = 0.2$, $\alpha_{12} = 0.02$, $\alpha_{13} = 0.2$, $\alpha_{20} = 0.01$ (unit $2/\omega_0$).

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