

GENERALIZED MECHANISM FOR μ^+ DEPOLARIZATION IN SOLUTIONS

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The formalism developed by Ivanter and Smilga^{1,2} to describe the "muonium mechanism" of positive muon depolarization is adapted and extended to include situations involving more than one strongly depolarizing influence (e.g., muonium and a radical). In such cases the Laplace transform method is inapplicable, and the explicit time dependence of the relevant spin systems must be solved. Calculations are shown for a plausible situation with the assumption of a transverse external magnetic field; the line of reasoning is outlined, and should be readily extendable to other cases, or to longitudinal field.

Consider an ensemble of polarized positive muons coming to rest in a target: without loss of generality, we may assume that they are 100% polarized, since imperfect polarization can be expressed as a multiplicative factor in all the formulas. The target may be gas, liquid, or solid, but we restrict this discussion to the case of liquids consisting of a reagent "X" dissolved in a solvent "S" in the "dilute limit"

(the concentration [X] of the reagent X is never high enough to significantly affect the density [S] of solvent molecules). This restriction facilitates treatment of muonium chemistry. All the muons capture electrons to form atomic muonium⁵, which may experience any of the subsequent fates outlined schematically in Fig. 1. This diagram is not intended to be all-inclusive; certain obvious possibilities, such as epithermal reactions with the reagent (causing a concentration-dependence of the "hot fraction", h) or chemical reactions with the reagent to form a second type of radical, have been omitted for the sake of simplicity; they are easily incorporated into the theory, if needed.

The "residual" polarization, P_{res} , is the value obtained by extrapolating the observed precession of the muon to zero time, and is thus independent of such extraneous phenomena as relaxation or "beating" due to local fields. P_{res} reflects only the adventures of the muons at very early times, and will differ in magnitude and direction from the beam polarization only if the muon spin experiences a strong influence such as the hyperfine interaction in muonium or a radical, which lasts for a time on the order of 1 nsec and then desists. Any muons still evolving rapidly in muonium or radicals at observation times are phenomenologically considered to be completely depolarized. In solutions, as we will see, this early behavior depends strongly upon the reagent concentration [X], a parameter easily varied by the experimenter.

Mathematically, the residual polarization P_{res} is obtained from the exact time-dependence $P(t)$ by dividing out the Larmor precession and letting the time go to infinity. When muonium is the only depolarizing influence, one can take advantage of this by using the Laplace transform technique

to circumvent the solution of the equations of motion; this method of solution for P_{res} depends upon the assumption that the muon spin evolves in only one environment until it gets into a diamagnetic compound, and can therefore not be used in the two-stage evolution involved here. With this in mind, we set out to obtain analytic formulas for all contributions at all times, with the residual polarization emerging as a special case.

Following Ivanter and Smilga¹, we define the density matrix in terms of the muon and electron polarizations \tilde{P}^μ and \tilde{P}^e and their "cross-correlation" b_{ij} :

$$\rho = 1/4 (1_u + \tilde{P}^\mu \cdot \tilde{\sigma}^\mu + \tilde{P}^e \cdot \tilde{\sigma}^e + \sum_{ij} b_{ij} \sigma_i^\mu \sigma_j^e) \quad (1)$$

and extract the Wangness-Bloch equations of motion:

$$\begin{aligned} \dot{\tilde{P}}_k^\mu &= \sum_{ij} \epsilon_{ijk} (-\frac{1}{2} \omega_0 b_{ij} - \zeta P_i^\mu \omega_j^e) \\ \dot{\tilde{P}}_k^e &= \sum_{ij} \epsilon_{ijk} (+\frac{1}{2} \omega_0 b_{ij} - P_i^e \omega_j^e) - 2\nu P_k^e \\ \dot{b}_{ij} &= \frac{1}{2} \omega_0 \sum_k \epsilon_{ijk} (P_k^\mu - P_k^e) + \sum_{mn} \omega_n^e (\epsilon_{mnj} b_{im} + \epsilon_{mni} b_{mj}) \\ &\quad - 2\nu b_{ij} \end{aligned} \quad (2)$$

where ω_0 is the hyperfine frequency in muonium, ζ is the ratio of μ^+ to electron magnetic moments, $\omega = eB/m_e c$ is the Larmor precession frequency of the electron in the external field, and ν is the frequency of electron "spin-flips" due to magnetic interactions with the medium. If the hyperfine interaction in the radical is a pure contact interaction, with strength $\hbar\omega_r$, then the equations of motion in the radical are identical

except for the substitution of ω_r for ω_o . When \underline{B} is perpendicular to the initial muon polarization, the equations of motion decouple into "parallel" and "transverse" sets of equations, and we can formulate the problem in terms of a set of four complex equations¹:

$$\hat{P} = \begin{pmatrix} P^\mu \\ P^e \\ P^t \\ P^\mu \end{pmatrix} = \begin{pmatrix} P^\mu + i P^y \\ P^e + i P^e \\ b_{xz} + i b_{yz} \\ b_{zx} + i b_{zy} \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad \text{at } t = 0 \quad (3)$$

where \hat{z} is the direction of \underline{B} , \hat{x} is the initial polarization direction of the muons, and \hat{y} is the cross-product of \hat{x} and \hat{z} . This complex 4-component vector then obeys the equation of motion $\dot{\hat{P}} = A_1 \hat{P}$, where

$$A_1 = \frac{i}{2} \omega_1 \begin{pmatrix} 2 \zeta x_1 & 0 & -1 & 1 \\ 0 & i\gamma_1 - 2x_1 & 1 & -1 \\ -1 & 1 & i\gamma_1 + 2\zeta x_1 & 0 \\ 1 & -1 & 0 & i\gamma_1 - 2x_1 \end{pmatrix} \quad (4)$$

for the i^{th} environment. Here $x_1 = B/B_1$ where B_1 is the hyperfine effective field in the i^{th} environment, and $\gamma_1 = 4\nu_1/\omega_1$, where ν_1 and ω_1 are the "spin-flip" frequency and the hyperfine frequency, respectively, in the i^{th} environment. For $i = m$ (muonium), for example, $\omega_m = \omega_o = 2.8 \times 10^{10}$ rad/sec, and $B_m = B_o = 1580$ Gauss. Both values are probably less in all other environments.

A_1 can be diagonalized (this is facilitated when $\nu \rightarrow 0$, as we believe to be the case for all liquids of interest, because then A_1 is just i times a real symmetric matrix.) to form the matrix D_1^i , as follows:

Let M be the matrix which diagonalizes A_m (muonium), and R be the matrix which diagonalizes A_r (radical); then $M^{-1}A_m M = D^m$ and $R^{-1}A_r R = D^r$, so that $D_{ij}^m = \delta_{ij} \lambda_i^m$ and $D_{ij}^r = \delta_{ij} \lambda_i^r$. In terms of these matrices we can define the finite time evolution operators in muonium or radical, respectively: $U_m(t, t') = M \exp[D^m(t - t')] M^{-1}$ and $U_r(t, t') = R \exp[D^r(t - t')] R^{-1}$ which operate upon $\hat{P}(t)$ in the appropriate environment: $\hat{P}(t) = U_i(t, t') \hat{P}(t')$. The time evolution operator for "hot" muonium is just unity (nothing happens on such a short time scale anyway), and that for muons in a diamagnetic compound is $U^d(t, t')$, defined by $U_{ij}^d(t, t') = \delta_{ij} \delta_{i1} \exp[i\omega_\mu(t - t')]$, where ω_μ is the free muon Larmor frequency [here we neglect the effects of chemical shielding].

Returning now to Fig. 1, we must construct a time evolution operator for every possible sequence of environments that a muon may pass through. This will in general just be a time-ordered product; for example, if we label the completely specified fate of a given muon (including times of transition from one environment to the next) as "q", consider "q₇": "hot" muonium \rightarrow thermalized muonium \rightarrow radical (at time t_1) [via normal chemistry] \rightarrow diamagnetic compound (at time t_2). The overall time evolution operator for this process will be $U_{q_7}(t, 0) = U^d(t, t_2) U^r(t_2, t_1) U^m(t_1, 0)$.

The muon polarization which emerges at the end of process "q" (of which the real part is the polarization in the initial direction and the imaginary part is the component in the direction perpendicular to it and the field) is just $\{U_q(t, 0) \hat{P}(0)\}_\mu$, where μ denotes the first component [see (3)]. When we multiply this by the fraction of the ensemble which

experiences fate "q" [which we denote $p(q)$], we obtain the contribution to the total complex muon polarization at time t , $P(t)$, from the muons experiencing fate "q", which we denote $P(q,t)$. That is,

$$P(t) = \sum_q P(q,t), \quad P(q,t) = p(q) \{U_q(t,0) \hat{P}(0)\}_\mu \quad (5)$$

The sum over q may of course involve integrations (e.g., over the unspecified internal times t_1 and t_2).

We now define some empirical quantities directly related to liquids: k_{md} is the chemical rate constant for the reaction $Mu + X \rightarrow$ Diamagnetic compound (Mu denotes muonium); k_{mr} is the chemical rate constant for the reaction $Mu + \text{Solvent} \rightarrow$ Radical; and k_{rd} is the chemical rate constant for the reaction $\text{Radical} + X \rightarrow$ Diamagnetic compound. In terms of these we define $1/\tau_{md} = k_{md}[X]$ = the rate at which muonium reacts chemically into a diamagnetic compound, $1/\tau_{mr} = k_{mr}[S]$ = the rate at which muonium reacts chemically into a radical, and $1/\tau_{rd} = k_{rd}[X]$ = the rate at which the radical reacts into a diamagnetic compound. We also define $1/\tau_m = 1/\tau_{md} + 1/\tau_{mr}$. The τ_i are typically in seconds, the k_i in liters/mole-sec, and the concentrations in moles/liter.

We now list all the contributions to $P(t)$ from processes shown in Fig. 1; note that we include contributions which become negligible at large times and thus do not enter the residual polarization, P_{res} ; if one is interested solely in P_{res} , these contributions need not be calculated.

1) STILL-FREE MUONIUM: "q₁": evolution in free Mu from $t = 0$ to t .

$$\{U_{q_1}(t,0) \hat{P}(0)\}_\mu = \sum_k F_k \exp[\lambda_k^m t]$$

where $F_k = \sum_j M_{1k}^{-1} [M^{-1}]_{kj} \hat{P}_j(0) = M_{1k}^{-1} [M^{-1}]_{k1}$. (6)

$$p(q_1) = (1 - h - r) \exp[-t/\tau_m]$$

thus $P(q_1, t) = (1 - h - r) \sum_k F_k \exp[(\lambda_k^m - 1/\tau_m)t]$

or $P(q_1, t) = \exp[i\omega_\mu t] (1 - h - r) \sum_k F_k \exp[\theta_k t]$ (7)

where we define $\theta_k = \lambda_k^m - 1/\tau_m - i\omega_\mu$. (8)

[The arrangement of terms to place the Larmor precession factor outside all the rest will be convenient later.]

- 2) HOT DIAMAGNETIC: "q₂": evolution in d.c. (diamagnetic compound)
since combining epithermally at $t \approx 0$.

$$\{U_{q_2}(t, 0) \hat{P}(0)\}_\mu = \exp[i\omega_\mu t]$$

$p(q_2) = h$, so $P(q_2, t) = h \exp[i\omega_\mu t]$ (9)

- 3) MUONIUM \rightarrow D.C. GEMMICALLY: "q₃": evolution in μ until time t_1 ,
followed by evolution in d.d. from t_1 to t .

$$\{U_{q_3}(t, 0) \hat{P}(0)\}_\mu = \exp[i\omega_\mu(t - t_1)] \sum_k F_k \exp[\lambda_k^m t_1]$$

$$p(q_3) = (1 - h - r) \frac{dt_1}{\tau_{md}} \exp[-t_1/\tau_m]$$

so $P(q_3, t) = \exp[i\omega_\mu t] (1 - h - r) \sum_k F_k \frac{dt_1}{\tau_{md}} \exp[\theta_k t_1]$

We integrate over t_1 from 0 to t to obtain $P_3(t)$, the contribution from the generic class of q_3 with all possible t_1 values:

$$P_3(t) = \exp[i\omega_\mu t] (1 - h - r) \sum_k \frac{1}{\tau_{md} \theta_k} F_k (\exp[\theta_k t] - 1) \quad (10)$$

- 4) STILL-FREE HOT RADICAL: "q₄": evolution in radical since
combining epithermally at $t \approx 0$.

This case is strictly analogous to case 1, and gives

$$P(q_4, t) = \exp[i\omega_\mu t] r \sum_k G_k \exp[\phi_k t] \quad (11)$$

where $G_k = R_{1k} [R^{-1}]_{k1}$ and $\phi_k = \lambda_k^r - 1/\tau_{rd} - i\omega_\mu$. (12)

- 5) HOT RADICAL \rightarrow D.C. CHEMICALLY: "q₅": epithermal entry into radical at $t \approx 0$, evolution in the radical until time t_1 , subsequent evolution in D.C.

This case is strictly analogous to case 3, and gives

$$P_5(t) = \exp[i\omega_\mu t] r \sum_k \frac{1}{\tau_{rd} \phi_k} G_k (\exp[\phi_k t] - 1) \quad (13)$$

- 6) STILL-FREE CHEMICAL RADICAL: "q₆": evolution until time t_1 in muonium, combination with S to form R' at time t_1 , subsequent evolution in R' (radical).

$$\begin{aligned} \{U_{q_6}(t, 0) \hat{P}(0)\}_\mu &= \{U^r(t, t_1) U^m(t_1, 0) \hat{P}(0)\}_\mu \\ &= \sum_{ijk} R_{1i} \exp[\lambda_i^r (t - t_1)] [R^{-1}]_{ij} M_{jk} \exp[\lambda_k^m t_1] [M^{-1}]_{k1} \\ &= \sum_{ik} W_{ik} \exp[\lambda_i^r t] \exp[(\lambda_k^m - \lambda_i^r) t_1] \end{aligned}$$

where $W_{ik} = \sum_j R_{1j} [R^{-1}]_{ij} M_{jk} [M^{-1}]_{k1}$ (14)

$$p(q_6) = (1 - h - r) \exp[-(t - t_1)/\tau_{rd}] \frac{dt_1}{\tau_{mr}} \exp[-t_1/\tau_m]$$

Thus $P(q_6, t) = \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr}} \sum_{ik} W_{ik} \exp[\phi_i t] \exp[\psi_{ik} t_1] dt_1$

where $\psi_{ik} = \lambda_k^m - \lambda_i^r + 1/\tau_{rd} - 1/\tau_m$. (15)

We integrate over t_1 from 0 to t to get $P_6(t)$, the contribution from all such types of q_6 with all possible t_1 values:

$$P_6(t) = \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr}} \sum_{ik} \frac{W_{ik}}{\psi_{ik}} \exp[\phi_i t] (\exp[\psi_{ik} t] - 1) \quad (16)$$

- 7) MUONIUM \rightarrow RADICAL \rightarrow D.C.: "q₇": evolution until time t₁ in muonium, followed by evolution from t₁ to t₂ in R', followed by evolution in d.c. from t₂ until t.

$$\begin{aligned} \{U_{q_7}(t, 0) \hat{P}(0)\}_\mu &= \{U^d(t, t_2) U^r(t_2, t_1) U^m(t_1, t) \hat{P}(0)\}_\mu \\ &= \exp[i\omega_\mu(t - t_2)] \sum_{ik} W_{ik} \exp[\lambda_1^r t_2] \exp[(\lambda_k^m - \lambda_1^r)t_1] \\ p(q_7) &= (1 - h - r) \frac{dt_2}{\tau_{rd}} \exp[-(t_2 - t_1)/\tau_{rd}] \frac{dt_1}{\tau_{mr}} \exp[-t_1/\tau_{mr}] \end{aligned}$$

giving $P(q_7, t) = \exp[i\omega_\mu t] (1 - h - r) \sum_{ik} W_{ik} \frac{dt_2}{\tau_{rd}} \exp[\phi_1 t_2] \frac{dt_1}{\tau_{mr}} \exp[\psi_{ik} t_1]$

The overall contribution from muons experiencing fates of the type "q₇" with all possible t₁ and t₂ is then

$$\begin{aligned} P_7(t) &= \int_0^t dt_2 \int_0^{t_2} dt_1 \frac{d^2 P(q_7, t)}{dt_2 dt_1} \\ &= \exp[i\omega_\mu t] \frac{(1 - h - r)}{\tau_{mr} \tau_{rd}} \sum_{ik} \frac{W_{ik}}{\psi_{ik}} \left\{ \frac{1}{\phi_1 + \psi_{ik}} \left(\exp[(\phi_1 + \psi_{ik})t] - 1 \right) \right. \\ &\quad \left. - \frac{1}{\phi_1} \left(\exp[\phi_1 t] - 1 \right) \right\} \quad (17) \end{aligned}$$

Assuming that Fig. 1 does not leave out any statistically significant processes, we now have the formula for the muon polarization at time t:

$$P(t) = P(q_1, t) + P(q_2, t) + P_3(t) + P(q_4, t) + P_5(t) + P_6(t) + P_7(t).$$

Note that this is the actual exact time dependence of the muon polarization, involving no approximations other than that Fig. 1 is complete.

Each term is conveniently of the form $\exp[i\omega_\mu t] P'$, making it easy to get P_{res} , the value obtained in precession experiments by

extrapolating to $t = 0$: keeping only those terms which are not still oscillating at a frequency beyond our practical resolution at large times, choosing a value for t which is $\gg \tau_m + \tau_{rd}$, and dividing out the Larmor precession term $\exp[i\omega_\mu t]$, we get

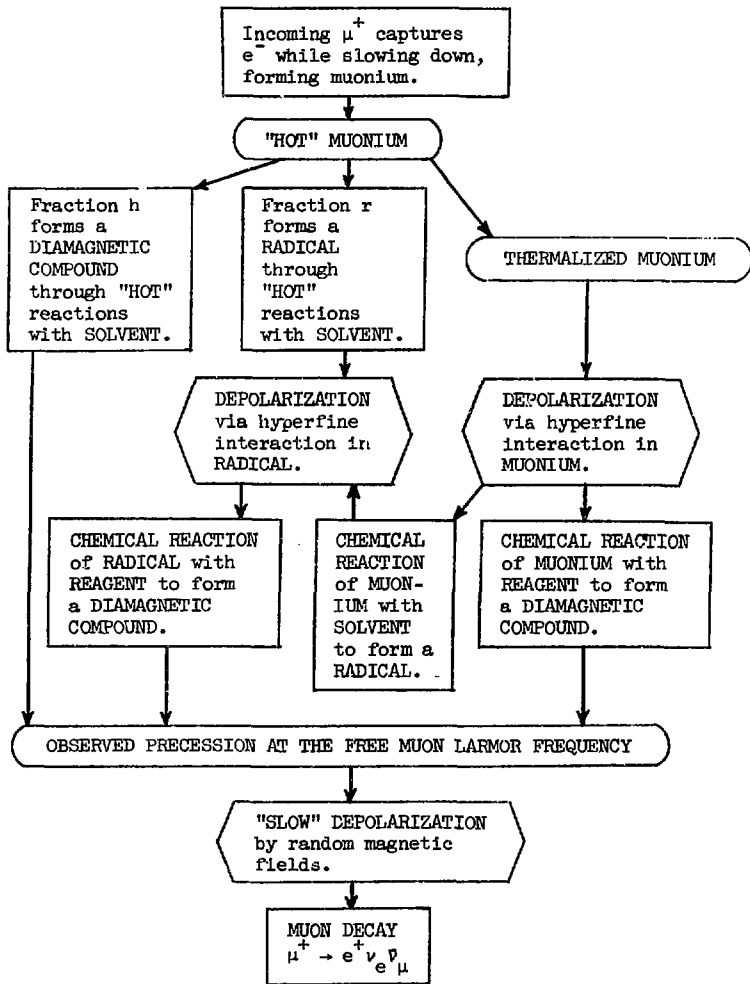
$$\begin{aligned}
 P_{res} &= \exp[-i\omega_\mu t] \left\{ P(q_2, t) + P_3(t) + P_7(t) \right\}_{t \rightarrow \infty} \\
 &= h + (1 - h - r) \sum_k \frac{F_k}{\tau_{md} \theta_k} \left\{ \exp[\theta_k t] - 1 \right\}_{t \rightarrow \infty} \\
 &+ \frac{(1 - h - r)}{\tau_{mr} \tau_{rd}} \sum_{ik} \frac{W_{ik}}{\Psi_{ik}} \left\{ \frac{1}{\phi_i + \Psi_{ik}} \left\{ \exp[(\phi_i + \Psi_{ik})t] - 1 \right\} \right. \\
 &\quad \left. - \frac{1}{\phi_i} \left\{ \exp[\phi_i t] - 1 \right\} \right\}_{t \rightarrow \infty} \quad (18)
 \end{aligned}$$

Setting $t = 10(\tau_m + \tau_{rd})$ seems to be an adequate approximation for $t \rightarrow \infty$.

These equations have been used to fit curves of P_{res} versus $[X]$ in several types of solutions. In most aqueous solutions, and in methanol⁶, the evidence does not suggest significant radical formation, and fits are made with the assumption of $r = k_{mr} = k_{rd} = 0$. In benzene, however, the experimental results flatly contradict the assumption of a pure muonium mechanism, and adequate fits are obtained only when we assume that considerable radical formation takes place.⁷

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Fig. 1