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Muonium spin exchange in spin-polarized media: Spin-flip and -nonflip collisions

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The transverse relaxation of the muon spin in muonium due to electron spin exchange with a polarized spin-$\frac{1}{2}$ medium is investigated. Stochastic calculations, which assume that spin exchange is a Poisson process, are carried out for the case where the electron spin polarization of the medium is on the same axis as the applied field. Two precession signals of muonium observed in intermediate fields ($B > 30$ G) are shown to have different relaxation rates which depend on the polarization of the medium. Furthermore, the precession frequencies are shifted by an amount which depends on the spin-nonflip rate. From the two relaxation rates and the frequency shift in intermediate fields, one can determine (i) the encounter rate of muonium and the paramagnetic species, (ii) the polarization of the medium, and most importantly (iii) the quantum-mechanical phase shift (and its sign) associated with the potential energy difference between electron singlet and triplet encounters. Effects of spin-nonflip collisions on spin dynamics are discussed for non-Poisson as well as Poisson processes. In unpolarized media, the time evolution of the muon spin in muonium is not influenced by spin-nonflip collisions, *if the collision process is Poissonian.* This seemingly obvious statement is not true anymore in non-Poissonian processes, i.e., it is necessary to specify both spin-flip and spin-nonflip rates to fully characterize spin dynamics.

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I. INTRODUCTION

Electron spin exchange is a quantum-mechanical process common in low-energy collisions between species with unpaired electron spins. Extensive theoretical and experimental work [1–6] has been done on the subject in conjunction with maser and optical pumping. Recently, electron spin exchange has been studied in systems containing hydrogen isotopes including muonium (Mu). Muonium is the bound state of a positive muon and an electron with the virtually same ionization potential as the hydrogen atom, and thus can be regarded as a light isotope of H. Muonium spin exchange has been studied in systems such as Mu+O_2 [7], Mu+NO [8–10], and Mu+Cs [11]. In these studies, the results were compared with corresponding H-atom systems, and isotope effects in spin exchange were discussed. More recently, optical pumping was used to produce spin-polarized Rb atoms as a means to polarize nuclear spins for nuclear-physics experiments [12–14], which makes it possible to study muonium spin exchange with polarized atoms. In the present work, it is shown that electron spin exchange of Mu in electron-polarized media can provide direct information on the spin-flip and spin-nonflip probabilities during collisions not obtainable from measurements in unpolarized media. In some cases, it is possible to determine the phase shift (including its sign) due to the difference in interaction potentials between spin singlet and triplet encounters.

Spin exchange is an electrostatic interaction arising from the quantum-mechanical requirement that the wave function be antisymmetric with respect to the interchange of two electrons. The antisymmetrized total electronic wave function of muonium with an α spin and a colliding gas atom with a β spin can be expressed by a Slater determinant $\|m\alpha,g\beta\|$, where $m(r_1)$ and $g(r_2)$ are the orbital wave functions of muonium and the paramagnetic gas atom, respectively. It is straightforward to show that this total wave function is a superposition of electron spin triplet and singlet parts [15]. Since the interaction energy between the two electrons depends on the total electron spin through Pauli's exclusion principle, the triplet and singlet parts of the wave function acquire different phase shifts Δ_T and Δ_S, respectively,

$$\|m\alpha,g\beta\| \rightarrow (\tfrac{1}{2})^{3/2}[m(1)g(2)+m(2)g(1)] \times[\alpha(1)\beta(2)-\alpha(2)\beta(1)]e^{i\Delta_S} + (\tfrac{1}{2})^{3/2}[m(1)g(2)-m(2)g(1)] \times[\alpha(1)\beta(2)+\alpha(2)\beta(1)]e^{i\Delta_T} , \quad (1)$$

where the phase shifts Δ_T and Δ_S are related to the interatomic potentials $V_T(r)$ and $V_S(r)$ by

$$\Delta_T = -\int [V_T(r)/\hbar]dt$$

and

$$\Delta_S = -\int [V_S(r)/\hbar]dt ,$$

respectively. By rearranging the right-hand side of Eq. (1), one obtains

$$\|m\alpha,g\beta\| \rightarrow \|m\alpha,g\beta\|(1+e^{i\Delta})/2 + \|m\beta,g\alpha\|(1-e^{i\Delta})/2 , \quad (2)$$

where Δ is the difference in the phase shift $\Delta=\Delta_S-\Delta_T$ [15,16]. The quantities

$$|(1-e^{i\Delta})/2|^2=\sin^2(\Delta/2)$$

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and

$$|(1+e^{i\Delta})/2|^2=\cos^2(\Delta/2)$$

can be regarded as the spin-flip and spin-nonflip probabilities, respectively, of the collision. If λ is defined as the encounter rate of muonium and paramagnetic gas molecules, the rates of spin-flip and spin-nonflip collisions are expressed by

$$\lambda_{SF}=\lambda\sin^2(\Delta/2) \text{ and } \lambda_{NF}=\lambda\cos^2(\Delta/2) . \quad (3)$$

II. THEORY

Spin dynamics of the muon in muonium undergoing repeated electron spin exchange has recently been treated by a stochastic time-ordered method [15] in which the muon spin polarization at time t after n collisions at $t_1,t_2,\ldots,t_n$ is calculated in terms of the phase shifts $\Delta_1,\Delta_2,\ldots,\Delta_n$, followed by statistical averaging over the distribution of $t_1,t_2,\ldots,t_n$, for a fixed n, and then over all possible n from 0 to infinity. Two basic assumptions are that the duration of a collision is much shorter than the average time between collisions and that the time evolution of spin states between collisions is determined by the muonium hyperfine interaction. In the past few years, this method was applied to spin exchange in unpolarized media with slow [15,16] and fast [17] spin-exchange rates and in intermediate fields [18]. The characteristic field dependence of the transverse relaxation rate predicted in intermediate fields was later confirmed [11,19] experimentally, providing a convenient method to distinguish relaxation due to spin exchange from that due to chemical reactions. In the present work, the method described in Ref. [15] is generalized to the case of electron-polarized media.

A. Time evolution of spin states

Let $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$ be the eigenstates of the muonium hyperfine interactions corresponding to the four branches of the Breit-Rabi diagram with energies ω_1, ω_2, ω_3, and ω_4. The muonium spin states $|\alpha_\mu\alpha_e\rangle$, $|\alpha_\mu\beta_e\rangle$, $|\beta_\mu\alpha_e\rangle$, and $|\beta_\mu\beta_e\rangle$ can be expressed as

$$|\alpha_\mu\alpha_e\rangle=|1\rangle ,$$

$$|\alpha_\mu\beta_e\rangle=s|2\rangle+c|4\rangle ,$$

$$|\beta_\mu\alpha_e\rangle=c|2\rangle-s|4\rangle ,$$

$$|\beta_\mu\beta_e\rangle=|3\rangle ,$$

where

$$c^2=(1+x/\sqrt{x^2+1})/2 ,$$

$$s^2=(1-x/\sqrt{x^2+1})/2 ,$$

$$x=B(\text{kG})/1.585$$

[15]. Therefore, the equations of time evolution for these spin states can be written as

$$|\alpha_\mu\alpha_e\rangle=e^{-i\omega_1 t}|1\rangle\to e^{-i\omega_{14}t}|1\rangle , \quad (4)$$

$$|\alpha_\mu\beta_e\rangle=se^{-i\omega_2 t}|2\rangle+ce^{-i\omega_4 t}|4\rangle$$
$$\to(s^2e^{-i\omega_{24}t}+c^2)|\alpha_\mu\beta_e\rangle$$
$$+(cse^{-i\omega_{24}t}-cs)|\beta_\mu\alpha_e\rangle , \quad (5)$$

$$|\beta_\mu\alpha_e\rangle=ce^{-i\omega_2}|2\rangle-se^{-i\omega_4 t}|4\rangle$$
$$\to(cse^{-i\omega_{24}t}-cs)|\alpha_\mu\beta_e\rangle$$
$$+(c^2e^{-i\omega_{24}t}+s^2)|\beta_\mu\alpha_e\rangle , \quad (6)$$

$$|\beta_\mu\beta_e\rangle=e^{-i\omega_3 t}|3\rangle\to e^{-i\omega_{34}t}|3\rangle , \quad (7)$$

where the overall phase $e^{-i\omega_4 t}$ is omitted and ω_{jk} is the transition frequency between the jth and kth levels of the Breit-Rabi diagram, $\omega_{jk}=\omega_j-\omega_k$.

B. Before the first collision

The positive muon produced in the decay of a pion at rest, $\pi^+\to\mu^++\nu_\mu$, is 100% spin polarized. In a transverse field, it is convenient to choose the initial muon spin polarization and the applied field direction along the x and z axes, respectively. The complex polarization $P_\mu=\sigma_\mu^x+i\sigma_\mu^y=\sigma_\mu^+$, defined in terms of Pauli's spin matrices, represents the subsequent time evolution of the muon polarization where the real and imaginary parts correspond to the x and y projections of the polarization, respectively. In this work, the electron polarization of the medium is assumed to be along the external field, i.e., along the z axis.

The initial muon spin, which points in the positive x axis, can be expressed [15] as $(\alpha_\mu+\beta_\mu)/\sqrt{2}$. At $t_0=0$, two different kinds of muonium atoms are formed with equal probabilities depending on the spin of the electron: (a) parallel muonium with its electron spin parallel to the muon spin, $(\alpha_\mu+\beta_\mu)(\alpha_e+\beta_e)/2$, and (b) antiparallel muonium, where the electron spin points in the negative x direction,

$$(\alpha_\mu+\beta_\mu)(-\alpha_e+\beta_e)/2 .$$

The properly antisymmetrized wave function of the colliding system can be written as [15]

$$\phi_\pm=\tfrac{1}{2}[\pm(\alpha_\mu+\beta_\mu)\|m\alpha,g_1\sigma\|+(\alpha_\mu+\beta_\mu)\|m\beta,g_1\sigma\|] , \quad (8)$$

where ϕ_+ and ϕ_- are, respectively, the wave functions for parallel and antiparallel muonium and g_1 is the orbital wave function of the paramagnetic gas atom with which the muonium atom undergoes the first collision. From this point on, the subscript e referring to electron spin is suppressed for the sake of simplicity. Since the wave functions $\alpha_\mu\|m\alpha,g_1\sigma\|$, $\alpha_\mu\|m\beta,g_1\sigma\|$, $\beta_\mu\|m\alpha,g_1\sigma\|$, and $\beta_\mu\|m\beta,g_1\sigma\|$ follow the equations of time evolution given in Eqs. (4)–(7), the time dependence of $\phi_\pm$ before the first collision can be written down as

$$\phi_{\pm}(t)=\tfrac{1}{2}[\pm\alpha_{\mu}\|m\alpha,g_1\sigma\|e^{-i\omega_{14}t}\pm\beta_{\mu}\|m\alpha,g_1\sigma\|(c^2e^{-i\omega_{24}t}+s^2)$$
$$\pm\alpha_{\mu}\|m\beta,g_1\sigma\|(cse^{-i\omega_{24}t}-cs)+\alpha_{\mu}\|m\beta,g_1\sigma\|(s^2e^{-i\omega_{24}t}+c^2)$$
$$+\beta_{\mu}\|m\alpha,g_1\sigma\|(cse^{-i\omega_{24}t}-cs)+\beta_{\mu}\|m\beta,g_1\sigma\|e^{-i\omega_{34}t}] \ . \tag{9}$$

The complex muon polarization observed at time of the first collision averaged over the probability that muonium is produced in the parallel-muonium state ($A_M=0.5$) or the antiparallel-muonium state ($B_M=0.5$) is given by

$$P(t_1)=A_M\langle\phi_+(t_1)|\sigma_{\mu}^{+}|\phi_+(t_1)\rangle+B_M\langle\phi_-(t_1)|\sigma_{\mu}^{+}|\phi_-(t_1)\rangle$$
$$=(c^2/2)(e^{i\omega_{12}t_1}+e^{-i\omega_{34}t_1})+(s^2/2)(e^{i\omega_{23}t_1}+e^{i\omega_{14}t_1})=G_T(0,t_1) \ . \tag{10}$$

The full expression of the quantity $G_T(P_G,t_1)$ for nonzero P_G will be given later.

C. After the first collision

If the first colliding atom has a β electron ($g_1\sigma=g_1\beta$), the first term of Eq. (9) will become after the first collision [Eq. (2)]

$$\alpha_{\mu}\|m\alpha,g_1\beta\|e^{-i\omega_{14}t_1}\rightarrow\alpha_{\mu}\|m\alpha,g_1\beta\|e^{-i\omega_{14}t_1}(1+e^{i\Delta_1})/2+\alpha_{\mu}\|m\beta,g_1\alpha\|e^{-i\omega_{14}t_1}(1-e^{i\Delta_1})/2 \ , \tag{11}$$

where Δ_1 is the phase shift of the first collision. After the first collision at t_1, the time evolution of this term is described in terms of Eqs. (4) and (5):

$$\alpha_{\mu}\|m\alpha,g_1\beta\|e^{-i\omega_{14}t_1}\rightarrow\alpha_{\mu}\|m\alpha,g_1\beta\|e^{-i\omega_{14}t_1}e^{-i\omega_{14}(t-t_1)}(1+e^{i\Delta_1})/2$$
$$+\alpha_{\mu}\|m\beta,g_1\alpha\|e^{-i\omega_{14}t_1}(s^2e^{-i\omega_{24}(t-t_1)}+c^2)(1-e^{i\Delta_1})/2$$
$$+\beta_{\mu}\|m\alpha,g_1\alpha\|e^{-i\omega_{14}t_1}(cse^{-i\omega_{24}(t-t_1)}-cs)(1-e^{i\Delta_1})/2 \ . \tag{12}$$

The full wave function of muonium (parallel or antiparallel) at time t after the first collision at t_1 with an atom with a β electron is expressed by

$$|\phi_{\pm}(t_1)b(t-t_1)\rangle=\tfrac{1}{2}[\pm\alpha_{\mu}\|m\alpha,g_1\beta\|e^{-i\omega_{14}t_1}e^{-i\omega_{14}(t-t_1)}(1+e^{i\Delta_1})/2$$
$$\pm\alpha_{\mu}\|m\beta,g_1\alpha\|e^{-i\omega_{14}t_1}(s^2e^{-i\omega_{24}(t-t_1)}+c^2)(1-e^{-i\Delta_1})/2$$
$$\pm\beta_{\mu}\|m\alpha,g_1\alpha\|e^{-i\omega_{14}t_1}(cse^{-i\omega_{24}(t-t_1)}-cs)(1-e^{i\Delta_1})/2$$
$$\pm\beta_{\mu}\|m\alpha,g_1\beta\|(c^2e^{-i\omega_{24}t_1}+s^2)(c^2e^{-i\omega_{24}(t-t_1)}+s^2)(1+e^{i\Delta_1})/2$$
$$\pm\alpha_{\mu}\|m\beta,g_1\beta\|(c^2e^{-i\omega_{24}t_1}+s^2)(cse^{-i\omega_{24}(t-t_1)}-cs)(1+e^{i\Delta_1})/2$$
$$\pm\beta_{\mu}\|m\beta,g_1\alpha\|(c^2e^{-i\omega_{24}t_1}+s^2)e^{-i\omega_{34}(t-t_1)}(1-e^{i\Delta_1})/2$$
$$\pm\alpha_{\mu}\|m\beta,g_1\beta\|(cse^{-i\omega_{24}t_1}-cs)(s^2e^{-i\omega_{24}(t-t_1)}+c^2)$$
$$\pm\beta_{\mu}\|m\alpha,g_1\beta\|(cse^{-i\omega_{24}t_1}-cs)(cse^{-i\omega_{24}(t-t_1)}-cs)$$
$$+\alpha_{\mu}\|m\beta,g_1\beta\|(s^2e^{-i\omega_{24}t_1}+c^2)(s^2e^{-i\omega_{24}(t-t_1)}+c^2)$$
$$+\beta_{\mu}\|m\alpha,g_1\beta\|(s^2e^{-i\omega_{24}t_1}+c^2)(cse^{-i\omega_{24}(t-t_1)}-cs)$$
$$+\beta_{\mu}\|m\alpha,g_1\beta\|(cse^{-i\omega_{24}t_1}-cs)(c^2e^{-i\omega_{24}(t-t_1)}+s^2)(1+e^{i\Delta_1})/2$$
$$+\alpha_{\mu}\|m\beta,g_1\beta\|(cse^{-i\omega_{24}t_1}-cs)(cse^{-i\omega_{24}(t-t_1)}-cs)(1+e^{i\Delta_1})/2$$
$$+\beta_{\mu}\|m\beta,g_1\alpha\|(cse^{-i\omega_{24}t_1}-cs)e^{-i\omega_{34}(t-t_1)}(1-e^{i\Delta_1})/2$$
$$+\beta_{\mu}\|m\beta,g_1\beta\|e^{-i\omega_{34}t_1}e^{-i\omega_{34}(t-t_1)}] \ . \tag{13}$$

Similarly, the wave function $|\phi_{\pm}(t_1)a(t-t_1)\rangle$ after collision with an α atom can be written down explicitly [15]. The muon polarization at the time of the second collision at t_2 averaged over the probability that the colliding gas atom is in the α state (A_G) or in the β state (B_G) can be expressed by

$$P(t_1,t_2)=A_M A_G\langle\phi_+(t_1)a(t_{21})|\sigma_\mu^+|\phi_+(t_1)a(t_{21})\rangle+A_M B_G\langle\phi_+(t_1)b(t_{21})|\sigma_\mu^+|\phi_+(t_1)b(t_{21})\rangle$$
$$+B_M A_G\langle\phi_-(t_1)a(t_{21})|\sigma_\mu^+|\phi_-(t_1)a(t_{21})\rangle+B_M B_G\langle\phi_-(t_1)b(t_{21})|\sigma_\mu^+|\phi_-(t_1)b(t_{21})\rangle\ , \quad (14)$$

where $t_{jk}=t_j-t_k$. Since σ_μ^+ is the raising operator which affects the muon spin state only, the terms of the form

$$\langle\|m\sigma_1,g\sigma_2\|\alpha_\mu|\sigma_\mu^+|\beta_\mu\|m\sigma_3,g\sigma_4\|\rangle=2\delta(\sigma_1,\sigma_3)\delta(\sigma_2,\sigma_4)$$

in Eq. (14) will survive, leading to

$$P(t_1,t_2)=\sin^2\frac{\Delta_1}{2}G_T(0,t_{10})G_T(P_G,t_{21})$$
$$+\cos^2\frac{\Delta_1}{2}G_T(0,t_{20})$$
$$+\sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}iP_G g_T(0,t_0,t_1,t_2)\ , \quad (15)$$

where $P_G=A_G-B_G$ is the electron polarization of the gas and the quantity $g_T(P_G,t_0,t_1,t_2)$ in the last term is defined in Appendix I. The quantity $G_T(P_G,t)$ is defined as

$$G_T(P_G,t)=\frac{c^2}{2}[(1+P_G)e^{i\omega_{12}t}+(1-P_G)e^{-i\omega_{34}t}]$$
$$+\frac{s^2}{2}[(1-P_G)e^{i\omega_{23}t}+(1+P_G)e^{i\omega_{14}t}]$$
$$=e^{i\phi(P_G,t)}A(P_G,t)\ . \quad (16)$$

The quantities $A(t)$ and $\phi(t)$ are expressed by

$$A(P_G,t)=\left[1-(1-\delta^2)\sin^2\left[\Omega t+\frac{\omega_0}{2}t\right]\right]^{1/2}$$
$$\times\left[1-(1-P_G^2)\sin^2\left[\frac{\omega_0}{2}t\right]\right]^{1/2}, \quad (17)$$

$$\phi(P_G,t)=\omega_-t-\tan^{-1}\left[\delta\tan\left[\Omega t+\frac{\omega_0}{2}t\right]\right]$$
$$+\tan^{-1}\left[P_G\tan\left[\frac{\omega_0}{2}t\right]\right], \quad (18)$$

where Ω and δ are defined by $\Omega=(\sqrt{1+x^2}-1)\omega_0/2$ and $\delta=x/\sqrt{1+x^2}$, respectively; $\omega_0/2\pi=4463$ MHz is the hyperfine frequency of muonium; and $\omega_-/2\pi=1.39$ MHz/G is the precession frequency of triplet muonium. The first term of Eq. (15) with the factor $\sin^2(\Delta/2)$ corresponds to the case where the first collision at t_1 is of spin-flip type. On the other hand, the second term with $\cos^2(\Delta/2)$ represents a spin-nonflip collision at t_1. In this case, the time evolution of the muon spin, represented by a single $G_T(0,t_2-t_0)$, is not disturbed by the spin-nonflip collision at t_1. The third term with

$$\sin(\Delta/2)\cos(\Delta/2)\sim\sqrt{\lambda_{SF}\lambda_{NF}}\ ,$$

which is called a "mixed term," can be regarded as a cross term arising from interference between the spin-flip and nonflip process. If $P_G=0$, the mixed term will vanish and Eq. (15) and similar equations (21) and (22) will reduce to the known results [15] in unpolarized media.

The wave function

$$|\phi_\pm(t_1)b(t_{21})a(t-t_2)\rangle$$

which represents the system at time t after a collision with a β electron at t_1 and a second collision with an α electron at t_2 can be constructed from Eq. (13). The Slater determinant of the second term, for example, in Eq. 13 before the second collision is expressed by $\pm\alpha_\mu\|m\beta,g_1\alpha,g_2\alpha\|$. After the second collision, this term will become a superposition of spin-flip and nonflip terms expressed in terms of the phase shift Δ_2:

$$\alpha_\mu\|m\beta,g_1\alpha,g_2\alpha\|\rightarrow\alpha_\mu\|m\beta,g_1\alpha,g_2\alpha\|(1+e^{i\Delta_2})/2$$
$$+\alpha_\mu\|m\alpha,g_1\alpha,g_2\beta\|(1-e^{i\Delta_2})/2\ . \quad (19)$$

At t_2, the gas atom $g_1\alpha$ which participated in the first collision is far away from the muonium atom, so that $g_1\alpha$ will not affect the second collision. It is still necessary to include $g_1\alpha$ in order to maintain the orthogonality of, say,

$$|\phi_\pm(t_1)b(t_{21})a(t-t_2)\rangle$$

and

$$|\phi_\pm(t_1)b(t_{21})b(t-t_2)\rangle\ .$$

After t_2, the first and second terms of Eq. (19) follow the time dependences given by Eqs. (5) and (4), respectively. It is straightforward to calculate the muon spin polarization observed at t_3 after two collisions at t_1 and t_2:

$$P(t_1,t_2,t_3)=A_M A_G A_G\langle\phi_+(t_1)a(t_{21})a(t_{32})|\sigma_\mu^+|\phi_+(t_1)a(t_{21})a(t_{32})\rangle$$
$$+A_M A_G B_G\langle\phi_+(t_1)a(t_{21})b(t_{32})|\sigma_\mu^+|\phi_+(t_1)a(t_{21})b(t_{32})\rangle$$
$$+A_M B_G A_G\langle\phi_+(t_1)b(t_{21})a(t_{32})|\sigma_\mu^+|\phi_+(t_1)b(t_{21})a(t_{32})\rangle$$
$$+A_M B_G B_G\langle\phi_+(t_1)b(t_{21})b(t_{32})|\sigma_\mu^+|\phi_+(t_1)b(t_{21})b(t_{32})\rangle$$
$$+B_M A_G A_G\langle\phi_-(t_1)a(t_{21})a(t_{32})|\sigma_\mu^+|\phi_-(t_1)a(t_{21})a(t_{32})\rangle$$
$$+B_M A_G B_G\langle\phi_-(t_1)a(t_{21})b(t_{32})|\sigma_\mu^+|\phi_-(t_1)a(t_{21})b(t_{32})\rangle$$
$$+B_M B_G A_G\langle\phi_-(t_1)b(t_{21})a(t_{32})|\sigma_\mu^+|\phi_-(t_1)b(t_{21})a(t_{32})\rangle$$
$$+B_M B_G B_G\langle\phi_-(t_1)b(t_{21})b(t_{32})|\sigma_\mu^+|\phi_-(t_1)b(t_{21})b(t_{32})\rangle\ , \quad (20)$$

where only surviving terms are

$$\langle \| m\sigma_1, g_1\sigma_2, g_2\sigma_3 \| \alpha_\mu | \sigma_\mu^+ | \beta_\mu \| m\sigma_4, g_1\sigma_5, g_2\sigma_6 \| \rangle = 2\delta(\sigma_1,\sigma_4)\delta(\sigma_2,\sigma_5)\delta(\sigma_3,\sigma_6) \ .$$

Assuming that parallel- and antiparallel-muonium atoms are produced $t=0$ with the equal probabilities $A_M = B_M = 0.5$, one obtains

$$\begin{aligned}
P(t_1,t_2,t_3) = {} & \sin^2\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}G_T(0,t_{10})G_T(P_G,t_{21})G_T(P_G,t_{32}) + \cos^2\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}G_T(0,t_{20})G_T(P_G,t_{32}) \\
& + \sin^2\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}G_T(0,t_{10})G_T(P_G,t_{31}) + \cos^2\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}G_T(0,t_{30}) \\
& + \cos^2\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}iP_G g_T(0,t_0,t_2,t_3) + \sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}iP_G g_T(0,t_0,t_1,t_3) \\
& + \sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}iP_G g_T(0,t_0,t_1,t_2)G_T(P_G,t_{32}) + \sin^2\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}iP_G G_T(0,t_{10})g_T(P_G,t_1,t_2,t_3) \\
& + \sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}(iP_G)^2 g_T(0,t_0,t_1,t_2,t_3) \ , \qquad (21)
\end{aligned}$$

where $g_T(P_G,t_0,t_1,t_2,t_3)$ in the last term is defined in Appendix I. The first term represents two spin-flip collisions at t_1 and t_2, while the fifth term, for example, is for one spin-nonflip collision at t_1 followed by a mixed collision at t_2. One can continue this procedure to calculate the polarization observed at t_4 after three collisions at t_1, t_2, and t_3 as

$$\begin{aligned}
P(t_1,t_2,t_3,t_4) = {} & \sin^2\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}\sin^2\frac{\Delta_3}{2}G_T(0,t_{10})G_T(P_G,t_{21})G_T(P_G,t_{32})G_T(P_G,t_{43}) \\
& + \sin^2\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}\cos^2\frac{\Delta_3}{2}G_T(0,t_{10})G_T(P_G,t_{21})G_T(P_G,t_{42}) \\
& + \cos^2\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}\sin^2\frac{\Delta_3}{2}G_T(0,t_{20})G_T(P_G,t_{32})G_T(P_G,t_{43}) \\
& + \sin^2\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}\sin^2\frac{\Delta_3}{2}G_T(0,t_{10})G_T(P_G,t_{31})G_T(P_G,t_{43}) \\
& + \cos^2\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}\cos^2\frac{\Delta_3}{2}G_T(0,t_{20})G_T(P_G,t_{42}) \\
& + \sin^2\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}\cos^2\frac{\Delta_3}{2}G_T(0,t_{10})G_T(P_G,t_{41}) + \cos^2\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}\sin^2\frac{\Delta_3}{2}G_T(0,t_{30})G_T(P_G,t_{43}) \\
& + \cos^2\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}\cos^2\frac{\Delta_3}{2}G_T(0,t_{40}) + \cos^2\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}\cos^2\frac{\Delta_3}{2}iP_G g_T(0,t_0,t_2,t_4) \\
& + \sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}\cos^2\frac{\Delta_3}{2}iP_G g_T(0,t_0,t_1,t_4) + \cos^2\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}\sin\frac{\Delta_3}{2}\cos\frac{\Delta_3}{2}iP_G g_T(0,t_0,t_3,t_4) \\
& + \cos^2\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}\sin^2\frac{\Delta_3}{2}iP_G g_T(0,t_0,t_2,t_3)G_T(P_G,t_{43}) \\
& + \sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}\sin^2\frac{\Delta_3}{2}iP_G g_T(0,t_0,t_1,t_3)G_T(P_G,t_{43}) \\
& + \sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}\cos^2\frac{\Delta_3}{2}iP_G g_T(0,t_0,t_1,t_2)G_T(P_G,t_{42}) \\
& + \sin^2\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}\cos^2\frac{\Delta_3}{2}iP_G G_T(0,t_{10})g_T(P_G,t_1,t_2,t_4) \\
& + \sin^2\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}\sin\frac{\Delta_3}{2}\cos\frac{\Delta_3}{2}iP_G G_T(0,t_{10})g_T(P_G,t_1,t_3,t_4) \\
& + \cos^2\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}\sin\frac{\Delta_3}{2}\cos\frac{\Delta_3}{2}iP_G G_T(0,t_{20})g_T(P_G,t_2,t_3,t_4) \\
& + \sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}\sin^2\frac{\Delta_3}{2}iP_G g_T(0,t_0,t_1,t_2)G_T(P_G,t_{32})G_T(P_G,t_{43})
\end{aligned}$$

$$
\begin{aligned}
&+\sin^2\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}\sin^2\frac{\Delta_3}{2}iP_G G_T(0,t_{10})g_T(P_G,t_1,t_2,t_3)G_T(P_G,t_{43})\\
&+\sin^2\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}\sin\frac{\Delta_3}{2}\cos\frac{\Delta_3}{2}iP_G G_T(0,t_{10})G_T(P_G,t_{21})g_T(P_G,t_2,t_3,t_4)\\
&+\cos^2\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}\sin\frac{\Delta_3}{2}\cos\frac{\Delta_3}{2}(iP_G)^2 g_T(0,t_0,t_2,t_3,t_4)\\
&+\sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\cos^2\frac{\Delta_2}{2}\sin\frac{\Delta_3}{2}\cos\frac{\Delta_3}{2}(iP_G)^2 g_T(0,t_0,t_1,t_3,t_4)\\
&+\sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}\cos^2\frac{\Delta_3}{2}(iP_G)^2 g_T(0,t_0,t_1,t_2,t_4)\\
&+\sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}\sin\frac{\Delta_3}{2}\cos\frac{\Delta_3}{2}(iP_G)^2 g_T(0,t_0,t_1,t_2)g_T(P_G,t_2,t_3,t_4)\\
&+\sin^2\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}\sin\frac{\Delta_3}{2}\cos\frac{\Delta_3}{2}(iP_G)^2 G_T(0,t_{10})g_T(P_G,t_1,t_2,t_3,t_4)\\
&+\sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}\sin^2\frac{\Delta_3}{2}(iP_G)^2 g_T(0,t_0,t_1,t_2,t_3)G_T(P_G,t_{43})\\
&+\sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}\sin\frac{\Delta_3}{2}\cos\frac{\Delta_3}{2}(iP_G)^3 g_T(0,t_0,t_1,t_2,t_3,t_4)\ .
\end{aligned}
\tag{22}
$$

The general expression for

$$P(t_1,t_2,t_3,\ldots,t_n,t)$$

can be written down by the following rules: Since each collision is one of three (spin-flip, spin-nonflip, and mixed) types, there are in total 3^n possible ways of distributing these three types among n collisions. Suppose a term in

$$P(t_1,t_2,t_3,\ldots,t_n,t)$$

has m spin-flip collisions at

$$t_{F_1},t_{F_2},t_{F_3},\ldots,t_{F_m}\ .$$

It can be seen that the m spin-flip collisions break the time interval $[0,t]$ into $m+1$ distinct segments

$$[0,t_{F_1}],[t_{F_1},t_{F_2}],\ldots,[t_{F_m},t]\ .$$

If there is no mixed collision between $t_{F_{k-1}}$ and t_{F_k}, the time evolution during this particular time segment is represented by $G(P_G,t_{F_k}-t_{F_{k-1}})$. If there are j mixed collisions between $t_{F_{k-1}}$ and t_{F_k} at $t_{M_1},t_{M_2},\ldots,t_{M_j}$, the time-evolution function for this segment is

$$g_T(P_G,t_{F_{k-1}},t_{M_1},t_{M_2},\ldots,t_{M_j},t_{F_k})\ .$$

If the segment happens to be the first one, i.e., $[0,t_{F_1}]$, the quantity P_G in the time-evolution function is set to zero, corresponding to the fact that muonium is formed with its electron unpolarized at $t=0$. Form the product of the $m+1$ time evolution functions and multiply by $(iP_G)^M$, where M is the total number of mix collisions from $t=0$ to t.

Figure 1 shows a term in $P(t_1,t_1,\ldots,t_8,t)$, in which two spin-flip collisions ($\rightarrow|\leftarrow$) take place at t_2 and t_4, two spin-nonflip collisions (-|-) at t_3 and t_7, and the collisions at t_1,t_5,t_6,t_8 are of mixed type (-●-). Following the procedure described above, one can write down this term as

$$
\begin{aligned}
&\sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\sin^2\frac{\Delta_2}{2}\cos^2\frac{\Delta_3}{2}\sin^2\frac{\Delta_4}{2}\sin\frac{\Delta_5}{2}\\
&\qquad\times\cos\frac{\Delta_5}{2}\sin\frac{\Delta_6}{2}\cos\frac{\Delta_6}{2}\cos^2\frac{\Delta_7}{2}\\
&\qquad\times\sin\frac{\Delta_8}{2}\cos\frac{\Delta_8}{2}(iP_G)^4 g_T(0,t_0,t_1,t_2)\\
&\qquad\times G_T(P_G,t_{42})g_T(P_G,t_4,t_5,t_6,t_8,t)\ .
\end{aligned}
$$

It should be noticed that this particular term is independent of t_3 and t_7 (spin-nonflip collisions).

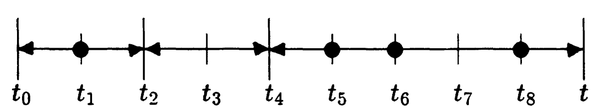

FIG. 1. This term in $P(t_1,t_2,\ldots,t_8,t)$ represents two spin-flip (long vertical lines at t_2 and t_4), two spin-nonflip (short vertical lines without a solid circle at t_3 and t_7), and four mixed (solid circles at t_1, t_5, t_6, and t_8) collisions corresponding to the phase functions $\sin^2(\Delta_k/2)$, $\cos^2(\Delta_k/2)$, and $\sin(\Delta_k/2)\cos(\Delta_k/2)$, respectively, where $t_0=0$ is the time of muonium formation. Spin flips at t_2 and t_4 divide the time interval $[t_0,t]$ into three distinct segments $[t_0,t_2]$, $[t_2,t_4]$, and $[t_4,t]$. The first, second, and third segments contain, respectively, one, zero, and three mixed collision corresponding to the time-evolution functions $g_T(0,t_0,t_1,t_2)$, $G_T(P_G,t_{42})$, and $g_T(P_G,t_4,t_5,t_6,t_8,t)$, where P_G in the first segment is set to zero. This term does not depend on the times of spin-nonflip collisions t_3 and T_7.

D. Statistical average

In order to obtain the statistically averaged polarization observed at t, the quantity

$$P(t_1,t_2,t_3,\ldots,t_n,t)$$

is averaged over all possible time distributions of $t_1,t_2,t_3,\ldots,t_n$ for a fixed n, then over all possible n with appropriate weights. Let $f(t_1,\ldots,t_n,t)$ denote the probability *density* that n collisions between $t=0$ and t are at $t_1,t_2,t_3,\ldots,t_n$. The average muon spin polarization observed at t is expressed by the time-ordered integral [21]

$$P(t)=\sum_{n=0}^{\infty}\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^{t}dt_n f(t_1,\ldots,t_n,t)\times P(t_1,\ldots,t_n,t)\ . \tag{23}$$

If the collision process is Markovian, the quantity $f(t_1,\ldots,t_n,t)$ can be expressed by

$$f(t_1,\ldots,t_n,t)=S(t-t_n)F(t_{n,n-1})\cdots F(t_{32})F(t_{21})F(t_{10})\ , \tag{24}$$

where the survival function $S(t)$ is the probability that after a collision at $t=0$ the particle undergoes no collision until time t and the collision time distribution

$$F(t)=-[dS(t)/dt] \tag{25}$$

is the probability *density* that the next collision after $t=0$ takes place at t [21]. The quantity $S(t-t_n)$ in Eq. (24) ensures that there is no collision after t_n until time t, thus limiting the number of collisions between $t=0$ and t strictly to n. It should be mentioned that each of n collisions can be either of spin-flip, spin-nonflip, or mixed type.

E. Spin exchange as a Poisson process

If the collision is Poissonian, the survival probability is given by $S(t)=\exp(-\lambda t)$ with $\lambda=\lambda_{SF}+\lambda_{NF}$. In this case, the quantity $f(t_1,t_2,\ldots,t_n,t)$ is simply given by

$$f(t_1,t_2,\ldots,t_n,t)=\lambda^n\exp(-\lambda t)$$

[18]. Therefore, the quantity $P(t)$ is expressed by

$$P(t)=\sum_{n=0}^{\infty}e^{-\lambda t}\lambda^n\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^{t}dt_n P_n(t_1,t_2,\ldots,t_n,t) \tag{26}$$

$$=\sum_{n=0}^{\infty}\left[e^{-\lambda t}\frac{(\lambda t)^n}{n!}\right]\frac{1}{t^n}\int_0^{t}dt_1\int_0^{t}dt_2\cdots\int_0^{t}dt_n T[P_n(t_1,t_2,\ldots,t_n,t)]\ . \tag{27}$$

The symbol $T[\cdots]$ maintains the chronological order of the collision events in the integrand, for example, $T[P_2(t_1,t_2,t)]=P_2(t_1,t_2,t)$ for $t_1<t_2$ and $T[P_2(t_1,t_2,t)]=P_2(t_2,t_1,t)$ for $t_2<t_1$. Since the quantity $\exp(-\lambda t)(\lambda t)^n/n!$ in the square brackets is the Poisson probability of having exactly n collisions between t_0 and t, the quantity

$$P_n(t)=\frac{1}{t^n}\int_0^{t}dt_1\int_0^{t}dt_2\int_0^{t}dt_3\cdots\int_0^{t}dt_n T[P_n(t_1,t_2,t_3,\ldots,t_n,t)] \tag{28}$$

can be regarded as the average muon spin polarization for a fixed number of collisions.

F. Poisson process in a weak transverse field

In low fields, where $\omega_{12}=\omega_{23}=\omega_M$ and $c^2=s^2=\frac{1}{2}$, the quantities $G(P_G,t)$ and $g_T(P_G,t_1,t_2,\ldots,t_n)$ become

$$G_T(P_G,t)=\tfrac{1}{2}e^{i\omega_M t}\ , \tag{29}$$

$$g_T(P_G,t_0,t_1,t_2)=\frac{1}{2^2}e^{i\omega_M t_{20}}\ , \tag{30}$$

$$g_T(P_G,t_0,t_1,t_2,t_3)=\frac{1}{2^3}e^{i\omega_M t_{30}}\ , \tag{31}$$

$$g_T(P_G,t_0,t_1,\ldots,t_n)=\frac{1}{2^n}e^{i\omega_M t_{n0}}\ , \tag{32}$$

where $\omega_M/2\pi=1.39$ MHz/G is the precession frequency of triplet muonium and fast oscillating terms containing ω_{14} and ω_{34} are ignored [15,18]. By substituting these into Eq. (15), one obtains the muon polarization observed at t_2 after one collision at t_1 as

$$P(t_1,t_2)=\tfrac{1}{2}e^{i\omega_M t_{20}}\left[1-\tfrac{1}{2}\sin^2\frac{\Delta_1}{2}+i\frac{P_G}{2}\sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\right]\ . \tag{33}$$

Similarly, Eq. (21) leads to

$$P(t_1,t_2,t_3)=\tfrac{1}{2}e^{i\omega_M t_{30}}\left[1-\tfrac{1}{2}\sin^2\frac{\Delta_1}{2}+i\frac{P_G}{2}\sin\frac{\Delta_1}{2}\cos\frac{\Delta_1}{2}\right]\left[1-\tfrac{1}{2}\sin^2\frac{\Delta_2}{2}+i\frac{P_G}{2}\sin\frac{\Delta_2}{2}\cos\frac{\Delta_2}{2}\right]\ . \tag{34}$$

In general, the muon polarization observed at time t after N collisions at $t_1,t_2,\ldots,t_n$ can be written down as

$$P(t_1,t_2,\ldots,t_n,t)=\tfrac{1}{2}e^{i\omega_M t}\prod_{n=1}^{n}\left[1-\tfrac{1}{2}\sin^2\frac{\Delta_n}{2}+i\frac{P_G}{2}\sin\frac{\Delta_n}{2}\cos\frac{\Delta_n}{2}\right]$$
$$=\tfrac{1}{2}e^{i\omega_M t}\left[1-\frac{1}{2}\left\langle\sin^2\frac{\Delta}{2}\right\rangle+i\frac{P_G}{2}\left\langle\sin\frac{\Delta}{2}\cos\frac{\Delta}{2}\right\rangle\right]^n , \tag{35}$$

where $\langle \cdots \rangle$ means the average value of the quantity in the brackets. Since the quantity $P(t_1,t_2,\ldots,t_n,t)$ is independent of $t_1,t_2,\ldots,t_n$, the multiple integral in Eq. (26) simply gives $t^n/n!$, leading to

$$P(t)=\sum_{n=0}^{\infty}P(t_1,t_2,\ldots,t_n,t)e^{-\lambda t}\frac{(\lambda t)^n}{n!}$$
$$=\tfrac{1}{2}e^{i\omega_M t}e^{-\lambda t}\sum_{n=0}^{\infty}\frac{(\lambda t)^n}{n!}\left[1-\frac{1}{2}\left\langle\sin^2\frac{\Delta}{2}\right\rangle+i\frac{P_G}{2}\left\langle\sin\frac{\Delta}{2}\cos\frac{\Delta}{2}\right\rangle\right]^n$$
$$=\tfrac{1}{2}e^{i\omega_M t}\exp\left[-\frac{\lambda_{SF}}{2}t\right]\exp\left[i\frac{P_G}{2}\lambda t\left\langle\sin\frac{\Delta}{2}\cos\frac{\Delta}{2}\right\rangle\right] , \tag{36}$$

where $\lambda_{SF}=\lambda\langle\sin^2(\Delta/2)\rangle$. The factor $\frac{1}{2}$ in front accounts for the fact that only triplet muonium is observed. The observed precession frequency and relaxation rate are expressed by

$$\omega_{\text{obs}}=\omega_M+\frac{P_G}{2}\lambda\left\langle\sin\frac{\Delta}{2}\cos\frac{\Delta}{2}\right\rangle=\omega_M+\frac{P_G}{2}\langle\sqrt{\lambda_{SF}\lambda_{NF}}\rangle , \tag{37}$$

$$\lambda_{\text{obs}}=\lambda_{SF}/2 , \tag{38}$$

where Eq. (37) defines the quantity $\langle\sqrt{\lambda_{SF}\lambda_{NF}}\rangle$ in terms of λ and Δ.

G. Intermediate transverse field

In intermediate fields, where $c^2=s^2=\frac{1}{2}$ but $\omega_{12}\neq\omega_{23}$, one obtains

$$G_T(P_G,t)=\tfrac{1}{4}[(1+P_G)e^{i\omega_{12}t}+(1-P_G)e^{i\omega_{23}t}] , \tag{39}$$

$$g_T(P_G,t_0,t_1,t_2)=\tfrac{1}{2}G_T(P_G,t_{20}) , \tag{40}$$

$$g_T(P_G,t_0,t_1,t_2,t_3)=\frac{1}{2^2}G_T(P_G,t_{30}) , \tag{41}$$

$$g_T(P_G,t_0,t_1,\ldots,t_n)=\frac{1}{2^{n-1}}G_T(P_G,t_{n0}) . \tag{42}$$

Direct substitution of these in Eqs. (15), (21), etc., leads to

$$P(t_1,t_2,\ldots,t_n,t)=\tfrac{1}{4}e^{i\omega_{12}t}\prod_{n=1}^{n}\left[1-\tfrac{1}{4}(3-P_G)\sin^2\frac{\Delta_n}{2}+i\frac{P_G}{2}\sin\frac{\Delta_n}{2}\cos\frac{\Delta_n}{2}\right]$$
$$+\tfrac{1}{4}e^{i\omega_{23}t}\prod_{n=1}^{n}\left[1-\tfrac{1}{4}(3+P_G)\sin^2\frac{\Delta_n}{2}+i\frac{P_G}{2}\sin\frac{\Delta_n}{2}\cos\frac{\Delta_n}{2}\right]$$
$$=\tfrac{1}{4}e^{i\omega_{12}t}\left[1-\tfrac{1}{4}(3-P_G)\left\langle\sin^2\frac{\Delta}{2}\right\rangle+i\frac{P_G}{2}\left\langle\sin\frac{\Delta}{2}\cos\frac{\Delta}{2}\right\rangle\right]^n$$
$$+\tfrac{1}{4}e^{i\omega_{23}t}\left[1-\tfrac{1}{4}(3+P_G)\left\langle\sin^2\frac{\Delta}{2}\right\rangle+i\frac{P_G}{2}\left\langle\sin\frac{\Delta}{2}\cos\frac{\Delta}{2}\right\rangle\right]^n . \tag{43}$$

It can be shown that all terms containing $t_1,t_2,\ldots,t_n$ can be ignored [18] in a field larger than $B=30$ G so that $(\omega_{23}-\omega_{12})t\gg 1$ at a typical observation time of, say, $t=1$ μs. For the Poisson process, $P(t)$ can be calculated from Eq. (26) as

$$P(t)=\sum_{n=0}^{\infty}P(t_1,t_2,\ldots,t_n,t)e^{-\lambda t}\frac{(\lambda t)^n}{n!}$$
$$=\tfrac{1}{4}e^{i(\omega_{12}+\delta\omega)t}\exp(-\lambda_{12}t)+\tfrac{1}{4}e^{i(\omega_{23}+\delta\omega)t}\exp(-\lambda_{23}t) , \tag{44}$$

where the frequency shift and the relaxation rates are given by

$$\delta\omega = \frac{P_G}{2}\lambda\left\langle \sin\frac{\Delta}{2}\cos\frac{\Delta}{2}\right\rangle = \frac{P_G}{2}\langle\sqrt{\lambda_{SF}\lambda_{NF}}\rangle = \frac{P_G}{4}\lambda\langle\sin\Delta\rangle \ , \tag{45}$$

$$\lambda_{12} = \lambda_{SF}\left[\frac{3}{4} - \frac{P_G}{4}\right] = \lambda\left[\frac{1-\langle\cos\Delta\rangle}{2}\right]\left[\frac{3}{4} - \frac{P_G}{4}\right] , \tag{46}$$

$$\lambda_{23} = \lambda_{SF}\left[\frac{3}{4} + \frac{P_G}{4}\right] = \lambda\left[\frac{1-\langle\cos\Delta\rangle}{2}\right]\left[\frac{3}{4} + \frac{P_G}{4}\right] . \tag{47}$$

H. Slow spin exchange in high fields

In high fields such that $c=1$ and $s=0$, the quantity $G(P_G,t)$ becomes

$$G(P_G,t) = \tfrac{1}{2}(1+P_G)e^{i\omega_{12}t} + \tfrac{1}{2}(1-P_G)e^{-i\omega_{34}t} . \tag{48}$$

If $s=0$, it can be shown that $g_T(P_G,t_1,t_2,\ldots,t_n)$ vanishes for all n (Appendix I). All terms containing $t_1,t_2,\ldots,t_n$ will be averaged to zero after integrations [18]. Therefore, one obtains

$$P_n(t_1,t_2,\ldots,t_n,t) = \frac{1}{2}\left[1-\tfrac{1}{2}(1-P_G)\left\langle\sin^2\frac{\Delta}{2}\right\rangle\right]^n e^{i\omega_{12}t} + \tfrac{1}{2}\left[1-\tfrac{1}{2}(1+P_G)\left\langle\sin^2\frac{\Delta}{2}\right\rangle\right]^n e^{-i\omega_{34}t} . \tag{49}$$

Following the same procedure as in the case of an intermediate field, one obtains

$$P(t) = \sum_{n=0}^{\infty} P_n(t_1,t_2,\ldots,t_n,t)e^{-\lambda t}\frac{(\lambda t)^n}{n!} = \tfrac{1}{2}e^{i\omega_{12}t}\exp(-\lambda_{12}t) + \tfrac{1}{2}e^{-i\omega_{34}t}\exp(-\lambda_{34}t) , \tag{50}$$

where the two relaxation rates are

$$\lambda_{12} = \lambda_{SF}(1-P_G)/2 \quad\text{and}\quad \lambda_{34} = \lambda_{SF}(1+P_G)/2 . \tag{51}$$

I. Spin-nonflip collisions in the Poisson process

If the collision process is Poissonian, the muon polarization given by Eq. (26) can be simplified by integrating out with respect to all spin-nonflip collision times (Appendix II). The result can be written down as

$$\begin{aligned} P(t) = {} & \sum_{m=0}^{\infty} e^{-\lambda_{SF}t}\lambda_{SF}^m \int_0^{t_2} dt_1 \cdots \int_0^t dt_m P_{SF}(t_1,t_2,\ldots,t_m,t) \\ & + (iP_G)^1 \sum_{m=1}^{\infty} e^{-\lambda_{SF}t}\lambda_{SF}^{m-1}\langle\sqrt{\lambda_{SF}\lambda_{NF}}\rangle^1 \int_0^{t_2} dt_1 \cdots \int_0^t dt_m P_{\rm mix}^{(1)}(t_1,t_2,\ldots,t_m,t) \\ & + (iP_G)^2 \sum_{m=2}^{\infty} e^{-\lambda_{SF}t}\lambda_{SF}^{m-2}\langle\sqrt{\lambda_{SF}\lambda_{NF}}\rangle^2 \int_0^{t_2} dt_1 \cdots \int_0^t dt_m P_{\rm mix}^{(2)}(t_1,t_2,\ldots,t_m,t) \\ & + (iP_G)^3 \sum_{m=3}^{\infty} e^{-\lambda_{SF}t}\lambda_{SF}^{m-3}\langle\sqrt{\lambda_{SF}\lambda_{NF}}\rangle^3 \int_0^{t_2} dt_1 \cdots \int_0^t dt_m P_{\rm mix}^{(3)}(t_1,t_2,\ldots,t_m,t) \\ & \vdots \ , \end{aligned} \tag{52}$$

where $P_{SF}(t_1,t_2,\ldots,t_m,t)$ is a simple product of $G_T(P_G,t)$'s given by

$$P_{SF}(t_1,\ldots,t_m,t) = G_T(0,t_{10})G_T(P_G,t_{21})G_T(P_G,t_{32}) \times \cdots G_T(P_G,t-t_m) , \tag{53}$$

representing m spin-flip collisions at $t_1,t_2,t_3,\ldots,t_m$. The quantity $P_{mix}^{(k)}(t_1,t_2,\ldots,t_m,t)$ in Eq. (52) contains all possible permutations of time-evolution functions for k mixed and $m-k$ spin-flip collisions. For example,

$$\begin{aligned} P_{\rm mix}^{(2)}(t_1,t_2,t_3,t) &= g_T(0,t_0,t_1,t_2,t_3)G_T(P_G,t-t_3) \\ &+ g_T(0,t_0,t_1,t_2)g_T(P_G,t_2,t_3,t) \\ &+ G_T(0,t_1-t_0)g_T(P_G,t_1,t_2,t_3,t) , \end{aligned} \tag{54}$$

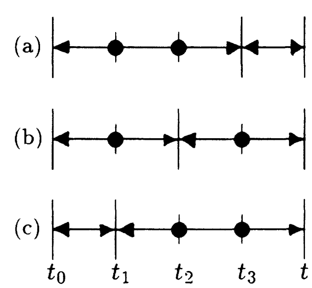

FIG. 2. The quantity $P_{\rm mix}^{(2)}(t_1,t_2,t_3,t)$ in Eq. (54) contains three terms (a) $g_T(0,t_0,t_1,t_2,t_3)G_T(P_G,t-t_3)$, (b) $g_T(0,t_0,t_1,t_2)g_T(P_G,t_2,t_3,t)$, (c) $G_T(0,t_1-t_0)g_T(P_G,t_1,t_2,t_3,t)$ representing all possible sequences of one spin-flip and two mixed collisions.

corresponding to the three diagrams in Fig. 2.

If $P_G=0$, $P(t)$ for the Poisson process is independent of λ_{NF}. For $P_G\neq0$, however, the average muon spin polarization $P(t)$ depends not only on the spin-flip rate but also on the spin-nonflip rate. As a consistency test, it is interesting to work out Eq. (52) for a weak transverse field. Using Eqs. (29)–(32), one can express

$$P_{\rm mix}^{(k)}(t_1,t_2,\ldots,t_m,t)=\frac{m!}{k!(m-k)!}\frac{1}{2^{m+1}}e^{i\omega_M t} . \quad (55)$$

Then, Eq. (52) will become

$$P(t)=\frac{e^{i\omega_M t}}{2}e^{-\lambda_{SF}t/2}\times\left[1+\frac{(iP_G)^1}{1!}\left[\frac{t}{2}\langle\sqrt{\lambda_{SF}\lambda_{NF}}\rangle\right]^1+\frac{(iP_G)^2}{2!}\left[\frac{t}{2}\langle\sqrt{\lambda_{SF}\lambda_{NF}}\rangle\right]^2+\frac{(iP_G)^3}{3!}\left[\frac{t}{2}\langle\sqrt{\lambda_{SF}\lambda_{NF}}\rangle\right]^3+\cdots\right] , \quad (56)$$

leading to the same result as Eq. (36).

J. Fast spin exchange

If the collision rate is much faster than the hyperfine frequency such that $\omega_{14}t\ll1$ and $\omega_{34}t\ll1$, the quantities $h_{12}(t)$, $h_{23}(t)$, and $g_T(P_G,t_1,t_2,\ldots,t_n)$ will vanish (see Appendix I). Therefore, the quantity $P(t_1,t_2,\ldots,t_n,t)$ contains no mixed collisions. In this case, one can calculate $P(t)$ by the first term of Eq. (52). It has been shown [17] that the relaxation rate and the precession frequency are related to the real and imaginary parts, respectively, of $\ln G_T(P_G,t)$ by

$$\lambda_{\rm obs}=-\lambda_{SF}\int_0^\infty dt\,\lambda_{SF}e^{-\lambda_{SF}t}{\rm Re}\ln G_T(P_G,t) , \quad (57)$$

$$\omega_{\rm obs}=-\lambda_{SF}\int_0^\infty dt\,\lambda_{SF}e^{-\lambda_{SF}t}{\rm Im}\ln G_T(P_G,t) . \quad (58)$$

Using

$${\rm Re}\ln G_T(P_G,t)=\ln A(P_G,t)$$

and

$${\rm Im}\ln G_T(P_G,t)=\phi(P_G,t) ,$$

with Eqs. (17) and (18), one can calculate $\lambda_{\rm obs}$ and $\omega_{\rm obs}$ in the same way as described in Ref. [17]:

$$\lambda_{\rm obs}=-\lambda_{SF}\int_0^\infty dt\,\lambda_{SF}e^{-\lambda_{SF}t}\ln|A(P_G,t)|=\frac{\omega_0^2}{4\lambda_{SF}}\left[\frac{1}{1+(1+x^2)\omega_0^2/\lambda_{SF}^2}+\frac{1-P_G^2}{1+\omega_0^2/\lambda_{SF}^2}\right] , \quad (59)$$

$$\omega_{\rm obs}=-\lambda_{SF}\int_0^\infty dt\,\lambda_{SF}e^{-\lambda_{SF}t}\phi(P_G,t)=-\omega_-+\lambda_{SF}\int_0^\infty dt\,\lambda_{SF}e^{-\lambda_{SF}t}\tan^{-1}\left[\delta\tan\left[\Omega t+\frac{\omega_0}{2}t\right]\right]-\lambda_{SF}\int_0^\infty dt\,\lambda_{SF}e^{-\lambda_{SF}t}\tan^{-1}\left[P_G\tan\left[\frac{\omega_0}{2}t\right]\right] . \quad (60)$$

III. DISCUSSION

Equations (37) and (45) show that in a weak or intermediate field, the precession frequency is shifted by an amount proportional to $P_G\langle\sin\Delta\rangle$. Thus, the frequency shift will vanish, if the collision is purely of spin-flip type, $\sin^2(\Delta/2)=1$, or purely of spin-nonflip type, $\cos^2(\Delta/2)=1$. While the relaxation rate in a weak field is not affected by the polarization of the medium, the two relaxation rates in an intermediate field depend on P_G. If $P_G=0$, the quantities λ_{12} and λ_{23} reduces to $3\lambda_{SF}/4$ with the characteristic factor $\frac{3}{4}$ of intermediate fields [18,19]. For $P_G\neq0$, one can determine both λ_{SF} and P_G from λ_{12} and λ_{23}. Suppose the phase shift Δ varies drastically from one collision to another so that Δ is distributed uniformly from zero to 2π. Then, the frequency shift will vanish, because the average value of $\sin\Delta$ is zero. In this case, one can see from Eq. (3) that $\lambda_{SF}=\lambda_{NF}=\lambda/2$. If, on the other hand, Δ is relatively constant, Eqs. (45)–(47) allow one to determine the phase shift Δ including its sign, the encounter rate λ, the polarization of the spin-exchange medium from the measured values of λ_{12}, λ_{23}, and $\delta\omega$.

If spin exchange is much faster than the hyperfine frequency, the spin-nonflip rate plays no role in spin dynamics, because all the mixed collision terms vanish (Appendix I). Still, the precession frequency and relaxation rate depend on P_G. The first two terms of Eq. (60) agree with the result in an unpolarized medium [17] and the last term can be thought of as a frequency shift due to additional field caused by the medium polarization. In the limit of extremely fast spin exchange $\lambda_{SF}\to\infty$, the quantity $\omega_{\rm obs}$ given by Eq. (60) approaches $\omega_{\rm obs}=+\omega_\mu-\omega_0P_G/2$, where $\omega_\mu/2\pi=0.0136$ MHz/G is the precession frequency of the positive muon. If $P_G=0$, this result will reduce to the known case of "quantum back swing," $\omega_{\rm obs}=+\omega_\mu$, where the muon spin in muonium cannot follow fast electron flips so that it will precess as if it were in a diamagnetic environment [16,17,20].

An equation similar to (52) is also valid for longitudinal fields. Mixed terms in longitudinal fields oscillate rapidly typically at frequencies comparable to the hyperfine frequency so that the effects of the spin-nonflip rate is averaged out in slow spin exchange [22]. In the limit of fast spin exchange [21] the mixed terms in longitudinal fields also vanish for the same reason as in transverse fields. It should be mentioned that Turner, Snider, and Fleming [23] briefly discussed muonium spin exchange in polarized media using a Boltzmann-equation approach without giving concrete expressions for experimentally observable quantities.

Equation (52) shows that if the process is Poissonian and $P_G=0$, the spin-nonflip rate has no effects on spin dynamics. If the collision process is not Poissonian, however, this seemingly obvious statement about the spin-nonflip rate is not true even for $P_G=0$. As a concrete example of a non-Poisson process, it is assumed that the survival probability is a linear function of time:

$$S(t)=\begin{cases}1-t/\tau=1-\lambda t & \text{if } t<\tau\\ 0 \ \text{if } t>\tau\ ,\end{cases} \tag{61}$$

which can be regarded as the first two terms of $\exp(-\lambda t)=1-\lambda t$ for $\lambda t \ll 1$. The probability density that a collision takes place at t is

$$F(t)=-\left[\frac{dS(t)}{dt}\right]=\begin{cases}1/\tau=\lambda & \text{if } t<\tau\\ 0 \ \text{if } t>\tau\ .\end{cases} \tag{62}$$

Therefore, the time distribution function $f_{\text{lin}}(t_1,t_2,t_3,\ldots,t_n,t)$ can be written down from Eq. (24):

$$f_{\text{lin}}(t_1,t_2,\ldots,t_n,t)$$
$$=F(t_{10})F(t_{21}),\ldots,F(t_{n,n-1})S(t-t_n)$$
$$=\frac{1}{\tau^n}\left[1-\frac{t-t_n}{\tau}\right]. \tag{63}$$

For the sake of simplicity, it is assumed that the field is weak and $P_G=0$, where the quantity $P(t_1,t_2,\ldots,t_n,t)$ is given from Eqs. (15), (21), (22), etc., as [15]

$$P(t_1,t_2,\ldots,t_n,t)=\tfrac{1}{2}e^{i\omega_M t}[1-\tfrac{1}{2}\sin^2(\Delta/2)]^n\ . \tag{64}$$

Using this in Eq. (23), one can work out $P(t)$ for $t<\tau$ as

$$P(t)=\tfrac{1}{2}e^{i\omega_M t}\sum_{n=0}^{\infty}\left[1-\tfrac{1}{2}\sin^2\frac{\Delta}{2}\right]^n\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^{t}dt_n\frac{1}{\tau^n}\left[1-\frac{t-t_n}{\tau}\right]$$
$$=\tfrac{1}{2}e^{i\omega_M t}\sum_{n=0}^{\infty}\left[1-\tfrac{1}{2}\sin^2\frac{\Delta}{2}\right]^n\left[\frac{1}{n!}\left[\frac{t}{\tau}\right]^n-\frac{1}{(n+1)!}\left[\frac{t}{\tau}\right]^{n+1}\right]$$
$$=\tfrac{1}{2}e^{i\omega_M t}\left[\frac{\lambda-\frac{1}{2}\lambda_{SF}\exp[(\lambda-\frac{1}{2}\lambda_{SF})t]}{\lambda-\frac{1}{2}\lambda_{SF}}\right]. \tag{65}$$

The quantity in the square brackets in the last expression, which represents the relaxation of the muon spin, explicitly contains both λ_{SF} and λ_{NF}. It should be mentioned that if $\lambda_{SF}=0$, the muon polarization shows no depolarization regardless of λ_{NF}.

In order to understand the effects of λ_{NF} on $P(t)$ more intuitively, it is instructive to investigate the time distribution function for *spin-flip* collisions only, which can be written as

$$F_{SF}(t)=F(t)\sin^2\frac{\Delta}{2}+\int_0^t dt_1F(t-t_1)F(t_1)\cos^2\frac{\Delta}{2}\sin^2\frac{\Delta}{2}$$
$$+\int_0^{t_2}dt_1\int_0^t dt_2F(t-t_2)F(t_2-t_1)F(t_1)\left[\cos^2\frac{\Delta}{2}\right]^2\sin^2\frac{\Delta}{2}+\cdots$$
$$=\sum_{n=0}^{\infty}\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^t dt_nF(t-t_n)\prod_{m=1}^{n}F(t_{m,m-1})\cos^{2n}\frac{\Delta}{2}\sin^2\frac{\Delta}{2}\ . \tag{66}$$

The term with $m=k$ in the summation represents the case where the first k collisions are of spin-nonflip type and the first flip takes place at the $(k+1)$th collision. One can obtain the survival function against spin-flip collisions $S_{SF}(t)$ by integrating Eq. (66) with respect to t and using the initial condition that $S_{SF}(0)=1$. The quantity $f_{SF}(t_1,\ldots,t_n,t)$ for spin-flip collisions is now expressed by

$$f_{SF}(t_1,\ldots,t_n,t)$$
$$=S_{SF}(t-t_n)F_{SF}(t_{n,n-1})\cdots F_{SF}(t_{21})F_{SF}(t_{10})\ . \tag{67}$$

If the collision process is Poissonian with a survival function (survival against any collision, spin flip and spin nonflip) $S(t)=\exp(-\lambda t)$ with $\lambda=\lambda_{SF}+\lambda_{NF}$, Eq. (66) can be summed up in a closed form as

$$F_{SF}(t)=\exp(-\lambda_{SF}t)\lambda_{SF}\ .$$

Therefore, both $S_{SF}(t)$ and $f_{SF}(t_1,t_2,\ldots,t_n,t)$ are independent of the spin-nonflip rate.

In the case of linear survival, as an example of non-Poissonian processes, one can use Eq. (62) in Eq. (66) to derive the time distribution of *spin-flip collisions* for $t<\tau=1/\lambda$:

$$F_{SF}(T)=\lambda\sin^2\frac{\Delta}{2}+\lambda^2t\cos^2\frac{\Delta}{2}\sin^2\frac{\Delta}{2}+\lambda^3\frac{t^2}{2!}\cos^4\frac{\Delta}{2}\sin^2\frac{\Delta}{2}$$
$$+\lambda^4\frac{t^3}{3!}\cos^6\frac{\Delta}{2}\sin^2\frac{\Delta}{2}+\cdots=\lambda_{SF}e^{\lambda_{NF}t}\ . \tag{68}$$

Thus, the survival probability and $f_{SF}(t_1,\ldots,t_n,t)$ for the linear decay are

$$S_{SF}(t)=[1+(\lambda_{SF}/\lambda_{NF})]-(\lambda_{SF}/\lambda_{NF})e^{\lambda_{NF}t}\ , \tag{69}$$

$$f_{SF}(t_1,\ldots,t_n,t)=\lambda_{SF}^n e^{\lambda_{NF}t_n}[1+(\lambda_{SF}/\lambda_{NF})(1-e^{\lambda_{NF}(t-t_n)})]\ . \tag{70}$$

The time distribution function for *spin-flip* collisions does contain λ_{NF}, i.e., it is necessary to specify both λ_{SF} and λ_{NF} to characterize the time distribution of spin-flip collisions.

The effects of λ_{NF} on the spin dynamics has recently been investigated numerically [21] for survival functions of the form $S(t)=\exp[-(\lambda t)^n]$, where $P(t)$ is found to become λ_{NF} independent only for $n=1$. Furthermore, in order that the quantity $P(t)$ does not depend on the spin-nonflip rate, it is essential that the process be stochastic. If the process is deterministic and chaotic, $P(t)$ is still affected by the spin-nonflip rate, even if the survival function is exponential [21].

Spin exchange during the slowing down of muonium is an example of a non-Poissonian process. Since the velocity muonium $v(E)$ and the collision cross section $\sigma(E)$ are time dependent during slowing down, the collision rate $\lambda\sim\sigma(E)v(E)$ is also time dependent. The survival function for this case is given in terms of the number density of the gas n as

$$S(t)=\exp[-\int_0^t nv(E)\sigma(E)dt]\ , \tag{71}$$

which is, in general, not simple exponential with respect to t. Other potentially non-Poissonian processes include the case where muonium repeats trapping, detrapping, and diffusion in solids and the case of spin exchange in high-pressure gases or in liquids, where intercollision times, if they can be defined at all, become comparable with the duration of a spin-exchange encounter.

IV. CONCLUDING REMARKS

Relaxation rate and frequency shift measurements of the two-frequency muonium precessions in a spin-polarized medium will provide (1) a simple method to determine the electron polarization of the media and (2) unique insight into the encounter rate with paramagnetic species and the phase shift due to the potential energy difference between electron-singlet and -triplet encounters, and thus into the spin-flip and spin-nonflip probabilities. The effects of the spin-nonflip rate on the relaxation rate and frequency shift are discussed in the Poisson as well as in non-Poisson processes.

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APPENDIX A: TIME EVOLUTION WITH MIXED COLLISIONS

$$g_T(P_G,t_0,t_1,t_2)=\tfrac{1}{2}(1+P_G)h_{12}(t_{10})h_{12}(t_{21})+\tfrac{1}{2}(1-P_G)h_{23}(t_{10})h_{23}(t_{21})$$

$$g_T(P_G,t_0,t_1,t_2,t_3)=\tfrac{1}{2}(1+P_G)h_{12}(t_{10})g_{12}(t_{21})h_{12}(t_{32})+\tfrac{1}{2}(1-P_G)h_{23}(t_{10})g_{23}(t_{21})h_{23}(t_{32})$$

$$g_T(P_G,t_0,t_1,t_2,t_3,t_4)=\tfrac{1}{2}(1+P_G)h_{12}(t_{10})g_{12}(t_{21})g_{12}(t_{32})h_{12}(t_{43})+\tfrac{1}{2}(1-P_G)h_{23}(t_{10})g_{23}(t_{21})g_{23}(t_{32})h_{23}(t_{43})$$

$$\vdots$$

$$g_T(P_G,t_0,t_1,t_2,\ldots,t_n)=\tfrac{1}{2}(1+P_G)h_{12}(t_{10})g_{12}(t_{21})\cdots g_{12}(t_{n-1,n-2})h_{12}(t_{n,n-1})+\tfrac{1}{2}(1-P_G)h_{23}(t_{10})g_{23}(t_{21})\cdots g_{23}(t_{n-1,n-2})h_{23}(t_{n,n-1})\ ,$$

where the quantities $h_{12}(t)$, $h_{23}(t)$, $g_{12}(t)$, and $g_{23}(t)$ are defined as

$$h_{12}(t)=cs(e^{i\omega_{12}t}-e^{i\omega_{14}t})$$

$$h_{23}(t)=cs(e^{i\omega_{23}t}-e^{-i\omega_{34}t})\ ,$$

$$g_{12}(t)=s^2e^{i\omega_{12}t}+c^2e^{i\omega_{14}t}\ ,$$

$$g_{23}(t)=c^2e^{i\omega_{23}t}+s^2e^{-i\omega_{34}t}\ .$$

At high fields $x\gg1$, where $c=1$, $s=0$, $h_{12}(t)=0$, and $h_{23}(t)=0$, the quantity $g_T(P_G,t_0,t_1,t_2,\ldots,t_n)$ vanishes for all n.

APPENDIX B: SPIN-NONFLIP COLLISIONS IN THE POISSON PROCESS

In order to prove Eq. (52), the integrals with respect to all spin-nonflip collisions in Eq. (26) are explicitly carried out. First, it is shown that all the terms without mixed collision will collapse into the first term of Eq. (52) after the integration with respect to all the times associated with spin-nonflip collisions. For the sake of simplicity, $G_T(P_G,t)$ is simply written as $G(t)$ in this section.

First, it is useful to arrange Eq. (27) according to the number of spin-flip collisions. Let us consider terms with m spin-flip collisions in $P_n(t_1,t_2,\ldots,t_n,t)$, where the total number of such terms in given by $n!/[m!(n-m)!]$. Let us pick one particular term in which collisions at $t_1,t_2,\ldots,t_m$ are of spin-flip type and those at $t_{m+1},t_{m+2},\ldots,t_n$ are of spin-nonflip type. Such a term in Eq. (26) is

$$G(t-t_m)G(t_{m,m-1})\cdots G(t_{32})G(t_{21})G(t_{10})\left[\sin^2\frac{\Delta}{2}\right]^m\left[\cos^2\frac{\Delta}{2}\right]^{n-m} . \tag{B1}$$

Here it is assumed that $\Delta_1=\Delta_2=\cdots=\Delta_m=\Delta$. Since this term does not contain $t_{m+1},t_{m+2},\ldots,t_n$ explicitly, the integrals with respect to these variables from 0 to t simply give a factor t^{n-m}. It is easy to see that all $n!/[m!(n-m)!]$ terms with m spin-flip collisions will lead to the same quantity after the time integrals. Therefore, Eq. (28) can be rewritten by

$$\begin{aligned}P_n(t)=&\sum_{m=0}^{n}\frac{n!}{m!(n-m)!}\left[\sin^2\frac{\Delta}{2}\right]^m\left[\cos^2\frac{\Delta}{2}\right]^{n-m}\frac{1}{t^m}\\&\times\int_0^t dt_1\int_0^t dt_2\int_0^t dt_3\cdots\int_0^t dt_m T[G(t-t_m)G(t_{m,m-1})\cdots G(t_{21})G(t_{10})] .\end{aligned} \tag{B2}$$

Using this result in Eq. (27), one obtains

$$P(t)=\sum_{n=0}^{\infty}\sum_{m=0}^{n}e^{-\lambda t}\frac{(\lambda_{NF}t)^{n-m}}{(n-m)!}\frac{\lambda_{SF}^m}{m!}\int_0^t dt_1\int_0^t dt_2\int_0^t dt_3\cdots\int_0^t dt_m T[G(t-t_m)G(t_{m,m-1})\cdots G(t_{21})G(t_{10})] . \tag{B3}$$

If the summation over n is carried out first for a fixed m, one obtains

$$\sum_{n=m}^{\infty}e^{-\lambda t}\frac{(\lambda_{NF}t)^{n-m}}{(n-m)!}=e^{-\lambda t}e^{\lambda_{NF}t}=e^{-\lambda_{SF}t} . \tag{B4}$$

This is the crucial step of the argument, where the quantity λ_{NF} drops out of the expression. Thus, $P(t)$ is expressed in terms of λ_{SF} by

$$\begin{aligned}P(t)=&\sum_{m=0}^{\infty}\left[e^{-\lambda_{SF}t}\frac{(\lambda_{SF}t)^m}{m!}\right]\frac{1}{t^m}\int_0^t dt_1\int_0^t dt_2\cdots\int_0^t dt_m T[G(t-t_m)G(t_{m,m-1})\cdots G(t_{21})G(t_{10})]\\=&\sum_{m=0}^{\infty}e^{-\lambda_{SF}t}\lambda_{SF}^m\int_0^{t_2}dt_1\cdots\int_0^t dt_m G(t-t_m)G(t_{m,m-1})\cdots G(t_{21})G(t_{10}) .\end{aligned} \tag{B5}$$

The same argument can be applied to prove other terms in Eq. (52) with mixed collisions. For the $(k+1)$th term of Eq. (52) which contains k mixed collisions, Eq. (B5) will become

$$\begin{aligned}&(iP_G)^k\sum_{m=k}^{\infty}\left[e^{-\lambda_{SF}t}\frac{(\lambda_{SF}t)^{m-k}}{m!}\right]\left[\lambda t\sin\frac{\Delta}{2}\cos\frac{\Delta}{2}\right]^k\frac{1}{t^m}\int_0^t dt_1\int_0^t dt_2\cdots\int_0^t dt_m T[P_{\text{mix}}^{(k)}(t_1,\ldots,t_m,t)]\\&\qquad=(iP_G)^k\sum_{m=k}^{\infty}e^{-\lambda_{SF}t}\lambda_{SF}^{m-k}(\sqrt{\lambda_{SF}\lambda_{NF}})^k\int_0^{t_2}dt_1\cdots\int_0^t dt_m P_{\text{mix}}^{(k)}(t_1,\ldots,t_m,t) .\end{aligned} \tag{B6}$$

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[1] E. M. Purcell and G. B. Field, Astrophys. J. **124**, 542 (1956).

[2] J. P. Wittke and R. H. Dicke, Phys. Rev. **103**, 620 (1956).

[3] A. Dalgarno, Proc. R. Soc. London, Ser. A **262**, 132 (1961).

[4] L. C. Balling, R. J. Hanson, and F. M. Pipkin, Phys. Rev. **133**, A607 (1964).

[5] L. C. Balling and F. M. Pipkin, Phys. Rev. A **136**, 46 (1964).

[6] W. Happer, Rev. Mod. Phys. **44**, 169 (1972).

[7] M. Senba, D. G. Fleming, D. J. Arseneau, D. M. Garner, and I. D. Reid, Phys. Rev. A **39**, 3871 (1989).

[8] D. G. Fleming, R. J. Mikula, and D. M. Garner, J. Chem. Phys. **73**, 2751 (1980).

[9] R. J. Mikula, D. M. Garner, and D. G. Fleming, J. Chem. Phys. **75**, 5362 (1981).

[10] M. Senba, A. C. Gonzalez, J. R. Kempton, D. J. Arseneau, J. J. Pan, A. Tempelmann, and D. G. Fleming, Hyperfine Interact. **65**, 979 (1990).

[11] J. J. Pan, M. Senba, D. J. Arseneau, J. R. Kempton, D. G. Fleming, S. Baer, A. C. Gonzalez, and R. Snooks, Phys. Rev. **48**, 1218 (1993).

[12] B. Larson, O. Häusser, P. P. J. Delheij, D. M. Whittal, and D. Thiessen, Phys. Rev. A **44**, 3108 (1991).

[13] A. S. Barton, P. Bogorad, G. D. Cates, H. Mabuchi, H. Middleton, N. R. Newbury, R. Holmes, J. McCracken, P.

A. Souder, J. Xu, and D. Tupa, Phys. Rev. Lett. **70**, 758 (1993).
[14] N. R. Newbury, A. S. Barton, P. Bogorad, G. D. Cates, M. Gatzke, H. Mabuchi, and B. Saam, Phys. Rev. A **48**, 558 (1993).
[15] M. Senba, J. Phys. B **23**, 4051 (1990).
[16] M. Senba, Hyperfine Interact. **65**, 779 (1990).
[17] M. Senba, J. Phys. B **24**, 3531 (1991).
[18] M. Senba, J. Phys. B **26**, 3213 (1993).
[19] M. Senba, J. J. Pan, D. J. Arseneau, S. Baer, M. Shelley, R. Snooks, and D. G. Fleming, Hyperfine Interact. (to be published).
[20] M. Senba, J. Phys. B **23**, 1545 (1990).
[21] M. Senba, Hyperfine Interact. (to be published).
[22] M. Senba, Hyperfine Interact. (to be published).
[23] R. E. Turner, R. F. Snider, and D. G. Fleming, Phys. Rev. A **41**, 1505 (1990).