Electron spin exchange with O_2: Effects on the muon spin rotation, the electron spin resonance, and the positronium lifetime

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Electron spin exchange with spin one paramagnetic species has been investigated with particular emphasis on the cases of hydrogen ($H=p^+e^-$), Mu ($Mu=\mu^+e^-$), positronium ($Ps=e^+e^-$) colliding with O_2. The effects of spin exchange on electron spin relaxation (ESR), muon spin relaxation (μSR), and positronium lifetime measurements are described in terms of the difference in phase shifts between quartet and doublet encounters (Δ), which will allow one to interpret ESR, μSR, and positron data in a unified way and help one to understand isotope mass effects not only in spin exchange but also in chemical reactions, which often compete with spin exchange. For instance, the ESR and μSR relaxation rates in high transverse fields are expressed, in terms of the rate of collisions λ, as $\lambda_T^e=(32/27)\lambda\,\sin^2(\Delta/2)$ and $\lambda_T^\mu=(16/27)\lambda\,\sin^2(\Delta/2)$, respectively, and the so-called statistical factors, such as (32/27) and (16/27), are strong functions of the magnitude and direction of the applied field.

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I. INTRODUCTION

Electron spin exchange [1–3] is not only an interesting quantum phenomenon but also an atomic process important in many fields of science, such as astrophysics [1], biochemistry [4], plasma, and optical pumping [5–8]. The muon spin rotation (μSR) technique [9–12] has been used extensively to investigate the spin exchange [13–19] and chemical reactions [20–24] of muonium ($Mu=\mu^+e^-$), which is the bound state of the positive muon and electron with the virtually identical ionization potential as hydrogen but with only $\frac{1}{9}$ of the hydrogen mass. One of the important areas of Mu studies is isotope mass effects in atomic and chemical reactions in comparison with the corresponding hydrogen reactions. Direct comparison of μSR results with data taken by other techniques, such as electron spin resonance (ESR), has often been hindered by the lack of knowledge of the statistical factor, which is essentially the proportionality constant between the observed relaxation rate and the rate of spin exchange, appropriate for the technique used in a given magnetic field value and direction.

In this work, the μSR and ESR relaxation rates in various field configurations and the change in *ortho*-positronium lifetime due to spin exchange are expressed in terms of a proper statistical factor so that one can directly compare data obtained by different experimental techniques. The formalism used here is based on the time-ordered stochastic method originally developed for Mu spin exchange with spin-$\frac{1}{2}$ species [25] in the gas phase. This method has been applied for extremely fast spin exchange [26], spin exchange in intermediate and high fields [27], and spin exchange in spin-polarized media [28,29]. The characteristic field dependence of the muon relaxation rate in transverse fields, predicted theoretically [27], has been observed experimentally [17,30]. The treatments of spin exchange presented in [26–29] have also proven to be useful in studies of hydrogen and Mu in semiconductors [31].

In the present work, the method developed in Ref. [25] has been generalized to the case of spin-1 paramagnetic species such as O_2 in order to calculate the muon spin relaxation due to electron spin exchange as well as the relaxation of the electron spin in hydrogenlike atoms (ESR). It should be mentioned that systems containing O_2 have been extensively studied by the μSR technique [15,16,19] and systematic ESR studies of the $H+O_2$ system in various media are of current interest [32], where results are to be compared with the corresponding $Mu+O_2$ results.

II. THEORY

A. Outline

One of the main goals of this work is to calculate the time evolution of the muon spin in Mu or of the electron spin in hydrogen in the presence of electron spin exchange with O_2. Since the total electron spin of O_2 is one ($S=1$), one can classify $Mu+O_2$ and $H+O_2$ collisions according to their total electron spin, $S=1+\frac{1}{2}=\frac{3}{2}$ (quartet) and $S=1-\frac{1}{2}=\frac{1}{2}$ (doublet). The difference in interaction energy between doublet and quartet encounters is responsible for spin exchange. A spin-exchange collision is characterized by a parameter Δ representing the difference in phase shifts between doublet and quartet encounters. It is convenient to assume that the duration of a collision is much shorter than the average time between collisions. Between collisions, the Mu or H atom in question will evolve with time as free particles, obeying the time evolution dictated by the Breit-Rabi energy diagram. The polarizations of the positive muon spin, $P^\mu(t_0,t_1,\ldots,t_n,t)$, or electron spin $P^e(t_0,t_1,\ldots,t_n,t)$, in hydrogen-like atoms observed at time t after n collisions at $t_1, t_2, \ldots t_n$ are expressed in terms of (the difference in) the phase shifts for individual collisions, $\Delta_1,\Delta_2,\ldots,\Delta_n$, where t_0 is the time of Mu or H formation. In order to obtain the polarization observed at t, the quantity $P^\mu(t_0,t_1,\ldots,t_n,t)$

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or $P^e(t_0,t_1,\ldots,t_n,t)$ is averaged over the Poisson distribution of $t_1,t_2,\ldots,t_n$ for a fixed n, then over all possible n from 0 to infinity.

The hyperfine eigenstates of muonium ($\mathrm{Mu}=\mu^+e^-$), hydrogen ($\mathrm{H}=p^+e^-$), or positronium ($\mathrm{Ps}=e^+e^-$) in a magnetic field applied in the z direction are expressed by

$$|1\rangle=|\alpha_p\alpha_e\rangle, \tag{1}$$

$$|2\rangle=s|\alpha_p\beta_e\rangle+c|\beta_p\alpha_e\rangle, \tag{2}$$

$$|3\rangle=|\beta_p\beta_e\rangle, \tag{3}$$

$$|4\rangle=c|\alpha_p\beta_e\rangle-s|\beta_p\alpha_e\rangle, \tag{4}$$

where α and β denote the spin state parallel and antiparallel, respectively, to the applied field and the subscripts p and e refer to the positive particle (muon, proton, or positron) and electron, respectively. Solving for $|\alpha_p\alpha_e\rangle$, $|\alpha_p\beta_e\rangle$, $|\beta_p\alpha_e\rangle$, and $|\beta_p\beta_e\rangle$, one can write

$$|\alpha_p\alpha_e\rangle=|1\rangle, \tag{5}$$

$$|\alpha_p\beta_e\rangle=s|2\rangle+c|4\rangle, \tag{6}$$

$$|\beta_p\alpha_e\rangle=c|2\rangle-s|4\rangle, \tag{7}$$

$$|\beta_p\beta_e\rangle=|3\rangle. \tag{8}$$

Here the quantities c and s [25] are given by $c^2=(1+x/\sqrt{x^2+1})/2$ and $s^2=(1-x/\sqrt{x^2+1})/2$, respectively, in terms of the magnitude of the applied magnetic field in units of the hyperfine field, $x=B/B_0$, where B_0 for H, Mu, and Ps are $B_0=0.5059$, 1.585, and 36.28 kG, respectively, corresponding to the hyperfine frequencies $\omega_0/2\pi=1.420$, 4.463, and 203.4 GHz.

Some of the important transition energies between the ith and jth levels of the Breit-Rabi diagram, $\omega_{ij}=\omega_i-\omega_j$, are given by

$$\omega_{12}=+\omega_0/2+\omega_M-\sqrt{\omega_0^2/4+\omega_+^2}, \tag{9}$$

$$\omega_{23}=-\omega_0/2+\omega_M+\sqrt{\omega_0^2/4+\omega_+^2}, \tag{10}$$

$$\omega_{14}=+\omega_0/2+\omega_M+\sqrt{\omega_0^2/4+\omega_+^2}, \tag{11}$$

$$\omega_{34}=+\omega_0/2-\omega_M+\sqrt{\omega_0^2/4+\omega_+^2}, \tag{12}$$

$$\omega_{24}=\sqrt{\omega_0^2+4\omega_+^2}, \tag{13}$$

where $\omega_M=(\omega_e-\omega_p)/2$ and $\omega_+=(\omega_e+\omega_p)/2$ are defined in terms of the absolute values of the precession frequencies associated with the electron and positive particle (muon, proton, or positron).

B. Spin exchange

Since the O_2 molecule has an electron spin of $S=1$, the total electronic spin for the $\mathrm{Mu}+O_2$ or $\mathrm{H}+O_2$ system is $S=\frac{3}{2}$ (quartet) or $S=\frac{1}{2}$ (doublet). It is useful to write down the Clebsch-Gordan coefficients for this system [33],

$$|\tfrac{3}{2},+\tfrac{3}{2}\rangle=\alpha_e(1,1), \tag{14}$$

$$|\tfrac{3}{2},+\tfrac{1}{2}\rangle=\sqrt{1/3}\beta_e(1,1)+\sqrt{2/3}\alpha_e(1,0), \tag{15}$$

$$|\tfrac{3}{2},-\tfrac{1}{2}\rangle=\sqrt{2/3}\beta_e(1,0)+\sqrt{1/3}\alpha_e(1,-1), \tag{16}$$

$$|\tfrac{3}{2},-\tfrac{3}{2}\rangle=\beta_e(1,-1), \tag{17}$$

$$|\tfrac{1}{2},+\tfrac{1}{2}\rangle=\sqrt{2/3}\beta_e(1,1)-\sqrt{1/3}\alpha_e(1,0), \tag{18}$$

$$|\tfrac{1}{2},-\tfrac{1}{2}\rangle=\sqrt{1/3}\beta_e(1,0)-\sqrt{2/3}\alpha_e(1,-1), \tag{19}$$

where $(1,m)$ denotes the spin state of O_2 with m being the z projection; α_e and β_e are spin states of the electron in Mu (H or Ps). The inverse relations of these equations are

$$\alpha_e(1,+1)=|\tfrac{3}{2},+\tfrac{3}{2}\rangle, \tag{20}$$

$$\alpha_e(1,0)=\sqrt{2/3}|\tfrac{3}{2},+\tfrac{1}{2}\rangle-\sqrt{1/3}|\tfrac{1}{2},+\tfrac{1}{2}\rangle, \tag{21}$$

$$\alpha_e(1,-1)=\sqrt{1/3}|\tfrac{3}{2},-\tfrac{1}{2}\rangle-\sqrt{2/3}|\tfrac{1}{2},-\tfrac{1}{2}\rangle, \tag{22}$$

$$\beta_e(1,+1)=\sqrt{1/3}|\tfrac{3}{2},+\tfrac{1}{2}\rangle+\sqrt{2/3}|\tfrac{1}{2},+\tfrac{1}{2}\rangle, \tag{23}$$

$$\beta_e(1,0)=\sqrt{1/3}|\tfrac{1}{2},-\tfrac{1}{2}\rangle+\sqrt{2/3}|\tfrac{3}{2},-\tfrac{1}{2}\rangle, \tag{24}$$

$$\beta_e(1,-1)=|\tfrac{3}{2},-\tfrac{3}{2}\rangle. \tag{25}$$

The properly antisymmetrized wave function for $|\frac{3}{2},\frac{3}{2}\rangle$ is expressed by

$$|\tfrac{3}{2},\tfrac{3}{2}\rangle=\|m\alpha,g_x\alpha,g_y\alpha\|,$$

where the right-hand side is a Slater determinant constructed from $m(r_1)$, $g_x(r_2)$, and $g_y(r_3)$, i.e., from the spatial wave functions of Mu (H or Ps) and two electron orbitals in O_2. In the ground state of O_2, two electrons are coupled to a spin triplet and to zero orbital angular momentum. The $|\frac{3}{2},-\frac{1}{2}\rangle$ state can be expressed in terms of Slater determinants as

$$|\tfrac{3}{2},-\tfrac{1}{2}\rangle=\sqrt{1/3}[\|m\alpha,g_x\beta,g_y\beta\|+\|m\beta,g_x\alpha,g_y\beta\| +\|m\beta,g_x\beta,g_y\alpha\|].$$

One can verify that the expectation value of the integration energy $V(r_1,r_2,r_3)=1/r_{12}+1/r_{23}+1/r_{31}$ is a function of total spin only, i.e.,

$$\langle\tfrac{3}{2},\tfrac{3}{2}|V|\tfrac{3}{2},\tfrac{3}{2}\rangle=\langle\tfrac{3}{2},-\tfrac{1}{2}|V|\tfrac{3}{2},-\tfrac{1}{2}\rangle,$$

$$\langle\tfrac{3}{2},\tfrac{1}{2}|V|\tfrac{3}{2},\tfrac{1}{2}\rangle\neq\langle\tfrac{1}{2},\tfrac{1}{2}|V|\tfrac{1}{2},\tfrac{1}{2}\rangle,$$

where the energy difference between quartet and doublet encounters is on the order of the exchange energy

$$E_{\mathrm{ex}}(m,g_x)=\int d^3r_1\int d^3r_2 m^*(r_1)g_x^*(r_2)\frac{1}{r_{12}}m(r_2)g_x(r_1).$$

When $|1\rangle=|\alpha_\mu\alpha_e\rangle$ Mu collides with a $(1,-1)$ O_2 molecule, the properly antisymmetric wave function of the initial

TABLE I. Transition matrix T_{11}: Mu (H or Ps) spin exchange with (1,1) O_2.

	$\|1\rangle(1,1)$	$\|2\rangle(1,1)$	$\|3\rangle(1,1)$	$\|4\rangle(1,1)$
$\|1\rangle(1,1)$	1	0	0	0
$\|1\rangle(1,0)$	0	$\sqrt{2}s(1-e^{i\Delta})/3$	0	$\sqrt{2}c(1-e^{i\Delta})/3$
$\|1\rangle(1,-1)$	0	0	0	0
$\|2\rangle(1,1)$	0	$1-2s^2(1-e^{i\Delta})/3$	0	$-2cs(1-e^{i\Delta})/3$
$\|2\rangle(1,0)$	0	0	$\sqrt{2}c(1-e^{i\Delta})/3$	0
$\|2\rangle(1,-1)$	0	0	0	0
$\|3\rangle(1,1)$	0	0	$(1+2e^{i\Delta})/3$	0
$\|3\rangle(1,0)$	0	0	0	0
$\|3\rangle(1,-1)$	0	0	0	0
$\|4\rangle(1,1)$	0	$-2cs(1-e^{i\Delta})/3$	0	$1-2c^2(1-e^{i\Delta})/3$
$\|4\rangle(1,0)$	0	0	$-\sqrt{2}s(1-e^{i\Delta})/3$	0
$\|4\rangle(1,-1)$	0	0	0	0

state is expressed by $\|m\alpha,g_x\beta,g_y\beta\|$, which is a superposition of quartet and doublet parts. During the collision the quartet part accumulates a different phase from the doublet part due to the difference in interaction energy. One can investigate effects of a collision on the state $|1\rangle(1,-1)$, without manipulating Slater determinants explicitly, by simply using Eq. (22),

$$|1\rangle(1,-1)=\alpha_\mu\alpha_e(1,-1)$$
$$=\sqrt{1/3}\alpha_\mu|\tfrac{3}{2},-\tfrac{1}{2}\rangle-\sqrt{2/3}\alpha_\mu|\tfrac{1}{2},-\tfrac{1}{2}\rangle. \quad (26)$$

During the collision the $S=\frac{3}{2}$ and $S=\frac{1}{2}$ parts of Eq. (26) acquire different phases,

$$\begin{aligned}|1\rangle(1,-1)&\rightarrow\sqrt{1/3}\alpha_\mu|\tfrac{3}{2},-\tfrac{1}{2}\rangle e^{i\Delta_Q}-\sqrt{2/3}\alpha_\mu|\tfrac{1}{2},-\tfrac{1}{2}\rangle e^{i\Delta_D}\\&=\sqrt{1/3}\alpha_\mu[\sqrt{2/3}\beta_e(1,0)+\sqrt{1/3}\alpha_e(1,-1)]e^{i\Delta_Q}-\sqrt{2/3}\alpha_\mu[\sqrt{1/3}\beta_e(1,0)-\sqrt{2/3}\alpha_e(1,-1)]e^{i\Delta_D}\\&=\alpha_\mu\alpha_e(1,-1)\tfrac{1}{3}[e^{i\Delta_Q}+2e^{i\Delta_D}]+\alpha_\mu\beta_e(1,0)\frac{\sqrt{2}}{3}[e^{i\Delta_Q}-e^{i\Delta_D}]\\&=|1\rangle(1,-1)\tfrac{1}{3}[e^{i\Delta_Q}+2e^{i\Delta_D}]+(s|2\rangle+c|4\rangle)(1,0)\frac{\sqrt{2}}{3}[e^{i\Delta_Q}-e^{i\Delta_D}],\end{aligned} \quad (27)$$

where the quartet and doublet phase shifts are defined in terms of the potential energy between Mu and O_2 as [1]

$$\Delta_{D,Q}=-\int dtV_{D,Q}(r)/\hbar=-\int dr(dt/dr)V_{D,Q}(r)/\hbar.$$

Multiplying Eq. (27) by $e^{-i\Delta_Q}$, one can write down the final spin state up to an overall phase factor

$$\begin{aligned}|1\rangle(1,-1)\rightarrow&|1\rangle(1,-1)(1+2e^{i\Delta})/3\\&+|2\rangle(1,0)\sqrt{2}s(1-e^{i\Delta})/3\\&+|4\rangle(1,0)\sqrt{2}c(1-e^{i\Delta})/3.\end{aligned} \quad (28)$$

The phase shift Δ is defined by $\Delta=\Delta_D-\Delta_Q$. The first term of Eq. (28) represents the process in which the spin states of Mu and the oxygen molecule are not affected by the collision, leaving Mu still in the $|1\rangle=\alpha_\mu\alpha_e$ state. The probability of having Mu in $|1\rangle$ after a collision with a $(1,-1)$ molecule is given by the coefficient of $|1\rangle(1,-1)$,

$$|(1+2e^{i\Delta})/3|^2=1-(8/9)\sin^2(\Delta/2). \quad (29)$$

The second and third terms represent, on the other hand, the process in which the electron spin of Mu is flipped from α_e to β_e, while the molecule changes its spin state from $(1,-1)$ to (1,0). The probabilities that the Mu atom is in the state $|2\rangle$ and $|4\rangle$ after the collision are given by $|\sqrt{2}s(1-e^{i\Delta})/3|^2=s^2(8/9)\sin^2(\Delta/2)$ and $|\sqrt{2}c(1-e^{i\Delta})/3|^2=c^2(8/9)\sin^2(\Delta/2)$, respectively. Similarly, one obtains for collisions of the type $|1\rangle+(1,0)$

$$\begin{aligned}|1\rangle(1,0)\rightarrow&|1\rangle(1,0)(2+e^{i\Delta})/3+|2\rangle(1,1)\sqrt{2}s(1-e^{i\Delta})/3\\&+|4\rangle(1,1)\sqrt{2}c(1-e^{i\Delta})/3.\end{aligned}$$

The effects of oxygen collisions on the eigenstates of Mu are summarized by the transition matrices T_{11}, T_{10}, and $T_{1\text{-}1}$, listed in Tables I–III. The state $|k\rangle(1,m)$ in the top row of the tables is the initial state of Mu and O_2. The state after a collision is given by a superposition of states $|k'\rangle(1,m')$ with coefficients listed in the column below. If, for example,

TABLE II. Transition matrix T_{10}: Mu (H or Ps) spin exchange with (1,0) O_2.

	$\|1\rangle(1,0)$	$\|2\rangle(1,0)$	$\|3\rangle(1,0)$	$\|4\rangle(1,0)$
$\|1\rangle(1,1)$	0	0	0	0
$\|1\rangle(1,0)$	$(2+e^{i\Delta})/3$	0	0	0
$\|1\rangle(1,-1)$	0	$\sqrt{2}s(1-e^{i\Delta})/3$	0	$\sqrt{2}c(1-e^{i\Delta})/3$
$\|2\rangle(1,1)$	$\sqrt{2}s(1-e^{i\Delta})/3$	0	0	0
$\|2\rangle(1,0)$	0	$(2+e^{i\Delta})/3$	0	0
$\|2\rangle(1,-1)$	0	0	$\sqrt{2}c(1-e^{i\Delta})/3$	0
$\|3\rangle(1,1)$	0	$\sqrt{2}c(1-e^{i\Delta})/3$	0	$-\sqrt{2}s(1-e^{i\Delta})/3$
$\|3\rangle(1,0)$	0	0	$(2+e^{i\Delta})/3$	0
$\|3\rangle(1,-1)$	0	0	0	0
$\|4\rangle(1,1)$	$\sqrt{2}c(1-e^{i\Delta})/3$	0	0	0
$\|4\rangle(1,0)$	0	0	0	$(2+e^{i\Delta})/3$
$\|4\rangle(1,-1)$	0	0	$-\sqrt{2}s(1-e^{i\Delta})/3$	0

the Mu state $|2\rangle$ collides with a (1,0) oxygen molecule, the final state can be constructed from the column under $|2\rangle(1,0)$ in Table II as

$$|2\rangle(1,0)\rightarrow|2\rangle(1,0)(2+e^{i\Delta})/3+|1\rangle(1,-1)\sqrt{2}s(1-e^{i\Delta})/3 +|3\rangle(1,1)\sqrt{2}c(1-e^{i\Delta})/3.$$

C. Time evolution of spin states

These 12×4 matrices, T_{11}, T_{10}, and T_{1-1}, operate on an arbitrary spin state expressed in terms of eigenstates of Mu and generate the state after a collision. Suppose the spin state of Mu at initial time t_0 is given by

$$\psi(0)=x_1|1\rangle+x_2|2\rangle+x_3|3\rangle+x_4|4\rangle=\begin{bmatrix}x_1\\x_2\\x_3\\x_4\end{bmatrix}, \tag{30}$$

where ψ is normalized to unity, $|x_1|^2+|x_2|^2+|x_3|^2+|x_4|^2=1$. The subsequent time evolution of this free Mu state is given by

$$\psi(t)=\begin{bmatrix}x_1e^{-i\omega_1 t}\\x_2e^{-i\omega_2 t}\\x_3e^{-i\omega_3 t}\\x_4e^{-i\omega_4 t}\end{bmatrix},$$

where $\hbar\omega_n$ is the energy eigenvalue of the Mu state $|n\rangle$. If the first collision takes place at time t_1, the spin state immediately after the collision is given by $T_{11}\psi(t_1)$, $T_{10}\psi(t_1)$, or $T_{1\text{-}1}\psi(t_1)$, depending on the spin of the colliding O_2 molecule. The operation of T_{1m} on $\psi(t_1)$ leads to a superposition of $|n\rangle(1,k)$ with $n=1,2,3,4$ and $k=1,0,-1$ with weighting factors given the table of T_{1m}. By calculating the coefficients of $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$, one can cast the result again in the form of Eq. (30). For instance, the state $\psi(t_1)$ will become, after collision with a (1,1) molecule at t_1,

$$T_{11}\psi(t_{10})=X_1(t_{10})|1\rangle+X_2(t_{10})|2\rangle+X_3(t_{10})|3\rangle+X_4(t_{10})|4\rangle =\begin{bmatrix}X_1(t_{10})\\X_2(t_{10})\\X_3(t_{10})\\X_4(t_{10})\end{bmatrix},$$

where $t_{ij}=t_i-t_j$ with $t_0=0$ and

$$X_1(t_{10})=x_1(1,1)_1e^{-i\omega_1 t_{10}}+x_2(1,0)_1e^{-i\omega_2 t_{10}}\sqrt{2}s(1-e^{i\Delta_1})/3 +x_4(1,0)_1e^{-i\omega_4 t_{10}}\sqrt{2}c(1-e^{i\Delta_1})/3$$

$$X_2(t_{10})=x_2(1,1)_1e^{-i\omega_2 t_{10}}[1-2s^2(1-e^{i\Delta_1})/3] -x_4(1,1)_1e^{-i\omega_4 t_{10}}2cs(1-e^{i\Delta_1})/3 +x_3(1,0)_1e^{-i\omega_3 t_{10}}\sqrt{2}c(1-e^{i\Delta_1})/3$$

$$X_3(t_{10})=x_3(1,1)_1e^{-i\omega_3 t_{10}}(1+2e^{i\Delta_1})/3$$

$$X_4(t_{10})=x_4(1,1)_1e^{-i\omega_4 t_{10}}[1-2c^2(1-e^{i\Delta_1})/3] -x_2(1,1)_1e^{-i\omega_2 t_{10}}2cs(1-e^{i\Delta_1})/3 -x_3(1,0)_1e^{-i\omega_3 t_{10}}\sqrt{2}s(1-e^{i\Delta_1})/3,$$

where $(1,m)_k$ and Δ_k are the final spin state of O_2 and the phase shift, respectively, associated with the kth collision. After the first collision at t_1, this state evolves as free Mu and the spin state at t_2 after t_1 is given by

$$T_{11}(t_{21})\psi(t_{10})=\begin{bmatrix}X_1(t_{10})e^{-i\omega_1 t_{21}}\\X_2(t_{10})e^{-i\omega_2 t_{21}}\\X_3(t_{10})e^{-i\omega_3 t_{21}}\\X_4(t_{10})e^{-i\omega_4 t_{21}}\end{bmatrix}.$$

It can easily be shown that $T_{11}(t_{21})\psi(t_{10})$, $T_{10}(t_{21})\psi(t_{10})$, and $T_{1\text{-}1}(t_{21})\psi(t_{10})$ are normalized and orthogonal to each other. This procedure can be repeated to produce the spin state at t after collisions at $t_1,t_2,t_3,\ldots,t_n$ as

TABLE III. Transition matrix $T_{1\text{-}1}$: Mu (H or Ps) spin exchange with $(1,-1)$ O_2.

	$\|1\rangle(1,-1)$	$\|2\rangle(1,-1)$	$\|3\rangle(1,-1)$	$\|4\rangle(1,-1)$
$\|1\rangle(1,1)$	0	0	0	0
$\|1\rangle(1,0)$	0	0	0	0
$\|1\rangle(1,-1)$	$(1+2e^{i\Delta})/3$	0	0	0
$\|2\rangle(1,1)$	0	0	0	0
$\|2\rangle(1,0)$	$\sqrt{2}s(1-e^{i\Delta})/3$	0	0	0
$\|2\rangle(1,-1)$	0	$1-2c^2(1-e^{i\Delta})/3$	0	$2cs(1-e^{i\Delta})/3$
$\|3\rangle(1,1)$	0	0	0	0
$\|3\rangle(1,0)$	0	$\sqrt{2}c(1-e^{i\Delta})/3$	0	$-\sqrt{2}s(1-e^{i\Delta})/3$
$\|3\rangle(1,-1)$	0	0	1	0
$\|4\rangle(1,1)$	0	0	0	0
$\|4\rangle(1,0)$	$\sqrt{2}c(1-e^{i\Delta})/3$	0	0	0
$\|4\rangle(1,-1)$	0	$2cs(1-e^{i\Delta})/3$	0	$1-2s^2(1-e^{i\Delta})/3$

$$T_{1m_n}(t-t_n)T_{1m_{n-1}}(t_{n,n-1})\cdots T_{1m_2}(t_{32})T_{1m_1}(t_{21})\psi(t_{10}),$$

where the kth collision is with a $(1,m_k)$ molecule.

D. Mu in a longitudinal field

The positive muon produced in the decay of a pion at rest, $\pi^+\to\mu^++\nu_\mu$, is 100% spin-polarized. In this section, it is assumed that the initial muon spin direction is in the z direction, which is also the direction of the applied field. If the muon captures an unpolarized electron, two kinds of muon atoms are formed with equal probabilities; (1) parallel Mu or A-Mu, where the captured electron has the same spin as the muon, $\alpha_\mu\alpha_e$, and (2) antiparallel Mu or B-Mu, in which the electron is pointing in the opposite direction to the muon spin, $\alpha_\mu\beta_e$. The initial spin state of A-Mu can be written following the notation of Eq. (30),

$$\psi_A(0)=\alpha_\mu\alpha_e=|1\rangle=\begin{bmatrix}1\\0\\0\\0\end{bmatrix}.$$

After its formation at $t_0=0$, this Mu atom evolves with time as

$$\psi_A(t)=\begin{bmatrix}e^{-i\omega_1 t}\\0\\0\\0\end{bmatrix}.$$

The muon spin polarization along the z axis is obtained from the expectation value of the quantity

$$\sigma_z^\mu=\begin{bmatrix}1&0&0&0\\0&s^2-c^2&0&2cs\\0&0&-1&0\\0&2cs&0&c^2-s^2\end{bmatrix}, \tag{31}$$

where the matrix elements are calculated among the eigenstates of free Mu, $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$. One can calculate the time evolution of the muon spin in A-Mu by taking the expectation value of σ_z^μ at time t,

$$G_A^\mu(t)=\langle\psi_A(t)|\sigma_z^\mu|\psi_A(t)\rangle=1,$$

which implies that the z component of the muon spin in A-Mu is conserved in a longitudinal field, if there is no collision. Similarly, for B-Mu

$$\psi_B(0)=\alpha_\mu\beta_e=s|2\rangle+c|4\rangle=\begin{bmatrix}0\\s\\0\\c\end{bmatrix}\to\psi_B(t)=\begin{bmatrix}0\\se^{-i\omega_2 t}\\0\\ce^{-i\omega_4 t}\end{bmatrix}.$$

The muon spin polarization in B-Mu at t is

$$G_B^\mu(t)=\langle\psi_B(t)|\sigma_z^\mu|\psi_B(t)\rangle=1-4c^2s^2(1-\cos\omega_{24}t). \tag{32}$$

If the captured electron is not polarized, the average muon spin polarization in Mu is

$$G_L^\mu(t)=[G_A^\mu(t)+G_B^\mu(t)]/2=1-2c^2s^2(1-\cos\omega_{24}t). \tag{33}$$

1. Muon polarization after one collision

The spin state immediately after the first collision can be generated by calculating $T_{11}\psi_A(t_{10})$, $T_{10}\psi_A(t_{10})$, $T_{1\text{-}1}\psi_A(t_{10})$, $T_{11}\psi_B(t_{10})$, $T_{10}\psi_B(t_{10})$, and $T_{1\text{-}1}\psi_B(t_{10})$, corresponding to six distinct mutually exclusive combinations of spin orientations, $A+(1,1)$, $A+(1,0)$, $A+(1,-1)$, $B+(1,1)$, $B+(1,0)$, and $B+(1,-1)$, respectively. For example, the state of originally A-Mu colliding with a (1,1) molecule at time t_1 is given by

$$T_{11}\psi_A(t_{10})=\begin{bmatrix}(1,1)_1e^{-i\omega_1t_{10}}\\0\\0\\0\end{bmatrix},$$

where the symbol $(1,m)_1$ denotes the final spin state of the molecule involved in the first collision. The time evolution of free Mu after t_1 is

$$T_{11}(t_{21})\psi_A(t_{10})=\begin{bmatrix}(1,1)_1e^{-i\omega_1t_{10}}e^{-i\omega_1t_{21}}\\0\\0\\0\end{bmatrix}.$$

The corresponding time evolution of the muon spin in Mu is calculated from the expectation value of σ_z^μ,

$$\langle\psi_A(t_{10})T_{11}(t_{21})|\sigma_z^\mu|T_{11}(t_{21})\psi_A(t_{10})\rangle=1,$$

which implies the muon spin in A-Mu is completely preserved after a collision with a (1,1) molecule.

If the first collision partner of A-Mu is a (1,0) molecule,

$$T_{10}(t_{21})\psi_A(t_{10})=\begin{bmatrix}(1,0)_1e^{-i\omega_1t_{10}}e^{-i\omega_1t_{21}}(2+e^{i\Delta_1})/3\\(1,1)_1e^{-i\omega_1t_{10}}e^{-i\omega_2t_{21}}\sqrt{2}s(1-e^{i\Delta_1})/3\\0\\(1,1)_1e^{-i\omega_1t_{10}}e^{-i\omega_4t_{21}}\sqrt{2}c(1-e^{i\Delta_1})/3\end{bmatrix}.$$

The muon polarization at t_2 is

$$\langle\psi_A(t_{10})T_{10}(t_{21})|\sigma_z^\mu|T_{10}(t_{21})\psi_A(t_{10})\rangle$$
$$=1-2c^2s^2(16/9)\sin^2(\Delta/2)(1-\cos\omega_{24}t_{21}).$$

Similarly for $A+(1,-1)$,

$$T_{1\text{-}1}(t_{21})\psi_A(t_{10})$$
$$=\begin{bmatrix}(1,-1)_1e^{-i\omega_1t_{10}}e^{-i\omega_1t_{21}}[1-2(1-e^{i\Delta_1})/3]\\(1,0)_1e^{-i\omega_1t_{10}}e^{-i\omega_2t_{21}}\sqrt{2}s(1-e^{i\Delta_1})/3\\0\\(1,0)_1e^{-i\omega_1t_{10}}e^{-i\omega_4t_{21}}\sqrt{2}c(1-e^{i\Delta_1})/3\end{bmatrix},$$

$$\langle\psi_A(t_{10})T_{1\text{-}1}(t_{21})|\sigma_z^\mu|T_{1-1}(t_{21})\psi_A(t_{10})\rangle$$
$$=1-2c^2s^2(16/9)\sin^2(\Delta/2)(1-\cos\omega_{24}t_{21}).\quad(34)$$

It is interesting to note that (1,0) and $(1,-1)$ molecules have the same effect on A-Mu.

If the electrons of O_2 are unpolarized, i.e., A-Mu collides with (1,1), (1,0), and $(1,-1)$ molecules with equal probabilities, the average muon spin polarization in A-Mu observed at t_2 after a collision at t_1 as

$$P_A^\mu(t_0,t_1,t_2)$$
$$=\frac{1}{3}\sum_{m=1,0,-1}\langle\psi_A(t_{10})T_{1m}(t_{21})|\sigma_z^\mu|T_{1m}(t_{21})\psi_A(t_{10})\rangle$$
$$=\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_A^\mu(t_{20})$$
$$+\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_L^\mu(t_{21})G_A^\mu(t_{10}).\quad(35)$$

Similarly, for B-Mu one obtains

$$P_B^\mu(t_0,t_1,t_2)=\frac{1}{3}\sum_{m=1,0,-1}\langle\psi_B(t_{10})T_{1m}(t_{21})|\sigma_z^\mu|T_{1m}(t_{21})\psi_B(t_{10})\rangle$$
$$=\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_B^\mu(t_{20})+\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_L^\mu()t_{21})G_B^\mu(t_{10}).\quad(36)$$

Assuming that all possible combinations of spin states, $A+(1,1)$, $A+(1,0)$, $A+(1,-1)$, $B+(1,1)$, $B+(1,0)$, and $B+(1,-1)$ take place with the same probabilities, i.e., the electrons of Mu and of O_2 are unpolarized, one can write the average muon spin polarization in Mu observed at t_2 after a collision at t_1 as

$$P_L^\mu(t_0,t_1,t_2)=\frac{1}{6}\sum_{M=A,B}\sum_{m=1,0,-1}\langle\psi_M(t_{10})T_{1m}(t_{21})|\sigma_z^\mu|T_{1m}(t_{21})\psi_M(t_{10})\rangle$$
$$=\frac{1}{2}[P_A^\mu(t_0,t_1,t_2)+P_B^\mu(t_0,t_1,t_2)]$$
$$=\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_L^\mu(t_{20})+\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_L^\mu(t_{21})G_L^\mu(t_{10}).\quad(37)$$

2. *Muon polarization after n collisions*

The spin state at t_3 of originally A-Mu colliding with (11) at time t_1 followed by a collision with (1,0) at t_2 can explicitly be written as

$$T_{10}(t_{32})T_{11}(t_{21})\psi_A(t_{10})=\begin{bmatrix}(1,1)_1(1,0)_2e^{-i\omega_1 t_{20}}e^{-i\omega_1 t_{32}}(2+e^{i\Delta_2})/3\\(1,1)_1(1,1)_2e^{-i\omega_1 t_{20}}e^{-i\omega_2 t_{32}}\sqrt{2}s(1-e^{i\Delta_2})/3\\0\\(1,1)_1(1,1)_2e^{-i\omega_1 t_{20}}e^{-i\omega_4 t_{32}}\sqrt{2}c(1-e^{i\Delta_2})/3\end{bmatrix},$$

where the subscript in $(1,m)_k$ denotes the final spin state of the kth colliding molecule. The muon spin polarization at t_3 is calculated to be

$$\langle\psi_A(t_{10})T_{11}(t_{21})T_{10}(t_{32})|\sigma_z^\mu|T_{10}(t_{32})T_{11}(t_{21})\psi_A(t_{10})\rangle=1-2c^2s^2(16/9)\sin^2(\Delta_2/2)(1-\cos\omega_{24}t_{32}). \tag{38}$$

The muon spin polarization in Mu at t_3 after two collisions at t_1 and t_2 averaged over all possible spin directions (18 in total) is

$$\begin{aligned}P_L^\mu(t_0,t_1,t_2,t_3)&=\frac{1}{18}\sum_{M=A,B}\sum_{k=1,0,-1}\sum_{m=1,0,-1}\langle\psi_M(t_{10})T_{1m}(t_{21})T_{1k}(t_{32})|\sigma_z^\mu|T_{1k}(t_{32})T_{1m}(t_{21})\psi_M(t_{10})\rangle\\&=\left[1-\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_L^\mu(t_{30})+\left[1-\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_L^\mu(t_{31})G_L^\mu(t_{10})\\&\quad+\left[\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_L^\mu(t_{32})G_L^\mu(t_{20})+\left[\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_L^\mu(t_{32})G_L^\mu(t_{21})G_L^\mu(t_{10}).\end{aligned} \tag{39}$$

In general, the muon spin polarization observed at time t after n collisions at $t_1,t_2,t_3,\ldots,t_n$ can be written symbolically by

$$\begin{aligned}P_L^\mu(t_0,t_1,t_2,\ldots,t_n,t)&\\=G_L^\mu(t-t_n)\prod_{k=1}^{n}&\left\{G_L^\mu(t_{k,k-1})\left[\frac{32}{27}\sin^2\frac{\Delta_k}{2}\right]\right.\\&\left.+G_L^\mu|t_{k,k-1})\left[1-\frac{32}{27}\sin^2\frac{\Delta_k}{2}\right]\right\},\end{aligned} \tag{40}$$

where $G_L^\mu(t_{32})G_L^\mu|t_{21})G_L^\mu|t_{10})=G_L^\mu(t_{31})G_L^\mu|t_{10})=G_L^\mu(t_{30})$.

E. Mu in a transverse field

In this section, the initial muon spin polarization is assumed in the positive x axis, where the applied magnetic field is still in the z direction. If the muon captures an unpolarized electron, two kinds of Mu atoms are formed with the same probabilities; (1) A-Mu, where the spin of the captured electron is in the positive x direction, and (2) B-Mu in which the electron spin is pointing in the negative x direction.

Since the spin pointing in the x direction [25] is represented by $(\alpha+\beta)/\sqrt{2}$, the spin state of A-Mu at the time of its formation ($t=0$) is expressed by

$$\phi_A(0)=\frac{1}{\sqrt{2}}(\alpha_\mu+\beta_\mu)\frac{1}{\sqrt{2}}(\alpha_e+\beta_e). \tag{41}$$

Using Eqs. (5)–(8), one can rewrite $\phi_A(0)$ in terms of the eigenstates of Mu $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$,

$$\phi_A(0)=\tfrac{1}{2}(|1\rangle+(c+s)|2\rangle+|3\rangle+(c-s)|4\rangle)=\tfrac{1}{2}\begin{bmatrix}1\\c+s\\1\\c-s\end{bmatrix}. \tag{42}$$

The A-Mu state at time t is given by

$$\phi_A(t)=\tfrac{1}{2}\begin{bmatrix}e^{-i\omega_1 t}\\(c+s)e^{-i\omega_2 t}\\e^{-i\omega_3 t}\\(c-s)e^{-i\omega_4 t}\end{bmatrix}. \tag{43}$$

It is convenient to define the complex muon polarization [25] in such a way that the real and imaginary parts correspond to the x and y components, respectively,

$$\sigma_+^\mu=\sigma_x^\mu+i\sigma_y^\mu=2\begin{bmatrix}0&c&0&-s\\0&0&s&0\\0&0&0&0\\0&0&c&0\end{bmatrix}, \tag{44}$$

where the bases for the matrix are the free Mu eigenstates $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$. One can derive the time evolution of the muon spin in A-Mu by calculating the expectation value of σ_+^μ at time t,

$$G_A^\mu(t)=\langle \phi_A(t)|\sigma_+^\mu|\phi_A(t)\rangle$$
$$=\tfrac{1}{2}[c(c+s)e^{i\omega_{12}t}+s(c+s)e^{i\omega_{23}t}$$
$$+c(c-s)e^{-i\omega_{34}t}+s(s-c)e^{i\omega_{14}t}]. \quad (45)$$

The electron spin pointing in the negative x direction is represented by $(-\alpha_e+\beta_e)/\sqrt{2}$. Therefore, for B-Mu,

$$\phi_B(0)=\frac{1}{\sqrt{2}}(\alpha_\mu+\beta_\mu)\frac{1}{\sqrt{2}}(-\alpha_e+\beta_e)\rightarrow\phi_B(t)$$
$$=\frac{1}{2}\begin{bmatrix} -e^{-i\omega_1 t} \\ (s-c)e^{-i\omega_2 t} \\ e^{-i\omega_3 t} \\ (c+s)e^{-i\omega_4 t}\end{bmatrix}.$$

The time evolution of the muon spin in B-Mu is

$$G_B^\mu(t)=\langle \phi_B(t)|\sigma_+^\mu|\phi_B(t)\rangle$$
$$=\tfrac{1}{2}[c(c-s)e^{i\omega_{12}t}+s(s-c)e^{i\omega_{23}t}$$
$$+c(c+s)e^{-i\omega_{34}t}+s(s+c)e^{i\omega_{14}t}]. \quad (46)$$

If the captured electrons are not polarized, the average time evolution of the muon spin in Mu is expressed by

$$G_T^\mu(t)=\tfrac{1}{2}[G_A^\mu(t)+G_B^\mu(t)]=(c^2/2)[e^{i\omega_{12}t}+e^{-i\omega_{34}t}]$$
$$+(s^2/2)[e^{i\omega_{23}t}+e^{i\omega_{14}t}]. \quad (47)$$

In the exact same manner as in the case of a longitudinal field, the muon spin polarization at t_2 of A-Mu after one collision at t_1 with a $(1,m)$ molecule can be calculated as

$$\langle \phi_A(t_{10})T_{1m}(t_{21})|\sigma_+^\mu|T_{1m}(t_{21})\phi_A(t_{10})\rangle .$$

Assuming six types of collisions, $A+(1,1)$, $A+(1,0)$, $A+(1,-1)$, $B+(1,1)$, $B+(1,0)$, and $B+(1,-1)$, occur with the same probabilities, one can write the muon spin polarization in Mu observed at t_2 after a collision at t_1 as

$$P_T^\mu(t_0,t_1,t_2)=\frac{1}{6}\sum_{M=A,B}\sum_{m=1,0,-1}$$
$$\times\langle \phi_M(t_{10})T_{1m}(t_{21})|\sigma_+^\mu|T_{1m}(t_{21})\phi_M(t_{10})\rangle$$
$$=\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_T^\mu(t_{20})$$
$$+\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_T^\mu(t_{21})G_T^\mu(t_{10}). \quad (48)$$

The muon spin polarization in Mu at t_3 after two collisions at t_1 and t_2 is

$$P_T^\mu(t_0,t_1,t_2,t_3)=\frac{1}{18}\sum_{M=A,B}\sum_{k=1,0,-1}\sum_{m=1,0,-1}\langle \phi_M(t_{10})T_{1m}(t_{21})T_{1k}(t_{32})|\sigma_+^\mu|T_{1k}(t_{32})T_{1m}(t_{21})\phi_M(t_{10})\rangle$$
$$=\left[1-\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_T^\mu(t_{30})$$
$$+\left[1-\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_T^\mu(t_{31})G_T^\mu(t_{10})+\left[\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_T^\mu(t_{32})G_T^\mu(t_{20})$$
$$+\left[\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_T^\mu(t_{32})G_T^\mu(t_{21})G_T^\mu(t_{10}). \quad (49)$$

It is tedious but straightforward to show that the muon polarization at t after n collisions at $t_1,t_2,t_3,\ldots,t_n$ can be written as

$$P_T^\mu(t_0,t_1,t_2,\ldots,t_n,t)$$
$$=G_T^\mu(t-t_n)\prod_{k=1}^{n}\left\{G_T^\mu(t_{k,k-1})\left[\frac{32}{27}\sin^2\frac{\Delta_k}{2}\right]\right.$$
$$\left.+G_T^\mu|t_{k,k-1})\left[1-\frac{32}{27}\sin^2\frac{\Delta_k}{2}\right]\right\}, \quad (50)$$

where $G_T^\mu(t_{32})G_T^\mu|t_{21})G_T^\mu|t_{10})=G_T^\mu(t_{31})G_T^\mu|t_{10})=G_T^\mu(t_{30})$.

F. Electron spin polarization in H atoms

In this section the electron polarization in H atoms in the presence of spin exchange with O_2 is investigated. The arguments in the preceding sections can be applied to H atoms with trivial substitutions in the Larmor precession and hyperfine frequency, i.e., $\omega_\mu\rightarrow\omega_p$ and $\omega_0/2\pi=4.463\rightarrow1.420$ GHz.

The situation considered here is that the electron spin in H is polarized in the positive x axis at $t_0=0$ by, for instance, a 90° pulse, while the proton spin is assumed to be random. Parallel and antiparallel hydrogen atoms have wave functions given by

$$\phi_A(0)=\frac{1}{\sqrt{2}}(\alpha_p+\beta_p)\frac{1}{\sqrt{2}}(\alpha_e+\beta_e)\rightarrow\phi_A(t)$$

$$=\frac{1}{2}\begin{bmatrix} e^{-i\omega_1 t} \\ (c+s)e^{-i\omega_2 t} \\ e^{-i\omega_3 t} \\ (c-s)e^{-i\omega_4 t}\end{bmatrix},$$

$$\phi_B(0)=\frac{1}{\sqrt{2}}(-\alpha_p+\beta_p)\frac{1}{\sqrt{2}}(\alpha_e+\beta_e)\rightarrow\phi_B(t)$$

$$=\frac{1}{2}\begin{bmatrix} -e^{-i\omega_1 t} \\ (c-s)e^{-i\omega_2 t} \\ e^{-i\omega_3 t} \\ -(c+s)e^{-i\omega_4 t}\end{bmatrix}.$$

The complex polarization of the electron spin in H is

$$\sigma_+^e=\sigma_x^e+i\sigma_y^e=2\begin{bmatrix} 0 & s & 0 & c \\ 0 & 0 & c & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & -s & 0\end{bmatrix}. \tag{51}$$

The time dependences of the electron spin in free A and B hydrogen are calculated in a straightforward manner as

$$G_A^e(t)=\langle\phi_A(t)|\sigma_+^e|\phi_A(t)\rangle$$
$$=\tfrac{1}{2}[s(c+s)e^{i\omega_{12}t}+c(c+s)e^{i\omega_{23}t}+c(c-s)e^{i\omega_{14}t}+s(s-c)e^{-i\omega_{34}t}],$$

$$G_B^e(t)=\langle\phi_B(t)|\sigma_+^e|\phi_B(t)\rangle$$
$$=\tfrac{1}{2}[s(s-c)e^{i\omega_{12}t}+c(c-s)e^{i\omega_{23}t}+c(c+s)e^{i\omega_{14}t}+s(c+s)e^{-i\omega_{34}t}].$$

If O_2 spins are not polarized, the average electron spin polarization in H is given by

$$G_T^e(t)=\tfrac{1}{2}[G_A^e(t)+G_B^e(t)]$$
$$=(s^2/2)[e^{i\omega_{12}t}+e^{-i\omega_{34}t}]+(c^2/2)[e^{i\omega_{23}t}+e^{i\omega_{14}t}]. \tag{52}$$

Following the same chain of argument as in the case of muon polarization, one can write the average spin polarization of the electron in H at t_2 after a collision at t_1 as

$$P_T^e(t_0,t_1,t_2)=\frac{1}{6}\sum_{M=A,B}\sum_{m=1,0,-1}\langle\phi_M(t_{10})T_{1m}(t_{21})|\sigma_+^e|T_{1m}(t_{21})\phi_M(t_{10})\rangle$$
$$=\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_T^e(t_{20})+\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]g_T^e(t_{21})g_T^e(t_{10}), \tag{53}$$

where the quantity $g_T^e(t)$ is given by

$$g_T^e(t)=\tfrac{1}{2}[G_A^e(t)-G_B^e(t)]=(cs/2)[e^{i\omega_{12}t}+e^{i\omega_{23}t}-e^{-i\omega_{34}t}-e^{i\omega_{14}t}]. \tag{54}$$

The electron spin polarization after two collisions at t_1 and t_2 can be expressed by

$$P_T^e(t_0,t_1,t_2,t_3)=\frac{1}{18}\sum_{M=A,B}\sum_{k=1,0,-1}\sum_{m=1,0,-1}\langle\phi_M(t_{10})T_{1m}(t_{21})T_{1k}(t_{32})|\sigma_+^e|T_{1k}(t_{32})T_{1m}(t_{21})\phi_M(t_{10})\rangle$$
$$=\left[1-\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]G_T^e(t_{30})+\left[1-\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]g_T^e(t_{31})g_T^e(t_{10})$$
$$+\left[\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[1-\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]g_T^e(t_{32})g_T^e(t_{20})+\left[\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right]\left[\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]g_T^e(t_{32})g_T^e(t_{21})g_T^e(t_{10}). \tag{55}$$

The expression after n collisions becomes

$$P_T^e(t_0,t_1,t_2,\ldots,t_n,t)=\prod_{k=1}^{n}\left[1-\frac{32}{27}\sin^2\frac{\Delta_k}{2}\right][G_T^e(t)-g_T^e(t)]$$
$$+g_T^e(t-t_n)\prod_{k=1}^{n}\left\{g_T^e(t_{k,k-1})\left[\frac{32}{27}\sin^2\frac{\Delta_k}{2}\right]+g_T^e|t_{k,k-1})\left[1-\frac{32}{27}\sin^2\frac{\Delta_k}{2}\right]\right\}, \tag{56}$$

where $g_T^\mu(t_{32})g_T^\mu|t_{21})g_T^\mu|t_{10})=g_T^\mu(t_{31})g_T^\mu|t_{10})=g_T^\mu(t_{30})$.

III. STATISTICAL AVERAGE

The quantity $P(t_0,t_1,t_2,\ldots,t_n,t)$ denotes the polarization in question at t after n collisions at $t_1,t_2,\ldots,t_n$. The experimentally observed polarization at t is obtained [28] by averaging over all possible time distributions of $t_1,t_2,t_3,\ldots t_n$ and over the number of collisions between $t_0=0$ and the time of observation t,

$$P(t)=\sum_{n=0}^{\infty}\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^{t}dt_n f(t_0,t_1,\ldots,t_n,t)\times P(t_0,t_1,\ldots,t_n,t), \tag{57}$$

where $f(t_0,t_1,t_2,\ldots,t_n,t)$ is the probability density that n collisions between $t_0=0$ and t take place at $t_1,t_2,\ldots t_n$. The derivation and properties of $f(t_0,t_1,t_2,\ldots,t_n,t)$ for several representative Markovian processes have been discussed in Refs. [28,34]. In this work, it is assumed that the collision is Poissonian, where the probability density is simply given by $f(t_0,t_1,t_2,\ldots,t_n,t)=\lambda^n\exp(-\lambda t)$. The quantity λ, which can be expressed in terms of the number density of O_2 (n), the relative velocity (v), and the collision cross section (σ) as $\lambda=nv\sigma$, is the encounter rate of Mu (or H) and O_2, i.e., the average rate of collisions, regardless of whether collisions are of spin flip or spin nonflip type. In this case Eq. (57) can be simplified to

$$P(t)=\sum_{n=0}^{\infty}\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^{t}dt_n e^{-\lambda t}\lambda^n\times P(t_0,t_1,\ldots,t_n,t). \tag{58}$$

A. Muon spin relaxation

In this section, the statistically averaged muon spin polarization is calculated using Eq. (58) in longitudinal and transverse fields. The muon spin-relaxation rate observed in each case is expressed in terms of the phase shift Δ and the rate of collisions λ.

1. Longitudinal field

The time evolution function $G_L^\mu(t)$ in Eq. (33) contains a term proportional to $\cos\omega_{24}t$ which oscillates, at least, at the Mu hyperfine frequency. Since the Mu hyperfine period ($2\pi/\omega_0=0.22$ ns) is much shorter than the typical time resolution of the conventional μSR apparatus, the term $\cos\omega_{24}t$ can be ignored as long as the collision rate is much less than ω_{24} [27]. In this case the time evolution function $G_L(t)$ can be simplified to

$$G_L^\mu(t)=1-2c^2s^2=(2x^2+1)/(2x^2+2). \tag{59}$$

Substituting Eq. (59) into Eqs. (37), (39), and (40), one obtains

$$P_L^\mu(t_0,t_1,t)=(1-2c^2s^2)\left[1-2c^2s^2\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right],$$

$$P_L^\mu(t_0,t_1,t_2,t)=(1-2e^2s^2)\left[1-2c^2s^2\frac{32}{27}\sin^2\frac{\Delta_1}{2}\right]\times\left[1-2c^2s^2\frac{32}{27}\sin^2\frac{\Delta_2}{2}\right],$$

$$P_L^\mu(t_0,t_1,t_2,\ldots,t_n,t)=(1-2c^2s^2)\prod_{k=1}^{n}\left[1-2c^2s^2\frac{32}{27}\sin^2\frac{\Delta_k}{2}\right]=(1-2c^2s^2)\left[1-2c^2s^2\frac{32}{27}\sin^2\frac{\Delta}{2}\right]^n, \tag{60}$$

where Δ is an average value of $\Delta_1,\Delta_2,\ldots,\Delta_n$. In this case the integrand of Eq. (58) is independent of $t_1,t_2,\ldots,t_n$ and the n-fold time integral simply gives $t^n/n!$. Thus,

$$P_L^\mu(t)=(1-2c^2s^2)\sum_{n=0}^{\infty}\left\{e^{-\lambda t}\frac{(\lambda t)^n}{n!}\right\}\times\left[1-2c^2s^2\frac{32}{27}\sin^2\frac{\Delta}{2}\right]^n. \tag{61}$$

The quantity in { } is the Poisson probability that there are exactly n collisions between $t_0=0$ and t. The summation over n can be calculated in a straightforward manner using $e^x=\Sigma x^n/n!$, which leads to

$$P_L^\mu(t)=(1-2c^2s^2)\exp\left[-2c^2s^2\frac{32}{27}\lambda\left(\sin^2\frac{\Delta}{2}\right)t\right]. \tag{62}$$

The observed muon spin-relaxation rate is expressed in terms of Δ as

$$\lambda_L^\mu=2c^2s^2\frac{32}{27}\lambda\sin^2\frac{\Delta}{2}=\frac{\lambda}{(1+x^2)}\frac{16}{27}\sin^2\frac{\Delta}{2}. \tag{63}$$

2. Weak transverse field

In a field of less than $B=10$ G, where $c^2\approx s^2\approx\frac{1}{2}$ and $\omega_{12}\approx\omega_{23}$, the time evolution function $G_T(t)$ can be simplified as

TABLE IV. Transition probability matrix K_{11}: spin exchange with a (1,1) O_2 molecule. The states $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$ on the top of the table are the initial Mu (H or Ps) states before a collision. The four numbers in the column below each $|n\rangle$ represent the probabilities of Mu being in a particular Mu eigenstate regardless of final O_2 spin states after a collision with (1,1).

	$\|1\rangle(1,1)$	$\|2\rangle(1,1)$	$\|3\rangle(1,1)$	$\|4\rangle(1,1)$
$\|1\rangle$	1	$s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	0	$c^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$
$\|2\rangle$	0	$1-s^2(1+2c^2)\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$c^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$2c^2s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$
$\|3\rangle$	0	0	$1-\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	0
$\|4\rangle$	0	$2c^2s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$1-c^2(1+2s^2)\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$

$$G_T(t)=\tfrac{1}{2}(e^{i\omega_M t}+\cos\omega_0 t). \tag{64}$$

The quantity ω_M is the precession frequency of triplet Mu given by $\omega_M=(\omega_e-\omega_\mu)/2$. The fast-oscillating term $\cos\omega_0 t$ can be ignored as long as the collision rate is much less than ω_0 [27]. Substituting $G_T(t)=\frac{1}{2}e^{i\omega_M t}$ in Eqs. (48)–(50), one can easily verify

$$P_T^\mu(t_0,t_1,t)=\frac{1}{2}e^{i\omega_M t}\left[1-\frac{16}{27}\sin^2\frac{\Delta_1}{2}\right], \tag{65}$$

$$P_T^\mu(t_0,t_1,t_2,t)=\frac{1}{2}e^{i\omega_M t}\left[1-\frac{16}{27}\sin^2\frac{\Delta_1}{2}\right]\left[1-\frac{16}{27}\sin^2\frac{\Delta_2}{2}\right], \tag{66}$$

$$P_T^\mu(t_0,t_1,t_2,\ldots,t_n,t)=\frac{1}{2}e^{i\omega_M t}\prod_{k=1}^{n}\left[1-\frac{16}{27}\sin^2\frac{\Delta_k}{2}\right]$$
$$=\frac{1}{2}e^{i\omega_M t}\left[1-\frac{16}{27}\sin^2\frac{\Delta}{2}\right]^n. \tag{67}$$

The integration in Eq. (58) can be carried out to give

$$P_T^\mu(t)=\frac{1}{2}e^{i\omega_M t}\sum_{n=0}^{\infty}\left\{e^{-\lambda t}\frac{(\lambda t)^n}{n!}\right\}\left[1-\frac{16}{27}\sin^2\frac{\Delta}{2}\right]^n. \tag{68}$$

One can carry out the summation with respect to the number of collisions,

$$P_T^\mu(t)=\tfrac{1}{2}e^{i\omega_M t}\exp[-\tfrac{16}{27}\lambda(\sin^2\Delta/2)t]. \tag{69}$$

The observed relaxation rate is expressed in terms of Δ as

$$\lambda_T^\mu=\tfrac{16}{27}\lambda\sin^2(\Delta/2). \tag{70}$$

3. *Intermediate transverse field*

If the applied field is such that $20<B\ll B_0=1.585$ kG, one observes the beating of two Mu frequencies ω_{12} and ω_{23},

$$G_T^\mu(t)=\tfrac{1}{4}(e^{i\omega_{12}t}+e^{i\omega_{23}t}+2\cos\omega_0 t). \tag{71}$$

If the two frequencies are well separated in the sense that the quantity $(\omega_{23}-\omega_{12})t$ is much larger than unity at a typical time of observation (e.g., $t=1$ μs), all the terms involving the frequency difference, $\exp[i(\omega_{23}-\omega_{12})t_{ij}]$, will vanish upon integration [27,28]. Substituting Eq. (71) in Eq. (50) and ignoring the fast hyperfine oscillation, one obtains

$$P_T^\mu(t_0,t_1,t_2,\ldots,t_n,t)=\tfrac{1}{4}(e^{i\omega_{12}t}+e^{i\omega_{23}t})\times[1-\tfrac{8}{9}\sin^2(\Delta/2)]^n. \tag{72}$$

The statistical average can easily be carried out,

TABLE V. Transition probability matrix K_{10}: spin exchange with a (1,0) O_2 molecule.

	$\|1\rangle(1,0)$	$\|2\rangle(1,0)$	$\|3\rangle(1,0)$	$\|4\rangle(1,0)$
$\|1\rangle$	$1-\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	0	$c^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$
$\|2\rangle$	$s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$1-\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$c^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	0
$\|3\rangle$	0	$c^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$1-\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$
$\|4\rangle$	$c^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	0	$s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$1-\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$

$$P_T^\mu(t)=\tfrac{1}{4}(e^{i\omega_{12}t}+e^{i\omega_{23}t})\exp[-\tfrac{8}{9}\lambda\sin^2(\Delta/2)t]. \quad (73)$$

The two precession frequencies relax with the same rate,

$$\lambda_T^\mu=\tfrac{8}{9}\lambda\sin^2(\Delta/2). \quad (74)$$

This value is 1.5 times higher than the low-field value.

4. High transverse field

In high fields $B \gg B_0=1.585$ kG, where $c=1$ and $s=0$, one can simplify $G_T(t)$ as

$$G_T^\mu(t)=\tfrac{1}{2}(e^{i\omega_{12}t}+e^{-i\omega_{34}t}). \quad (75)$$

In this case, one obtains

$$P_T^\mu(t_0,t_1,t_2,\ldots,t_n,t)=\tfrac{1}{2}(e^{i\omega_{12}t}+e^{-i\omega_{34}t})\times[1-\tfrac{16}{27}\sin^2(\Delta/2)]^n. \quad (76)$$

Therefore,

$$P_T^\mu(t)=\tfrac{1}{2}(e^{i\omega_{12}t}+e^{-i\omega_{34}t})\exp[-\tfrac{16}{27}\lambda(\sin^2\Delta/2)t]. \quad (77)$$

The relaxation rate in a high field is

$$\lambda_T^\mu=\tfrac{16}{27}\lambda\sin^2(\Delta/2). \quad (78)$$

B. Electron spin relaxation in a high transverse field

In this section, the case of a high field is considered where most ESR measurements are performed. If $B \gg B_0=0.5059$ kG, where $c\approx 1$ and $s\approx 0$, the quantities $G_T^e(t)$ and $g_T^e(t)$ are simplified, respectively, to

$$G_T^e(t)=\tfrac{1}{2}[e^{i\omega_{23}t}+e^{i\omega_{14}t}] \text{ and } g_T^e(t)=0.$$

In this case, $P_T^e(t_0,t_1,t_2,\ldots t_n,t)$ can be expressed by

$$P_T^e(t_0,t_1,t_2,\ldots,t_n,t)=\tfrac{1}{2}[e^{i\omega_{23}t}+e^{i\omega_{14}t}]\times[1-\tfrac{32}{27}\sin^2(\Delta/2)]^n.$$

The averaged electron polarization at t is calculated from Eq. (58) as

$$P_T^e(t)=\tfrac{1}{2}[e^{i\omega_{23}t}+e^{i\omega_{14}t}]\sum_{n=0}^{\infty}\left\{e^{-\lambda t}\frac{(\lambda t)^n}{n!}\right\}\times[1-\tfrac{32}{27}\sin^2(\Delta/2)]^n$$
$$=\tfrac{1}{2}[e^{i\omega_{23}t}+e^{i\omega_{14}t}]\exp[-\tfrac{32}{27}\lambda(\sin^2\Delta/2)t], \quad (79)$$

where the observed relaxation rate of the electron spin is

$$\lambda_T^e=\tfrac{32}{27}\lambda\sin^2(\Delta/2). \quad (80)$$

C. Renormalized encounter rate

Equations (37) and (48) give an interesting insight into the nature of spin exchange with O_2. If $\sin^2(\Delta_1/2)=0$, the muon spin polarization at t_2 is simply given by $P(t_0,t_1,t_2)=G(t_{20})$, indicating that the collision at t_1 has no effect at all on the muon spin at t_2. The situation $\sin^2(\Delta_k/2)=0$, therefore, can be regarded as the case where the kth collision is of pure spin nonflip type. If $\sin^2(\Delta_1/2)=\frac{27}{32}$, on the other hand, the spin nonflip term vanishes and the polarization at t_3 is given by a simple product of $G(t)$'s, i.e., $P(t_0,t_1,t_2)=G(t_{21})G(t_{10})$. It has been shown [25,28] that the product $G(t_{21})G(t_{10})$ represents a spin-flip collision at t_1. This is in contrast to the case of Mu spin exchange with spin-$\frac{1}{2}$ species, where $\sin^2(\Delta/2)=1$ corresponds to pure spin flip. For general values of Δ, the observed polarization at t_2 is a superposition of spin-nonflip and spin-flip terms, i.e., $G(t_{20})$ and $G(t_{21})G(t_{10})$, with appropriate weighting factors, $1-\frac{32}{27}\sin^2(\Delta/2)$ and $\frac{32}{27}\sin^2(\Delta/2)$, respectively. The second term in Eq. (39) or (49) represents the process where the first and second collisions are, respectively, of spin-flip and spin-nonflip type. Such a term depends on t_1 but not on t_2, reflecting the fact that the spin-nonflip collision at t_2 has no effect on spin dynamics of the muon and electron. If the collision process is Poissonian, one can carry out all the time integrals with respect to the times associated with spin-nonflip collisions in Eq. (58) so that the result is expressed in terms of the times associated with spin-flip collisions only. Following the procedure described in Ref. [28] for Mu spin exchange with spin-$\frac{1}{2}$ species, one can eliminate all the dependences on the spin-nonflip times from $P(t)$. The result for the muon spin polarization in a transverse or longitudinal field is

TABLE VI. Transition probability K_{1-1}: spin exchange with a $(1,-1)$ O_2 molecule.

	$\|1\rangle(1,-1)$	$\|2\rangle(1,-1)$	$\|3\rangle(1,-1)$	$\|4\rangle(1,-1)$
$\|1\rangle$	$1-\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	0	0	0
$\|2\rangle$	$s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$1-c^2(1+2s^2)\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	0	$2c^2s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$
$\|3\rangle$	0	$c^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	1	$s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$
$\|4\rangle$	$c^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	$2c^2s^2\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$	0	$1-s^2(1+2c^2)\frac{8}{9}\sin^2\left(\frac{\Delta}{2}\right)$

$$P^{\mu}(t)=\sum_{m=0}^{\infty}\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^{t}dt_m e^{-\lambda_{SF}t}\lambda_{SF}^m \times P^{\mu}\{t_0,t_1,\ldots,t_m,t\}, \quad (81)$$

where λ_{SF} is the renormalized encounter rate given by

$$\lambda_{SF}=\lambda\tfrac{32}{27}\sin^2(\Delta/2), \quad (82)$$

which is a measure of the frequency of spin-flip collisions. The quantity $P^{\mu}\{t_0,t_1,\ldots,t_m,t\}$ is a simple product of $G^{\mu}(t)$'s,

$$P^{\mu}\{t_0,t_1,\ldots,t_m,t\} =G^{\mu}(t-t_m)G^{\mu}(t_{m,m-1})\cdots G^{\mu}(t_{21})G^{\mu}(t_{10}), \quad (83)$$

representing the muon spin polarization after m spin-flip collisions [25,28] at $t_1,t_2,t_3,\ldots,t_m$. The quantity $G^{\mu}(t)$ is either $G_T^{\mu}(t)$ or $G_L^{\mu}(t)$, depending on the field geometry used. It should be mentioned that Eq. (83) consists of only one term as opposed to 2^n terms in the case of 40 or 50.

A similar procedure can be carried out for the electron spin polarization in H in a transverse field and the result can be written down as

$$P_T^e(t)=[G_T^e(t)-g_T^e(t)]\exp[-\lambda_{SF}t] +\sum_{m=0}^{\infty}\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^{t}dt_m e^{-\lambda_{SF}t}\lambda_{SF}^m \times p_T^e\{t_0,t_1,\ldots,t_m,t\}, \quad (84)$$

where

$$p_T^e\{t_0,t_1,\ldots,t_m,t\} =g_T^e(t-t_m)g_T^e(t_{m,m-1})\cdots g_T^e(t_{21})g_T^e(t_{10}). \quad (85)$$

The first term of Eq. (84) represents the portion of H atoms which do not undergo a collision until t and the second term, which has in general a different relaxation rate from the first term, is for the H atoms which participated in, at least, one collision with O_2. It should be mentioned that for non-Poisson processes including the case of deterministic chaos [34], Eqs. (81) and (84) are not valid and the observed polarization $P(t)$ depends not only on λ_{SF} but also on $\lambda_{NF}=\lambda[1-\frac{32}{27}\sin^2(\Delta/2)]$ [28,34], which is a measure of the frequency of spin-nonflip collisions. Equation (81) together with the renormalized encounter rate λ_{SF} (rather than the bare encounter rate λ) will lead to the same expressions for $P_L^{\mu}(t)$, $P_T^{\mu}(t)$, and $P_T^e(t)$ discussed in the preceding sections, once the remaining integrals with respect to times for spin-flip collisions are carried out.

D. Positronium lifetime

Positronium (Ps) occurs in two distinct spin states: (1) *ortho*-Ps is a spin triplet state with annihilation lifetime $1/\lambda_1=140$ ns and (2) *para*-Ps with zero total spin with $1/\lambda_0=0.12$ ns. As a result of spin exchange with O_2, *ortho*-Ps can be converted to *para*-Ps, which causes a reduction in the apparent lifetime of *ortho*-Ps.

The absolute squared values of matrix elements in T_{11}, T_{10}, and $T_{1\text{-}1}$ represent the transition probabilities among the states $|n\rangle(1,m)$. One can construct tables of the transition probabilities, K_{11}, K_{10}, and $K_{1\text{-}1}$ among the Ps eigenstates regardless of the final O_2 spin state after a collision with (1,1), (1,0), and $(1,-1)$ molecules, respectively (Tables IV–VI). The labels on the top $|1\rangle$, $|2\rangle$, $|3\rangle$, or $|4\rangle$, are the Ps states before the collision and the column below each label gives the distribution of Ps states after one collision. If the polarization of O_2 spins is negligible, the average transition probability matrix (Table VII) can be constructed simply by

$$K=[K_{11}+K_{10}+K_{1\text{-}1}]/3.$$

This simple sum of three K_{1n}'s can be justified, because two different initial states lead to two different mutually exclusive sets of final states, e.g., $|1\rangle(1,0)\rightarrow|1\rangle(1,0)$, $|2\rangle(1,1)$, $|4\rangle(1,1)$ (Table II), while $|1\rangle(1,-1)\rightarrow|1\rangle(1,-1)$, $|2\rangle(1,0)$, $|4\rangle(1,0)$ (Table III), so that there is no interference in the final states.

The quantity B_0 for Ps is 36.28 kG, corresponding to the hyperfine frequency $\omega_0/2\pi=203.4$ GHz. In this work, the applied field is assumed to be weak ($B\ll B_0$) so that the system is in the low-field limit, $x=0$ and $c=s=1/\sqrt{2}$. In this limit, the states $|1\rangle$, $|2\rangle$, and $|3\rangle$ are slowly decaying triplet states and $|4\rangle$ is the fast decaying singlet. The rate equations for the occupation numbers, $n_1(t)$, $n_2(t)$, $n_3(t)$, and $n_4(t)$, in the Ps eigenstates, $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$ can be constructed from Table VII as

$$\frac{dn_1}{dt}=-\lambda_T n_1(t)-[2n_1(t)-n_2(t)-n_4(t)]\lambda\tfrac{8}{27}\sin^2(\Delta/2),$$

$$\frac{dn_2}{dt}=-\lambda_T n_2(t)-[3n_2(t)-n_1(t)-n_3(t)-n_4(t)]\lambda\tfrac{8}{27}\sin^2(\Delta/2),$$

$$\frac{dn_3}{dt}=-\lambda_T n_3(t)-[2n_3(t)-n_2(t)-n_4(t)]\lambda\tfrac{8}{27}\sin^2(\Delta/2),$$

$$\frac{dn_4}{dt}=-\lambda_S n_4(t)-[3n_4(t)-n_1(t)-n_2(t)-n_3(t)]\lambda\tfrac{8}{27}\sin^2(\Delta/2),$$

where $\lambda=nv\sigma$ is the rate of collisions and the quantities λ_T and λ_S are the density-dependent (including the pick-off process) *ortho*- and *para*-Ps lifetimes, respectively, in the absence of spin exchange. Since the main interest here is the change of *ortho*-Ps lifetime, one is interested in a time regime comparable to the *ortho*-Ps lifetime ($1/\lambda_T$) and much larger than $1/\lambda_S$. This assumption amounts to setting $n_4(t)=0$, leading to

$$n_T(t)=n_T(0)\exp[-\lambda_T t-\lambda t\tfrac{8}{27}\sin^2(\Delta/2)],$$

where $n_T(t)=n_1(t)+n_2(t)+n_3(t)$ is the population in the triplet states. The apparent lifetime of *ortho*-Ps in the presence of O_2 spin exchange is

$$\lambda_{\text{O-Ps}}=\lambda_T+\tfrac{8}{27}\lambda \sin^2(\Delta/2). \tag{86}$$

Such changes in Ps lifetimes upon addition of small amount of O_2 in Ar in the gas phase have been observed [35] and attributed to the presence of unpaired electrons in O_2 [36]. A more general treatment of *ortho*- and *para*-like Ps lifetimes in a magnetic field is presented elsewhere [37].

IV. DISCUSSION

For Mu spin exchange with spin-$\frac{1}{2}$ species such as Mu+ e^-, λ_{SF} and λ_{NF} are defined as $\lambda_{SF}=\lambda \sin^2(\Delta/2)$ and $\lambda_{NF}=\lambda \cos^2(\Delta/2)$, respectively, with $\lambda=nv\sigma$, where the quantity v is the relative velocity, n is the number density of paramagnetic species, and σ is the collision cross section. If the medium is 100% spin polarized antiparallel to the Mu electron, λ_{SF} and λ_{NF} are related to the spin-flip and spin-nonflip cross sections by $\lambda_{SF}=nv\sigma_{SF}$ and $\lambda_{NF}=nv\sigma_{NF}$, respectively. In the partial wave analysis, σ_{SF}, σ_{NF}, and σ can be expressed by [37,38]

$$\sigma_{SF}=\frac{1}{k^2}\sum_l (2l+1)\sin^2(\delta_{l+}-\delta_{l-}),$$

$$\sigma_{NF}=\frac{1}{k^2}\sum_l (2l+1)[2 \sin^2\delta_{l+}+2 \sin^2\delta_{l-} - \sin^2(\delta_{l+}-\delta_{l-})],$$

$$\sigma=\sigma_{SF}+\sigma_{NF}=\frac{2}{k^2}\sum_l (2l+1)[\sin^2\delta_{l+}+\sin^2\delta_{l-}],$$

where k is the wave number, and the plus and minus signs after the partial wave label l correspond to singlet and triplet encounters. The spin-flip rate λ_{SF}, defined as a quantity independent of the spin polarization of the paramagnetic species, represents the rate of collisions which influence spin dynamics in both spin-unpolarized and spin-polarized media [28,29] alike.

It is possible for spin-$\frac{1}{2}$ species such as Cs to flip the electron spin of Mu in one collision, e.g., $\text{Mu}^{\uparrow}+\text{Cs}^{\downarrow}\rightarrow \text{Mu}^{\downarrow}+\text{Cs}^{\uparrow}$ [25]. For Mu+O_2 collisions; however, the situation is more complex than Mu+Cs. As can be seen from Table VI or Eq. (29), the transition probability $|1\rangle(1,-1)\rightarrow|1\rangle(1,-1)$, $1-\frac{8}{9}\sin^2(\Delta/2)$, will never vanish regardless of the value of Δ, which implies that the electron spin in Mu cannot be flipped completely in a Mu+O_2 collision and that there is no clear separation between spin-flip and spin-nonflip collisions at the microscopic state-to-state level. In spite of this complexity, it is still possible to define $\lambda_{SF}=\frac{32}{27}\lambda\sin^2(\Delta/2)$ as a measure of the spin-flip rate for Mu+O_2. It is interesting to express λ_T^e, λ_T^μ, λ_L^μ, etc., in terms of λ_{SF},

$$\lambda_T^e=\tfrac{32}{27}\lambda \sin^2(\Delta/2)=\lambda_{SF}, \quad \text{ESR in high fields,} \tag{87}$$

$$\lambda_T^\mu=\tfrac{16}{27}\lambda \sin^2(\Delta/2) =\lambda_{SF}/2, \quad \mu\text{SR in low transverse fields,} \tag{88}$$

$$\lambda_T^\mu=\tfrac{24}{27}\lambda \sin^2(\Delta/2) =3\lambda_{SF}/4, \quad \mu\text{SR in intermediate transverse fields,} \tag{89}$$

$$\lambda_T^\mu=\tfrac{16}{27}\lambda \sin^2(\Delta/2) =\lambda_{SF}/2, \quad \mu\text{SR in high transverse fields,} \tag{90}$$

$$\lambda_L^\mu=\frac{\lambda}{1+x^2}\frac{16}{27}\sin^2(\Delta/2) =\frac{\lambda_{SF}/2}{1+x^2}, \quad \mu\text{SR in longitudinal fields,} \tag{91}$$

$$\lambda_{\text{O-Ps}}=\lambda_T+\tfrac{8}{27}\lambda \sin^2(\Delta/2)=\lambda_T +\lambda_{SF}/4, \quad \textit{ortho}\text{-Ps in zero field.} \tag{92}$$

It is important to note the relaxation rate of the electron spin in H in high transverse fields is different from the muon relaxation rate in low, intermediate, and high fields, which will have important consequences in comparing ESR and μSR relaxation data [32]. This difference in Δ dependences between μSR and ESR is due to the fact that μSR is sensitive to electron spin dynamics indirectly through the time evolution of the muon spin, while ESR observes the relaxation of the electron spin directly, where the transition $|\alpha_\mu\alpha_e\rangle\rightarrow|\alpha_\mu\beta_e\rangle$ may be a case in point. In a high longitudinal field, where both initial and final states are eigenstates, the electron spin polarization is completely lost in one collision in the sense that the spin of the final state is opposite to that of the initial state. On the other hand, the muon spin is not affected at all by this transition, since the final state is also an eigenstate.

It should be noted that the expressions for the relaxation rates λ_T^μ and λ_L^μ expressed in terms of $\lambda_{SF}=\frac{32}{27}\lambda \sin^2(\Delta/2)$, are identical to the case of spin-$\frac{1}{2}$ species [25,27] expressed in terms of $\lambda_{SF}=\lambda \sin^2(\Delta/2)$. If one rewrites Table VII (transition probabilities) using λ_{SF}, the resulting matrix (Table VIII) for O_2 is identical to that for spin-$\frac{1}{2}$ paramagnetic species [37]. One is tempted to speculate that the transition rate matrix and the muon and electron spin relaxation rates for Mu (H) spin exchange with species of any arbitrary spin J are identical to those of spin-$\frac{1}{2}$ paramagnetic species, if λ_{SF} is defined as

$$\lambda_{SF}=\frac{2}{f}\lambda \sin^2(\Delta/2)=2\frac{8J(J+1)}{3(2J+1)^2}\lambda \sin^2(\Delta/2), \tag{93}$$

where f is the statistical factor defined in Ref. [41]. For $J=\frac{1}{2}$ and 1, this equation gives the correct statistical factors 1 and $\frac{32}{27}$, respectively.

The transverse muon spin relaxation rate at intermediate fields, $\lambda_T^\mu=\frac{8}{9}\lambda \sin^2(\Delta/2)=\frac{3}{4}\lambda_{SF}$, is 1.5 times faster than that in low fields, which is a distinct signature for spin exchange absent in Mu relaxations due to chemical reactions [30]. Such a field dependence for spin exchange was predicted theoretically for spin-$\frac{1}{2}$ species [27] and subsequently confirmed experimentally in the Mu+Cs system [17], serving as a convenient tool to distinguish spin exchange from chemical

TABLE VII. Average transition probability matrix $K=[K_{11}+K_{10}+K_{1-1}]/3$: spin exchange with unpolarized O_2 molecules.

	$\|1\rangle O_2$	$\|2\rangle O_2$	$\|3\rangle O_2$	$\|4\rangle O_2$
$\|1\rangle$	$1-\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$	$s^2\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$	0	$c^2\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$
$\|2\rangle$	$s^2\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$	$1-(1+2c^2s^2)\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$	$c^2\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$	$2c^2s^2\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$
$\|3\rangle$	0	$c^2\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$	$1-\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$	$s^2\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$
$\|4\rangle$	$c^2\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$	$2c^2s^2\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$	$s^2\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$	$1-(1+2c^2s^2)\frac{16}{27}\sin^2\left(\frac{\Delta}{2}\right)$

reactions as the cause of observed relaxations. A similar field dependence has been observed experimentally for $Mu+O_2$ [30] and the present work confirms the ratio of relaxation rates in intermediate and low fields is also 1.5 as in spin-$\frac{1}{2}$ species. It is interesting to point out that this characteristic field dependence in transverse relaxation rates is absent in Ps spin exchange because of the degeneracy $\omega_1=\omega_3$ for Ps [37].

Ps spin exchange in zero field enhances the *ortho*-Ps annihilation rate by $\frac{8}{27}\lambda\ \sin^2(\Delta/2)=\lambda_{SF}/4$ [Eq. (86)], indicating that the average rate of *ortho*- to *para*-Ps conversion is $\lambda_{SF}/4$. This straightforward interpretation is not valid for Ps spin exchange in external magnetic fields, where the $|2\rangle$ and $|4\rangle$ states do not represent pure *ortho*- and *para*-Ps [37].

In most experimental situations, one obtains λ_{SF}, which is a product from λ and $\sin^2(\Delta/2)$. One notable exception to this is Mu spin exchange with spin-polarized media, where measurements in an intermediate field can determine λ and $\sin^2(\Delta/2)$ separately [28].

Treatment by Turner *et al.* [41] defines λ_{SF} and $\lambda_{SF}=\lambda\ \sin^2(\Delta/2)$ and expressed the observed relaxation rate in low fields by $\lambda_T^{\mu}=\frac{16}{27}\lambda_{SF}$, which is in agreement with Eq. (70).

It is instructive to estimate the phase shift $-\Delta=\int dt[V_D(r)-V_Q(r)]/\hbar\approx\delta t[V_D(r)-V_Q(r)]/\hbar$ for a typical experimental situation. It is assumed that the difference in the potential energy is on the order of 1 eV and that the integral with respect to time is calculated over the time period for thermal Mu to travel over the size of O_2, which is about $\delta t\approx 10^{-13}$ s. Under these assumptions, one obtains $-\Delta\approx 150$, which is much larger than 2π. If δt is very different from one collision to another, the quantity Δ takes random values in the reduced zone from 0 to 2π. This implies that the average value of $\sin^2(\Delta/2)$ is $\frac{1}{2}$, a case of strong collisions [1], leading to $\lambda_T^e=\frac{16}{27}\lambda$ for the electron spin polarization in high transverse fields and $\lambda_T^{\mu}=\frac{8}{27}\lambda$, $\frac{4}{9}\lambda$, and $\frac{8}{27}\lambda$ for the muon spin polarization in low, intermediate, and high fields, respectively, where λ is the bare rate of encounters.

The case of very fast spin exchange with O_2, in which one has to deal with a very large number of collisions, can most conveniently be investigated with the simplified Eq. (81). The comparison of Eq. (81) with Ref. [26] reveals that the only change to be made for O_2 spin exchange is to replace $\lambda_{SF}=\lambda\ \sin^2(\Delta/2)$ by $\lambda_{SF}=\lambda\frac{32}{27}\sin^2(\Delta/2)$. The observed precession frequency and relaxation rate of the muon spin in Mu in a transverse field are related to the imaginary and real part, respectively, of $\ln G_T^{\mu}(t)$ by

$$\begin{aligned}\omega_{obs}&=-\lambda_{SF}\int_0^{\infty}dt\ \lambda_{SF}e^{-\lambda_{SF}t}\ \mathrm{Im}\ \ln G_T^{\mu}(t)\\&=-\omega_M+\lambda_{SF}\int_0^{\infty}dt\ \lambda_{SF}e^{-\lambda_{SF}t}\\&\quad\times\tan^{-1}\left[\frac{x}{\sqrt{x^2+1}}\tan(\omega_0 t\sqrt{x^2+1}/2)\right]\\&\approx\omega_{\mu}+\tfrac{1}{4}(\omega_e+\omega_{\mu})(\omega_0/\lambda_{SF})^2,\end{aligned}\tag{94}$$

TABLE VIII. Average transition rate matrix expressed in terms of the spin-flip rate (renormalized encounter rate) λ_{SF}: Mu (H or Ps) in collision with unpolarized species. This matrix is valid not only for O_2 but also for paramagnetic species of any spin J, if λ_{SF} is defined by Eq. (93).

	$\|1\rangle O_2$	$\|2\rangle O_2$	$\|3\rangle O_2$	$\|4\rangle O_2$
$\|1\rangle$	$\lambda-\lambda_{SF}/2$	$s^2\lambda_{SF}/2$	0	$c^2\lambda_{SF}/2$
$\|2\rangle$	$s^2\lambda_{SF}/2$	$\lambda-(1+2c^2s^2)\lambda_{SF}/2$	$c^2\lambda_{SF}/2$	$2c^2s^2\lambda_{SF}/2$
$\|3\rangle$	0	$c^2\lambda_{SF}/2$	$\lambda-\lambda_{SF}/2$	$s^2\lambda_{SF}/2$
$\|4\rangle$	$c^2\lambda_{SF}/2$	$2c^2s^2\lambda_{SF}/2$	$s^2\lambda_{SF}/2$	$\lambda-(1+2c^2s^2)\lambda_{SF}/2$

$$\lambda_{obs} = -\lambda_{SF}\int_0^\infty dt\ \lambda_{SF} e^{-\lambda_{SF}t}\ \mathrm{Re}\ \ln G_T^\mu(t)$$
$$= \frac{\omega_0^2}{4\lambda_{SF}}\left[1+\frac{1}{1+\omega_{24}^2/\lambda_{SF}^2}\right]$$
$$\approx \frac{\omega_0^2}{2\lambda_{SF}}[1-\tfrac{1}{2}(x^2+1)(\omega_0/\lambda_{SF})^2]. \qquad (95)$$

If the renormalized encounter rate λ_{SF} is much larger than the Mu hyperfine frequency $\omega_0/2\pi = 4.463$ GHz, the muon spin cannot follow the rapid repeated electron flips so that the muon spin in Mu precesses with the precession frequency of the bare positive muon [25,26,39,40]. This phenomenon analogous to motional narrowing in NMR has previously been investigated in details for spin-$\frac{1}{2}$ species [26]. Comparing Eq. (94) in the limit of $\lambda_{SF} \gg \omega_0$ with the corresponding expression by Nosov and Yakovleva [42] ($\omega_0^2/4\nu$), one concludes that their phenomenological parameter ν corresponds to $\nu = \lambda_{SF}/2 = \lambda\frac{16}{27}\sin^2(\Delta/2)$ in the case of O_2 spin exchange. In a longitudinal field, where there is no precession, the relaxation rate is given by

$$\lambda_{obs} = -\lambda_{SF}\int_0^\infty dt\ \lambda_{SF} e^{-\lambda_{SF}t}\ \mathrm{Re}\ \ln G_L^\mu(t)$$
$$= \frac{\omega_0^2}{2\lambda_{SF}}\frac{1}{1+\omega_{24}^2/\lambda_{SF}^2}.$$

V. CONCLUDING REMARKS

The (statistical) factors which connect experimentally observed rates to the collision rate and $\sin^2(\Delta/2)$ are derived for Mu+O_2 (μSR), H+O_2 (ESR), and Ps+O_2 (Ps lifetime), which enables one to interpret spin-exchange data obtained by three different techniques in a coherent manner. Even though Mu (H or Ps) spin exchange with O_2 is much more complex than that with spin-$\frac{1}{2}$ species, it is still possible to define the spin-flip rate as $\lambda_{SF} = \lambda\frac{32}{27}\sin^2(\Delta/2)$. Once expressed in terms of λ_{SF}, the expressions of λ_T^e, λ_T^μ, λ_L^μ, and $\lambda_{\text{O-Ps}}$ for spin-1 molecules become identical to those for spin-$\frac{1}{2}$ species expressed in terms of $\lambda_{SF} = \lambda\sin^2(\Delta/2)$ appropriate for spin-$\frac{1}{2}$.

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