Anisotropic muonium atoms: Energy levels and electron spin exchange

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The time evolution of the muon spin in fully anisotropic muonium ($\mathrm{Mu}=\mu^{+}+e^{-}$) in the presence of Heisenberg spin exchange has been investigated theoretically. First, the energy levels of anisotropic Mu as a function of field are investigated analytically with a particular emphasis on the crossing and avoidance of energy levels at certain magnetic fields, which have important consequences in muon spin dynamics. Second, the knowledge of the energy levels is applied to investigate the muon spin depolarization due to electron spin exchange with spin-$\frac{1}{2}$ paramagnetic species, where the muon spin depolarization rate and the precession amplitude observed by the muon-spin-rotation (μSR) technique are explicitly expressed solely in terms of the matrix that diagonalizes the anisotropic Mu hyperfine Hamiltonian. The treatment presented here represents a special systematic and practical method that allows one to investigate the time evolution of the muon spin in anisotropic Mu in the presence of electron spin exchange. Several concrete examples are discussed in detail, including those in which all the μSR observables can be obtained *analytically*. The method developed in this work is used to explain the relaxation rate maximum in anisotropic Mu in semiconductors observed at the longitudinal fields at which two of the Mu energy levels avoid each other due to a strong level mixing or avoidance, where the present formalism takes the tensor nature of the anisotropic hyperfine interaction fully into account without invoking the convenient but not necessarily correct notion of an effective magnetic field in an anisotropic Mu. Also discussed is the possibility of observing additional relaxation maximum at a low-avoidance field, where the effective magnetic-field approximation completely breaks down. Observation of such a maximum will provide valuable information on the parameters characterizing the anisotropic Mu in question. The formalism presented here can also be applied to anisotropic positronium on surfaces, anisotropic Mu undergoing both charge exchange and spin exchange, and fast spin exchange.

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I. INTRODUCTION

The muon-spin-rotation (μSR) technique [1–5] takes advantage of two important consequences of the parity violation in the weak interaction: first, the spin of the muon produced in the pion decay $\pi^{+}\rightarrow\mu^{+}+\nu_{\mu}$ is nearly 100% polarized in the rest frame of the pion, and second, the decay positron from the muon decay $\mu^{+}\rightarrow e^{+}+\nu_{e}+\overline{\nu_{\mu}}$ is emitted preferentially in the direction of the muon spin [6]. By measuring the counting rate of the decay positrons as a function of time, one can study the time evolution of the muon spin polarization.

Muonium ($\mathrm{Mu}=\mu^{+}+e^{-}$) is a hydrogenlike bound state of a positive muon and an electron, analogous to hydrogen ($\mathrm{H}=p^{+}+e^{-}$). Since μ^{+} is about 200 times heavier than e^{-}, the reduced mass of Mu is essentially the electron mass. Thus Mu has a virtually identical ionization potential to H. In this sense, Mu can be regarded as a light isotope of H. Since the advent of the μSR technique, the atomic and chemical properties of Mu in the gas phase have been investigated extensively and results are compared to those of H in the context of isotope mass effects [7].

The Mu atom in vacuum has an isotropic hyperfine interaction characterized by the interaction energy $\omega_{\mathrm{hf}}/2\pi=4.463\,\mathrm{GHz}$. The chemical reaction rates of isotropic Mu have been measured in reactions such as $\mathrm{Mu}+\mathrm{H}_2\rightarrow\mathrm{MuH}+\mathrm{H}$ [8] and $\mathrm{Mu}+\mathrm{X}_2\rightarrow\mathrm{MuX}+\mathrm{X}$ (where X=F, Cl, Br) [9], in the gas phase. If reaction partners of Mu are paramagnetic species having at least one unpaired electron, Mu undergoes electron spin-flip collisions, which affects, through the Mu hyperfine interaction, the muon spin polarization. The spin-flip cross section has been obtained for systems such as $\mathrm{Mu}+\mathrm{O}_2$ [10], Mu+Cs [11], and Mu+NO [12] in the gas phase from the muon-spin depolarization rate caused by electron spin exchange.

Mu has also been observed in condensed media, including semiconductors [13–20] and fullerenes [23–25]. In particular, Mu states in semiconductors have been studied extensively in order to obtain insights into H states that affect the electrical and optical properties of technologically important material [14,21]. Two different Mu states, labeled as Mu_T^0 and $\mathrm{Mu}_{\mathrm{BC}}^0$, are observed in Si, Ge, diamond, GaAs, and GaP, where the superscript zero refers to neutral Mu and the subscripts T and BC denote the *tetrahedral* and *bond-center* positions, respectively. Mu_T^0, which diffuses rapidly among tetrahedral interstitial sites, has an isotropic hyperfine interaction with a reduced hyperfine interaction $\omega_{\mathrm{hf}}/2\pi$ (=2.0 GHz in Si [13]) compared to Mu in vacuum (4.463 GHz). $\mathrm{Mu}_{\mathrm{BC}}^0$, localized on the time scale of the muon lifetime (2.2 μs) near a bond-center position [15], has an anisotropic hyperfine interaction with an axial symmetry characterized by $\omega_{\parallel}$ and $\omega_{\perp}$, where the values in Si are $\omega_{\parallel}/2\pi=-16.82\,\mathrm{MHz}$ and $\omega_{\perp}/2\pi=-92.59\,\mathrm{MHz}$ [19,20]. $\mathrm{Mu}_{\mathrm{BC}}^0$ is also called anomalous muonium denoted by Mu*.

In the past, the connection between the depolarization rate observed by μSR and the spin-flip cross section that charac-

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terizes spin exchange at the quantum-mechanical level has been studied theoretically by two different methods: a Boltzmann equation approach [26–30] and a time-ordered stochastic method [31–42]. The Boltzmann equation method, which deals with paramagnetic species of any spin ($S=\frac{1}{2}$, 1, $\frac{3}{2}$, etc.), has been applied to μSR in a transverse as well as longitudinal field, H-maser [43], and stored beam experiments [44]. The second method, which will be used in this work, calculates explicitly the muon spin polarization after n consecutive binary collisions with paramagnetic species, $P_\mu(t_1,t_2,\ldots,t_n,t)$, where t_k is the time of the kth collision and t is the time of observation. One obtains the muon polarization observed at time t by the average of $P_\mu(t_1,t_2,\ldots,t_n,t)$ weighted (i) over all possible Poisson distributions of $t_1,t_2,\ldots,t_n$ under the condition $0\leqslant t_1\leqslant t_2 \leqslant\cdots\leqslant t_n\leqslant t$, and (ii) over all possible n from 0 to ∞. The method was developed first for Mu spin exchange with spin-$\frac{1}{2}$ species (e^-, Cs, NO, etc.) in transverse and longitudinal fields [31], where paramagnetic species are unpolarized, and later extended to a number of cases: fast Mu spin exchange [34], the transverse field dependence of the relaxation rate [35], Mu spin exchange with spin polarized paramagnetic species [37], Mu spin exchange with spin one ($S=1$) paramagnetic species (O_2) [40], spin exchange of H detected by the electron spin resonance (ESR) technique [40], spin exchange of positronium (Ps$=e^++e^-$) studied by the positron lifetime (PLT) technique [40,41]. The transverse field dependence of the muon spin depolarization rate, predicted theoretically in Ref. [35], proved to be a convenient tool to use to distinguish spin exchange from chemical reactions as causes of Mu spin depolarization [11,12,36,45]. The work based on the time-ordered stochastic method described in Refs. [40,41] lead to direct comparisons of the spin-flip cross sections in Mu$+O_2$ [10], H$+O_2$ [40,46], and Ps$+O_2$ [42,47], studied by three different experimental techniques, i.e., μSR, ESR, and PLT, respectively, where the spin-flip cross section for Ps$+O_2$ was found to be 1000 times smaller than that for Mu$+O_2$ [42,47].

Even though anisotropic Mu has been investigated experimentally in recent years, the theoretical and quantitative understanding of anisotropic Mu undergoing electron spin exchange, which is much more complex than the case of isotropic Mu, is still lacking. The present work will extend the above-mentioned time-ordered stochastic method to the case of anisotropic Mu, in order to provide a systematic and practical scheme that allows one to calculate, often analytically, the relaxation rate, amplitude, and phase of muon spin precessions in the presence of spin exchange directly in terms of the matrix that diagonalizes the anisotropic Hamiltonian. Here, we confine ourselves to the case of anisotropic Mu or Mu radicals, such as $\mathrm{Mu}^0_{\mathrm{BC}}$, MuC_{70}, MuCO, and MuO_2, where the only spins in the system are carried by the muon and electrons; i.e., there is no nuclear moment.

II. THEORY

It is convenient to use the spin functions $\alpha_\mu\alpha_e$, $\alpha_\mu\beta_e$, $\beta_\mu\alpha_e$, and $\beta_\mu\beta_e$, as the basis for expressing the Hamiltonian, where $\alpha_\mu(\alpha_e)$ and $\beta_\mu(\beta_e)$ represent the z components of the muon (electron) spin in the laboratory frame of reference (x,y,z). First, the 4×4 Hamiltonian (H) matrix of a fully anisotropic Mu in a magnetic field applied in the z direction is expressed in terms of the Euler angles, α, β, and γ, which relate the principal axes (X,Y,Z) of the Mu hyperfine tensor to the laboratory system (x,y,z). By solving the 4×4 secular equation analytically [41], one investigates the four eigenvalues ($\hbar\omega_k$ with $k=1$, 2, 3, and 4) of Mu as a function of the magnetic-field strength and the orientation of the Mu principal axes with respect to the field direction. Of particular interest are crossing and avoidance of energy levels that will have important consequences in the muon spin depolarization observed by μSR. Once an eigenenergy $\hbar\omega_j$ is obtained for a given magnetic field and Mu orientation, it is possible to obtain, numerically or analytically, the eigenstate $|j\rangle$ corresponding to $\hbar\omega_j$ as a superposition of $\alpha_\mu\alpha_e$, $\alpha_\mu\beta_e$, $\beta_\mu\alpha_e$, and $\beta_\mu\beta_e$, as $|j\rangle=U_{j1}\alpha_\mu\alpha_e+U_{j2}\alpha_\mu\beta_e+U_{j3}\beta_\mu\alpha_e+U_{j4}\beta_\mu\beta_e$ with $j=1,2,3,4$.

After investigating the transitions among $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$ induced by electron spin-exchange collisions, the time-ordered stochastic method will be used to study anisotropic Mu. One of the main goals here is to show that the experimental observables of the μSR technique, including the relaxation rate due to spin exchange, the amplitude, and the phase of μSR signals, can be expressed explicitly in terms of U_{jk}'s. Several concrete cases are presented as examples, including some special cases, where U_{jk}'s, thus all observables of μSR also, can be obtained analytically.

In this work, anisotropic Mu is assumed to be stationary in the (x,y,z) system as in the case of Mu^0_{BC} in semiconductors. The spin exchange of rapidly rotating MuCO, MuO_2, etc., will be discussed elsewhere.

A. Euler angles

Let (X,Y,Z) be the coordinate system fixed to anisotropic Mu, while (x,y,z) is attached to the laboratory system. The unit vectors along the x, y, and z axes are expressed in terms of the direction cosines in the (X,Y,Z) system:

$$\hat{x}=(\cos\alpha_x,\cos\beta_x,\cos\gamma_x),\quad \hat{y}=(\cos\alpha_y,\cos\beta_y,\cos\gamma_y),$$

$$\hat{z}=(\cos\alpha_z,\cos\beta_z,\cos\gamma_z). \tag{1}$$

Similarly, the unit vectors along the X, Y, and Z axes with respect to the (x,y,z) system are

$$\hat{X}=(\cos\alpha_x,\cos\alpha_y,\cos\alpha_z),\quad \hat{Y}=(\cos\beta_x,\cos\beta_y,\cos\beta_z),$$

$$\hat{Z}=(\cos\gamma_x,\cos\gamma_y,\cos\gamma_z). \tag{2}$$

Since $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors that are mutually orthogonal, one obtains

$$\cos\alpha_n\cos\alpha_m+\cos\beta_n\cos\beta_m+\cos\gamma_n\cos\gamma_m=\delta_{nm}, \tag{3}$$

where δ_{nm} is Kronecker's δ function and n, $m=x$, y, and z. Since the vector product $\hat{x}\times\hat{y}$ is equal to $\hat{z}$, one obtains

$$\cos\alpha_x\cos\beta_y - \cos\beta_x\cos\alpha_y = \cos\gamma_z,$$
$$\cos\gamma_x\cos\alpha_y - \cos\alpha_x\cos\gamma_y = \cos\beta_z, \quad (4)$$
$$\cos\beta_x\cos\gamma_y - \cos\gamma_x\cos\beta_y = \cos\alpha_z.$$

Similar relations can be obtained by cyclic permutations $x,y,z \rightarrow y,z,x \rightarrow z,x,y$.

The components of a spin angular-momentum vector seen in the (X,Y,Z) system are expressed in terms of the components of the same vector seen in the (x,y,z) system as

$$\begin{bmatrix} s_X \\ s_Y \\ s_Z \end{bmatrix} = D(\alpha,\beta,\gamma)\begin{bmatrix} s_x \\ s_y \\ s_z \end{bmatrix}. \quad (5)$$

The transformation matrix $D(\alpha,\beta,\gamma)$ can be expressed by

$$D(\alpha,\beta,\gamma) = \begin{bmatrix} \cos\alpha_x & \cos\alpha_y & \cos\alpha_z \\ \cos\beta_x & \cos\beta_y & \cos\beta_z \\ \cos\gamma_x & \cos\gamma_y & \cos\gamma_z \end{bmatrix}$$
$$= \begin{bmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{bmatrix}, \quad (6)$$

where α, β, and γ are the Euler angles of the three consecutive rotations around the Z, Y, and Z axes of the (X,Y,Z) coordinate system, which initially coincides with the (x,y,z) system. It should be emphasized that the matrix $D(\alpha,\beta,\gamma)$ represents rotations of the coordinate system with the object of interest fixed in space.

B. Hamiltonian for anisotropic Mu

The hyperfine interaction between the muon spin and the electron spin consists of the scaler Fermi contact term and traceless dipolar terms. In an external magnetic field applied (B) in the z direction, the Hamiltonian of anisotropic Mu can bewritten down in terms of the Pauli spin operators as

$$H = \frac{\hbar}{2}\omega_e\sigma_z^e - \frac{\hbar}{2}\omega_\mu\sigma_z^\mu + \frac{\hbar}{4}\omega_X\sigma_X^\mu\sigma_X^e + \frac{\hbar}{4}\omega_Y\sigma_Y^\mu\sigma_Y^e + \frac{\hbar}{4}\omega_Z\sigma_Z^\mu\sigma_Z^e, \quad (7)$$

where ω_e (ω_μ) is the Larmor precession angular velocity defined in terms of the absolute value of the gyromagnetic ratio of the electron (muon) as $\omega_e = \gamma_e B$ ($\omega_\mu = \gamma_\mu B$), σ^e and σ^μ are Pauli's spin matrices for the electron and positive muon, respectively, the lower case subscripts x,y,z refer to the axes fixed in the laboratory frame of reference, while X,Y,Z is the system fixed in Mu, in which the hyperfine interaction tensor is diagonal with the principal values $\hbar\omega_X$, $\hbar\omega_Y$, and $\hbar\omega_Z$. Using the transformation matrix given in Eq. (5) one can rewrite the vector components referring to the Mu (X,Y,Z) axes, σ_X^μ, σ_Y^μ, σ_Z^μ, σ_X^e, σ_Y^e, and σ_Z^e, in terms of the corresponding quantities in the laboratory (x,y,z) system. The matrix representation of the Hamiltonian expressed on the basis set $(\alpha_\mu\alpha_e, \alpha_\mu\beta_e, \beta_\mu\alpha_e, \beta_\mu\beta_e)$ is

$$\frac{H}{\hbar} = \begin{bmatrix} \omega_- + \Omega_{zz} & \Omega_{zx} - i\Omega_{yz} & \Omega_{zx} - i\Omega_{yz} & \Omega_{xx} - \Omega_{yy} - 2i\Omega_{xy} \\ \Omega_{zx} + i\Omega_{yz} & -\omega_+ - \Omega_{zz} & \Omega_{xx} + \Omega_{yy} & -(\Omega_{zx} - i\Omega_{yz}) \\ \Omega_{zx} + i\Omega_{yz} & \Omega_{xx} + \Omega_{yy} & \omega_+ - \Omega_{zz} & -(\Omega_{zx} - i\Omega_{yz}) \\ \Omega_{xx} - \Omega_{yy} + 2i\Omega_{xy} & -(\Omega_{zx} + i\Omega_{yz}) & -(\Omega_{zx} + i\Omega_{yz}) & -\omega_- + \Omega_{zz} \end{bmatrix}, \quad (8)$$

where $\omega_\pm$ are defined by $\omega_\pm = (\omega_e \pm \omega_\mu)/2$ and Ω_{xx}, Ω_{yy}, Ω_{zz}, Ω_{xy}, Ω_{yz}, Ω_{zx} are defined by

$$\Omega_{xx} = \tfrac{1}{4}[\omega_X\cos^2\alpha_x + \omega_Y\cos^2\beta_x + \omega_Z\cos^2\gamma_x], \quad \Omega_{yy} = \tfrac{1}{4}[\omega_X\cos^2\alpha_y + \omega_Y\cos^2\beta_y + \omega_Z\cos^2\gamma_y],$$
$$\Omega_{zz} = \tfrac{1}{4}[\omega_X\cos^2\alpha_z + \omega_Y\cos^2\beta_z + \omega_Z\cos^2\gamma_z], \quad \Omega_{xy} = \tfrac{1}{4}[\omega_X\cos\alpha_x\cos\alpha_y + \omega_Y\cos\beta_x\cos\beta_y + \omega_Z\cos\gamma_x\cos\gamma_y], \quad (9)$$
$$\Omega_{yz} = \tfrac{1}{4}[\omega_X\cos\alpha_y\cos\alpha_z + \omega_Y\cos\beta_y\cos\beta_z + \omega_Z\cos\gamma_y\cos\gamma_z],$$
$$\Omega_{zx} = \tfrac{1}{4}[\omega_X\cos\alpha_z\cos\alpha_x + \omega_Y\cos\beta_z\cos\beta_x + \omega_Z\cos\gamma_z\cos\gamma_x].$$

The following quantity in Eq. (8) is of particular interest for later discussions:

$$\Omega_{zx}+i\Omega_{yz}=-e^{i\alpha}\sin\beta\times\tfrac{1}{4}[(\omega_X\cos^2\gamma+\omega_Y\sin^2\gamma-\omega_Z)\cos\beta+(\omega_X-\omega_Y)i\cos\gamma\sin\gamma]. \tag{10}$$

If Mu is isotropic ($\omega_X=\omega_Y=\omega_Z=\omega_0$), it can easily be verified from the orthogonality of $\hat{X}$, $\hat{Y}$, and $\hat{Z}$ [Eq. (3)] that $\Omega_{xx}=\Omega_{yy}=\Omega_{zz}=\omega_0/4$ and $\Omega_{xy}=\Omega_{yz}=\Omega_{zx}=0$.

C. Energy levels

One can obtain the energy eigenvalues by solving the secular equation $|H-\hbar\lambda I|=0$ for λ, where I is the 4×4 unit matrix. By a straightforward calculation, one can show that the secular equation will reduce to $\lambda^4+a_1\lambda^3+a_2\lambda^2+a_3\lambda+a_4=0$, where

$$\begin{aligned}
&a_1=0,\quad a_2=-[\omega_+^2+\omega_-^2+\tfrac{1}{8}(\omega_X^2+\omega_Y^2+\omega_Z^2)],\\
&a_3=2\Omega_{zz}(\omega_+^2-\omega_-^2)+\tfrac{1}{8}\omega_X\omega_Y\omega_Z,\\
&a_4=\omega_+^2\omega_-^2+\omega_+^2[(\Omega_{xx}-\Omega_{yy})^2-\Omega_{zz}^2+4\Omega_{xy}^2]\\
&\quad+\omega_-^2[(\Omega_{xx}-\Omega_{yy})^2-\Omega_{zz}^2+4\Omega_{xx}\Omega_{yy}]\\
&\quad+\tfrac{1}{4}(-\omega_X-\omega_Y-\omega_Z)\tfrac{1}{4}(-\omega_X+\omega_Y+\omega_Z)\\
&\quad\times\tfrac{1}{4}(\omega_X-\omega_Y+\omega_Z)\tfrac{1}{4}(\omega_X+\omega_Y-\omega_Z).
\end{aligned} \tag{11}$$

The quartic equation that determines the energy levels can be solved analytically, even though this is rarely done because of complexities in choosing the right phases in the solutions of the auxiliary cubic equation associated with the quartic equation. In this work, the quartic equation has been solved analytically according to the phase convention described in Ref. [41]. Figures 1(a)–1(c) show the magnetic-field dependence of the energy levels ($E/h=\omega/2\pi$ in units of MHz) of axially symmetric Mu with the principal values $\omega_X/2\pi=80$, $\omega_Y/2\pi=80$, and $\omega_Z/2\pi=130$ MHz for Euler angles $(\alpha,\beta,\gamma)=(0°,0°,0°)$, (0°,10°,0°), and (0°,90°,0°), where the energy levels E_1, E_2, E_3, and E_4 are labeled in the decreasing order of energy at a given field. In Fig. 1(a), where the Z axis is in the direction of $B(z)$, one observes that the energy levels E_2 and E_3 *cross* near $B=1.5$ mT (low-field crossing). In Fig. 1(b), where the Z symmetry axis of Mu is tilted away from the direction of B, the E_2 and E_3 do not cross anymore, but they *avoid* each other (low-field avoidance). Similar crossing and avoidance of energy levels are observed between E_1 and E_2 at much higher fields (high-field crossing or avoidance), as shown in Fig. 1(d), where the difference E_1-E_2 is plotted as a function B for Euler angles $(0°,\beta,0°)$. It can be seen that these two levels cross only when one of the principal axes coincides with the direction of the field: $\beta=0°$ and $\beta=90°$. Figures 2(a)–2(d) show similar low-field crossing or avoidance among E_1, E_2, and E_3 for fully anisotropic Mu with $\omega_X/2\pi=80$, $\omega_Y/2\pi=100$, and $\omega_Z/2\pi=130$ MHz for Euler angles $(\alpha,\beta,\gamma)=(30°,0°,0°)$, (30°,10°,0°), (30°,80°,0°), and (30°,90°,0°). For the Euler angles $0°<\beta<90°$, when the Z axis of Mu does not point in the field direction, these energy levels will avoid rather than cross. Crossing and avoidance are also observed between E_1 and E_2 at a high field analogous to the case of axially symmetric Mu. For $\omega_X=\omega_Y$, where any direction in the XY plane can be regarded as a principal axis, a level crossing is observed, either between E_2 and E_3 at a low field or between E_1 and E_2 at a high field, when the B field is in the XY (symmetry) plane. For isotropic Mu, where any direction in space can be regarded as a principal axis, the high-field crossing between E_1 and E_2 occurs at a field given by $\omega_0=2\omega_e\omega_\mu/(\omega_e-\omega_\mu)\approx2\omega_\mu$ regardless of (α,β,γ) and no level avoidance will take place. As seen in a later section, these low-field as well as high-field avoidances of energy levels will drastically affect the amplitude and relaxation rate of μSR signals.

D. Eigenstates

The eigenstates of the Hamiltonian $|n\rangle$ corresponding to ω_n can be expressed as

$$|n\rangle=U_{n1}(\alpha,\beta,\gamma)\alpha_\mu\alpha_e+U_{n2}(\alpha,\beta,\gamma)\alpha_\mu\beta_e+U_{n3}(\alpha,\beta,\gamma)\beta_\mu\alpha_e+U_{n4}(\alpha,\beta,\gamma)\beta_\mu\beta_e, \tag{12}$$

where the coefficients U_{n1}, U_{n2}, U_{n3}, U_{n4} are obtained by solving the eigenvalue equations

$$\begin{bmatrix} H_{11}-\hbar\omega_n & H_{12} & H_{13} & H_{14}\\ H_{21} & H_{22}-\hbar\omega_n & H_{23} & H_{24}\\ H_{31} & H_{32} & H_{33}-\hbar\omega_n & H_{34}\\ H_{41} & H_{42} & H_{43} & H_{44}-\hbar\omega_n \end{bmatrix}\times\begin{bmatrix}U_{n1}\\U_{n2}\\U_{n3}\\U_{n4}\end{bmatrix}=0 \tag{13}$$

under the normalization condition $|U_{n1}|^2+|U_{n2}|^2+|U_{n3}|^2+|U_{n4}|^2=1$. Writing

$$\|1\rangle=\alpha_\mu\alpha_e,\quad \|2\rangle=\alpha_\mu\beta_e,\quad \|3\rangle=\beta_\mu\alpha_e,\quad \|4\rangle=\beta_\mu\beta_e, \tag{14}$$

one can cast Eq. (12) and its inverse relation in a more compact form:

$$|n\rangle=\sum_{j=1}^{4}U_{nj}(\alpha,\beta,\gamma)\|j\rangle,\quad \|j\rangle=\sum_{k=1}^{4}U_{kj}^{*}(\alpha,\beta,\gamma)|k\rangle, \tag{15}$$

respectively. It is straightforward to show that $[U]$ satisfies the orthonormality condition

$$\sum_{j=1}^{4}U_{nj}(\alpha,\beta,\gamma)U_{kj}^{*}(\alpha,\beta,\gamma)=\delta_{nk} \tag{16}$$

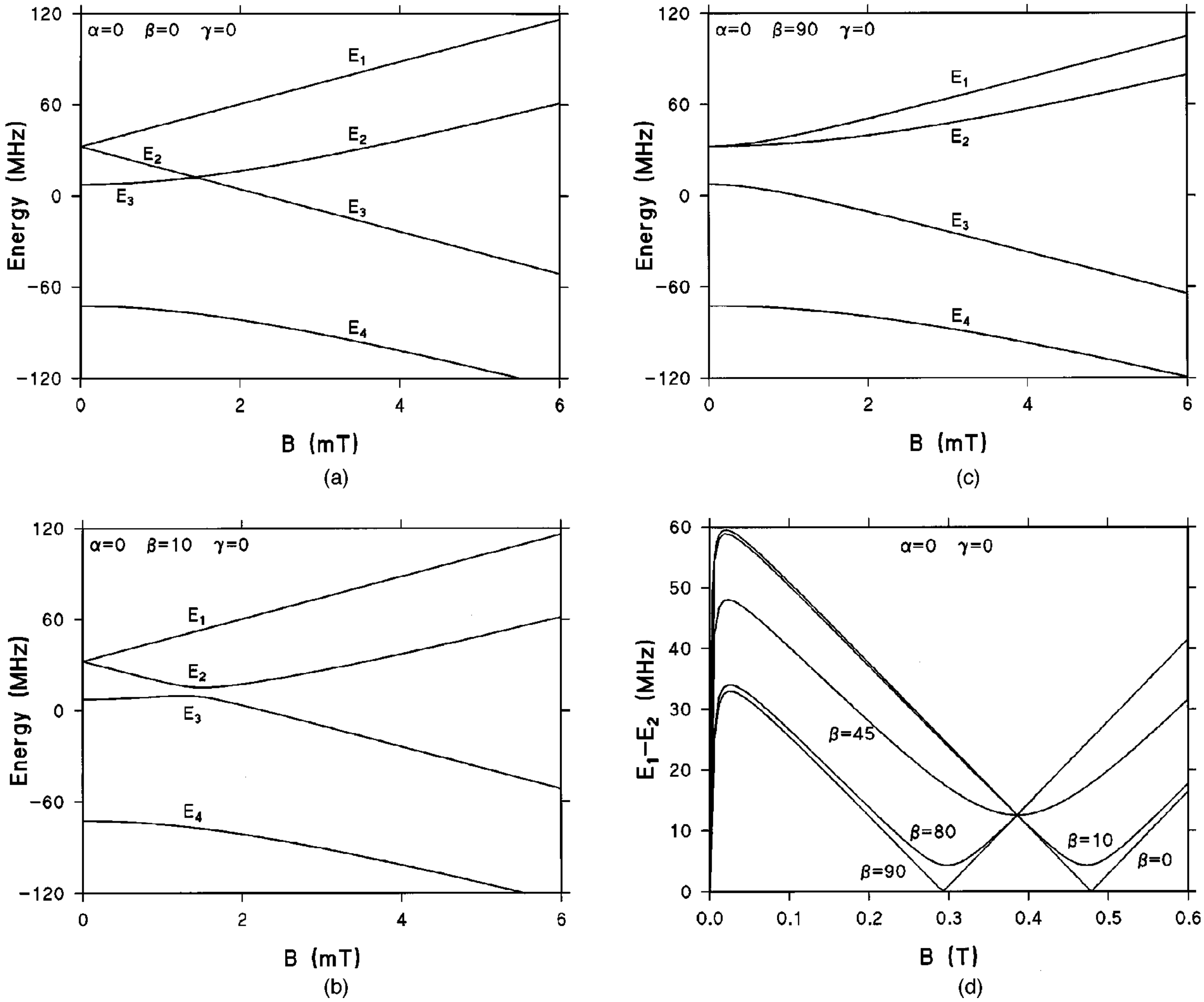

FIG. 1. Energy levels of axially symmetric Mu with $\omega_X/2\pi = 80$ MHz, $\omega_Y/2\pi = 80$ MHz, $\omega_Z/2\pi = 130$ MHz with the applied magnetic field in the z direction in the laboratory frame, where the energy levels $E_j = \hbar\omega_j$ are labeled in the descending order in energy at each field. (a) Euler angles are in units of degree $(\alpha,\beta,\gamma) = (0°,0°,0°)$, where the Z symmetry axis of Mu is in the field direction. Two levels E_2 and E_3 cross (low-field crossing) at a field near $B = 1.5$ mT. (b) $(\alpha,\beta,\gamma) = (0°,10°,0°)$, where the Z symmetry axis points away from the field. The two levels E_2 and E_3 now avoid (low-field avoidance) each other, rather than cross, at a field near $B = 1.5$ mT. (c) $(\alpha,\beta,\gamma) = (0°,90°,0°)$. (d) The difference $E_1 - E_2$ is plotted as a function of field with $(\alpha,\beta,\gamma) = (0°,\beta,0°)$, showing a high-field crossing or avoidance between E_1 and E_2 depending on β value.

and that U^*HU^T is diagonal with $\langle j|U^*HU^T|k\rangle = \Sigma_{nm} U^*_{jn} H_{nm} U_{km} = E_j \delta_{jk}$, where U^T is the transpose of the matrix U and δ_{jk} is Kronecker delta.

Once the eigenvalues are calculated analytically, U can be obtained either numerically with standard routines [48] or often analytically. In this work, the muon spin relaxation rate due to spin exchange and the initial amplitude of each precession component observed by μSR are expressed explicitly in terms of the matrix elements U_{jk} only. It is instructive at this stage to investigate special cases in which the matrix U can be obtained analytically: (i) isotropic Mu, (ii) axially symmetric anisotropic Mu in zero field, (iii) fully anisotropic Mu in zero field, (iv) anisotropic Mu with one of its principal axes in the z direction, and (v) Mu in a high field.

1. Isotropic Mu: $\omega_X = \omega_Y = \omega_Z = \omega_0$

In this case, the secular equation can be solved analytically [40,42]. The corresponding eigen-states $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$, labeled in the decreasing order of their energy eigenvalues below the high-field crossing are given by [31]

$$|1\rangle = \alpha_\mu \alpha_e, \quad |2\rangle = s\,\alpha_\mu \beta_e + c\,\beta_\mu \alpha_e,$$
$$|3\rangle = \beta_\mu \beta_e, \quad |4\rangle = c\,\alpha_\mu \beta_e - s\,\beta_\mu \alpha_e, \tag{17}$$

where c and s are field-dependent positive quantities defined by $c^2 = (1 + x/\sqrt{x^2+1})/2$ and $s^2 = (1 - x/\sqrt{x^2+1})/2$ expressed in terms of $x = B(\gamma_e + \gamma_\mu)/\omega_0$. Thus comparing this result with Eq. (12) one obtains the matrix $[U_{jk}]$ as

$$[U_{jk}] = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & s & c & 0 \\ 0 & 0 & 0 & 1 \\ 0 & c & -s & 0 \end{bmatrix}. \tag{18}$$

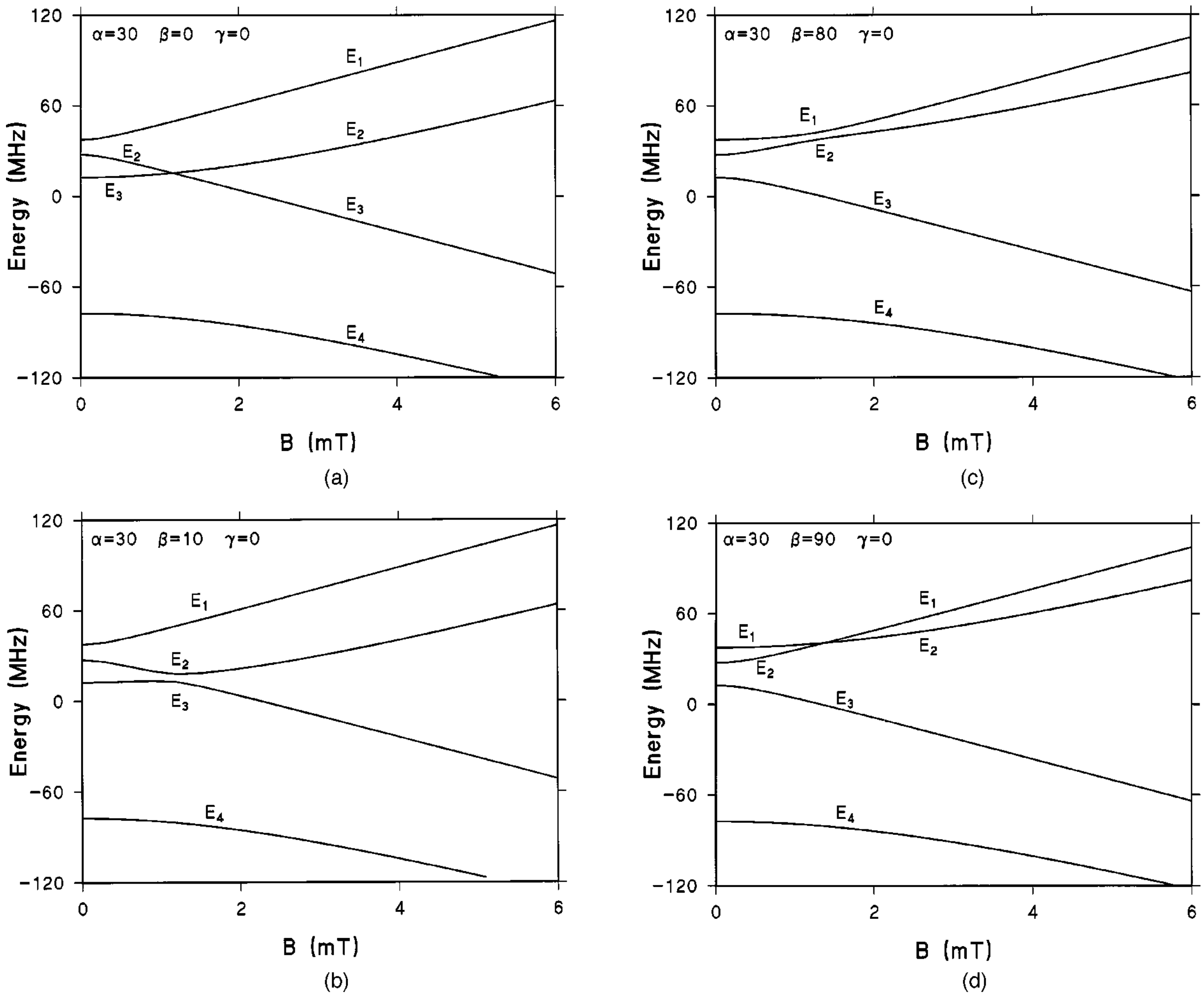

FIG. 2. Energy levels of fully anisotropic Mu with $\omega_X/2\pi = 80$ MHz, $\omega_Y/2\pi = 100$ MHz, $\omega_Z/2\pi = 130$ MHz. (a) Euler angles $(\alpha,\beta,\gamma) = (30°,0°,0°)$, where the Z symmetry axis of Mu points in the field direction. A level crossing occurs between E_2 and E_3 below $T = 2$ mT. (b) $(\alpha,\beta,\gamma) = (30°,10°,0°)$, where the Z axis points away from the field direction. The two levels E_2 and E_3 avoid, rather than cross. (c) $(\alpha,\beta,\gamma) = (30°,80°,0°)$. (d) $(\alpha,\beta,\gamma) = (30°,90°,0°)$. In this case, the $-X$ symmetry axis of Mu is in the field (z) direction, leading to a level *crossing* between E_1 and E_2.

2. Axially symmetric Mu in zero field

In zero field, where $\omega_+ = \omega_- = 0$, two eigenenergies of axially anisotropic Mu are degenerate. In the case of $\omega_X = \omega_Y$, the eigenvalues ω_1, ω_2, ω_3, and ω_4 are obtained as

$$\omega_1 = \omega_Z/4, \quad \omega_2 = \omega_Z/4, \quad \omega_3 = (2\omega_X - \omega_Z)/4, \quad \omega_4 = -(2\omega_X + \omega_Z)/4. \tag{19}$$

One can show that, in zero field, the singlet Mu state $|S_0\rangle = (\alpha_\mu\beta_e - \beta_\mu\alpha_e)/2$ is the energy eigen-state corresponding to the eigenenergy ω_4, regardless of the orientation of Mu. This means that the other three eigenstates, $|1\rangle$, $|2\rangle$, and $|3\rangle$, are linear combinations of the triplet states only, which implies from Eq. (12) that $U_{j2} = U_{j3}$ for $j = 1$, 2, and 3. One can directly solve Eqs. (13) to obtain

$$[U_{jk}] = \frac{1}{\sqrt{2}} \begin{bmatrix} (\cos\gamma_x - i\cos\gamma_y)/\sin\gamma_z & 0 & 0 & (\cos\gamma_x + i\cos\gamma_y)/\sin\gamma_z \\ (\cos\gamma_x - i\cos\gamma_y)/\tan\gamma_z & \sin\gamma_z & \sin\gamma_z & -(\cos\gamma_x + i\cos\gamma_y)/\tan\gamma_z \\ -\cos\gamma_x + i\cos\gamma_y & \cos\gamma_z & \cos\gamma_z & \cos\gamma_x + i\cos\gamma_y \\ 0 & 1 & -1 & 0 \end{bmatrix}. \tag{20}$$

From Eqs. (3) and (4), it is straightforward to show that $U^* H U^T$ is a diagonal matrix with the jj elements being $\hbar\omega_j$.

3. Fully anisotropic Mu in zero field

In this case, the solutions of the secular equation are given by

$$\omega_1=(-\omega_X+\omega_Y+\omega_Z)/4,\quad \omega_2=(\omega_X-\omega_Y+\omega_Z)/4, \tag{21}$$

$$\omega_3=(\omega_X+\omega_Y-\omega_Z)/4,\quad \omega_4=(-\omega_X-\omega_Y-\omega_Z)/4, \tag{22}$$

and the simultaneous Eqs. (13) for $[U_{jk}]$ can analytically be solved to give

$$[U_{jk}]=\frac{1}{\sqrt{2}}\begin{bmatrix} -\cos\alpha_x+i\cos\alpha_y & \cos\alpha_z & \cos\alpha_z & \cos\alpha_x+i\cos\alpha_y \\ -\cos\beta_x+i\cos\beta_y & \cos\beta_z & \cos\beta_z & \cos\beta_x+i\cos\beta_y \\ -\cos\gamma_x+i\cos\gamma_y & \cos\gamma_z & \cos\gamma_z & \cos\gamma_x+i\cos\gamma_y \\ 0 & 1 & -1 & 0 \end{bmatrix}. \tag{23}$$

4. One of the principal axes in the field direction

If one of the principal axes coincides with the field (z) direction, one can easily verify from Eq. (10) that $\Omega_{yz}=\Omega_{zx}=0$, thus the Hamiltonian matrix given by Eq. (8) becomes

$$\frac{H}{\hbar}=\begin{bmatrix} \omega_-+\Omega_{zz} & 0 & 0 & \Omega_{xx}-\Omega_{yy}-2i\Omega_{xy} \\ 0 & -\omega_+-\Omega_{zz} & \Omega_{xx}+\Omega_{yy} & 0 \\ 0 & \Omega_{xx}+\Omega_{yy} & \omega_+-\Omega_{zz} & 0 \\ \Omega_{xx}-\Omega_{yy}+2i\Omega_{xy} & 0 & 0 & -\omega_-+\Omega_{zz} \end{bmatrix}, \tag{24}$$

where the matrix takes a block form, i.e., the $\|2\rangle\|3\rangle$ subspace spanned by $\|2\rangle=\alpha_\mu\beta_e$ and $\|3\rangle=\beta_\mu\alpha_e$ is completely decoupled from the $\|1\rangle\|4\rangle$ subspace. In this case, the eigenenergies can easily be calculated within each subspace separately:

$$\omega_1=\Omega_-+\Omega_{zz},\quad \omega_2=-\Omega_+-\Omega_{zz},\quad \omega_3=\Omega_+-\Omega_{zz},\quad \omega_4=-\Omega_-+\Omega_{zz}, \tag{25}$$

where Ω_+ and Ω_- are defined as

$$\Omega_+=\sqrt{\omega_+^2+(\Omega_{xx}+\Omega_{yy})^2},\quad \Omega_-=\sqrt{\omega_-^2+(\Omega_{xx}-\Omega_{yy})^2+4\Omega_{xy}^2}. \tag{26}$$

One can obtain the matrix $[U_{jk}]$ by straightforward calculations as

$$\begin{bmatrix} (\omega_-+\Omega_-)/N_- & 0 & 0 & (\Omega_{xx}-\Omega_{yy}+2i\Omega_{xy})/N_- \\ 0 & (\omega_++\Omega_+)/N_+ & -(\Omega_{xx}+\Omega_{yy})/N_+ & 0 \\ 0 & (\Omega_{xx}+\Omega_{yy})/N_+ & (\omega_++\Omega_+)/N_+ & 0 \\ -(\Omega_{xx}-\Omega_{yy}-2i\Omega_{xy})/N_- & 0 & 0 & (\omega_-+\Omega_-)/N_- \end{bmatrix}, \tag{27}$$

where N_+ and N_- are defined as $N_+=\sqrt{2\Omega_+(\omega_++\Omega_+)}$ and $N_-=\sqrt{2\Omega_-(\omega_-+\Omega_-)}$. Here, the order of ω_1, ω_2, ω_3, and ω_4 is chosen such that $[U_{jk}]$ becomes diagonal in the high-field limit.

If $\Omega_{zz}>0$, the eigenenergies ω_1 and ω_3 will become equal at a high field approximately given by $\omega_\mu=2\Omega_{zz}$. Since the eigenstates corresponding to ω_1 and ω_3, i.e., $|1\rangle=U_{11}\|1\rangle+U_{14}\|4\rangle$ and $|3\rangle=U_{32}\|2\rangle+U_{33}\|3\rangle$, belong to the mutually independent $\|1\rangle\|4\rangle$ and $\|2\rangle\|3\rangle$ subspaces, respectively, the states $|1\rangle$ and $|3\rangle$ do not mix even at $\omega_1=\omega_3$, thus leading to a crossing of energy levels, rather than an avoidance, as exemplified by Figs. 1(a), 1(d), 2(a), and 2(d). If the principal axis does not point exactly in the field direction, nonzero off-diagonal matrix elements cause a strong mixing between $|1\rangle$ and $|3\rangle$ near the field at which the matrix elements $H_{11}=\omega_-+\Omega_{zz}$ and $H_{33}=\omega_+-\Omega_{zz}$ become identical, leading to a level avoidance, as shown in Figs. 1(b), 1(d), 2(b), and 2(c). If $\Omega_{zz}<0$, the crossing is between $|2\rangle$ and $|4\rangle$ at $\omega_2=\omega_4$.

5. High field

If the applied field is high such that $\omega_\pm\gg\omega_X,\omega_Y,\omega_Z$, the Hamiltonian matrix [Eq. (8)] becomes diagonal with the diagonal elements $\omega_1=\omega_+-\Omega_{zz}$, $\omega_2=\omega_-+\Omega_{zz}$, $\omega_3=-\omega_-+\Omega_{zz}$, $\omega_4=-\omega_+-\Omega_{zz}$, where $\omega_1,\omega_2,\omega_3,\omega_4$ are labeled in the decreasing order in the high-field limit. In this case, the matrix U_{jk} is given by

$$[U_{jk}]=\begin{bmatrix}0&0&1&0\\1&0&0&0\\0&0&0&1\\0&1&0&0\end{bmatrix}. \tag{28}$$

E. Matrix elements of the spin operators on the ($|1\rangle$, $|2\rangle$, $|3\rangle$, $|4\rangle$) basis

It is customary to express the muon spin polarization in the xy plane by a complex number, where the x and y projections correspond to the real and imaginary parts, respectively, $\sigma_+^\mu=\sigma_x^\mu+i\sigma_y^\mu$ [2,31]. It is convenient to express the spin operators σ_+^μ and σ_z^μ on the basis set ($|1\rangle$,$|2\rangle$,$|3\rangle$,$|4\rangle$). For instance, the quantity $\langle j|\sigma_+^\mu|k\rangle$ is the jk matrix element of σ_+^μ with respect to the eigenstates $|j\rangle$ and $|k\rangle$:

$$\langle j|\sigma_+^\mu|k\rangle=2(U_{j1}^*U_{k3}+U_{j2}^*U_{k4}), \tag{29}$$

$$\langle j|\sigma_z^\mu|k\rangle=U_{j1}^*U_{k1}+U_{j2}^*U_{k2}-U_{j3}^*U_{k3}-U_{j4}^*U_{k4}, \tag{30}$$

where $\langle \alpha_\mu|\sigma_+^\mu|\beta_\mu\rangle=2$ is used.

F. Time evolution of the muon spin in Mu

The time evolution of the muon spin in anisotropic Mu will be discussed in the general case, where the initial muon spin in Mu is in the direction specified by a unit vector $\hat{S}_0=(\cos\alpha_0,\cos\beta_0,\cos\gamma_0)$, where the components of $\hat{S}_0$ are the direction cosines in the laboratory system. The following identity will turn out to be useful for later discussions:

$$\begin{aligned}\hat{S}_0&=(\cos\alpha_0,\cos\beta_0,\cos\gamma_0)\\&=\hat{X}(\hat{X}\cdot\hat{S}_0)+\hat{Y}(\hat{Y}\cdot\hat{S}_0)+\hat{Z}(\hat{Z}\cdot\hat{S}_0),\end{aligned} \tag{31}$$

where the angles α_0, β_0, and γ_0 should not be confused with the Euler angles α, β, and γ, which specify the orientation of the Mu atom in the laboratory frame.

1. Initial spin state of Mu

The muon spin states ϕ_μ^+ and ϕ_μ^- in which the muon spin points in an arbitrary direction specified by the unit vectors $\hat{S}_0$ [Eq. (31)] and $-\hat{S}_0$ can be written down as [49]

$$\begin{aligned}\phi_\mu^+&=\cos\frac{\gamma_0}{2}\alpha_\mu+\frac{\cos\alpha_0+i\cos\beta_0}{2\cos(\gamma_0/2)}\beta_\mu\\&=\cos\frac{\gamma_0}{2}\alpha_\mu+e^{i\delta_0}\sin\frac{\gamma_0}{2}\beta_\mu,\end{aligned} \tag{32}$$

$$\begin{aligned}\phi_\mu^-&=\sin\frac{\gamma_0}{2}\alpha_\mu-\frac{\cos\alpha_0+i\cos\beta_0}{2\sin(\gamma_0/2)}\beta_\mu\\&=\sin\frac{\gamma_0}{2}\alpha_\mu-e^{i\delta_0}\cos\frac{\gamma_0}{2}\beta_\mu,\end{aligned} \tag{33}$$

respectively, where $\cos\delta_0$ and $\sin\delta_0$ are defined by $\cos\delta_0=\cos\alpha_0/\sin\gamma_0$ and $\sin\delta_0=\cos\beta_0/\sin\gamma_0$. One can obtain a similar set of equations for the electron by replacing the subscript "μ" by "e." Even though the muon is initially 100% spin polarized, the spins of electrons involved in Mu formations are not necessarily polarized. This leads to two possible Mu spin states at the time of a Mu formation: (i) A-Mu (parallel Mu), in which the electron spin is parallel to the muon spin and (ii) B-Mu (antiparallel Mu), where the two spins are antiparallel to each other. In this work, the electrons are assumed to be unpolarized so that A-Mu and B-Mu are produced with the same probabilities, even though it is possible to extend the argument presented in this work to the case of polarized electrons by using a method developed for isotropic Mu [37].

2. Time evolution of the spin

From Eq. (32), the initial state of this A-Mu atom in which both muon and electron spins are in the $\hat{S}_0$ direction [Eq. (31)] can be written by

$$\begin{aligned}\phi^A(0)=&\left[\cos\frac{\gamma_0}{2}\alpha_\mu+e^{i\delta_0}\sin\frac{\gamma_0}{2}\beta_\mu\right]\\&\times\left[\cos\frac{\gamma_0}{2}\alpha_e+e^{i\delta_0}\sin\frac{\gamma_0}{2}\beta_e\right],\end{aligned} \tag{34}$$

where $\cos\delta_0$ and $\sin\delta_0$ are defined in Eqs. (32) and (33). By rewriting $\alpha_\mu\alpha_e$, $\alpha_\mu\beta_e$, $\beta_\mu\alpha_e$, and $\beta_\mu\beta_e$ in Eq. (34) in terms of $|n\rangle$ [Eq. (15)], one can cast $\phi^A(0)$ in the following form:

$$\phi^A(0)=A_1|1\rangle+A_2|2\rangle+A_3|3\rangle+A_4|4\rangle=\begin{bmatrix}A_1\\A_2\\A_3\\A_4\end{bmatrix},$$

where A_k is the coefficient of $|k\rangle$ given by

$$\begin{aligned}A_k=&U_{k1}^*\cos^2\frac{\gamma_0}{2}+\tfrac{1}{2}(U_{k2}^*+U_{k3}^*)e^{i\delta_0}\sin\gamma_0\\&+U_{k4}^*e^{2i\delta_0}\sin^2\frac{\gamma_0}{2}.\end{aligned} \tag{35}$$

Since $|k\rangle$ is an eigenstate of the Hamiltonian with the eigenenergy $\hbar\omega_k$, the spin state at time t, $\phi^A(t)$, is obtained from the time-dependent Schrödinger equation as

$$\begin{aligned}\phi^A(t)=&\begin{bmatrix}e^{-i\omega_1t}A_1\\e^{-i\omega_2t}A_2\\e^{-i\omega_3t}A_3\\e^{-i\omega_4t}A_4\end{bmatrix}\\=&e^{-i\omega_1t}A_1|1\rangle+e^{-i\omega_2t}A_2|2\rangle+e^{-i\omega_3t}A_3|3\rangle\\&+e^{-i\omega_4t}A_4|4\rangle,\end{aligned} \tag{36}$$

where the kth component of $\phi^A(t)$ is $\langle k|\phi^A(t)\rangle=e^{-i\omega_kt}A_k$. The expectation value of the muon spin polarization σ^μ can be calculated as

$$G^A_{\alpha_0\beta_0\gamma_0}(t)=\langle\phi^A(t)|\sigma^\mu|\phi^A(t)\rangle$$
$$=\sum_{jk}\langle\phi^A(t)|j\rangle\langle j|\sigma^\mu|k\rangle\langle k|\phi^A(t)\rangle$$
$$=\sum_{jk}e^{i\omega_{jk}t}A_j^*A_k\langle j|\sigma^\mu|k\rangle, \tag{37}$$

where σ^μ is either σ^μ_+ [Eq. (29)] or σ^μ_z [Eq. (30)] and $\omega_{jk}=\omega_j-\omega_k$ is the energy difference between the $|j\rangle$ and $|k\rangle$ states.

Similarly, the initial spin state for antiparallel Mu (B-Mu) with the electron spin in the $-\hat{S}_0$ direction is

$$\phi^B(0)=\left[\cos\frac{\gamma_0}{2}\alpha_\mu+e^{i\delta_0}\sin\frac{\gamma_0}{2}\beta_\mu\right]\times\left[\sin\frac{\gamma_0}{2}\alpha_e-e^{i\delta_0}\cos\frac{\gamma_0}{2}\beta_e\right]=\begin{bmatrix}B_1\\B_2\\B_3\\B_4\end{bmatrix}.$$

where B_k is

$$B_k=(U^*_{k1}-U^*_{k4}e^{2i\delta_0})\cos\frac{\gamma_0}{2}\sin\frac{\gamma_0}{2}-\left(U^*_{k2}\cos^2\frac{\gamma_0}{2}-U^*_{k3}\sin^2\frac{\gamma_0}{2}\right)e^{i\delta_0}. \tag{38}$$

The muon spin in B-Mu at time t, $G^B_{\alpha_0\beta_0\gamma_0}(t)$, is obtained by replacing the quantity A_k in Eq. (37) by B_k. If A-Mn and B-Mn are produced with the same probability, the average expectation value of σ^μ is

$$G^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t)=\frac{1}{2}[G^A_{\alpha_0\beta_0\gamma_0}(t)+G^B_{\alpha_0\beta_0\gamma_0}(t)]$$
$$=\sum_{jk}\underbrace{e^{i\omega_{jk}t}}_{\text{time evolution}}\underbrace{\frac{1}{2}[A_j^*A_k+B_j^*B_k]}_{\text{initial state}}\underbrace{\langle j|\sigma^\mu|k\rangle}_{\text{quantity observed at }t} \tag{39}$$

From Eqs. (35) and (38) the quantity $(A_j^*A_k+B_j^*B_k)/2$ can be expressed in terms of $[U_{jk}]$ as

$$\tfrac{1}{2}(A_j^*A_k+B_j^*B_k)=\tfrac{1}{2}(U_{j1}U^*_{k1}+U_{j2}U^*_{k2})\cos^2\frac{\gamma_0}{2}+\tfrac{1}{2}(U_{j3}U^*_{k3}+U_{j4}U^*_{k4})\sin^2\frac{\gamma_0}{2}+\tfrac{1}{2}(U_{j1}U^*_{k3}+U_{j2}U^*_{k4})\times\tfrac{1}{2}(\cos\alpha_0+i\cos\beta_0)+\tfrac{1}{2}(U_{j3}U^*_{k1}+U_{j4}U^*_{k2})\times\tfrac{1}{2}(\cos\alpha_0-i\cos\beta_0)\equiv\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle. \tag{40}$$

The notation $\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle$ is introduced to represent the initial muon spin state in the $\hat{S}_0$ direction. It should be noted that $\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle=\langle k|\phi(\alpha_0,\beta_0,\gamma_0)|j\rangle^*$. The time evolution of the muon spin initially in the direction specified by $\hat{S}_0$ observed at time t is expressed in terms of $\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle$ as

$$G^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t)=\sum_{jk}\underbrace{e^{i\omega_{jk}t}}_{\text{time evolution}}\underbrace{\langle k|\phi(\alpha_0,\beta_0,\gamma_0)|j\rangle}_{\text{initial state}}\underbrace{\langle j|\sigma^\mu|k\rangle}_{\text{observed at }t}=\sum_{jk}e^{i\omega_{jk}t}\quad I^{\sigma^\mu}_{jk}(\alpha_0,\beta_0,\gamma_0), \tag{41}$$

where σ^μ is either σ^μ_z [Eq. (30)] or σ^μ_+ [Eq. (29)]. It should be noted that the amplitude given by

$$I^{\sigma^\mu}_{jk}(\alpha_0,\beta_0,\gamma_0)=\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle\langle j|\sigma^\mu|k\rangle \tag{42}$$

is completely specified by the matrix elements $[U_{jk}]$ through Eqs. (29), (30), and (40). Concerning Eq. (40), the following two special cases are of practical interest: (i) the transverse field, where $(\alpha_0,\beta_0,\gamma_0)=(0°,90°,90°)$ and (ii) the longitudinal field, where $(\alpha_0,\beta_0,\gamma_0)=(90°,90°,0°)$:

$$\langle j|\phi(0°,90°,90°)|k\rangle=\tfrac{1}{4}[(U_{j1}+U_{j3})(U^*_{k1}+U^*_{k3})+(U_{j2}+U_{j4})(U^*_{k2}+U^*_{k4})], \tag{43}$$

$$\langle j|\phi(90°,90°,0°)|k\rangle=\tfrac{1}{2}(U_{j1}U^*_{k1}+U_{j2}U^*_{k2}). \tag{44}$$

Unlike in the case of isotropic Mu, the muon spin in anisotropic Mu in a transverse (longitudinal) field does not necessarily remain in the xy plane (z axis), i.e., both $I^{\sigma^\mu_z}_{jk}(0°,90°,90°)$ and $I^{\sigma^\mu_+}_{jk}(90°,90°,0°)$, can be nonvanishing, which reflects the tensor nature of the anisotropic hyperfine interaction.

G. Transitions induced by spin exchange

When Mu collides with a paramagnetic species with an unpaired electron, there is a finite probability that two unpaired electrons are exchanged [31,37,41,40,42]:

$$\alpha_e\alpha\rightarrow\alpha_e\alpha(1+e^{i\Delta})/2+\alpha_e\alpha(1-e^{i\Delta})/2,$$
$$\alpha_e\beta\rightarrow\alpha_e\beta(1+e^{i\Delta})/2+\beta_e\alpha(1-e^{i\Delta})/2, \tag{45}$$

$$\beta_e\alpha \rightarrow \beta_e\alpha(1+e^{i\Delta})/2+\alpha_e\beta(1-e^{i\Delta})/2,$$
$$\beta_e\beta \rightarrow \beta_e\beta(1+e^{i\Delta})/2+\beta_e\beta(1-e^{i\Delta})/2, \tag{46}$$

where the subscripts ''e'' refer to the electron spin in the Mu atom, while the electron spin states without a subscript represent those of paramagnetic species. This phenomenon, called Heisenberg spin exchange, arises from the fact that electrons obey the Pauli principle [31,42], where the quantity Δ is the difference in phase shifts between electron spin triplet and singlet encounters [31,42,50]. The probability that a collision is of the spin-flip type is given by $|(1-e^{i\Delta})/2|^2=\sin^2(\Delta/2)$, while the spin nonflip probability is $|(1+e^{i\Delta})/2|^2=\cos^2(\Delta/2)$. The case with $\Delta=\pi$ ($\Delta=0$) corresponds to a purely spin-flip (or nonflip) collision. It is customary to define the spin-flip and spin nonflip rates as

$$\lambda_{\rm SF}=\lambda\sin^2(\Delta/2)=nv\sigma\sin^2(\Delta/2)=nv\sigma_{\rm SF}, \tag{47}$$

$$\lambda_{\rm NF}=\lambda\cos^2(\Delta/2)=nv\sigma\cos^2(\Delta/2)=nv\sigma_{\rm NF}, \tag{48}$$

where n is the number density of the paramagnetic species, v is the relative velocity, λ and σ are the rate and cross section for collisions, while $\sigma_{\rm SF}$, and $\sigma_{\rm NF}$ are the spin-flip and spin nonflip cross sections, respectively. It should be emphasized that λ includes collisions of both spin-flip and spin nonflip types: $\lambda=\lambda_{\rm SF}+\lambda_{\rm NF}$. More detailed interpretation for $\lambda_{\rm SF}$ and $\lambda_{\rm NF}$ and the quantum-mechanical expressions for σ, $\sigma_{\rm SF}$, and $\sigma_{\rm NF}$ in terms of partial-wave phase shifts can be found in Ref. [42].

It is important to study the effects of a collision, which can be either of spin-flip or spin nonflip type, on the eigenstates of Mu. Suppose that Mu is in the $|n\rangle$ state and that the muonium atom is to collide a paramagnetic species with an α electron. Using Eq. (15), one can write down the initial state as

$$|n\rangle\alpha=U_{n1}\alpha_\mu\alpha_e\alpha+U_{n2}\alpha_\mu\beta_e\alpha+U_{n3}\beta_\mu\alpha_e\alpha+U_{n4}\beta_\mu\beta_e\alpha. \tag{49}$$

Substituting Eqs. (45) and (46) in the right-hand side of this equation, one can write the wave function after the collision as

$$|n\rangle\alpha \rightarrow |n\rangle\alpha\frac{1+e^{i\Delta}}{2}+(U_{n1}\alpha_\mu\alpha_e\alpha+U_{n2}\alpha_\mu\alpha_e\beta + U_{n3}\beta_\mu\alpha_e\alpha+U_{n4}\beta_\mu\alpha_e\beta)\frac{1-e^{i\Delta}}{2}. \tag{50}$$

Using Eq. (15), one can express the states $\alpha_\mu\alpha_e$ and $\beta_\mu\alpha_e$ in the second term as $\alpha_\mu\alpha_e=\Sigma_{j=1}^4 U_{j1}^*|j\rangle$ and $\beta_\mu\alpha_e=\Sigma_{j=1}^4 U_{j3}^*|j\rangle$. Thus the net effect of a collision with an α paramagnetic species can be written as

$$|n\rangle\alpha \rightarrow \frac{1+e^{i\Delta}}{2}|n\rangle\alpha+\frac{1-e^{i\Delta}}{2}\sum_{j=1}^{4}[(U_{n1}U_{j1}^*+U_{n3}U_{j3}^*)|j\rangle\alpha + (U_{n2}U_{j1}^*+U_{n4}U_{j3}^*)|j\rangle\beta]. \tag{51}$$

Here, one introduces a 4×4 matrix T^α, which operates on a Mu spin state expressed in terms of a superposition of the Mu hyperfine eigenstates

$$\psi=X_1|1\rangle+X_2|2\rangle+X_3|3\rangle+X_4|4\rangle=\begin{bmatrix}X_1\\X_2\\X_3\\X_4\end{bmatrix} \tag{52}$$

and produces the spin state immediately after a collision with an α paramagnetic species. In this notation, Eq. (51) can also be written in the following form:

$$|n\rangle\alpha \rightarrow T^\alpha|n\rangle=T^\alpha\begin{bmatrix}\delta_{1n}\\\delta_{2n}\\\delta_{3n}\\\delta_{4n}\end{bmatrix}=\begin{bmatrix}T^\alpha_{1n}\\T^\alpha_{2n}\\T^\alpha_{3n}\\T^\alpha_{4n}\end{bmatrix}, \tag{53}$$

where the matrix element T^α_{jn} can be obtained from Eq. (51) as

$$T^\alpha_{jn}=\delta_{jn}\,\alpha(1+e^{i\Delta})/2+[(U_{j1}^*U_{n1}+U_{j3}^*U_{n3})\alpha + (U_{j1}^*U_{n2}+U_{j3}^*U_{n4})\beta](1-e^{i\Delta})/2. \tag{54}$$

Thus the effect of operating T^α on ψ [Eq. (52)] can be written down as

$$T^\alpha\psi=T^\alpha\begin{bmatrix}X_1\\X_2\\X_3\\X_4\end{bmatrix}=\begin{bmatrix}\sum_j^4 T^\alpha_{1j}X_j\\\sum_j^4 T^\alpha_{2j}X_j\\\sum_j^4 T^\alpha_{3j}X_j\\\sum_j^4 T^\alpha_{4j}X_j\end{bmatrix}. \tag{55}$$

Assuming now Eq. (52) is the Mu spin state at time t_n just before a collision, one can obtain the kth component of $T^\alpha\psi$ at t_n immediately after the collision and at time t after t_n as

$$\langle k|T^\alpha\psi(t_n)\rangle=\sum_j^4 T^\alpha_{kj}X_j(t_n),$$

$$\langle k|T^\alpha(t-t_n)\psi(t_n)\rangle=e^{-i\omega_k(t-t_n)}\sum_j^4 T^\alpha_{kj}X_j(t_n), \tag{56}$$

respectively. It should be noted that the coefficients T^α_{kj} ($j,k=1,2,3,4$) contain α and β, which refer to the electron spin of the paramagnetic species after the collision, and that $T^\alpha(t-t_n)\psi(t_n)$ is normalized, provided that $\psi(t_n)$ before the collision is normalized.

Similarly, one can define a matrix T^β_{nj}, which describes the effect of a collision with a β paramagnetic species, by

$$T^{\beta}_{jn}=\delta_{jn}\beta(1+e^{i\Delta})/2+[(U^*_{j2}U_{n2}+U^*_{j4}U_{n4})\beta+(U^*_{j2}U_{n1}+U^*_{j4}U_{n3})\alpha](1-e^{i\Delta})/2. \tag{57}$$

The operator T^{β} converts the spin state given by Eq. (52) to $T^{\beta}\psi$, where the kth components of $T^{\beta}\psi$ immediately after the collision at t_n and that at t after t_n are

$$\langle k|T^{\beta}\psi(t_n)\rangle=\sum_{j}^{4} T^{\beta}_{kj}X_j,$$

$$\langle k|T^{\beta}(t-t_n)\psi(t_n)\rangle=e^{-i\omega_k(t-t_n)}\sum_{j}^{4} T^{\beta}_{kj}X_j. \tag{58}$$

The matrices T^{α} and T^{β} introduced here represent an extension to anisotropic Mu of similar quantities considered earlier for isotropic hydrogenlike atoms (H,Mu,Ps) undergoing spin exchange with spin-$\frac{1}{2}$ [41,42] and spin-1 [40] paramagnetic species.

H. Effects of spin exchange on the muon spin

One considers now an A-Mu atom, produced at time $t=0$ with the muon spin pointing in the $\hat{S}_0$ direction [Eq. (31)], undergoes the first collision at t_1. The state of this Mu just before the first collision at t_1, $\phi^A(t_{10})$, is given by Eq. (36), where the jth component (jth row) is $e^{-i\omega_j t_{10}}A_j$. Suppose now that the first collision takes place with a paramagnetic species with an α electron. The spin state immediately after the first collision at t_1 with an α paramagnetic species and that immediately before the second collision at t_2 can be written from Eq. (56) as

$$\langle k|T^{\alpha}\phi^A(t_{10})\rangle=\sum_{k_1}^{4} e^{-i\omega_{k_1}t_{10}}T^{\alpha}_{kk_1}A_{k_1} \quad \text{and} \tag{59}$$

$$\begin{aligned}\langle k|T^{\alpha}(t_{21})\phi^A(t_{10})\rangle&=e^{-i\omega_k t_{21}}\sum_{k_1}^{4} e^{-i\omega_{k_1}t_{10}}T^{\alpha}_{kk_1}A_{k_1}\\ &=[(1+e^{i\Delta})/2]e^{-i\omega_k t_{20}}A_k\alpha^1+[(1-e^{i\Delta})/2]\sum_{k_1}^{4} e^{-i\omega_k t_{21}}e^{-i\omega_{k_1}t_{10}}(U^*_{k1}U_{k_11}+U^*_{k3}U_{k_13})A_{k_1}\alpha^1\\ &\quad+[(1-e^{i\Delta})/2]\sum_{k_1}^{4} e^{-i\omega_k t_{21}}e^{-i\omega_{k_1}t_{10}}(U^*_{k1}U_{k_12}+U^*_{k3}U_{k_14})A_{k_1}\beta^1,\end{aligned} \tag{60}$$

respectively, where α^1 and β^1 represent the spin states after t_1 of the paramagnetic species involved in the first collision at t_1. From Eq. (16), one can show that the state $T^{\alpha}(t_{21})\phi^A(t_{10})$ is normalized. The expectation value of a muon spin operator σ^{μ} [Eq. (29) or (30)] at t_2 after a collision at t_1 with α paramagnetic species can be calculated as

$$\begin{aligned}\langle\phi^A(t_{10})T^{\alpha}(t_{21})|\sigma^{\mu}|T^{\alpha}(t_{21})\phi^A(t_{10})\rangle&=\sum_{jk}\langle\phi^A(t_{10})T^{\alpha}(t_{21})|j\rangle\langle j|\sigma^{\mu}|k\rangle\langle k|T^{\alpha}(t_{21})\phi^A(t_{10})\rangle\\ &=\cos^2(\Delta/2)\sum_{jk} e^{i\omega_{jk}t_{20}}A^*_jA_k\langle j|\sigma^{\mu}|k\rangle\\ &\quad+\sin^2(\Delta/2)\sum_{jk} e^{i\omega_{jk}t_{21}}\sum_{j_1k_1} e^{i\omega_{j_1k_1}t_{10}}A^*_{j_1}A_{k_1}\langle j_1k_1|\Lambda_{\alpha}|jk\rangle\langle j|\sigma^{\mu}|k\rangle\\ &\quad+(1+e^{-i\Delta})(1-e^{i\Delta})/4\sum_{jk} e^{i\omega_{jk}t_{21}}\sum_{k_1} e^{i\omega_{jk_1}t_{10}}A^*_jA_{k_1}(U^*_{k1}U_{k_11}+U^*_{k3}U_{k_13})\langle j|\sigma^{\mu}|k\rangle\\ &\quad+(1+e^{i\Delta})(1-e^{-i\Delta})/4\sum_{jk} e^{i\omega_{jk}t_{21}}\sum_{j_1} e^{i\omega_{j_1k}t_{10}}A_kA^*_{j_1}(U_{j1}U^*_{j_11}+U_{j3}U^*_{j_13})\langle j|\sigma^{\mu}|k\rangle,\end{aligned} \tag{61}$$

where $\langle j_1k_1|\Lambda_{\alpha}|jk\rangle$ is expressed by U_{jk} by

$$\langle j_1k_1|\Lambda_{\alpha}|jk\rangle=(U_{j1}U^*_{j_11}+U_{j3}U^*_{j_13})(U^*_{k1}U_{k_11}+U^*_{k3}U_{k_13})+(U_{j1}U^*_{j_12}+U_{j3}U^*_{j_14})(U^*_{k1}U_{k_12}+U^*_{k3}U_{k_14}). \tag{62}$$

For the case where the first collision at t_1 is with a β paramagnetic species, one can write down the expectation value of the muon spin polarization at t_2 by replacing T^{α} in Eq. (61) by T^{β}:

$$\langle \phi^A(t_{10})T^{\beta}(t_{21})|\sigma^{\mu}|T_{\beta}(t_{21})\phi^A(t_{10})\rangle = \cos^2(\Delta/2)\sum_{jk} e^{i\omega_{jk}t_{20}}A_j^*A_k\langle j|\sigma^{\mu}|k\rangle$$
$$+\sin^2(\Delta/2)\sum_{jk} e^{i\omega_{jk}t_{21}}\sum_{j_1k_1} e^{i\omega_{j_1k_1}t_{10}}A_{j_1}^*A_{k_1}\langle j_1k_1|\Lambda_{\beta}|jk\rangle\langle j|\sigma^{\mu}|k\rangle$$
$$+(1+e^{-i\Delta})(1-e^{-i\Delta})/4\sum_{jk} e^{i\omega_{jk}t_{21}}\sum_{k_1} e^{i\omega_{jk_1}t_{10}}A_j^*A_{k_1}(U_{k2}^*U_{k_12}+U_{k4}^*U_{k_14})\langle j|\sigma^{\mu}|k\rangle$$
$$+(1+e^{i\Delta})(1-e^{-i\Delta})/4\sum_{jk} e^{i\omega_{jk}t_{21}}\sum_{j_1} e^{i\omega_{j_1k}t_{10}}A_kA_{j_1}^*(U_{j2}U_{j_12}^*+U_{j4}U_{j_14}^*)\langle j|\sigma^{\mu}|k\rangle \quad (63)$$

where $\langle j_1k_1|\Lambda_{\beta}|jk\rangle = (U_{j2}U_{j_11}^*+U_{j4}U_{j_13}^*)(U_{k2}^*U_{k_11}+U_{k4}^*U_{k_13})+(U_{j2}U_{j_12}^*+U_{j4}U_{j_14}^*)(U_{k2}^*U_{k_12}+U_{k4}^*U_{k_14}).$ (64)

If the spin of the paramagnetic species is not polarized so that collisions with α and β paramagnetic species occur with the same probabilities, the average of the muon spin polarization can be obtained from Eqs. (61) and (63):

$$P^A_{\alpha_0\beta_0\gamma_0}(t_1,t_2) = \tfrac{1}{2}[\langle \phi^A(t_{10})T^{\alpha}(t_{21})|\sigma^{\mu}|T^{\alpha}(t_{21})\phi^A(t_{10})\rangle + \langle \phi^A(t_{10})T^{\beta}(t_{21})|\sigma^{\mu}|T^{\beta}(t_{21})\phi^A(t_{10})\rangle]$$
$$= \cos^2(\Delta/2)\sum_{jk} e^{i\omega_{jk}t_{20}}A_j^*A_k\langle j|\sigma^{\mu}|k\rangle + \sin^2(\Delta/2)\sum_{jk} e^{i\omega_{jk}t_{21}}\sum_{j_1k_1} e^{i\omega_{j_1k_1}t_{10}}A_{j_1}^*A_{k_1}\langle j_1k_1|\Lambda|jk\rangle\langle j|\sigma^{\mu}|k\rangle, \quad (65)$$

where the last two terms of Eqs. (61) cancel against those of Eq. (63) because of the orthogonality given by Eq. (16). In Eq. (65), the quantity $\langle j_1k_1|\Lambda|jk\rangle$ is defined as

$$2\langle j_1k_1|\Lambda|jk\rangle = \langle j_1k_1|\Lambda_{\alpha}|jk\rangle + \langle j_1k_1|\Lambda_{\beta}|jk\rangle. \quad (66)$$

By rearranging Eqs. (62) and (64), one can express $\langle j_1k_1|\Lambda|jk\rangle$ as

$$2\langle j_1k_1|\Lambda|jk\rangle = (U_{j_11}^*U_{k_11}+U_{j_12}^*U_{k_12})(U_{j1}U_{k1}^*+U_{j2}U_{k2}^*)+(U_{j_11}^*U_{k_13}+U_{j_12}^*U_{k_14})(U_{j1}U_{k3}^*+U_{j2}U_{k4}^*)$$
$$+(U_{j_13}^*U_{k_11}+U_{j_14}^*U_{k_12})(U_{j3}U_{k1}^*+U_{j4}U_{k2}^*)+(U_{j_13}^*U_{k_13}+U_{j_14}^*U_{k_14})(U_{j3}U_{k3}^*+U_{j4}U_{k4}^*). \quad (67)$$

It is important to recognize that $\langle j_1k_1|\Lambda|jk\rangle = \langle jk|\Lambda|j_1k_1\rangle^*$. One can obtain the muon spin of B-Mu after one collision at t_1 by replacing A_jA_k in Eq. (65) by B_jB_k. The muon spin polarization observed at t_2 after one collision at t_1 averaged over the spin direction of the paramagnetic species and over A- and B-Mu is

$$P^{\sigma^{\mu}}_{\alpha_0\beta_0\gamma_0}(t_1,t_2) = \tfrac{1}{2}[P^A_{\alpha_0\beta_0\gamma_0}(t_1,t_2)+P^B_{\alpha_0\beta_0\gamma_0}(t_1,t_2)] = \cos^2(\Delta/2)\sum_{jk} e^{i\omega_{jk}t_{20}}\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle\langle j|\sigma^{\mu}|k\rangle + \sin^2(\Delta/2)$$
$$\times\sum_{jk} e^{i\omega_{jk}t_{21}}\sum_{j_1k_1} e^{i\omega_{j_1k_1}t_{10}}\langle j_1|\phi(\alpha_0,\beta_0,\gamma_0)|k_1\rangle\langle j_1k_1|\Lambda|jk\rangle\langle j|\sigma^{\mu}|k\rangle, \quad (68)$$

where $\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle$ is defined by Eq. (40). The coefficient of $\cos^2(\Delta/2)$ in Eq. (68) can be recognized as $G^{\sigma^{\mu}}_{\alpha_0\beta_0\gamma_0}(t_{20})$ [Eq. (41)], which represents the time evolution from $t_0=0$ to t_2 unaffected by the collision at t_1, consistent with the interpretation of $\cos^2(\Delta/2)$ being the spin nonflip probability, while the second terms of Eq. (68) describe a spin-flip collision at t_1. With two terms together, Eq. (68) represents the weighted average of spin-flip and nonflip contributions. The quantities $\langle nm|\Lambda|jk\rangle$ contain all the information on spin exchange. It is interesting to note that in each term of Eq. (68) three pieces of information concerning the initial wave function, spin-exchange collision, and the physical quantity observed at t enter the expression as a simple product. Extending this to the case of two collisions, one can write the muon spin polarization at t_3 after two collisions at t_1 and t_2 as

$$
\begin{aligned}
P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t_1,t_2,t_3) = {} & \cos^2(\Delta_1/2)\cos^2(\Delta_2/2)\sum_{jk} e^{i\omega_{jk}t_{30}}\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle\langle j|\sigma^\mu|k\rangle \\
& + \cos^2(\Delta_1/2)\sin^2(\Delta_2/2)\sum_{jk} e^{i\omega_{jk}t_{32}}\sum_{j_1k_1} e^{i\omega_{j_1k_1}t_{20}}\langle j_1|\phi(\alpha_0,\beta_0,\gamma_0)|k_1\rangle\langle j_1k_1|\Lambda|jk\rangle\langle j|\sigma^\mu|k\rangle \\
& + \sin^2(\Delta_1/2)\cos^2(\Delta_2/2)\sum_{jk} e^{i\omega_{jk}t_{31}}\sum_{j_1k_1} e^{i\omega_{j_1k_1}t_{10}}\langle j_1|\phi(\alpha_0,\beta_0,\gamma_0)|k_1\rangle\langle j_1k_1|\Lambda|jk\rangle\langle j|\sigma^\mu|k\rangle \\
& + \sin^2(\Delta_1/2)\sin^2(\Delta_2/2)\sum_{jk} e^{i\omega_{jk}t_{32}}\sum_{j_1k_1} e^{i\omega_{j_1k_1}t_{21}}\sum_{j_2k_2} e^{i\omega_{j_2k_2}t_{10}}\langle j_2|\phi(\alpha_0,\beta_0,\gamma_0)|k_2\rangle\langle j_2k_2|\Lambda|j_1k_1\rangle \\
& \times\langle j_1k_1|\Lambda|jk\rangle\langle j|\sigma^\mu k\rangle, \qquad (69)
\end{aligned}
$$

where σ^μ is either σ^μ_+ [equation (29)] or σ^μ_z [equation (30)]. The first term of Eq. (69) is independent of t_1 and t_2, representing two spin nonflip collisions, where spin dynamics is not affected by the two collisions. The fourth term gives the muon spin polarization in anisotropic Mu after two spin-flip collisions at t_1 and t_2. In the case of isotropic Mu, Eq. (69) reduces to a much simpler equation discussed earlier in Ref. [31].

One can obtain the muon spin polarization in anisotropic Mu observed at t by averaging the quantity $P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t_1,t_2,\dots,t_n,t)$ over all possible time distributions of $t_1,t_2,\dots,t_n$ for a fixed n, then over n from zero to infinity. If the collision process is Poissonian, the statistically averaged muon polarization is given by [31]

$$
P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t)=\sum_{n=0}^{\infty}\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^{t_n}dt_{n-1}\int_0^{t}dt_n\, e^{-\lambda t}\lambda^n P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t_1,t_2,\dots,t_n,t), \qquad (70)
$$

where λ is the average collision rate regardless of the types of collisions, spin flip or spin nonflip. As evident from Eq. (69), the quantity $P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t_1,t_2,\dots,t_n,t)$ contains 2^{n-1} spin nonflip collisions. Since $P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t_1,t_2,\dots,t_n,t)$ does not depend on t_k, at which spin nonflip collisions take place, one can carry out all the integrations with respect to times associated with spin nonflip collisions in a straightforward manner [37,41]. In the present case, the result of such integrations can be written down as

$$
P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t)=\sum_{n=0}^{\infty}\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^{t_n}dt_{n-1}\int_0^{t}dt_n\, e^{-\lambda_{SF}t}\lambda^n_{\rm SF} P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}\{t_1,t_2,\dots,t_n,t\}, \qquad (71)
$$

where $P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}\{t_1,t_2,\dots,t_n,t\}$ is defined by

$$
\begin{aligned}
P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}\{t_1,t_2,\cdots,t_n,t\} = {} & \sum_{jk}\sum_{j_1k_1}\cdots\sum_{j_nk_n}\overbrace{e^{i\omega_{jk}(t-t_n)}\,e^{i\omega_{j_1k_1}t_{n\,n-1}}\cdots e^{i\omega_{j_{n-1}k_{n-1}}t_{21}}\,e^{i\omega_{j_nk_n}t_{10}}}^{\text{time evolution}} \\
\times & \underbrace{\langle j_n|\phi(\alpha_0,\beta_0,\gamma_0)|k_n\rangle}_{\text{initial state}}\underbrace{\langle j_nk_n|\Lambda|j_{n-1}k_{n-1}\rangle\cdots\langle j_2k_2|\Lambda|j_1k_1\rangle\,\langle j_1k_1|\Lambda|jk\rangle}_{n\text{ consecutive spin flips}}\underbrace{\langle j|\sigma^\mu|k\rangle}_{\text{quantity observed at }t} \qquad (72)
\end{aligned}
$$

Equation (71) shows that for a Poisson process the muon spin polarization observed at t depends on the spin-flip rate ($\lambda_{\rm SF}$) but not on the spin nonflip rate ($\lambda_{\rm NF}$). It should be emphasized, however, that for non-Poissonian processes the quantity $P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t)$ can depend not only on the spin-flip rate but also on the spin nonflip rate [37]. The quantity $P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}\{t_1,t_2,\dots,t_n,t\}$ represents the muon spin polarization after n consecutive *spin-flip* collisions. It can easily be shown from Eqs. (29), (30), (40), and (67) that

$$
\sum_{j_1k_1}\langle j_2k_2|\Lambda|j_1k_1\rangle\langle j_1k_1|\Lambda|jk\rangle=\langle j_2k_2|\Lambda|jk\rangle, \qquad (73)
$$

$$
\sum_{j_1k_1}\langle j_1|\phi(\alpha_0,\beta_0,\gamma_0)|k_1\rangle\langle j_1k_1|\Lambda|jk\rangle =\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle, \qquad (74)
$$

$$
\sum_{jk}\langle j_1k_1|\Lambda|jk\rangle\langle j|\sigma^\mu|k\rangle=\langle j_1|\sigma^\mu|k_1\rangle. \qquad (75)
$$

I. Slow spin exchange

In order to obtain the expression for the muon spin polarization observed at time t from Eq. (71), it is convenient to treat slow and fast spin exchange separately. In this work, only slow spin exchange is treated in detail, and the case of fast spin exchange will be discussed elsewhere.

If λ_{SF} is much less than $|\omega_X|$, $|\omega_Y|$, and $|\omega_Z|$, only terms in Eq. (72) with $j=j_1=j_2=\cdots=j_n$ and $k=k_1=k_2=\cdots=k_n$ will survive the integrations with respect to $t_1,t_2,\ldots,t_n$ in Eq. (71) as discussed in Ref. [31]. In this case, Eq. (72) can be simplified as

$$P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}\{t_1,t_2,\ldots,t_n,t\}=\sum_{jk} e^{i\omega_{jk}t}\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle \times\langle jk|\Lambda|jk\rangle^n\langle j|\sigma^\mu|k\rangle. \quad (76)$$

Since this quantity is independent of $t_1,t_2,\ldots,t_n$, the integrals in Eq. (71) lead to $\int_0^{t_2}dt_1\int_0^{t_3}dt_2\cdots\int_0^t dt_n\rightarrow t^n/n!$. Thus $P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t)$ in Eq. (71) can be written as

$$\begin{aligned}P^{\sigma^\mu}_{\alpha_0\beta_0\gamma_0}(t)&=\sum_{jk} e^{i\omega_{jk}t}\langle j|\phi(\alpha_0,\beta_0,\gamma_0)|k\rangle\\&\quad\times\langle j|\sigma^\mu|k\rangle\sum_n^\infty \frac{e^{-\lambda_{\mathrm{SF}}t}}{n!}[\lambda_{\mathrm{SF}}\langle jk|\Lambda|jk\rangle t]^n\\&=\sum_{jk} e^{i\omega_{jk}t}I^{\sigma^\mu}_{jk}(\alpha_0\beta_0\gamma_0)\\&\quad\times\exp[-\lambda_{\mathrm{SF}}(1-\langle jk|\Lambda|jk\rangle)t],\end{aligned} \quad (77)$$

where $I^{\sigma^\mu}_{jk}(\alpha_0\beta_0\gamma_0)=\langle j|\phi(\alpha_0\beta_0\gamma_0)|k\rangle\langle j|\sigma^\mu|k\rangle$ is the initial amplitude for $e^{i\omega_{jk}t}$ defined by Eq. (42). Equation (77) shows that the relaxation rate for the $e^{i\omega_{jk}t}$ precession is given by

$$\lambda^{\mathrm{obs}}_{jk}=\lambda_{\mathrm{SF}}(1-\langle jk|\Lambda|jk\rangle), \quad (78)$$

where λ^{obs}_{jk} can be expressed in terms of the U matrix elements through Eq. (67), which also shows that $\langle jk|\Lambda|jk\rangle=\langle jk|\Lambda|jk\rangle^*$, i.e., $\langle jk|\Lambda|jk\rangle$ is a real quantity. Furthermore, it can be shown $\langle jk|\Lambda|jk\rangle=\langle kj|\Lambda|kj\rangle$, so that the two precessing components $e^{i\omega_{jk}t}$ and $e^{i\omega_{kj}t}$ have the same relaxation rate, even though their amplitudes $I^{\sigma^\mu}_{jk}(\alpha_0\beta_0\gamma_0)$ and $I^{\sigma^\mu}_{kj}(\alpha_0\beta_0\gamma_0)$ may differ from each other as shown in Fig. 3(a). Since $\langle nm|\Lambda|jk\rangle$ can be regarded from Eq. (72) as the probability that a spin-flip collision converts $e^{i\omega_{nm}t}$ to $e^{i\omega_{jk}t}$, the quantity $\langle jk|\Lambda|jk\rangle$ is the survival probability that the precession $e^{i\omega_{jk}t}$ is not affected by a spin-flip collision. The quantity $1-\langle jk|\Lambda|jk\rangle$ in Eq. (78), therefore, represents the probability that $e^{i\omega_{jk}t}$ is converted to other precession components, thus causing dephasing.

The above argument leading to Eq. (77) is strictly for the case where the precession frequencies ω_{jk} are all different. If some of ω_{jk}'s happen to be the same, a little more careful analysis is required. For the sake of argument, let ω_{12} be identical to ω_{23} as in the case of isotropic Mu in low fields. The component that precesses coherently with the precession frequency $\omega_{12}=\omega_{23}$ before the first collision [Eq. (41)] can be written out as

$$\begin{aligned}e^{i\omega_{12}t}I^{\sigma^\mu}_{12,23}&=e^{i\omega_{12}t}\langle 1|\phi|2\rangle\langle 1|\sigma|2\rangle+e^{i\omega_{23}t}\langle 2|\phi|3\rangle\langle 2|\sigma|3\rangle\\&=e^{i\omega_{12}t}[\langle 1|\phi|2\rangle,\langle 2|\phi|3\rangle]\begin{bmatrix}\langle 1|\sigma^\mu|2\rangle\\\langle 2|\sigma^\mu|3\rangle\end{bmatrix},\end{aligned} \quad (79)$$

where the amplitude $I_{12,23}$ is a product from a row vector with a column vector. After one spin flip, the corresponding coherent terms in $P^{\sigma^\mu}\{t_1,t\}$ can be found from Eq. (72) to be

$$\begin{aligned}&e^{i\omega_{12}(t-t_1)}e^{i\omega_{12}t_1}\langle 1|\phi|2\rangle\langle 12|\Lambda|12\rangle\langle 1|\sigma^\mu|2\rangle\\&\quad+e^{i\omega_{12}(t-t_1)}e^{i\omega_{23}t_1}\langle 1|\phi|2\rangle\langle 12|\Lambda|23\rangle\langle 2|\sigma^\mu|3\rangle\\&\quad+e^{i\omega_{23}(t-t_1)}e^{i\omega_{12}t_1}\langle 2|\phi|3\rangle\langle 23|\Lambda|12\rangle\langle 1|\sigma^\mu|2\rangle\\&\quad+e^{i\omega_{23}(t-t_1)}e^{i\omega_{23}t_1}\langle 2|\phi|3\rangle\langle 23|\Lambda|23\rangle\langle 2|\sigma^\mu|3\rangle\\&=e^{i\omega_{12}t}[\langle 1|\phi|2\rangle,\langle 2|\phi|3\rangle][\Lambda^{2\times 2}_{12,23}]\begin{bmatrix}\langle 1|\sigma^\mu|2\rangle\\\langle 2|\sigma^\mu|3\rangle\end{bmatrix}\\&=e^{i\omega_{12}t}I^{\sigma^\mu}_{12,23}R_1^{12,23},\end{aligned} \quad (80)$$

where $[\Lambda^{2\times 2}_{12,23}]$ is a 2×2 matrix defined as

$$[\Lambda^{2\times 2}_{12,23}]=\begin{bmatrix}\langle 12|\Lambda|12\rangle & \langle 12|\Lambda|23\rangle\\\langle 23|\Lambda|12\rangle & \langle 23|\Lambda|23\rangle\end{bmatrix}. \quad (81)$$

Extending this argument to the case of many collisions, one can show in a straightforward manner that this component after n spin-flip collisions will become

$$\begin{aligned}&e^{i\omega_{12}t}[\langle 1|\phi|2\rangle,\langle 2|\phi|3\rangle][\Lambda^{2\times 2}_{12,23}]^n\begin{bmatrix}\langle 1|\sigma^\mu|2\rangle\\\langle 2|\sigma^\mu|3\rangle\end{bmatrix}\\&\quad=e^{i\omega_{12}t}I^{\sigma^\mu}_{12,23}(R_n^{12,23})^n,\end{aligned} \quad (82)$$

where $R_n^{12,23}$ is a scaler quantity defined by this equation. If $R_1^{12,23}=R_2^{12,23}=\cdots=R_n^{12,23}=R_{12,23}$, one can carry out, using Eq. (71), the calculation for the Poisson average for this component as

$$P^{\sigma^\mu}_{12,23}(t)=e^{\omega_{12}t}I^{\sigma^\mu}_{12,23}\exp[-(1-R_{12,23})\lambda_{\mathrm{SF}}t]. \quad (83)$$

If, on the other hand, the condition $R_1^{12,23}=R_2^{12,23}=\cdots=R_n^{12,23}=R_{12,23}$ is not satisfied, the relaxation is not simply exponential.

Equation (72) has a nonoscillating (DC) component arising from terms with $j=k$, $j_1=k_1$, $j_2=k_2,\ldots$, $j_n=k_n$ that survives the integrations with respect to $t_1,t_2,\ldots,t_n$. The relaxation rate for this component can be calculated in the following way. The time-independent muon spin polarization before the first collision [Eq. (41)] is expressed by

$$I_{\rm DC}^{\sigma^\mu}=\sum_j \langle j|\phi|j\rangle\langle j|\sigma^\mu|j\rangle$$

$$=[\langle 1|\phi|1\rangle,\langle 2|\phi|2\rangle,\langle 3|\phi|3\rangle,\langle 4|\phi|4\rangle]\begin{bmatrix}\langle 1|\sigma^\mu|1\rangle\\ \langle 2|\sigma^\mu|2\rangle\\ \langle 3|\sigma^\mu|3\rangle\\ \langle 4|\sigma^\mu|4\rangle\end{bmatrix}. \quad (84)$$

The DC component after one spin-flip collision can be written from Eq. (72) as

$$P_{\rm DC}^{\sigma^\mu}\{t_1,t\}=\sum_j\sum_{j_1}\langle j_1|\phi|j_1\rangle\langle j_1j_1|\Lambda|jj\rangle\langle j|\sigma^\mu|j\rangle$$

$$=[\langle 1|\phi|1\rangle,\langle 2|\phi|2\rangle,\langle 3|\phi|3\rangle,\langle 4|\phi|4\rangle][\Lambda_{\rm DC}^{4\times4}]$$

$$\times\begin{bmatrix}\langle 1|\sigma^\mu|1\rangle\\ \langle 2|\sigma^\mu|2\rangle\\ \langle 3|\sigma^\mu|3\rangle\\ \langle 4|\sigma^\mu|4\rangle\end{bmatrix}=I_{\rm DC}^{\sigma^\mu}R_1^{\rm DC}, \quad (85)$$

where $[\Lambda_{\rm DC}^{4\times4}]$ is a 4×4 matrix defined by

$$[\Lambda_{\rm DC}^{4\times4}]=\begin{bmatrix}\langle 11|\Lambda|11\rangle & \langle 11|\Lambda|22\rangle & \langle 11|\Lambda|33\rangle & \langle 11|\Lambda|44\rangle\\ \langle 22|\Lambda|11\rangle & \langle 22|\Lambda|22\rangle & \langle 22|\Lambda|33\rangle & \langle 22|\Lambda|44\rangle\\ \langle 33|\Lambda|11\rangle & \langle 33|\Lambda|22\rangle & \langle 33|\Lambda|33\rangle & \langle 33|\Lambda|44\rangle\\ \langle 44|\Lambda|11\rangle & \langle 44|\Lambda|22\rangle & \langle 44|\Lambda|33\rangle & \langle 44|\Lambda|44\rangle\end{bmatrix}, \quad (86)$$

and the quantity $\langle jj|\Lambda|kk\rangle$ is given by Eq. (67). After n spin-flip collisions, the DC component of the muon spin polarization is

$$P_{\rm DC}^{\sigma^\mu}\{t_1,\ldots,t_n,t\}=\sum_j\sum_{j_1}\cdots\sum_{j_n}\langle j_n|\phi|j_n\rangle$$

$$\times\langle j_nj_n|\Lambda|j_{n-1}j_{n-1}\rangle\cdots\langle j_1j_1|\Lambda|jj\rangle$$

$$\times\langle j|\sigma^\mu|j\rangle$$

$$=[\langle 1|\phi|1\rangle,\langle 2|\phi|2\rangle,\langle 3|\phi|3\rangle,\langle 4|\phi|4\rangle]$$

$$\times[\Lambda_{\rm DC}^{4\times4}]^n\begin{bmatrix}\langle 1|\sigma^\mu|1\rangle\\ \langle 2|\sigma^\mu|2\rangle\\ \langle 3|\sigma^\mu|3\rangle\\ \langle 4|\sigma^\mu|4\rangle\end{bmatrix}$$

$$=I_{\rm DC}^{\sigma^\mu}(R_n^{\rm DC})^n. \quad (87)$$

If $R_1^{\rm DC}=R_2^{\rm DC}=\cdots=R_n^{\rm DC}=R_{\rm DC}$, one can express the relaxation of the DC component as

$$P_{\rm DC}^{\sigma^\mu}(t)=I_{\rm DC}^{\sigma^\mu}\exp[-(1-R_{\rm DC})\lambda_{\rm SF}t]. \quad (88)$$

III. DISCUSSION

Using the method developed above, one can express the initial amplitudes and the relaxation rates due to electron spin exchange explicitly in terms of the matrix $[U_{jk}]$, which diagonalizes the Hamiltonian. In this section, this method is applied to several specific cases of experimental relevance, including the cases where all the experimental observables of the muon spin rotation techniques can be expressed analytically.

A. Axially symmetric Mu in zero field

If the Mu atom is axially asymmetric with $\omega_X=\omega_Y\neq\omega_Z$, the $[U_{jk}]$ matrix is given by Eq. (20). In this case, one can show from Eq. (40) that

$$\langle j|\phi(\alpha_0\beta_0\gamma_0)|k\rangle=\frac{1}{4}\begin{bmatrix}1 & \hat{Z}\cdot\hat{S}_0 & C & iD\\ \hat{Z}\cdot\hat{S}_0 & 1 & -iD & -C\\ C & iD & 1 & \hat{Z}\cdot\hat{S}_0\\ -iD & -C & \hat{Z}\cdot\hat{S}_0 & 1\end{bmatrix}, \quad (89)$$

where $C=\cos\alpha\cos\beta\cos\alpha_0+\sin\alpha\cos\beta\cos\beta_0-\sin\beta\cos\gamma_0$ and $D=\sin\alpha\cos\alpha_0-\cos\alpha\cos\beta_0$. The matrix $\langle j|\sigma_+^\mu|k\rangle$ can be calculated from Eq. (29) as

$$\langle j|\sigma_+^\mu|k\rangle=\begin{bmatrix}0 & e^{i\alpha}\sin\beta & e^{i\alpha}\cos\beta & -e^{i\alpha}\\ e^{i\alpha}\sin\beta & 0 & e^{i\alpha} & -e^{i\alpha}\cos\beta\\ e^{i\alpha}\cos\beta & -e^{i\alpha} & 0 & e^{i\alpha}\sin\beta\\ e^{i\alpha} & -e^{i\alpha}\cos\beta & e^{i\alpha}\sin\beta & 0\end{bmatrix}, \quad (90)$$

while the matrix $\langle j|\sigma_z^\mu|k\rangle$ is from Eq. (30):

$$\langle j|\sigma_z^\mu|k\rangle=\begin{bmatrix}0 & \cos\beta & -\sin\beta & 0\\ \cos\beta & 0 & 0 & \sin\beta\\ -\sin\beta & 0 & 0 & \cos\beta\\ 0 & \sin\beta & \cos\beta & 0\end{bmatrix}. \quad (91)$$

For $\omega_X=\omega_Y$, the two energy levels are degenerate as seen from Eq. (19) and Figs. 1(a)–1(c), where $\omega_{12}=\omega_{21}=0$, ω_{13}

$=\omega_{23}$, and $\omega_{14}=\omega_{24}$. From Eqs. (20) and (67) one can show $\langle 13|\Lambda|13\rangle=\langle 14|\Lambda|14\rangle=\langle 23|\Lambda|23\rangle=\langle 24|\Lambda|24\rangle=\langle 34|\Lambda|34\rangle=\frac{1}{4}$ and $\langle 13|\Lambda|23\rangle=\langle 23|\Lambda|13\rangle=\langle 14|\Lambda|24\rangle=\langle 24|\Lambda|14\rangle=0$. Thus the precession components $e^{i\omega_{34}t}$ and $e^{i\omega_{43}t}$ have a relaxation rate $3\lambda_{SF}/4$ given by Eq. (78). The relaxation rate of the $e^{i\omega_{13}t}$ ($e^{i\omega_{23}t}$) component is obtained from a matrix similar to Eq. (81):

$$[\Lambda^{2\times 2}_{13,23}]=\begin{bmatrix}\langle 13|\Lambda|13\rangle & \langle 13|\Lambda|23\rangle\\ \langle 23|\Lambda|13\rangle & \langle 23|\Lambda|23\rangle\end{bmatrix}=\frac{1}{4}\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix},$$

from which one obtains $R_1^{13,23}=R_2^{13,23}=\cdots R_n^{13,23}=R_{13,23}=\frac{1}{4}$. The observed relaxation rate is, therefore, $(1-R_{13,23})\lambda_{SF}=3\lambda_{SF}/4$ from Eq. (83). It turns out that all the precession components have the same relaxation rate.

There are six nonoscillating terms corresponding to $e^{i\omega_{11}}$, $e^{i\omega_{22}}$, $e^{i\omega_{33}}$, $e^{i\omega_{44}}$, $e^{i\omega_{12}}$, and $e^{i\omega_{21}}$. Here, one considers the expectation value of σ_+^μ. The amplitude of the nonoscillating component before the first collision is obtained in an expression similar to Eq. (84):

$$I_{DC}^{\sigma_+^\mu}=[\langle 1|\phi|1\rangle,\langle 2|\phi|2\rangle,\langle 3|\phi|3\rangle,\langle 4|\phi|4\rangle,\langle 1|\phi|2\rangle,\langle 2|\phi|1\rangle]\times[\langle 1|\sigma_+^\mu|1\rangle,\langle 2|\sigma_+^\mu|2\rangle,\langle 3|\sigma_+^\mu|3\rangle,\langle 4|\sigma_+^\mu|4\rangle,\langle 1|\sigma_+^\mu|2\rangle,\langle 2|\sigma_+^\mu|1\rangle]^T, \quad (92)$$

where T means the transpose of the row vector. Since the diagonal elements of $\langle j|\sigma_+^\mu|k\rangle$ vanish, this expression reduces to

$$I_{DC}^{\sigma_+^\mu}(t)=[\langle 1|\phi|2\rangle,\langle 2|\phi|1\rangle]\begin{bmatrix}\langle 1|\sigma_+^\mu|2\rangle\\ \langle 2|\sigma_+^\mu|1\rangle\end{bmatrix}=\tfrac{1}{2}(\hat{Z}\cdot\hat{S}_0)e^{i\alpha}\sin\beta. \quad (93)$$

One can verify directly that $\langle 12|\Lambda|kk\rangle=\langle 21|\Lambda|kk\rangle=\langle kk|\Lambda|12\rangle=\langle kk|\Lambda|21\rangle=0$ for $k=1$, 2, 3, and 4. Thus the DC components after n spin-flip collisions can be simplified to

$$P_{DC}^{\sigma_+^\mu}\{t_1,t_2,\ldots,t_n,t\}=[\langle 1|\phi|2\rangle,\langle 2|\phi|1\rangle]\times[\Lambda^{2\times 2}_{12,21}]^n\begin{bmatrix}\langle 1|\sigma_+^\mu|2\rangle\\ \langle 2|\sigma_+^\mu|1\rangle\end{bmatrix}=(\tfrac{1}{2})^n\tfrac{1}{2}(\hat{Z}\cdot\hat{S}_0)e^{i\alpha}\sin\beta, \quad (94)$$

where

$$[\Lambda^{2\times 2}_{12,21}]=\begin{bmatrix}\langle 12|\Lambda|12\rangle & \langle 12|\Lambda|21\rangle\\ \langle 21|\Lambda|12\rangle & \langle 21|\Lambda|21\rangle\end{bmatrix}=\begin{bmatrix}1/4 & 1/4\\ 1/4 & 1/4\end{bmatrix}. \quad (95)$$

Equation (94) means $R_1^{DC}=R_2^{DC}=\cdots R_n^{DC}=R_{DC}^{+}=\frac{1}{2}$. Therefore, the relaxation rate for the DC component is $\lambda_{SF}(1-R_{DC}^{z})=\lambda_{SF}/2$. Combining the oscillating and nonoscillating components calculated above and taking the real part of $P_{\alpha_0\beta_0\gamma_0}^{\sigma_+^\mu}(t)$, one can rewrite the x component of the polarization at time t as

$$P_{\alpha_0\beta_0\gamma_0}^{\sigma_x^\mu}(t)=(\tfrac{1}{2})e^{-3\lambda_{SF}t/4}[\cos\alpha_x(\hat{X}\cdot\hat{S}_0)(\cos\omega_{23}t+\cos\omega_{24}t)]+(\tfrac{1}{2})e^{-3\lambda_{SF}t/4}[\cos\beta_x(\hat{Y}\cdot\hat{S}_0)\times(\cos\omega_{23}t+\cos\omega_{24}t)]+(\tfrac{1}{2})e^{-3\lambda_{SF}t/4}[\cos\gamma_x(\hat{Z}\cdot\hat{S}_0)\cos\omega_{34}t]+(\tfrac{1}{2})e^{-\lambda_{SF}t/2}\cos\gamma_x(\hat{Z}\cdot\hat{S}_0), \quad (96)$$

where ω_{jk} are obtained from Eq. (19). It should be noted that the oscillating and nonoscillating components have different relaxation rates. The quantities $P_{\alpha_0\beta_0\gamma_0}^{\sigma_y^\mu}(t)$ and $P_{\alpha_0\beta_0\gamma_0}^{\sigma_z^\mu}(t)$ can be obtained by replacing the subscript x in Eq. (96) by y and z, respectively. If many anisotropic Mu atoms are oriented randomly, while $\hat{S}_0$ is fixed in the (x,y,z) system, the quantity $P_{\alpha_0\beta_0\gamma_0}^{\sigma_x^\mu}(t)$ averaged over the Euler angles, α, β, and γ, can be obtained by

$$\langle P_{\alpha_0\beta_0\gamma_0}^{\sigma_x^\mu}(t)\rangle_{\alpha\beta\gamma}=\frac{1}{8\pi^2}\int_0^{2\pi}d\alpha\int_0^{\pi}\sin\beta d\beta\int_0^{2\pi}d\gamma P_{\alpha_0\beta_0\gamma_0}^{\sigma_x^\mu}(t)=\tfrac{1}{6}\cos\alpha_0[e^{-\lambda_{SF}t/2}+e^{-3\lambda_{SF}t/4}\times(2\cos\omega_{23}t+2\cos\omega_{24}t+\cos\omega_{34}t)], \quad (97)$$

The angle-average quantities along the y and z direction are obtained by replacing $\cos\alpha_0$ in this equation by $\cos\beta_0$ and $\cos\gamma_0$, respectively.

B. Fully anisotropic Mu in zero field

Using Eqs. (13) and (40), one can verify directly that

$$\langle j|\phi(\alpha_0\beta_0\gamma_0)|k\rangle=\frac{1}{4}\begin{bmatrix}1 & i\hat{Z}\cdot\hat{S}_0 & -i\hat{Y}\cdot\hat{S}_0 & \hat{X}\cdot\hat{S}_0\\ -i\hat{Z}\cdot\hat{S}_0 & 1 & i\hat{X}\cdot\hat{S}_0 & \hat{Y}\cdot\hat{S}_0\\ i\hat{Y}\cdot\hat{S}_0 & -i\hat{X}\cdot\hat{S}_0 & 1 & \hat{Z}\cdot\hat{S}_0\\ \hat{X}\cdot\hat{S}_0 & \hat{Y}\cdot\hat{S}_0 & \hat{Z}\cdot\hat{S}_0 & 1\end{bmatrix}, \quad (98)$$

$$\langle j|\sigma_z^{\mu}|k\rangle = \begin{bmatrix} 0 & -i\cos\gamma_z & i\cos\beta_z & \cos\alpha_z \\ i\cos\gamma_z & 0 & -i\cos\alpha_z & \cos\beta_z \\ -i\cos\beta_z & i\cos\alpha_z & 0 & \cos\gamma_z \\ \cos\alpha_z & \cos\beta_z & \cos\gamma_z & 0 \end{bmatrix}, \tag{99}$$

where similar matrices $\langle j|\sigma_x^{\mu}|k\rangle$ and $\langle j|\sigma_y^{\mu}|k\rangle$ are obtained by replacing the subscript z by x and y. Since the diagonal elements of $\langle j|\sigma_+^{\mu}|k\rangle$ and $\langle j|\sigma_z^{\mu}|k\rangle$ vanish, all the initial amplitudes for the nonprecessing components $I_{jj}^{\sigma^{\mu}} = \langle j|\phi|j\rangle\langle j|\sigma^{\mu}|j\rangle$ will vanish. From Eqs. (23) and (67) one obtains $\langle jk|\Lambda|jk\rangle = \frac{1}{4}$, i.e., all the precessing components have the same relaxation rate, $3\lambda_{\mathrm{SF}}/4$. Thus the muon spin polarization in the z direction is written down as

$$\begin{aligned} P_{\alpha_0\beta_0\gamma_0}^{\sigma_z^{\mu}}(t) = {}& \cos\alpha_z(\hat{X}\cdot\hat{S}_0)e^{-3\lambda_{\mathrm{SF}}t/4}(\tfrac{1}{2})[\cos\omega_{14}t + \cos\omega_{23}t] \\ & + \cos\beta_z(\hat{Y}\cdot\hat{S}_0)e^{-3\lambda_{\mathrm{SF}}t/4}(\tfrac{1}{2})[\cos\omega_{13}t \\ & + \cos\omega_{24}t] + \cos\gamma_z(\hat{Z}\cdot\hat{S}_0)e^{-3\lambda_{\mathrm{SF}}t/4}(\tfrac{1}{2}) \\ & \times[\cos\omega_{12}t + \cos\omega_{34}t]. \end{aligned} \tag{100}$$

One observes up to six precession frequencies. If one of the symmetry axes of Mu (X,Y,Z) is chosen as the z (detection) direction, only two oscillation frequencies are observed. In the special case of $\lambda_{\mathrm{SF}}=0$, Eq. (100) should be compared to the result by Macrae *et al.* [24]. One can obtain the x and y components of the muon spin polarization simply by replacing the subscripts z in Eq. (100) by x and y, respectively. Three detectors placed on the X, Y, and Z axes of the Mu frame observe different sets of oscillation frequencies, e.g., the $X(Y)$ detector sees only ω_{14} and ω_{23} (ω_{13} and ω_{24}), a manifestation of the tensor nature of the anisotropic interaction. The angle-averaged quantity can be written by

$$\begin{aligned} \langle P_{\alpha_0\beta_0\gamma_0}^{\sigma_z^{\mu}}(t)\rangle_{\alpha\beta\gamma} &= \frac{1}{8\pi^2}\int_0^{2\pi} d\alpha \int_0^{\pi}\sin\beta d\beta \int_0^{2\pi} d\gamma P_{\alpha_0\beta_0\gamma_0}^{\sigma_z^{\mu}}(t) \\ &= \tfrac{1}{6}\cos\gamma_0 e^{-3\lambda_{\mathrm{SF}}t/4}[\cos\omega_{12}t + \cos\omega_{13}t + \cos\omega_{14}t \\ &\quad + \cos\omega_{23}t + \cos\omega_{24}t + \cos\omega_{34}t]. \end{aligned}$$

Similar quantities $\langle P_{\alpha_0\beta_0\gamma_0}^{\sigma_x^{\mu}}(t)\rangle_{\alpha\beta\gamma}$ and $\langle P_{\alpha_0\beta_0\gamma_0}^{\sigma_y^{\mu}}(t)\rangle_{\alpha\beta\gamma}$ can be obtained by replacing the $\cos\gamma_0$ by $\cos\alpha_0$ and $\cos\beta_0$, respectively.

High field

From Eq. (28) the matrices $\langle j|\phi|k\rangle$, $\langle j|\sigma_+^{\mu}|k\rangle$, and $\langle j|\sigma_z^{\mu}|k\rangle$ are written down as

$$\langle j|\phi|k\rangle = \begin{bmatrix} \frac{1}{2}\sin^2\frac{\gamma_0}{2} & \frac{1}{4}(\cos\alpha_0 - i\cos\beta_0) & 0 & 0 \\ \frac{1}{4}(\cos\alpha_0 + i\cos\beta_0) & \frac{1}{2}\cos^2\frac{\gamma_0}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2}\sin^2\frac{\gamma_0}{2} & \frac{1}{4}(\cos\alpha_0 - i\cos\beta_0) \\ 0 & 0 & \frac{1}{4}(\cos\alpha_0 + i\cos\beta_0) & \frac{1}{2}\cos^2\frac{\gamma_0}{2} \end{bmatrix}, \tag{101}$$

$$\langle j|\sigma_+^{\mu}|k\rangle = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{bmatrix}, \quad \langle j|\sigma_z^{\mu}|K\rangle = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}. \tag{102}$$

From Eq. (42) the only precession components observed are $e^{i\omega_{21}t}$ and $e^{i\omega_{43}t}$ in the xy components, while one can directly calculate $\langle 21|\Lambda|21\rangle = \langle 43|\Lambda|43\rangle = \frac{1}{2}$; the relaxation rate for oscillating components are $\lambda_{\mathrm{SF}}/2$. One can write

$$\begin{aligned} P_{\alpha_0\beta_0\gamma_0}^{\sigma_+^{\mu}}(t) &= \tfrac{1}{2}(\cos\alpha_0 + i\cos\beta_0)e^{-\lambda_{\mathrm{SF}}t/2}(e^{i\omega_{21}t} + e^{i\omega_{43}}), \\ P_{\alpha_0\beta_0\gamma_0}^{\sigma_z^{\mu}}(t) &= \cos\gamma_0. \end{aligned} \tag{103}$$

C. Transverse fields

For this field configuration of practical importance [Eq. (43)], where σ_+^{μ} is measured, the amplitude for the precession component $e^{i\omega_{jk}t}I_{jk}^{\sigma_+^{\mu}}(0°,90°,90°)$ is simplified as I_{jk}^{+T}. Using Eqs. (29) and (42), one can show that $I_{jk}^{+T} + (I_{kj}^{+T})^* \geqslant 0$ for $j \neq k$, that is, the imaginary parts of I_{jk}^{+T} and I_{kj}^{+T} are identical. Figure 3(a) shows the absolute value of the precession amplitudes I_{jk}^{+T} for axially symmetric Mu with $\omega_X/2\pi$

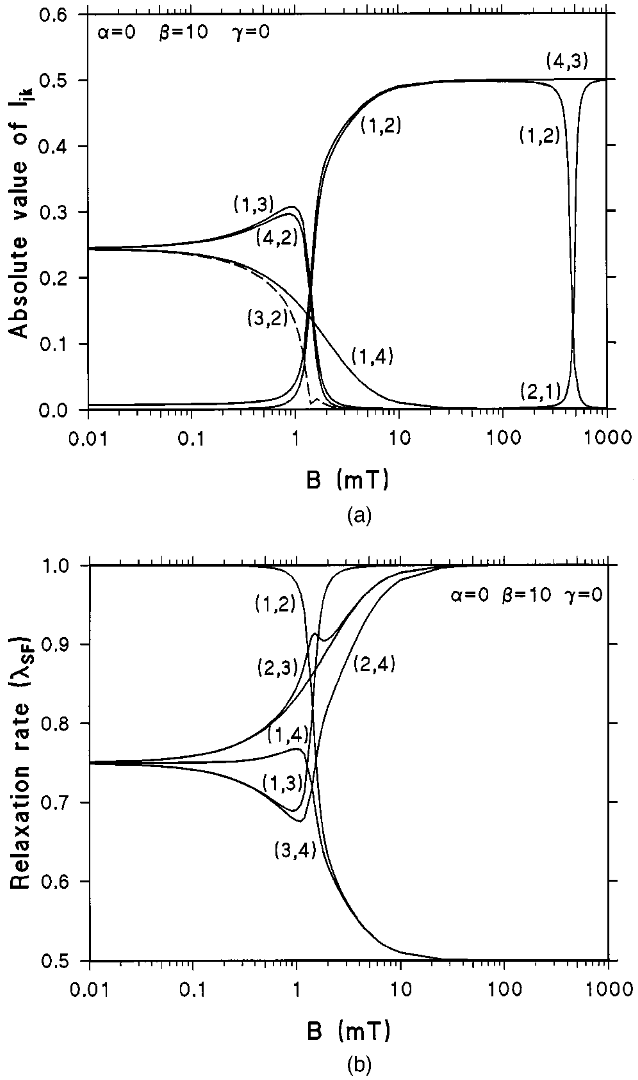

FIG. 3. Axially symmetric Mu with $\omega_X/2\pi = 80$ MHz, $\omega_Y/2\pi = 80$ MHz, $\omega_Z/2\pi = 130$ MHz at the Euler angles $(\alpha,\beta,\gamma) = (0°,10°,0°)$. (a) The absolute value of the amplitude $|I_{jk}^{+T}|$ for the precession component $e^{i\omega_{jk}t}$ for the transverse field configuration [Eq. (43)], where σ_+^μ is measured. The label (j,k) represents $|I_{jk}^{+T}|$. Above the high-field avoidance at $B = 0.48$ T only I_{21}^{+T} and I_{43}^{+T} are observable. (b) The transverse relaxation rate in units of λ_{SF} calculated from Eq. (78). Because of $\langle jk|\Lambda|jk\rangle = \langle kj|\Lambda|kj\rangle$, the two precessing components $e^{i\omega_{jk}t}$ and $e^{i\omega_{kj}t}$ have the same relaxation rate.

$= 80$ MHz, $\omega_Y/2\pi = 80$ MHz, and $\omega_Z/2\pi = 130$ MHz for Euler angles $(\alpha,\beta,\gamma) = (0°,10°,0°)$, where the matrix $[U_{jk}]$ was calculated numerically. Near the low-field avoidance near $B = 1.5$ mT, the amplitudes I_{jk}^{+T} show complex field dependencies because of the avoidance between E_2 and E_3 shown in Fig. 1(b). Above the high-field avoidance $B > 480$ mT, only I_{21}^{+T} and I_{43}^{+T} are observable in agreement with Eq. (103). Figure 3(b) shows the transverse relaxation rate for the same Mu in units of the spin-flip rate λ_{SF}. From Eq. (67) one can show the precession components $I_{jk}^{+T} e^{i\omega_{jk}t}$ and $I_{kj}^{+T} e^{i\omega_{kj}t}$ have the same relaxation rate. The low-field relaxation rate is $3\lambda_{SF}/4$ as given by Eq. (100). The relaxation rates show complex field dependencies near the low-field crossing, while the high-field crossing has no effect.

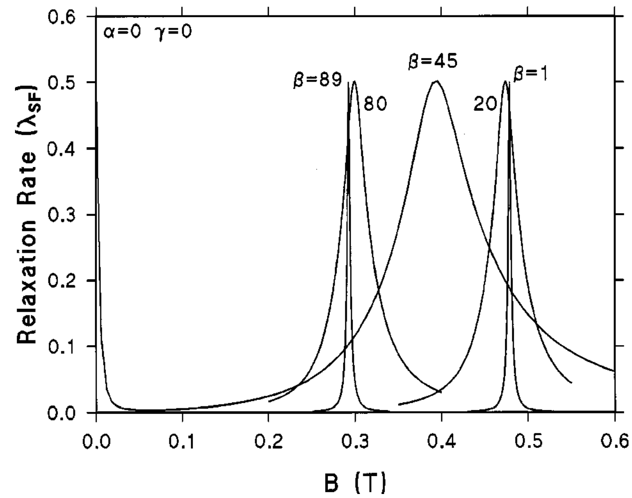

FIG. 4. The relaxation rate for the nonoscillating (DC) component in the longitudinal configuration near the high-field avoiding or crossing field for an axially symmetric Mu with $\omega_X/2\pi = 80$ MHz, $\omega_Y/2\pi = 80$ MHz, $\omega_Z/2\pi = 130$ MHz.

D. Longitudinal fields

In this section, one investigates the nonoscillating component of $P_{\alpha_0\beta_0\gamma_0}^{\sigma_z^\mu}(t)$ in the case where the initial muon spin polarization is in the z direction [Eq. (44)]. Using Eqs. (30) and (71), one can write the DC term before the first collision as

$$I_{\rm DC} = \sum_j \tfrac{1}{2}(U_{j1}U_{j1}^* + U_{j2}U_{j2}^*) \times (U_{j1}^*U_{j1} + U_{j2}^*U_{j2} - U_{j3}^*U_{j3} - U_{j4}^*U_{j4}). \quad (104)$$

The DC component after one and n spin-flip collisions can be obtained from Eqs. (85) and (87), respectively. The quantities $R_1^{\rm DC}, R_2^{\rm DC}, R_3^{\rm DC},\ldots$ are calculated numerically for the cases of $\omega_X/2\pi = 80$ MHz, $\omega_Y/2\pi = 80$ MHz, $\omega_Z/2\pi = 130$ MHz for $\beta = 1°$, 10°, 45°, 80°, and 89° with fixed $\alpha = 0°$ and $\gamma = 0°$, where it is found $R_1^{\rm DC} = R_2^{\rm DC} = R_3^{\rm DC} = \cdots = R_{DC}$. Figure 4 shows the longitudinal relaxation rate, $\lambda_{SF}(1 - R_{\rm DC})$, calculated numerically in units of λ_{SF}, where a relaxation maximum occurs at the field of energy level avoidance between E_1 and E_2. As the angle β approaches 0° or 90°, the peak narrows considerably and eventually disappears at $\beta = 0°$ or 90°, where the Z or X axis points in the field direction. Such a relaxation rate maximum was observed experimentally in axially symmetric Mu in n-type Si by Chow *et al.* [16] and Krasnoperov [22] and the phenomenon was satisfactorily interpreted by an effective magnetic-field approximation [16] that replaces the anisotropic hyperfine interaction (tensor) by an effective field (vector). In the

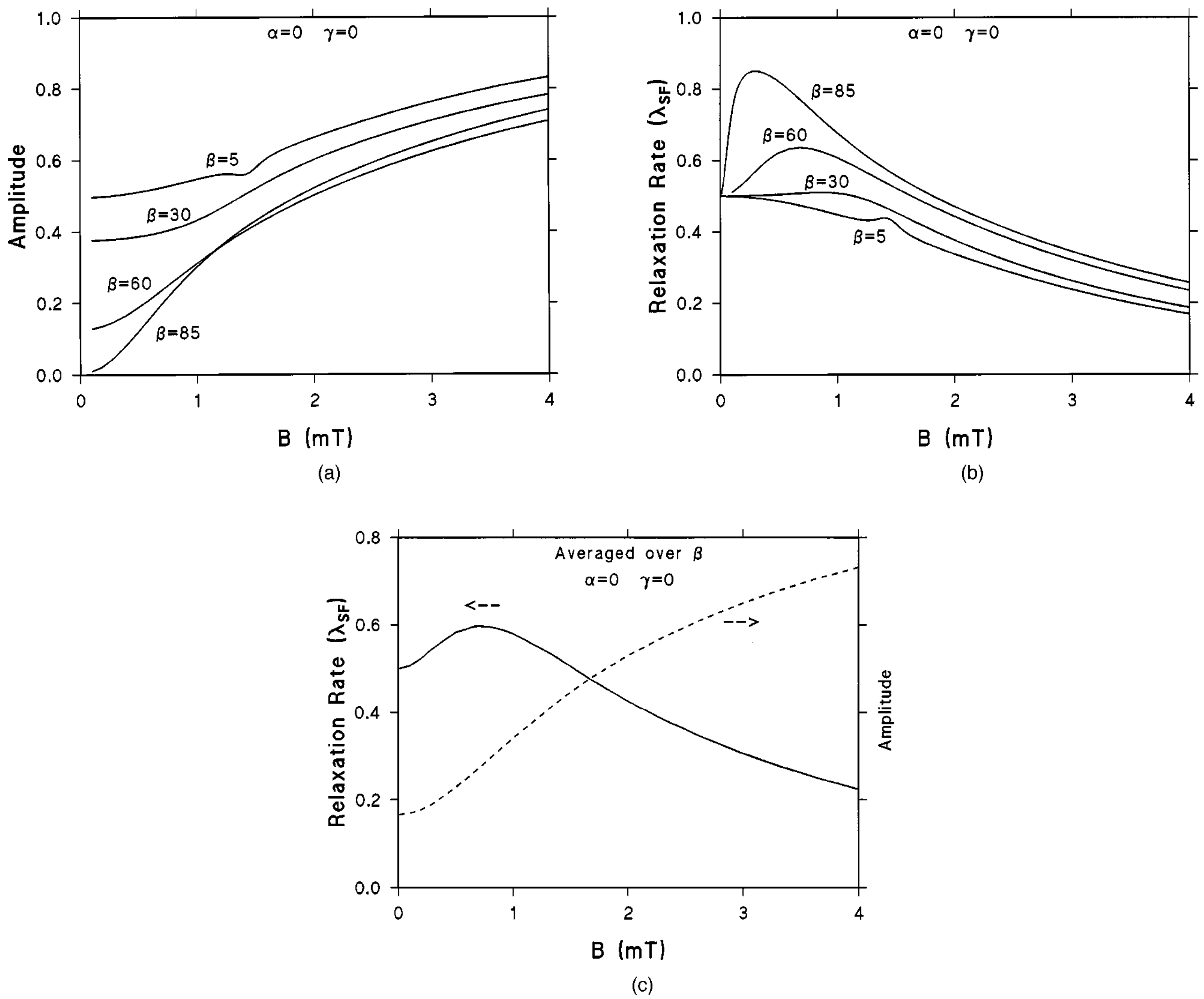

FIG. 5. The amplitude and relaxation rate of the DC component near the low-field avoiding/crossing field for an axially symmetric Mu with $\omega_X/2\pi = 80$ MHz, $\omega_Y/2\pi = 80$ MHz, $\omega_Z/2\pi = 130$ MHz at the Euler angles $(\alpha,\beta,\gamma) = (0°,\beta,0°)$. (a) The amplitude for Euler angle $\beta = 5°$, 30°, 60°, and 85°. (b) The relaxation rate for $\beta = 5°$, 30°, 60°, and 85°. (c) The amplitude and the relaxation rate averaged over the random uniform distribution of β, showing a relaxation rate maximum below the low-field crossing or avoidance.

following, an alternative interpretation of the maximum is given, where the tensor nature of the anisotropic interaction is fully taken into account.

Here one considers a high field so that $\omega_\mu \gg |\omega_X|,|\omega_Y|,|\omega_Z|$ so that all the off-diagonal elements of the Hamiltonian [Eq. (8)] are characterized by a small parameter ϵ. Furthermore, it is assumed that one of the principal axes makes a small angle η with the z axis. Because of Eq. (10) with $\beta = \eta$, the matrix elements $\Omega_{zx} + i\Omega_{yz}$ and $\Omega_{zx} - i\Omega_{yz}$ are proportional to the small parameter η. Thus one can write down the equations that determine the eigenstate $|j\rangle$ in the following form:

$$\begin{bmatrix} \omega_- + \Omega_{zz} - \omega_j & \eta\epsilon g_{12} & \eta\epsilon g_{12} & \epsilon g_{14} \\ \eta\epsilon g_{12}^* & -\omega_+ - \Omega_{zz} - \omega_j & \epsilon g_{23} & -\eta\epsilon g_{12} \\ \eta\epsilon g_{12}^* & \epsilon g_{23}^* & \omega_+ - \Omega_{zz} - \omega_j & -\eta\epsilon g_{12} \\ \epsilon g_{14}^* & -\eta\epsilon g_{12}^* & -\eta\epsilon g_{12}^* & -\omega_- + \Omega_{zz} - \omega_j \end{bmatrix} \begin{bmatrix} U_{j1} \\ U_{j2} \\ U_{j3} \\ U_{j4} \end{bmatrix} = 0. \qquad (105)$$

Since the Hamiltonian $[H]$ in this case is *almost diagonal* because of $\omega_\pm \gg \epsilon|g_{jk}| \gg \eta\epsilon|g_{jk}|$, the four eigenvalues are approximately $\omega_1=\omega_- + \Omega_{zz}$, $\omega_2=-\omega_+ - \Omega_{zz}$, $\omega_3=\omega_+ - \Omega_{zz}$, and $\omega_4=-\omega_- + \Omega_{zz}$. If $\Omega_{zz}>0$, the H_{11} and H_{33} matrix elements become identical near the crossing or avoiding field $\omega_+ - \omega_- = \omega_\mu = 2\Omega_{zz}$. For $j=1$ or 3, the two diagonal elements of $[h]=[H-\hbar\omega_j I]$, i.e., $h_{11}=\omega_- + \Omega_{zz} - \omega_j$ and $h_{33}=\omega_+ - \Omega_{zz} - \omega_j$, simultaneously become small quantities near the high-field crossing or avoidance, while the other two diagonal elements h_{22} and h_{44} remain much larger. If h_{11} and h_{33} become much smaller than the off-diagonal element $h_{13}=\eta\epsilon g_{12}$ at a certain field, one obtains $U_{12}\approx U_{14}\approx U_{32}\approx U_{34}\approx 0$ and $|U_{11}|^2 \approx |U_{13}|^2 \approx |U_{31}|^2 \approx |U_{33}|^2 \approx \frac{1}{2}$, thus one can choose $|1\rangle \approx (\alpha_\mu\alpha_e + \beta_\mu\alpha_e)/\sqrt{2}$ and $|3\rangle \approx (\alpha_\mu\alpha_e - \beta_\mu\alpha_e)/\sqrt{2}$, which means a strong mixing of $\alpha_\mu\alpha_e$ and $\beta_\mu\alpha_e$ in $|1\rangle$ and $|3\rangle$ near the avoidance field. If the angle η between the principal axes and the z axis becomes extremely small, the condition for strong mixing, $|h_{11}|, |h_{33}| \ll \eta\epsilon|g_{12}|$, is satisfied only for a small range of magnetic field near $\omega_\mu = 2\Omega_{zz}$. This explains why the relaxation peaks for the Euler angle $\beta=1$ and 89 in Fig. 4 are narrow. If $\eta=0$, the Hamiltonian H reduces to a block form and the two states $\alpha_\mu\alpha_e$ and $\beta_\mu\alpha_e$ cannot mix, leading to $|1\rangle \approx \alpha_\mu\alpha_e$ and $|3\rangle \approx \beta_\mu\alpha_e$ even at the crossing field. In this case, both A-Mu$(\alpha_\mu\alpha_e)$ and B-Mu$(\alpha_\mu\beta_e)$ are nearly eigenstates. Thus electron spin-flip collisions that change the electron spin but not the muon spin will have no effects on the muon spin, which accounts for the disappearance of the relaxation peak at $\beta=\eta=0$. It should be mentioned that longitudinal field dependences of the relaxation rate similar to those in Fig. 4 are discussed by Roduner [51] in the context of the reorientational dynamics of radicals containing Mu.

Figures 5(a)–5(c) show the amplitude and relaxation rate of the DC component in axially symmetric Mu with $\omega_X/2\pi = 80$ MHz, $\omega_Y/2\pi = 80$ MHz, $\omega_Z/2\pi = 130$ MHz in the longitudinal configuration near the low-field crossing avoiding, where the amplitude $I(\beta)$ and the relaxation rate $\lambda(\beta)$ are calculated directly from $[U_{jk}]$ numerically as a function of Euler angle β for fixed $\alpha=0°$ and $\gamma=0°$. Once $I(\beta)$ and $\lambda(\beta)$ are calculated, the time dependence of the muon polarization averaged for β can be expressed as

$$P(t)=\frac{1}{2}\int_0^\pi d\beta \sin\beta\, I(\beta)\exp[-\lambda(\beta)t]. \qquad (106)$$

The quantity $P(t)$ calculated in this way was found to decay with time nearly exponentially. The the averaged initial amplitude $I=P(0)$ and the average decay constant calculated from $\lambda=-(1/t)\ln P(t)$ are plotted in Fig. 5(c). The relaxation maximum near the low-field crossing/avoiding field [Figs. 5(b) and 5(c)], which has not been investigated experimentally, should provide valuable information on the energy levels and spin dynamics in anisotropic Mu.

IV. CONCLUDING REMARKS

It was shown that the energy levels for anisotropic Mu can be obtained analytically and that the matrix $[U_{jk}]$ that diagonalizes the Hamiltonian can be written down analytically for several important cases. Once $[U_{jk}]$ is obtained, analytically or otherwise, all the experimental observables in μSR, including the amplitude, phase, and relaxation rate, can explicitly be expressed in terms of the matrix elements $[U_{jk}]$. The amplitude and relaxation rate near level crossing or avoidance fields are discussed in detail. Finally, it should be mentioned that the method developed here is currently applied to the cases: (i) the lifetimes of anisotropic positronium on surfaces, (ii) anisotropic Mu undergoing both spin exchange and charge exchange, (iii) spin exchange of Mu radicals containing nuclear spins, and (iv) muon spin dynamics on anisotropic Mu in the gas phase.

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