Rotation operator approach to spin dynamics and the Euler geometric equations

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The rotation operator approach proposed previously is applied to spin dynamics in a time-varying magnetic field. The evolution of the wave function is described, and that of the density operator is also treated in terms of a spherical tensor operator base. It is shown that this formulation provides a straightforward calculation of accumulated phases and probabilities of spin transitions and coherence evolutions. The technique focuses, not on the rotation matrix, but on the three Euler angles and its characteristic equations are equivalent to the Euler geometric equations long known to describe the motion of a rigid body. The method usually depends on numerical calculations, but analytical solutions exist in some situations. In this paper, as examples, a hyperbolic secant pulse is solved analytically, and a Gaussian-shaped pulse is calculated numerically.

I. INTRODUCTION

The behavior of a spin system in an arbitrary time-varying magnetic field was first studied by Majorana in 1932.[1] He showed that the motion of a spin-I system could be reduced to that of a superposition of $2I$ spin-$\frac{1}{2}$ system. Therefore the motion of a spin-$\frac{1}{2}$ could be used to describe the motion of a spin of arbitrary magnitude. Majorana also gave an expression for the spin transition probabilities, now known as the Majorana formula.[2] A number of equivalent results and extensions of these ideas have been developed since then.[2]

Spin dynamics in the time-varying magnetic field has applications to nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), quantum optics, and relevant two-level problems. In recent years, shaped radiofrequency pulses,[3–9] rotational resonance in magic angle spinning (MAS) solid state NMR,[10–12] and geometric phases[13–15] are all quite interesting examples concerned.

In order to treat these applications, a number of useful approaches have been developed. These include the average Hamiltonian theory,[16] the Floquet theory,[11,12,16–18] the Wei–Norman method,[5,19–21] and a variety of approaches to geometric phases.[15,22–24] In addition, basic quantum-mechanical treatments or classical descriptions to these problems often lead to equivalent formulations.[25–30]

The Hamiltonians of Zeeman-type interactions obey a SU(2) algebra structure, which contain only terms linear in the spin operator components. This implies that these problems are, in essence, some rotations in a three-dimensional space; hence, their propagators can be cast into a clear form described by the Wigner rotation operator[31–33] in which all the dynamic information is included. Such an approach leads to a separate accumulated phase factor from the probability amplitude characterizing a state evolution. Moreover, for any such interactions it is easy to cast the problem into three differential equations for the Euler angles.[32] These equations are concise and transparent, and are identical to the classical equations of motion for rigid bodies.[34] This method, called the rotation operator approach, is detailed in this paper.

The coherence evolutions under shaped pulses, which are frequently described by the density operator formalism, are of great importance to NMR spectroscopy and imaging. The rotation operator approach is in form simple and comprehensible, and is readily applicable to both the wave function and the density operator. Another purpose of this paper is to apply this approach to spin dynamics in shaped pulses and to solve the characteristic equations concerned.

II. ROTATION OPERATOR APPROACH AND THE EULER GEOMETRIC EQUATIONS

By ignoring relaxation effects, the evolution of the wave function $\psi(t)$ of the spin system is characterized by the Schrödinger equation

$$i\hbar \frac{d\psi(t)}{dt} = \mathscr{H}(t)\psi(t), \tag{1}$$

and equivalently the evolution of the density operator $\rho(t)$ by the Liouville-von Neumann equation

$$i\hbar \frac{d\rho(t)}{dt} = [\mathscr{H}(t), \rho(t)]. \tag{2}$$

In both cases, the formal solutions can be written by the unitary operator

$$U(t,t_0) = T \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} \mathscr{H}(t')dt'\right), \tag{3}$$

and the initial states $\psi(t_0)$ or $\rho(t_0)$ as

$$\psi(t) = U(t,t_0)\psi(t_0) \tag{4}$$

and

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$$\rho(t)=U(t,t_0)\rho(t_0)U^+(t,t_0), \tag{5}$$

where $U(t,t_0)$ is commonly called a propagator and T is the bothersome Dyson time-ordering operator which arises from the time-dependent Hamiltonian.

The aforementioned brief description defines only the problems, and further treatment depends on the form of $\mathscr{H}(t)$. The problems we treat in this paper can be expressed by a time-dependent Hamiltonian in the form

$$\mathscr{H}(t)/\hbar=-\omega_x(t)I_x-\omega_y(t)I_y-\omega_z(t)I_z, \tag{6}$$

which contains only the three components of an arbitrary angular momentum operator **I**. The three frequencies are, in the most general case, time-dependent by virtue of the time-varying magnetic field

$$\mathbf{B}(t)=\mathbf{i}B_x(t)+\mathbf{j}B_y(t)+\mathbf{k}B_z(t)$$

with $\omega_i(t)=\gamma_I B_i(t)$. Because the Hamiltonian (6) contains only terms linear in the spin operator components, the propagator must take the form of a rotation operator,[31–33]

$$\begin{aligned}U(t,t_0)&=\mathscr{D}[\alpha(t),\beta(t),\gamma(t)]\\&=\exp[i\gamma(t)I_z]\exp[i\beta(t)I_y]\exp[i\alpha(t)I_z],\end{aligned} \tag{7}$$

where $\alpha(t)$, $\beta(t)$, and $\gamma(t)$ are the three time-dependent Euler angles. It is clear that in the rotation operator approach, all the effects of the time-varying field are contained in the rotation operator with the three time-dependent Euler angles and satisfying the equation of motion

$$i\hbar\frac{d}{dt}\mathscr{D}(\alpha,\beta,\gamma)=\mathscr{H}(t)\mathscr{D}(\alpha,\beta,\gamma). \tag{8}$$

Insertion of Eq. (7) into the left side of Eq. (8) and the equalization of the result with Eq. (6) yield

$$\begin{aligned}&\dot\gamma+\dot\alpha\cos\beta=\omega_z(t),\\&\dot\beta=\omega_x(t)\sin\gamma+\omega_y(t)\cos\gamma,\\&\dot\alpha\sin\beta=-\omega_x(t)\cos\gamma+\omega_y(t)\sin\gamma,\end{aligned} \tag{9}$$

which can be recognized as the classical equations of motion for rigid bodies with angular velocities $\omega_x(t)$, $\omega_y(t)$, and $\omega_z(t)$,[34] usually known as the Euler geometric equations.[33] Solving these characteristic equations requires some initial conditions which, for our problems concerned, are

$$\alpha(t_0)=\xi,\quad \beta(t_0)=0,\quad \gamma(t_0)=-\xi, \tag{10}$$

where ξ is constant. The above derivations clearly show the resulting characteristic equations and their initial conditions, hence solutions, are independent of the spin magnitudes I and the initial states $\psi(t_0)$ or $\rho(t_0)$, instead depend only on the three frequencies in Hamiltonian (6).

III. SPIN TRANSITION AND COHERENCE EVOLUTION

A. General

It is known that any state $\psi(t)$ of the spin system can be expanded in a complete set of its eigenstates $(\psi_{Im}:-I\leqslant m\leqslant I)$,

$$\psi(t)=\sum_m C_{Im}(t)\psi_{Im}. \tag{11}$$

Equivalently, the density operator can be characterized by a linear superposition of irreducible tensor operators ($Y^{(k)q}$: $k=0,1,\ldots,2I$; $-k\leqslant q\leqslant k$),

$$\rho(t)=\sum_{kq}\phi_q^k(t)Y^{kq}(\mathbf{I}). \tag{12}$$

Although numerous choices are possible for the expansion of the density operator, a proper selection may be essential to ease the solution of a particular problem.[16] Since spherical tensors are irreducible under the rotation group, we formulate the density operator theory using them. It is shown that the tensor rank k and spherical component q play an analogous role in operator space to I and m in state space and, moreover, q labels the qth multiquantum coherence.

Inserting of Eqs. (7) and (11) into (4), we can give an expression for the evolution of the wave function,

$$C_{Im}(t)=\sum_{m'}\mathscr{D}^{(I)}_{mm'}(\alpha\beta\gamma)C_{Im'}(t_0), \tag{13}$$

where $\mathscr{D}^{(I)}(\alpha\beta\gamma)$ is the Wigner rotation matrices whose elements obey

$$\mathscr{D}^{(I)}_{mm'}(\alpha\beta\gamma)=e^{i(m\gamma+m'\alpha)}d^{(I)}_{mm'}(\beta).$$

Similarly, for the evolution of the density operator,

$$\phi_q^k(t)=\sum_{q'}\mathscr{D}^{(k)}_{qq'}(\alpha\beta\gamma)\phi^K_{q'}(t_0). \tag{14}$$

If the spin system is initially only in one eigenstate $\psi_{Im'}$, the probability and accumulated phase for the transition from eigenstate $\psi_{Im'}$ to ψ_{Im} are, respectively, $[d^{(I)}_{mm'}(\beta)]^2$ and $(m\gamma+m'\alpha)$ since the reduced Wigner rotation matrix element $d^{(I)}_{mm'}(\beta)$ is real. The reduced rotation matrix element $d^{(I)}_{mm'}(\beta)$ can thus be known as a pure probability amplitude. Similarly, those for the evolution from multiple-quantum coherence $Y^{(k)q'}(\mathbf{I})$ to $Y^{(k)q}(\mathbf{I})$ are $d^{(k)}_{qq'}(\beta)$ and $(q\gamma+q'\alpha)$.

B. Coherence evolution

Later we discuss the coherence evolutions in more detail. Suppose that α, β, and γ are the Euler angles for a shaped pulse in the rotating frame, the evolutions of various multiple-quantum coherences under this pulse can be described by means of Eqs. (12) and (14), called the multipole NMR,[35] or in terms of the tensor operator formalism,[16]

$$Y^{kq}(\mathbf{I})\xrightarrow{\text{shaped pulse}}\sum_{q'}\mathscr{D}^{(k)}_{q'q}(\alpha\beta\gamma)Y^{kq'}(\mathbf{I}). \tag{15}$$

In the multipole NMR, the object of spin dynamics is to evaluate the polarizations $\hat\phi_q^k$ that determine the state, where the caret denotes the rotating frame. If our problems are concerned only with $\hat\phi_q^1$, Eqs. (12) and (14) can be reduced, by the use of the matrix $d^{(1)}(\beta)$, to

$$\hat\rho(t)=\hat\phi_x(t)I_x+\hat\phi_y(t)I_y+\hat\phi_z(t)I_z \tag{16}$$

and

$$\begin{pmatrix} \hat{\phi}_x(t) \\ \hat{\phi}_y(t) \\ \hat{\phi}_z(t) \end{pmatrix} = \begin{pmatrix} -\sin\alpha\sin\gamma+\cos\alpha\cos\beta\cos\gamma & \cos\alpha\sin\gamma+\sin\alpha\cos\beta\cos\gamma & -\sin\beta\cos\gamma \\ -\sin\alpha\cos\gamma-\cos\alpha\cos\beta\sin\gamma & \cos\alpha\cos\gamma-\sin\alpha\cos\beta\sin\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix} \begin{pmatrix} \hat{\phi}_x(t_0) \\ \hat{\phi}_y(t_0) \\ \hat{\phi}_z(t_0) \end{pmatrix}, \tag{17}$$

where both $\hat{\phi}_x$ and $\hat{\phi}_y$ are referred to as the transverse polarization or magnetization, and $\hat{\phi}_z$ as the longitudinal one. The equilibrium state of the spin system is described by the longitudinal magnetization, while the single-quantum coherence observed usually corresponds to the transverse magnetization.

The response of the equilibrium state to the shaped pulse, such as excitation ($\hat{\phi}_z \to \hat{\phi}_x, \hat{\phi}_y$) and inversion ($\hat{\phi}_z \to -\hat{\phi}_z$), is a basic problem for spin dynamics under the shaped pulse. For this special situation, we have

$$\begin{aligned} &\hat{\phi}_z(t)/\hat{\phi}_z(t_0)=\cos\beta, \\ &\hat{\phi}_\perp(t)/\hat{\phi}_z(t_0)=\sin\beta, \\ &tg^{-1}[\hat{\phi}_y(t)/\hat{\phi}_x(t)]=\pi-\gamma, \end{aligned} \tag{18}$$

where $\hat{\phi}_\perp$ is the transverse projection of the magnetization vector under the shaped pulse, namely the amplitude of the excited transverse magnetization. It follows that both excitation and inversion depend on β and γ only and, moreover, $\cos\beta$, $\sin\beta$, and $\pi-\gamma$ are three factors characterizing these processes, where $\cos\beta$ denotes the remained longitudinal magnetization, $\sin\beta$ the excited transverse magnetization and $\pi-\gamma$ its phase.

In contrast, the responses of other initial states to this shaped pulse, e.g., deexcitation ($\hat{\phi}_x, \hat{\phi}_y \to \hat{\phi}_z$) and refocusing ($\hat{\phi}_x \to \hat{\phi}_x, \hat{\phi}_y \to -\hat{\phi}_y$) or ($\hat{\phi}_x \to -\hat{\phi}_x, \hat{\phi}_y \to \hat{\phi}_y$), must depend on α, β, and γ. Therefore shaped pulses designed for excitation and deexcitation, as well as inversion and refocusing, should be different.[6,7]

IV. NUMERICAL CALCULATION TO SHAPED PULSES

The rotation operator approach leads to the well-known Euler geometric equations and the explicit form of the rotation operator depends on their solutions. In this section, based on the analytic solutions to a constant pulse,[32] a Gaussian-shaped pulse is calculated numerically, for which analytical solutions are unknown.

In the rotating frame, the Hamiltonian of an arbitrary amplitude-, phase- and/or frequency-modulated pulse[2–9] can be represented by

$$\hat{\mathscr{H}}(t)/\hbar=\Delta\omega(t)I_z-\omega_1(t)[I_x\cos\phi(t)+I_y\sin\phi(t)]. \tag{19}$$

Comparing with Eq. (6), we have $\omega_z(t)=-\Delta\omega(t)$, $\omega_x(t)=\omega_1(t)\cos\phi(t)$, and $\omega_y(t)=\omega_1(t)\sin\phi(t)$, hence the Euler geometric equations (9) become

$$\begin{aligned} &\dot{\gamma}+\dot{\alpha}\cos\beta=-\Delta\omega(t), \\ &\dot{\beta}=\omega_1(t)\sin[\gamma+\phi(t)], \\ &\dot{\alpha}\sin\beta=-\omega_1(t)\cos[\gamma+\phi(t)]. \end{aligned} \tag{20}$$

The usual NMR case involving the constant pulse, whose resonance offset $\Delta\omega$, pulse amplitude ω_1 and pulse phase ϕ are all constant, and whose initial conditions (10) can be chosen as $\xi=\phi-\pi/2$, can be exactly solved as done in our previous work.[32] The solutions depending on the effective precession frequency $\Omega=(\Delta\omega^2+\omega_1^2)^{1/2}$ are

$$\begin{aligned} &\cos\beta=\frac{1}{\Omega^2}[\Delta\omega^2+\omega_1^2\cos\Omega(t-t_0)], \\ &\alpha=-tg^{-1}\left(\frac{\Delta\omega}{\Omega}tg\,\frac{\Omega(t-t_0)}{2}\right)+\phi-\frac{\pi}{2}, \\ &\gamma=-tg^{-1}\left(\frac{\Delta\omega}{\Omega}tg\,\frac{\Omega(t-t_0)}{2}\right)-\phi+\frac{\pi}{2}. \end{aligned} \tag{21}$$

The aforementioned results are given since they are needed later. By defining

$$\alpha'=-tg^{-1}\left(\frac{\Delta\omega}{\Omega}tg\,\frac{\Omega(t-t_0)}{2}\right)\ \frac{\pi}{2},$$

the propagator can be expressed as

$$\hat{U}(t,t_0)=\mathscr{D}(\alpha'+\phi,\beta,\alpha'-\phi+\pi),$$

which agrees with that in our earlier works.[32,35]

In another special situation of an amplitude-modulated pulse on resonance, its initial conditions can also be selected as $\xi=\phi-\pi/2$, and three Euler angles α_0, β_0, and γ_0 can be given by

$$\begin{aligned} &\alpha_0(t)=\phi-\frac{\pi}{2}, \\ &\beta_0(t)=\int_{t_0}^{t}\omega_1(t')dt', \\ &\gamma_0(t)=\frac{\pi}{2}-\phi. \end{aligned} \tag{22}$$

For the majority of shaped pulses, whose offset $\Delta\omega(t)$, amplitude $\omega_1(t)$, and phase $\phi(t)$ are all time dependent, the solutions must resort to the numerical calculation. As usual, let a pulse duration be divided into n intervals, $\Delta t_i=t_i-t_{i-1}$ $(i=1,2,\ldots,n)$, each of which is short enough, $\Delta t_i\to 0$, so that its parameters can be considered as constant, $\Delta\omega(t)=\Delta\omega(t_i)$, $\omega_1(t)=\omega_1(t_i)$, and $\phi(t)=\phi(t_i)$. In this way, any shaped pulse can be described by a product of n rotations,

$$\mathscr{D}(\alpha_n\beta_n\gamma_n)=\prod_{i=1}^{n}\mathscr{D}(\Delta\alpha_i\Delta\beta_i\Delta\gamma_i), \tag{23}$$

and each rotation has, by virtue of Eqs. (21), analytic solutions,

$$\cos \Delta\beta_i = \frac{1}{\Omega(t_i)^2}[\Delta\omega(t_i)^2 + \omega_1(t_i)^2 \cos \Omega(t_i)\Delta t_i],$$

$$\Delta\alpha_i = -tg^{-1}\left(\frac{\Delta\omega(t_i)}{\Omega(t_i)} tg \frac{\Omega(t_i)\Delta t_i}{2}\right) + \phi(t_i) - \frac{\pi}{2}, \quad (24)$$

$$\Delta\gamma_i = -tg^{-1}\left(\frac{\Delta\omega(t_i)}{\Omega(t_i)} tg \frac{\Omega(t_i)\Delta t_i}{2}\right) - \phi(t_i) + \frac{\pi}{2},$$

with $\Omega(t_i) = (\Delta\omega(t_i)^2 + \omega_1(t_i)^2)^{1/2}$. Calculations follow from the initial conditions, evaluating the Euler angles at each step,

$$(\xi, 0, -\xi) \rightarrow (\alpha_0\beta_0\gamma_0),$$
$$(\Delta\alpha_1\Delta\beta_1\Delta\gamma_1) \text{ and } (\alpha_0\beta_0\gamma_0) \rightarrow (\alpha_1\beta_1\gamma_1),$$
$$(\Delta\alpha_2\Delta\beta_2\Delta\gamma_2) \text{ and } (\alpha_1\beta_1\gamma_1) \rightarrow (\alpha_2\beta_2\gamma_2),$$
$$(\Delta\alpha_i\Delta\beta_i\Delta\gamma_i) \text{ and } (\alpha_{i-1}\beta_{i-1}\gamma_{i-1}) \rightarrow (\alpha_i\beta_i\gamma_i),$$
$$(\Delta\alpha_n\Delta\beta_n\Delta\gamma_n) \text{ and } (\alpha_{n-1}\beta_{n-1}\gamma_{n-1}) \rightarrow (\alpha_n\beta_n\gamma_n).$$

In fact, the procedure to the rotation composition is the same as the multipole theory of composite pulses.[35]

Later, as an example, we consider a Gaussian-shaped pulse,

$$\omega_1(t) = \omega_{1\,\max} \exp[-a(t-t_c)^2] \prod \Pi(t_0, t_n), \quad (25)$$

where the pulse center $t_c = (t_0 + t_n)/2$ and

$$\prod (t_0, t_n) = \begin{cases} 1 & t_0 \leqslant t \leqslant t_n \\ 0 & \text{otherwise}. \end{cases}$$

For the sake of convenience, we rewrite Eq. (25) in a dimensionless expression

$$A(\tau) = A_{\max} \exp[-b(\tau - 0.5)^2] \prod (0,1), \quad (26)$$

where the maximum pulse area $A_{\max} = \omega_{1\,\max}\Delta T$, $b = a\Delta T^2$, $\tau = (t - t_0)/\Delta T$, the total duration $\Delta T = t_n - t_0$, and $\Pi(0,1)$ has the similar definition to $\Pi(t_0, t_n)$. The parameter b is related to the pulse truncation tr otherwise $A_{\max}$ depends on both tr and the pulse area β_0, i.e.,

$$b = -4 \ln(\text{tr}),$$

$$A_{\max} = \frac{\beta_0}{S},$$

where the parameter S is

$$S = \int_0^1 \exp[-b(\tau - 0.5)^2] d\tau.$$

For example, the π Gaussian-shaped pulse truncated at 2.5% has $b = 14.755\,52$, $S = 0.458\,374\,6$, and $A_{\max} = 2.181\,622\pi$. In the limit of the constant pulse, we have tr=100%, $b = 0$, $S = 1$, and $A_{\max} = \beta_0 = \pi$.

The three Euler angles of the $\pi/2$ Gaussian-shaped pulse, whose truncation is at 2.5% and duration is 25 ms, is illustrated in Fig. 1(a). As stated earlier, the three Euler angles can be used to describe arbitrary coherence evolutions. Figure 1(b) shows the response of the longitudinal magnetization to this pulse, which is usually known as the excitation. We can see that its excitation selectivity is evident and the phase of the transverse magnetization is almost linear in the region of interest. Similarly, the three Euler angles of, and the response of the longitudinal magnetization to, the π Gaussian-shaped pulse are shown in Fig. 2. Obviously its inversion selectivity is not as good as the excitation selectivity and, in particular, there are two regions outside the inversion region, where the excited transverse magnetization is stronger.

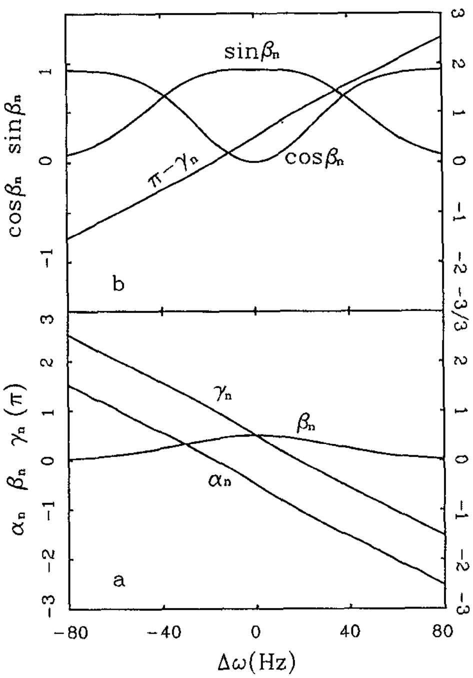

FIG. 1. (a) The three Euler angles ($\alpha_n, \beta_n, \gamma_n$) of, and (b) the response of the equilibrium state to, the $\pi/2$ Gaussian-shaped pulse truncated at 2.5% as functions of the offsets $\Delta\omega$. The pulse duration ΔT and phase ϕ are 25 ms and 0, respectively. The parameters for the numerical calculation are $n = 200$ and $\Delta\omega = 5$ Hz.

The Gaussian-shaped pulse is one of the selective pulses employed most commonly in NMR spectroscopy and imaging.[4,7,36–38] The response of the spin system to this pulse has already been calculated using the different techniques, in which the most simple method may be to integrate the classical Bloch equations.[36,37] In the rotation operator formulation, the parametrization of this pulse by the three Euler angles is implemented by solving the Euler geometric equations. The response of any initial state can be predicted all together. It is thus clear that a pulse sequence involving Gaussian and other shaped pulses can be well treated.

V. TRANSFORMATIONS AND ANALYTIC SOLUTIONS

Some important cases of hyperbolic secant,[3–5,28] chirp,[29,30,39] and exponential[5,26] pulses have been solved analytically by means of different methods. Those analytical solutions are quite useful for rationalizing relevant problems. In this section, based on some realistic transformations, the Euler geometric equations for a hyperbolic secant pulse are solved as an example.

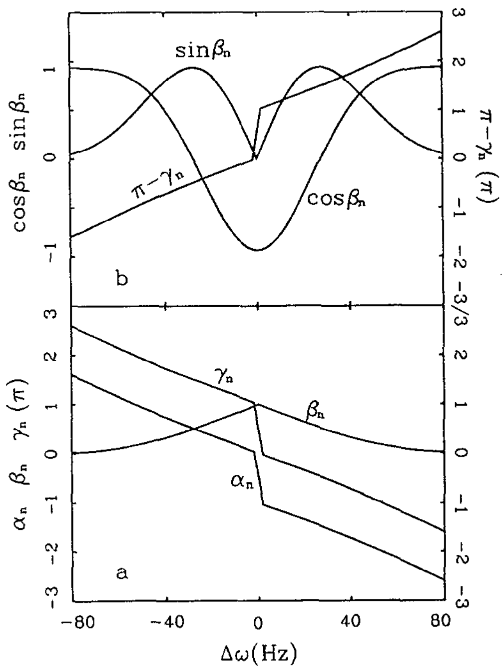

FIG. 2. (a) The three Euler angles $(\alpha_n, \beta_n, \gamma_n)$ of, and (b) the response of the equilibrium state to, the π Gaussian-shaped pulse. The employed parameters are the same as those in Fig. 1.

A. Transformations

Obviously the Euler geometric equations can be combined into two ordinary differential equations as

$$\begin{aligned}\dot{\beta}&=\omega_x(t)\sin\gamma+\omega_y(t)\cos\gamma,\\ \dot{\gamma}&=\omega_z(t)+[\omega_x(t)\cos\gamma-\omega_y(t)\sin\gamma]ctg\beta.\end{aligned} \tag{27}$$

By defining a complex function

$$f=-tg\,\frac{\beta}{2}\,e^{i\gamma}, \tag{28}$$

Equation (27) can be cast into the Riccati equation

$$\dot{f}=\frac{i}{2}\,\Omega_1(t)f^2+i\omega_z(t)f-\frac{i}{2}\,\Omega_1^*(t), \tag{29}$$

where $\Omega_1(t)=\omega_x(t)+i\omega_y(t)$ and $\Omega_1^*(t) = \omega_x(t) - i\omega_y(t)$ and, correspondingly, the initial conditions (10) of the Euler geometric equations into that of the Riccati equation,

$$f(t_0)=0. \tag{30}$$

By defining again

$$f=\frac{2i\;\;\dot{W}}{\Omega_1(t)W}, \tag{31}$$

where $W=W(t)$ is an unknown function to be solved, the Riccati equation can be written as a second-order linear differential equation,

$$\ddot{W}-\left(i\omega_z(t)+\frac{\dot{\Omega}_1(t)}{\Omega_1(t)}\right)\dot{W}+\tfrac{1}{4}|\Omega_1(t)|^2W=0. \tag{32}$$

We can see that the Euler geometric equations can be easily solved analytically once the analytic solution of Eq. (32) is found. Equation (28) shows that the module and radial angles (nonprinciple values) of the complex function f can be written, respectively, as

$$|f|=\left|tg\,\frac{\beta}{2}\right|,$$

and

$$\mathrm{Arg}(f)=\gamma-\pi.$$

Therefore, we have

$$\begin{aligned}\cos\beta&=\frac{1-|f|^2}{1+|f|^2},\\ \gamma&=\pi+\mathrm{Arg}(f).\end{aligned} \tag{33}$$

The aforementioned relationships may provide us a simple way to obtain the three Euler angles by virtue of the complex function f. In fact, as pointed out in Sec. III, the excitation and inversion behaviors of the spin system can be determined by means of Eq. (33) provided the complex function f is obtained.

B. Hyperbolic secant pulse

A complex hyperbolic secant pulse is of the envelop

$$\Omega_1(t)=\omega_{1\,\max}[\mathrm{sech}\;\delta(t-t_c)]^{1+i\mu}, \tag{34}$$

which is amplitude and frequency modulated.[3–5,28] For such a shaped pulse, the second-order differential equation (32) becomes

$$\begin{aligned}&\ddot{W}+[i\Delta\omega+(1+i\mu)\delta th\,\delta(t-t_c)]\dot{W}\\ &\quad+\tfrac{1}{4}\omega_{1\,\max}^2\mathrm{sech}^2\delta(t-t_c)W=0,\end{aligned} \tag{35}$$

where $\Delta\omega$ is constant. Defining a new variable

$$x=\tfrac{1}{2}[1+th\,\delta(t-t_c)], \tag{36}$$

we can obtain the hypergeometric or Gauss equation,[40]

$$\begin{aligned}&x(1-x)\ddot{W}+\left[-x(1-i\mu)+\frac{1}{2}\right.\\ &\quad\left.+\frac{i}{2}\left(\frac{\Delta\omega}{\delta}-\mu\right)\right]\dot{W}+\left(\frac{\omega_{1\,\max}}{2\delta}\right)^2 W=0,\end{aligned} \tag{37}$$

which is similar to that in the earlier papers[3–5] and whose solution is

$$\begin{aligned}W(x)=&AF(a,b;c;x)+Bx^{1-c}F(a-c+1,b-c+1;2\\ &-c;x),\end{aligned} \tag{38}$$

where F is the hypergeometric or Gauss function, A and B are two arbitrary constants, and the three parameters a, b, and c are defined by

$$a=-i\frac{\mu}{2}+\left[\left(\frac{\omega_{1\ \max}}{2\delta}\right)^2-\left(\frac{\mu}{2}\right)^2\right]^{1/2},$$
$$b=-i\frac{\mu}{2}-\left[\left(\frac{\omega_{1\ \max}}{2\delta}\right)^2-\left(\frac{\mu}{2}\right)^2\right]^{1/2}, \tag{39}$$
$$c=\frac{1}{2}+\frac{i}{2}\left(\frac{\Delta\omega}{\delta}-\mu\right).$$

Using the differential property of the hypergeometric function and the initial condition $f(t_0=-\infty)=f(x_0=0)=0$, we have

$$f(t)=p(t)\ \frac{F(a+1,b+1;c+1;x)}{F(a,b;c;x)}, \tag{40}$$

where

$$p(t)=\frac{i\delta}{\omega_{1\ \max}}\frac{ab}{c}\left[4x(1-x)\right]^{1-i\mu/2}.$$

The behavior of the inversion of the longitudinal magnetization can thus be predicted by means of Eqs. (33) and (40), as detailed in two previous contributions.[3,4] In this case, the initial state is the equilibrium state.

The rotation operator approach to spin dynamics provides a general treatment to various initial states. In NMR spectroscopy and imaging, the refocusing $(\hat{\phi}_1^1\leftrightarrow\hat{\phi}_{-1}^1)$ of the transverse magnetization is an important subject. Using the multipole NMR, we have

$$|\hat{\phi}_1^1(t)/\hat{\phi}_{-1}^1(t_0)|=|\hat{\phi}_{-1}^1(t)/\hat{\phi}_1^1(t_0)|=\tfrac{1}{2}(1-\cos\beta), \tag{41}$$

which shows that $\frac{1}{2}(1-\cos\beta)$ is a factor specifying the refocusing of the single-quantum coherence. Therefore the refocusing ignoring the accumulated phase has nearly the same frequency selectivity to the inversion.

VI. CONCLUSIONS

The rotation operator approach, like the Wei–Norman and Floquet theory, has the advantage of removing the Dyson time-ordering operator in the propagator. Although these methods treating the time-dependent Zeeman Hamiltonian are essentially complementary,[21,41] the rotation operator approach offers a clear physical interpretation and recognizes that the propagator must be a rotation operator from which the accumulated phase factors are clearly identifiable so that this approach is well suited for describing coherence evolutions. In addition, the equations for the Euler angles are enormously concise and physically relevant.

On the other hand, the rotation operator formulation shifts the problem from solving the equations of motion for the coefficients $C_{Im}(t)$ or $\phi_q^k(t)$ to studying the characteristic equations for the three Euler angles. Although either choice cannot readily be solved, the rotation operator approach is a powerful technique for calculating spin dynamics since its characteristic equations are independent of the spin magnitudes I and, moreover, relevant solutions are not related to the initial states of the spin system. The rotation operator formulation therefore is relatively simple and general, and its further applications are now in progress.

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