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Exponential Operator Approach to the General Solution to Off-Resonance RF Field Interaction

J. ZHOU,* H. GAO,* AND B. C. SANCTUARY†

*Wuhan Institute of Physics, The Chinese Academy of Sciences, P.O. Box 71010, 430071 Wuhan, Hubei, People's Republic of China; and †Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal H3A 2K6, Canada

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Using the properties of exponential operators, a very concise solution is found for the effect of a general NMR pulse on a spin of arbitrary magnitude I at arbitrary resonance offset. The solution agrees with previous calculations, has clear physical interpretation, and is readily incorporated into the formulation of multipole NMR.

INTRODUCTION

In 1932 (*1*), Majorana showed that an RF field applied to a system containing nuclear spins of arbitrary magnitude I can be solved exactly. Moreover, he showed that the Euler angles responsible for a transformation of the spin state are independent of the spin magnitude. Subsequent work (*2*) recognized these transformations as Wigner rotation matrices. However, the treatment of Majorana is long and tedious to follow. Even though techniques in angular-momentum theory and the rotation group were later used in the treatments of RF pulses, the case most often treated was that of a spin-$\frac{1}{2}$ and on-resonance. Later, using a spherical-tensor-operator basis, Sanctuary (*3*) derived the general case and expressed the Euler angles for arbitrary off-resonance conditions.[1] The advantage of using a spherical-tensor-operator basis, called multipole NMR, is that the higher-rank tensor components, present for spins of magnitude greater than $\frac{1}{2}$, are all transformed under the influence of an RF pulse by Wigner rotation matrices.

The solution presented in the multipole approach (*3*), although more concise than Majorana's calculation, is still somewhat involved and not easily followed without considerable effort. One reason for this is that the time evolution of the density operator was presented as a set of differential equations for the various nuclear magnetic polarizations using a spherical-tensor-operator basis. In contrast, most NMR spectroscopists are familiar with the properties of exponential operators (*4*), which have found wide application in many areas of NMR theory, in particular multi-spin-$\frac{1}{2}$ problems (*5*) and fictitious-spin-$\frac{1}{2}$ approaches (*6*) to mention only two. The use of exponential operators, however, is free of any basis representation.

In this paper, the well-known properties of exponential operators are used to obtain the full solution to NMR pulses. The derivation is concise and clear. It is easy to see where various initial conditions and arbitrary phase choices arise. This approach leads to three simple differential equations for the Euler angles and thereby avoids the more cumbersome solution presented earlier, in which differential equations for the nuclear polarizations were solved in a spherical-tensor-operator representation.

THE EULER ANGLES FOR AN NMR PULSE

To be clear, the details of the Zeeman field are given. The Zeeman interaction is $\mathscr{H}(t) = -\hbar\gamma\mathbf{I}\cdot\mathbf{H}(t)$, where the symbols have their usual meanings. The time-dependent magnetic field has a constant z component H_0 and a component oscillating in the xy plane of amplitude H_1, carrier frequency ω, and phase ϕ:

$$H(t) = H_0\hat{z} + H_1[\hat{x}\cos(\omega t - \phi) - \hat{y}\sin(\omega t - \phi)]. \quad [1]$$

Finally, the Larmor frequency is defined as $\omega_0 = \gamma H_0$ and the RF amplitude as $\omega_1 = \gamma H_1$.

The resulting Hamiltonian can be cast into a rotating frame to give

$$\hat{\mathscr{H}}/\hbar = \Delta\omega I_z - \omega_1(I_x\cos\phi + I_y\sin\phi), \quad [2]$$

where the resonance offset is $\Delta\omega = (\omega - \omega_0)$ and the rotating frame is defined by

[1] Edmonds [Ref. (*9*)], in the first printing of the second edition, 1960, defines the rotation matrices (4.1.9)

$$\mathsf{D}(\alpha\beta\gamma) = \exp[i\alpha J_z]\exp[i\beta J_y]\exp[i\gamma J_z],$$

while in the 1974 revised second edition, Edmonds uses

$$\mathsf{D}(\alpha\beta\gamma) = \exp[i\gamma J_z]\exp[i\beta J_y]\exp[i\alpha J_z].$$

Reference (*3*) uses the former definition, while from 1985 the later definition is used. Here we use the latter definition and the Euler angles obtained agree with those given in (*12*).

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$$\hat{A}(t) = e^{-i\omega t I_z} A(t) e^{+i\omega t I_z}. \qquad [3]$$

The quantum Liouville equation gives the evolution of the density operator in the rotating frame as

$$i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\hat{\mathscr{H}}, \hat{\rho}(t)]_{-}. \qquad [4]$$

From [2], $\hat{\mathscr{H}}$ is time independent. As a result of this, it is possible to write the propagator as

$$\exp[-i\hat{\mathscr{H}} t/\hbar] = e^{-i\phi I_z} \exp[-i(\Delta\omega I_z - \omega_1 I_x)t] e^{i\phi I_z}. \qquad [5]$$

The RF phase determines, via a rotation about the z axis, where the RF pulse is oriented in the xy plane. The rest of the propagator is also of the form of a rotation and thus can be expressed as

$$\exp[-i(\Delta\omega I_z - \omega_1 I_x)t] = \exp[i\gamma(t) I_z] \exp[i\beta(t) I_y] \exp[i\alpha(t) I_z]. \qquad [6]$$

The problem is now shifted to calculating the three time-dependent Euler angles $\alpha(t)$, $\beta(t)$, and $\gamma(t)$. Differentiating [6] and using the properties of exponential operators (*4*)

$$\exp[i\gamma I_z] I_y \exp[i\beta I_y] \exp[i\alpha I_z] = (I_y \cos\gamma - I_x \sin\gamma) \exp[i\gamma(t) I_z] \times \exp[i\beta(t) I_y] \exp[i\alpha(t) I_z] \qquad [7]$$

and

$$\exp[i\gamma I_z] \exp[i\beta I_y] I_z \exp[i\alpha I_z] = [I_z \cos\beta - (I_x \cos\gamma - I_y \sin\gamma)\sin\beta] \times \exp[i\gamma(t) I_z] \exp[i\beta(t) I_y] \exp[i\alpha(t) I_z] \qquad [8]$$

leads directly to three simple differential equations:

$$\dot{\gamma} + \dot{\alpha}\cos\beta = -\Delta\omega \qquad [9]$$

$$\dot{\beta} = \omega_1 \sin\gamma \qquad [10]$$

$$\dot{\alpha}\sin\beta = -\omega_1 \cos\gamma \qquad [11]$$

which are the Euler geometrical equations (*9*). To solve these, initial conditions are required. At time $t = 0$, no propagation occurs, and hence

$$\beta(0) = 0. \qquad [12]$$

From [6], it is clear that $\alpha(0) = +\xi$ and $\gamma(0) = -\xi$. To be consistent with earlier conventions, we choose

$$\alpha(0) = -\frac{\pi}{2} \qquad [13]$$

$$\gamma(0) = +\frac{\pi}{2}. \qquad [14]$$

The three Euler angles are found by solving [8]–[10]. The solutions are presented in the appendix and give

$$\cos\beta = \frac{1}{\Omega^2}(\Delta\omega^2 + \omega_1^2 \cos\Omega t) \qquad [15]$$

$$\alpha = -\tan^{-1}\left(\frac{\Delta\omega}{\omega\Omega_1} \tan\frac{\Omega t}{2}\right) - \frac{\pi}{2} \qquad [16]$$

$$\gamma = -\tan^{-1}\left(\frac{\Delta\omega}{\omega\Omega_1} \tan\frac{\Omega t}{2}\right) + \frac{\pi}{2} - \alpha + \pi, \qquad [17]$$

where $\Omega = \sqrt{\Delta\omega^2 + \omega_1^2}$.

In summary, the RF propagator in the rotating frame is given in terms of the Euler angles by

$$\exp[-i\hat{\mathscr{H}} t/\hbar] = \exp[i(\alpha - \phi + \pi)I_z] \exp[i\beta I_y] \exp[i(\alpha + \phi)I_z] = \mathbf{D}(\alpha + \phi, \beta, \alpha - \phi + \pi), \qquad [18]$$

in agreement with earlier work reviewed in (*12*).

APPLICATION TO MULTIPOLE NMR

The treatment in the above section does not depend on any choice of basis states. At this stage, any representation can be used and the corresponding matrix elements calculated. In this section, it is shown that the choice of a spherical-tensor-operator basis is the obvious one for treating pure pulses, which was the original motivation behind the multipole approach (*7*).

Since spherical tensor operators are irreducible under the rotation group, and since the propagator [18] is a rotation operator, the spin-density operator is expanded in a spherical-tensor-operator basis:

$$\hat{\sigma}(t) = \sum_{kq} \hat{\phi}_q^k(t) \mathscr{Y}^{(k)q}(\mathbf{I}). \qquad [19]$$

These components obey the adjoint property

$$\mathscr{Y}^{(k)q\dagger}(\mathbf{I}) = (-1)^{k-q} \mathscr{Y}^{(k)-q}(\mathbf{I}), \qquad [20]$$

which is different from the convention used by Schwinger (*8*) but the same as that used by Edmonds (*9*).

The orthonormal property is (tr = trace)

$$\mathrm{tr}\{\mathscr{Y}^{(k')q'*}(\mathbf{I}) \mathscr{Y}^{(k)q}(\mathbf{I})\} = (2I + 1)\delta_{kk'}\delta_{qq'}. \qquad [21]$$

For each spherical-tensor-operator component, the RF pulse propagator can be expressed as a sum over Wigner rotation matrices (*9, 10*):

$$\begin{aligned}\exp[-i\mathscr{H}t/\hbar]\mathscr{Y}^{(k)q}(\mathbf{I})\exp[i\mathscr{H}t/\hbar] &= \mathbf{D}(\alpha+\phi, \beta, \alpha-\phi+\pi)\mathscr{Y}^{(k)q}(\mathbf{I}) \\ &\quad \times \mathbf{D}^{\dagger}(\alpha+\phi, \beta, \alpha-\phi+\pi) \\ &= \sum_{q'} \mathscr{D}^{(k)}_{q'q}(\alpha+\phi, \beta, \alpha-\phi+\pi)\mathscr{Y}^{(k)q'}(\mathbf{I}). \quad [22]\end{aligned}$$

Using [19] and [21] gives

$$\begin{aligned}\tilde{\sigma}(t) &= \exp[-i\mathscr{H}t/\hbar]\sigma(0)\exp[i\mathscr{H}t/\hbar] \\ &= \sum_{kq} \phi^k_q(0) \sum_{q'} \mathscr{D}^{(k)}_{q'q}(\alpha+\phi, \beta, \alpha-\phi+\pi) \\ &\qquad \times \mathscr{Y}^{(k)q'}(\mathbf{I}), \quad [23]\end{aligned}$$

which, with [21], gives directly the result reported earlier (*12*),

$$\tilde{\phi}^k_q(t) = \sum_{q'} \mathscr{D}^{(k)}_{qq'}(\alpha+\phi, \beta, \alpha-\phi+\pi)\hat{\phi}^k_{q'}(0). \quad [24]$$

CONCLUSIONS

The derivation of the Euler angles for the off-resonance propagation presented here and which uses the well-known properties of exponential operators is much more concise and clear than previous approaches. In addition, it leaves the propagator in a form which is independent of the choice of representation of the spin states. In the case of a spherical-tensor basis, the propagator is represented by a Wigner rotation matrix as expected.

APPENDIX

Here we solve the differential equations [9]–[11] for the Euler angles. It follows from the square of [11] and the use of [10] that

$$\dot{\beta}^2 + \dot{\alpha}^2\sin^2\beta = \omega_1^2. \quad [A1]$$

Next, the following is needed. Using [9] and [10] we obtain

$$\dot{\gamma}(\omega_1 \sin\gamma) = -(\Delta\omega + \dot{\alpha}\cos\beta)\dot{\beta}. \quad [A2]$$

Then by using $(\cos\gamma)' = -\dot{\gamma}\sin\gamma$ and [11], we derive

$$(\dot{\alpha}\sin\beta)' = -\Delta\omega\dot{\beta} - \dot{\alpha}(\sin\beta)'. \quad [A3]$$

Multiplication by $\sin\beta$ leads to

$$(\dot{\alpha}\sin\beta\sin\beta)' = \Delta\omega(\cos\beta)', \quad [A4]$$

which, with the initial condition that $\beta = 0$ at $t = 0$, gives

$$\dot{\alpha}\sin^2\beta = \Delta\omega(\cos\beta - 1). \quad [A5]$$

Solve for $\cos\beta$: Use of [A1] and the square of [A5] and letting $u = \cos\beta$ give

$$(\dot{u})^2 = -\Omega^2u^2 + 2\Delta\omega^2u + (\omega_1^2 - \Delta\omega^2), \quad [A6]$$

which can be directly integrated using Eq. 2.261 of (*11*) to give [15].

Solve for α and γ: Use of [A5] and substituting $\cos\beta$ from [15] give

$$\dot{\alpha} = -\frac{\Delta\omega}{1+\cos\beta} = -\frac{\Delta\omega\Omega^2}{(\Omega^2+\Delta\omega^2)+\omega_1^2\cos\Omega t}, \quad [A7]$$

which can be integrated using Eq. 2.553.3 of (*11*) and the initial condition in [13] to give [16]. Likewise for γ we find

$$\dot{\gamma} = \frac{\Delta\omega}{1+\cos\beta}, \quad [A8]$$

which integrates in the same way as $\dot{\alpha}$ but with initial [14] to give [17].

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