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Beyond Euler angles: Exploiting the angle–axis parametrization in a multipole expansion of the rotation operator

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Abstract

Euler angles (α, β, γ) are cumbersome from a computational point of view, and their link to experimental parameters is oblique. The angle–axis $\{\Phi, \hat{\mathbf{n}}\}$ parametrization, especially in the form of quaternions (or Euler–Rodrigues parameters), has served as the most promising alternative, and they have enjoyed considerable success in rf pulse design and optimization. We focus on the benefits of angle–axis parameters by considering a multipole operator expansion of the rotation operator $\hat{\mathscr{D}}(\Phi, \hat{\mathbf{n}})$, and a Clebsch–Gordan expansion of the rotation matrices $\mathscr{D}^J_{MM'}(\Phi, \hat{\mathbf{n}})$. Each of the coefficients in the Clebsch–Gordan expansion is proportional to the product of a spherical harmonic of the vector $\hat{\mathbf{n}}$ specifying the axis of rotation, $Y_{\lambda\mu}(\hat{\mathbf{n}})$, with a fixed function of the rotation angle Φ, a Gegenbauer polynomial $C^{\lambda+1}_{2J-\lambda}(\cos\frac{\Phi}{2})$. Several application examples demonstrate that this Clebsch–Gordan expansion gives easy and direct access to many of the parameters of experimental interest, including coherence order changes (isolated in the Clebsch–Gordan coefficients), and rotation angle (isolated in the Gegenbauer polynomials).

Keywords: Wigner rotation matrices; Euler angles; Angle–axis parameters; Multipole expansion; Rotation operator; Spherical tensors

1. Introduction

Whether spin dynamics are described from a classical or a quantum mechanical point of view, a suitable parametrization of rotations is an indispensable part of the mathematical formalism used for the theoretical description and analysis of NMR phenomena [1,2]. This is particularly so for many solid-state NMR experiments, which often involve coherent averaging in either spin space, coordinate space, or both [3]. The most convenient and insightful description of these experiments expresses the internal Hamiltonians involved in terms of spin and spatial irreducible spherical tensor operators, whose behaviour under rotations in spin and coordinate space is well understood. From the very inception of NMR some 60 years ago, almost the entire edifice of this formalism has been built with the use of the Euler angle (α, β, γ) parametrization. Are Euler angles actually the most useful parametrization of rotations?

Since the Euler parameters are not uniquely defined whenever the second Euler angle equals 0 or π, the case for all rotations in all the dihedral groups and in all the crystallographic point groups for example, Altmann and Herzig [4] note that certainly for the finite point groups, "... the Euler angle parametrization is as cumbersome as it is defective." Some 20 years ago, well recognizing just how cumbersome Euler angles were in NMR applications, Blümich and Spiess [5] introduced the use of quaternions for the calculus of rotations in NMR. This introduction of quaternions to NMR, first by Blümich and Spiess [5], followed shortly thereafter by Counsell et al. [6] in the form of the Euler–Rodrigues (ER) parameters

$$\{\lambda, \mathbf{\Lambda}\} \equiv \{\lambda(\Phi, \hat{\mathbf{n}}), \mathbf{\Lambda}(\Phi, \hat{\mathbf{n}})\} = \left\{\cos\frac{\Phi}{2}, \hat{\mathbf{n}}\sin\frac{\Phi}{2}\right\} \tag{1}$$

subsequently unleashed a host of novel NMR applications (reviewed in [1,2]). These applications highlighted the simplicity and computational efficiency of the angle/axis parameters $\{\Phi, \hat{\mathbf{n}}\}$. The next step to complete this parametrization revolution has yet to be taken, and that would be to use the angle–axis parameters $\{\Phi, \hat{\mathbf{n}}\}$ for the rotation

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operator $\hat{\mathscr{D}}(\Phi,\hat{\mathbf{n}})$, and the associated transformation matrices $\mathscr{D}^{J}_{MM'}(\Phi,\hat{\mathbf{n}})$

$$e^{-i\Phi(\hat{\mathbf{n}}\cdot\mathbf{J})} \equiv \hat{\mathscr{D}}(\Phi,\hat{\mathbf{n}}) = \hat{\mathscr{D}}(\alpha,\beta,\gamma) \equiv e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z}, \tag{2}$$

$$\mathscr{D}^{J}_{MM'}(\Phi,\hat{\mathbf{n}}) = \mathscr{D}^{J}_{MM'}(\alpha,\beta,\gamma). \tag{3}$$

The transformation matrices are important because the irreducible spherical tensor operators $\hat{T}_{LM}$ which define NMR interaction Hamiltonians, and which refer to either spin or spatial degrees of freedom, transform under rotations R, specified by the Euler parameters $\{\alpha,\beta,\gamma\}$, the Cayley–Klein parameters $\{a,b\}$, the angle–axis parameters $\{\Phi,\hat{\mathbf{n}}\}$, or the ER parameters $\{\lambda,\boldsymbol{\Lambda}\}$ according to

$$\hat{T}'_{LM'} = \sum_{M=-L}^{L} \mathscr{D}^{L}_{MM'}(R)\hat{T}_{LM} \tag{4}$$

$$= \sum_{M=-L}^{L} \mathscr{D}^{L}_{MM'}(\alpha,\beta,\gamma)\hat{T}_{LM} \tag{5}$$

$$= \sum_{M=-L}^{L} \mathscr{D}^{L}_{MM'}(a,b)\hat{T}_{LM} \tag{6}$$

$$= \sum_{M=-L}^{L} \mathscr{D}^{L}_{MM'}(\Phi,\hat{\mathbf{n}})\hat{T}_{LM} \tag{7}$$

$$= \sum_{M=-L}^{L} \mathscr{D}^{L}_{MM'}(\lambda,\boldsymbol{\Lambda})\hat{T}_{LM}. \tag{8}$$

Exploiting this property of irreducible spherical tensor operators greatly facilitates the transformation of spatial tensors in particular from one reference frame to another, most often from the principal axis systems to the laboratory frame. At this point, we have included other possible parametrizations of the transformation matrices in Eqs. (6)–(8) for completeness, but at best, they would be regarded as an exotic curiosities since only the Euler angle parametrized version is ever used in practice. Why is that?

The foundation of angular momentum theory laid in the classic texts by Rose [7], Edmonds [8], and Brink and Satchler [9], gives short shrift to the angle–axis parametrization. Only one of these texts even acknowledges the existence of the angle–axis parameters $\{\Phi,\hat{\mathbf{n}}\}$ as an alternative to the Euler parameters $\{\alpha,\beta,\gamma\}$ for describing the rotation operator. This acknowledgement by Rose [7] could not be more perfunctory or dismissive: "It is well known that three parameters are needed to specify a rotation. These may be the three components of the vector $\Phi\hat{\mathbf{n}}$, where Φ gives the magnitude and $\hat{\mathbf{n}}$ the direction of the rotation. The most useful description is, however, in terms of the Euler angles ...". Later reviews and texts on angular momentum theory (see [10] for example) often repeat this canard, without any critical comment or examination. Does current practice, and our current state of knowledge, provide any justification for concluding that the Euler parameters are really the best and most useful choice? Reasonable criteria for "best" and "useful" would surely include measures of computational ease, simplicity and above all, insight.

If the choice of rotation parameters was merely a matter of taste, this question would hardly be worth answering. However, the well-established success of the quaternion (ER) parameters in the analysis and design of NMR pulse sequences inevitably raises the following questions: first, can we dispense with the Euler parameters entirely, and second, what might be gained by an angle–axis parametrization of the quantum mechanical rotation operator and the associated rotation matrices? A definitive and complete answer to the first question is beyond the scope of this article, but we at least begin to answer it by addressing the second question in some detail.

In the case of the rotation operator and the rotation matrices, what might we ask of a better alternative to the Euler parameters? Above all, a more direct connection to the experimental parameters such as nutation frequency ω_1, rotation angle Φ, resonance offset Δ, and phase ϕ, and a facile method of calculating rotation matrix elements. Ideally, analytical expressions for the matrix elements should clearly separate the rotation angle (Φ) dependence from the rotation axis ($\hat{\mathbf{n}} \equiv \hat{\mathbf{n}}(\theta,\phi)$) dependence. Surprisingly, such an alternative already exists, in the form of a multipole operator expansion of the rotation operator $\hat{\mathscr{D}}(\Phi,\hat{\mathbf{n}})$, and a Clebsch–Gordan expansion of the rotation matrices $\mathscr{D}^{J}_{MM'}(\Phi,\hat{\mathbf{n}})$ [11,12]. Each of the coefficients in the latter Clebsch–Gordan expansion is proportional to the product of a spherical harmonic of the vector $\hat{\mathbf{n}}$ specifying the axis of rotation, $Y_{\lambda\mu}(\hat{\mathbf{n}})$, with a fixed function of the rotation angle Φ, a Gegenbauer polynomial $\mathrm{C}^{\lambda+1}_{2J-\lambda}(\cos\frac{\Phi}{2})$. As far as we are aware, these expansions have yet to be applied in NMR.

The primary purpose of this communication is to introduce these expansions, and by way of a few simple examples, to illustrate their rich potential for NMR applications. The secondary purpose is to extend the seminal work of Blümich and Spiess [5] and Counsell et al. [6] on quaternions into the realm of the transformation matrices $\mathscr{D}^{J}_{MM'}(\Phi,\hat{\mathbf{n}})$. For this purpose, we go beyond mere tabulations of $\mathscr{D}^{J}_{MM'}(\Phi,\hat{\mathbf{n}})$ to consider how these matrices might be used in NMR applications. Section 2 provides the necessary theoretical and computational background, including a summary of noncanonical parametrizations of $SU(2,c)$ and their use in deriving the conventional irreducible representations of the rotation group in Section 2.1, a brief summary of the known pathologies of the Euler parameters in both classical and quantum mechanical contexts in Section 2.2, statements of the multipole operator and Clebsch–Gordan expansions in Section 2.3, and methods for evaluating the Clebsch–Gordan expansions of the $\mathscr{D}^{J}_{MM'}(\Phi,\hat{\mathbf{n}})$ matrix elements in Section 2.4. Section 3, the essential core of this communication, discusses several NMR applications of the multipole operator and Clebsch–Gordan expansions, and Section 4 concludes with a summary of the most advantageous features of the angle–axis expansions, with an eye towards future applications.