Tensors and Rotations in NMR

LEONARD J. MUELLER

Department of Chemistry, University of California, Riverside, CA 92521

ABSTRACT: The transformation of second-rank Cartesian tensors under rotation plays a fundamental role in the theoretical description of nuclear magnetic resonance experiments, providing the framework for describing anisotropic phenomena such as single crystal rotation patterns, tensor powder patterns, sideband intensities under magic-angle sample spinning, and as input for relaxation theory. Here, two equivalent procedures for effecting this transformation—direct rotation in Cartesian space and the decomposition of the Cartesian tensor into irreducible spherical tensors that rotate in subgroups of rank 0, 1, and 2—are reviewed. In a departure from the standard formulation, the explicit use of the spherical tensor basis for the decomposition of a spatial Cartesian tensor is introduced, helping to delineate the rotational properties of the basis states from those of the matrix elements. The result is a uniform approach to the rotation of a physical system and the corresponding transformation of the spatial components of the NMR Hamiltonian, expressed as either Cartesian or spherical tensors. This clears up an apparent inconsistency in the NMR literature, where the rotation of a spatial tensor in spherical tensor form has typically been partnered with the inverse rotation in Cartesian form to produce equivalent transformations. © 2011 Wiley Periodicals, Inc. Concepts Magn Reson Part A 38: 221–235, 2011.

KEY WORDS: irreducible spherical tensor; Cartesian tensor; rotation matrices; Wigner rotation matrix elements

INTRODUCTION

The NMR Hamiltonian is anisotropic, giving rise to spectroscopic lines that depend not only on local molecular and chemical structure, but also on orientation within the static magnetic field (*1–7*). For example, single crystals have resonance frequencies that are periodic under rotation, while powdered samples of randomly oriented crystallites give broad, but typically structured, resonances. Time-dependent modulation of the orientation through sample spinning can average the position and breadth of these peaks, but even for samples in rapid isotropic motion, vestiges of anisotropic interactions remain as routes to relaxation (*1*, *2*, *5*, *8*).

Anisotropic interactions in the NMR Hamiltonian are represented by second-rank Cartesian tensors whose transformational properties under rotation play a fundamental role in the theoretical description of NMR experiments (*1–7*). Two approaches to treating these rotations are the direct transformation of the second-rank spatial tensor in Cartesian form and the

Received 3 June 2011; revised 31 July 2011; accepted 1 August 2011

Correspondence to: Leonard J. Mueller. E-mail: Leonard.Mueller@ucr.edu

Concepts in Magnetic Resonance Part A, Vol. 38A(5) 221–235 (2011)

DOI 10.1002/cmr.a.20224

decomposition of the Cartesian tensor into irreducible spherical tensor components that rotate in subgroups of rank 0, 1, and 2 (*9–13*). While these two approaches must give equivalent results, there is an apparent and curious need in the NMR literature to partner the rotation in one representation with its inverse rotation in the other to find consistency in the final transformed tensor. Here, the transformation of second-rank tensors in Cartesian and spherical forms are reviewed and it is shown that discrepancies in their sense of rotation can be reconciled by explicitly writing the Cartesian tensor as an expansion in the irreducible spherical tensor basis and taking care to distinguish the rotational properties of the underlying spherical tensor basis components from those of the expansion coefficients. The result is a uniform and consistent approach to the rotation of the physical system and the corresponding transformation of the spatial components of the NMR Hamiltonian, expressed as either Cartesian or spherical tensors.

This review begins with a brief introduction to second-rank Cartesian tensors in the NMR Hamiltonian and rotation matrices and operators from both the active and passive points of view. Next, the spherical tensor basis is introduced and explicit relations for the transformation of spherical tensor matrix elements under rotation of the physical system are derived. The resulting *coefficient equation* differs from the customary equation used in the theoretical description of NMR experiments, and the relationship between the two is shown, highlighting the error in the sense of rotation for the latter. A worked example for the transformation of an ab initio chemical shielding tensor is then presented to illustrate the consistency of this approach, before final comments on the Hamiltonian in spherical tensor form and the choice of reference frame.

THE NMR HAMILTONIAN AND ROTATIONS

The general form of a term in the NMR Hamiltonian (*3*, *4*, *6*, *7*) is

$$H^{\lambda} = c^{\lambda}\, I \cdot \mathbf{A}^{\lambda} \cdot S^{\lambda}, \qquad [1]$$

where c^{λ} is a constant specific to a given interaction, I is a spin angular momentum vector operator, and S^{λ} is another vector, which, depending on the particular interaction, may be the same spin angular momentum operator (quadrupolar interaction), a different spin angular momentum operator (J coupling or dipolar coupling), the static magnetic field (chemical shielding interaction), or the molecular angular momentum vector (spin-rotation interaction). $\mathbf{A}^{\lambda}$ is a second-rank Cartesian tensor and is a molecular level property that depends on local geometry, electronic structure, and molecular orientation. For example, the Hamiltonian for the chemical shielding interaction has the form,

$$\begin{aligned} H^{\mathrm{CS}} &= \gamma\, I \cdot \boldsymbol{\sigma} \cdot B \\ &= \gamma \begin{pmatrix} I_x & I_y & I_z \end{pmatrix} \cdot \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ B_z \end{pmatrix} \\ &= \gamma \left(I_x \sigma_{xz} B_z + I_y \sigma_{yz} B_z + I_z \sigma_{zz} B_z \right), \end{aligned} \qquad [2]$$

for the static, laboratory-frame magnetic field aligned along the z-axis. The chemical shielding interaction results from currents in the electron density induced by the external magnetic field, which in turn produce an additional magnetic field that interacts with the nuclear spin. Although the induced field is not necessarily aligned along the lab-frame magnetic field, it is truncated under the secular approximation (*3*), in which terms that do not commute with the Zeeman interaction are discarded, to give

$$H^{\mathrm{CS,secular}} = \gamma\, I_z \sigma_{zz} B_z. \qquad [3]$$

The theoretical description of NMR spectroscopy relies on the transformation of spatial tensors under rotation. Two equivalent ways to treat this transformation are the direct rotation of the second-rank spatial tensor in Cartesian form and the decomposition of the Cartesian tensor into irreducible spherical tensor components that are independently rotated and recombined to form the transformed Cartesian tensor. For the direct rotation, the initial ($\mathbf{A}$) and transformed ($\mathbf{A}'$) tensors are related by (*14*)

$$\mathbf{A}' = \mathbf{R}\mathbf{A}\,\mathbf{R}^{-1}, \qquad [4]$$

where $\mathbf{R}$ is the corresponding rotation matrix. For the transformation in irreducible spherical tensor form, the individual spherical tensor components $\mathbf{A}_{kq}$ transform in an analogous fashion to the angular momentum basis kets, with the q^{th} tensor component of a rank-k spherical tensor rotating into a sum of the other tensor components of the same rank,

$$\mathbf{A}^{R}_{k\,q} = \sum_{p=-k}^{k} D^{(k)}_{p\,q}(\Omega_R)\; \mathbf{A}_{k\,p}, \qquad [5]$$

with weightings determined by the Wigner rotation matrix elements, $D^{(k)}_{pq}(\Omega_R)$ (*9–13*). As will be discussed in detail below, Eq. [5] is not completely analogous to Eq. [4]; $\mathbf{A}^R_{kq}$ describes what the q^{th}-component of the rank-k tensor, $\mathbf{A}_{kq}$, transforms into and should not be confused with the q^{th}-component of the transformed tensor.

The precise meanings of Eqs. [4] and [5] depend on whether the transformation is considered to be the result of a rotation of the object (the active point of view) or a rotation of the coordinate frame of reference (the passive point of view) (*14*, *15*), which are reviewed in the following sections. For a physical rotation of the object, Eq. [4] expresses the Cartesian tensor after the rotation, $\mathbf{A}'$, in terms of the tensor for the object in its original orientation, $\mathbf{A}$, while Eq. [5] describes what the initial $\mathbf{A}_{kq}$ spherical-tensor component rotates into. For a coordinate frame transformation, Eq. [4] describes the tensor in the rotated frame, $\mathbf{A}'$, in terms of the elements of the tensor in the original frame, $\mathbf{A}$; Eq. [5] expresses what a single tensor component of the original frame, $\mathbf{A}_{kq}$, looks like in the rotated frame.

To compare the Cartesian and spherical tensor representations of a rotational transformation first requires explicit expressions for the rotation matrices and the corresponding Wigner rotation matrix elements. Significant confusion over this correspondence exists in the literature due in part to mistakes in two standard texts on angular momentum, the first by Rose (*10*) and the second by Edmonds (*12*) (although the text by Edmonds was subsequently revised (*16*)). Bouten (*15*) points out these well-hidden errors and explicitly writes out the form of the rotation matrices and quantum mechanical operators that define the Wigner rotation matrices from both the active and passive points of view. Bouten's expressions agree with those given by Fano and Racah (*9*), Wigner (*11*), and the revised version of Edmonds (*16*). As these matrices are essential to this discussion, they are presented below.

Rotation Matrices in Cartesian Space

Rotations in three-dimensional (3D) space can be parameterized by three Euler angles, $\Omega = \{\alpha,\beta,\gamma\}$, that relate the orientation of a stationary set of axes, *Oxyz*, to a rotatable set, *OXYZ*. Following Bouten (*15*), if the two frames are initially coincident, then the Euler angles describe the following successive rotations as the *OXYZ* axes are transformed to their final orientation: first, a rotation about the z-axis by an angle α (using a right-hand rule) that reorients the X and Y axes, with the transformed Y axis defining an intermediate axis u; second, a rotation about the u axis by an angle β, placing the Z axis in its final orientation; and third, a rotation about the transformed Z axis by an angle γ to place the *OXYZ* axes in their final orientation. These are illustrated in Figure 1.

Two points of view exist for how these Euler angles describe the orientation of an object, defined by a body-fixed set of axes, relative to an observer-fixed reference frame in which the object is viewed. Under the active rotation convention, different orientations of the object are the result of rotations of the object in the observer-fixed frame. In this case, the body-fixed axes are associated with the rotatable *OXYZ* frame above, and the reference axes with the stationary *Oxyz* frame. Such a transformation is defined by the active rotation matrix in 3D space,

$$\mathbf{R}_{\mathrm{A}}(\alpha,\beta,\gamma) = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & \cos\alpha\sin\beta \\ \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\alpha\sin\beta \\ -\sin\beta\cos\gamma & \sin\beta\sin\gamma & \cos\beta \end{pmatrix}. \qquad [6]$$

As expected, an active $\pi/2$ rotation about the z axis takes an initial vector aligned along x to one along y, i.e., $\mathbf{R}_{\mathrm{A}}\left(\frac{\pi}{2},0,0\right)\begin{pmatrix}1\\0\\0\end{pmatrix} = \begin{pmatrix}0\\1\\0\end{pmatrix}$.

From the standpoint of passive rotation it is the observer-fixed frame that rotates relative to the body-fixed frame. In this case, the body-fixed axes are associated with the stationary *Oxyz* frame and the reference axes with the rotatable *OXYZ* frame. Different orientations of the object are effected by different sets of Euler angles that transform the observer-fixed frame from initial coincidence with the body-fixed frame to its new perspective on the object. The transformation is defined by the passive rotation matrix in 3D space,

$$\mathbf{R}_{\mathrm{P}}(\alpha,\beta,\gamma) = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix}. \qquad [7]$$

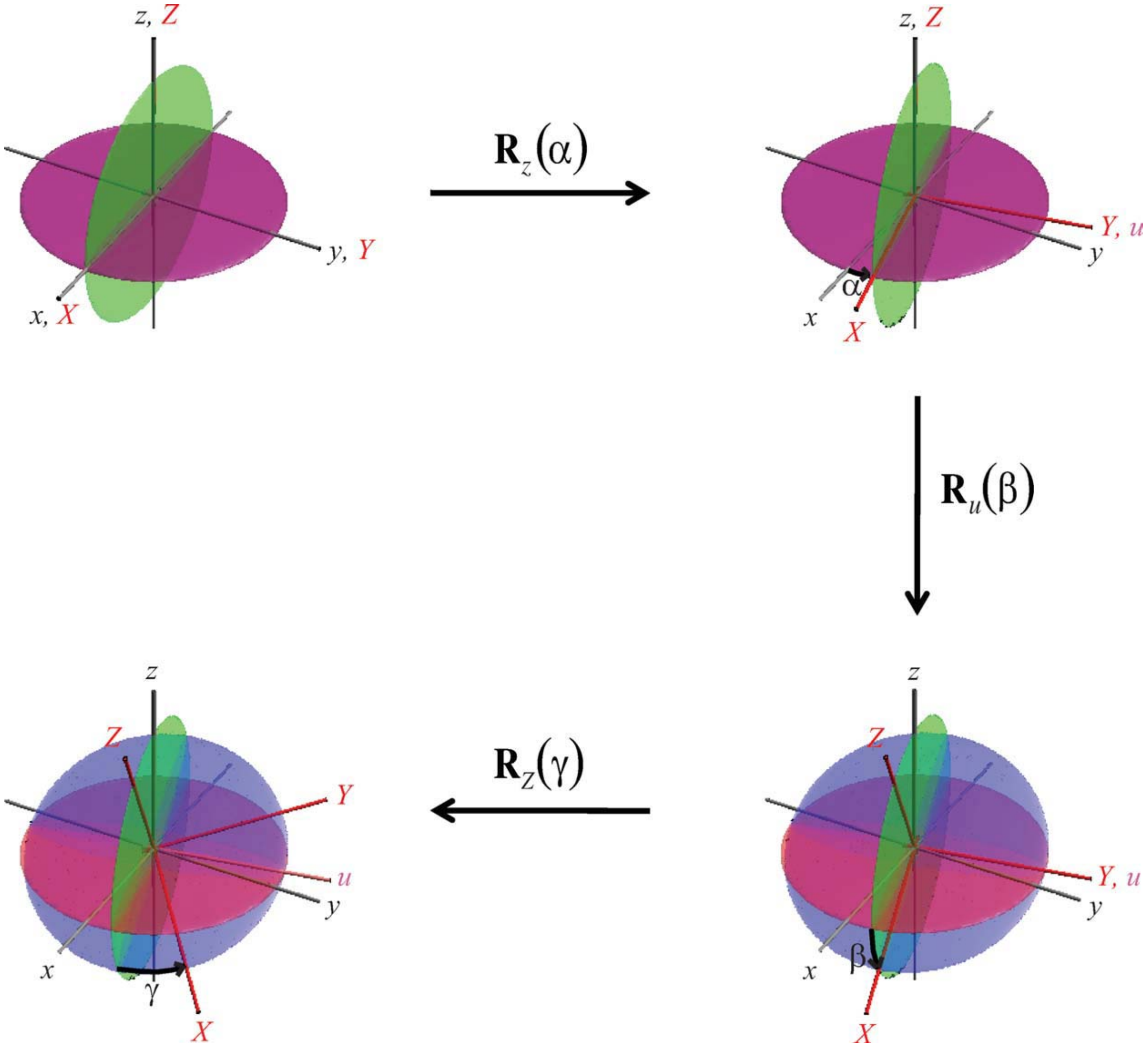

Figure 1 Rotation in three-dimensional space parameterized by the Euler angles, $\Omega = \{\alpha,\beta,\gamma\}$, that relate the orientation of a rotatable set of axes, *OXYZ*, to a stationary set, *Oxyz*.

In the passive convention, a rotation of $\pi/2$ about Z takes an X-vector to $-Y$, $\mathbf{R}_{\mathrm{P}\left(\frac{\pi}{2},0,0\right)} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ -1 \\ 0 \end{pmatrix}$.

In both the active and passive contexts, the coordinates of the object are written in the observer-fixed reference frame, which is *Oxyz* for an active rotation and *OXYZ* for passive, and so any transformation that takes an initial vector $\vec{a}$ to a final vector $\vec{b}$,

$$\mathbf{R} \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} = \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix}, \qquad [8]$$

must have the same numerical values for its rotation matrix elements regardless of whether it is considered to be the result of an active or a passive transformation; it is only the values ascribed to the specific Euler angles that are different. In this sense, there is considerable latitude in choosing a convention when setting up transformations in the laboratory frame; problems involving coordinate frame transformations can often be recast as physical rotations and vice versa (see Question 1 for an example of this). It is also worth noting that if one were to perform an active rotation followed by a passive rotation with the same three Euler angles, the object would be restored to its original orientation in the observer-fixed frame, a consequence of the fact that

Table 1 Wigner Rotation Matrix Elements (17)

Active: $D^{(k)}_{pq}(\alpha,\beta,\gamma) = e^{-i\alpha p}\,e^{-i\gamma q}\,d^{(k)}_{pq}(\beta)$ *Passive:* $D^{(k)}_{pq}(\alpha,\beta,\gamma) = e^{i\gamma p}\,e^{i\alpha q}\,d^{(k)}_{pq}(-\beta)$

$$d^{(0)}_{0\,0}(\beta) = 1$$

$$d^{(1)}_{1\,1}(\beta) = d^{(1)}_{-1\,-1}(\beta) = \cos^2\left(\frac{\beta}{2}\right)$$

$$d^{(1)}_{1\,-1}(\beta) = d^{(1)}_{-1\,1}(\beta) = \sin^2\left(\frac{\beta}{2}\right)$$

$$d^{(1)}_{0\,1}(\beta) = d^{(1)}_{-1\,0}(\beta) = -d^{(1)}_{0\,-1}(\beta) = -d^{(1)}_{1\,0}(\beta) = \frac{1}{\sqrt{2}}\sin\beta$$

$$d^{(1)}_{0\,0}(\beta) = \cos\beta$$

$$d^{(2)}_{2\,2}(\beta) = d^{(2)}_{-2\,-2}(\beta) = \cos^4\left(\frac{\beta}{2}\right)$$

$$d^{(2)}_{2\,1}(\beta) = -d^{(2)}_{1\,2}(\beta) = -d^{(2)}_{-2\,-1}(\beta) = d^{(2)}_{-1\,-2}(\beta) = -\frac{1}{2}\sin\beta\,(1+\cos\beta)$$

$$d^{(2)}_{2\,0}(\beta) = d^{(2)}_{0\,2}(\beta) = d^{(2)}_{-2\,0}(\beta) = d^{(2)}_{0\,-2}(\beta) = \sqrt{\frac{3}{8}}\sin^2\beta$$

$$d^{(2)}_{2\,-1}(\beta) = d^{(2)}_{1\,-2}(\beta) = -d^{(2)}_{-2\,1}(\beta) = d^{(2)}_{-1\,2}(\beta) = \frac{1}{2}\sin\beta\,(-1+\cos\beta)$$

$$d^{(2)}_{2\,-2}(\beta) = d^{(2)}_{-2\,2}(\beta) = \sin^4\left(\frac{\beta}{2}\right)$$

$$d^{(2)}_{1\,1}(\beta) = d^{(2)}_{-1\,-1}(\beta) = \frac{1}{2}(2\cos\beta - 1)\,(\cos\beta + 1)$$

$$d^{(2)}_{1\,-1}(\beta) = d^{(2)}_{-1\,1}(\beta) = \frac{1}{2}(2\cos\beta + 1)\,(1 - \cos\beta)$$

$$d^{(2)}_{1\,0}(\beta) = d^{(2)}_{0\,-1}(\beta) = -d^{(2)}_{0\,1}(\beta) = -d^{(2)}_{-1\,0}(\beta) = -\sqrt{\frac{3}{2}}\sin\beta\cos\beta$$

$$d^{(2)}_{0\,0}(\beta) = \frac{1}{2}\left(3\cos^2\beta - 1\right)$$

$$\mathbf{R}_{\mathrm{P}}(\alpha,\beta,\gamma) = \mathbf{R}_{\mathrm{A}}^{-1}(\alpha,\beta,\gamma). \qquad [9]$$

Wigner Rotation Matrices

To calculate the Wigner matrix elements for the rotation of the spherical tensor components requires an expression for the quantum mechanical rotation operator. For every rotation of a physical system in real space, there corresponds a unitary quantum mechanical operator in the state space of the physical system that transforms a ket according to

$$|\psi'\rangle = O(\alpha,\beta,\gamma)\ |\psi\rangle \qquad [10]$$

The active and passive representations of this operator are again derived by Bouten (*15*) respectively as,

$$O_{\mathrm{A}}(\alpha,\beta,\gamma) = e^{-i\alpha I_z}e^{-i\beta I_y}e^{-i\gamma I_z}, \qquad [11]$$

and,

$$O_{\mathrm{P}}(\alpha,\beta,\gamma) = e^{i\gamma I_z}e^{i\beta I_y}e^{i\alpha I_z}. \qquad [12]$$

The former is familiar from NMR as the form of the active rotations used in Liouville space transformations (*5*). Note that both are defined in terms of the angular momentum operators in the observer-fixed frame of reference, taken to be *Oxyz* in both cases now. As well, both are unitary and each other's inverse

$$O_{\mathrm{A}}(\alpha,\beta,\gamma)=O_{\mathrm{P}}^{-1}(\alpha,\beta,\gamma). \qquad [13]$$

The Wigner rotation matrix elements are defined in terms of the matrix elements of these operators in the generalized angular momentum basis $|kq\rangle$,

$$D^{(k)}_{p\,q}(\Omega_R)=\langle k\,p|O_R|k\,q\rangle, \qquad [14]$$

which arise naturally under the application of closure to the rotation of an initial angular momentum ket

$$\begin{aligned}|k\,q\rangle^R = O_R|k\,q\rangle &= \sum_{k'}\sum_{p=-k'}^{k'}|k'\,p\rangle\langle k'\,p|O_R|k\,q\rangle\\ &=\sum_{p=-k}^{k}|k\,p\rangle\langle k\,p|O_R|k\,q\rangle=\sum_{p=-k}^{k}D^{(k)}_{p\,q}(\Omega_R)\;|k\,p\rangle. \qquad [15]\end{aligned}$$

Table 1 summarizes the Wigner rotation matrices for both the active and passive rotation operators. Note that it is the first index of the Wigner rotation matrix that is summed over in Eq. [15], just as in Eq. [5]. Also, by definition, Eq. [15] describes the rotation of the q^{th}-basis or vector component, not the q^{th}-basis component of the rotated vector in state space. This is similarly true for the rotation of the spherical tensor components in Eq. [5], a point that is often confused in the NMR literature (although by no means unique to NMR) with Eq. [5] frequently taken to mean the q^{th} component of the transformed tensor. To avoid confusion, the transformed tensor will be referred to as $\mathbf{A}' = \mathbf{RA}\,\mathbf{R}^{-1}$ and its tensor components as $\mathbf{A}'_{kq}$, while a rotated tensor component will be designated as $\mathbf{A}^R_{kq}$.

It is also important to distinguish the tensor components, which are themselves tensors, from matrix elements of the tensors, which are scalars associated with the magnitude of a specific tensor component. The latter will be denoted by lower case letters, e.g., a_{xx}. The analogy is to vectors in Cartesian space, with the vector $\vec{\mathbf{v}}=v_x\hat{\mathbf{x}}+v_y\hat{\mathbf{y}}+v_z\hat{\mathbf{z}}$ having an x-vector component $v_x\hat{\mathbf{x}}$ and an x-scalar component (or matrix element/coefficient) v_x.

THE SPHERICAL TENSOR BASIS AND THE ROTATION OF SPHERICAL TENSORS

To derive equations for the transformation in the spherical tensor representation, it is useful to introduce the irreducible spherical tensor basis (*18*, *19*), which forms a matrix basis for the decomposition of Cartesian tensors. The spherical tensor basis (STB) is related to the 2nd-rank Cartesian tensor basis (CTB) by

$$\begin{aligned}\mathbf{T}_{0\,0}&=-\tfrac{1}{\sqrt{3}}\left[\mathbf{T}_{x\,x}+\mathbf{T}_{y\,y}+\mathbf{T}_{z\,z}\right]\\ \mathbf{T}_{1\,0}&=-\tfrac{i}{\sqrt{2}}\left[\mathbf{T}_{x\,y}-\mathbf{T}_{y\,x}\right]\\ \mathbf{T}_{1\,\pm1}&=-\tfrac{1}{2}\left[\mathbf{T}_{z\,x}-\mathbf{T}_{x\,z}\pm i\left(\mathbf{T}_{z\,y}-\mathbf{T}_{y\,z}\right)\right]\\ \mathbf{T}_{2\,0}&=\tfrac{1}{\sqrt{6}}\left[3\mathbf{T}_{z\,z}-\left(\mathbf{T}_{x\,x}+\mathbf{T}_{y\,y}+\mathbf{T}_{z\,z}\right)\right]\\ \mathbf{T}_{2\,\pm1}&=\mp\tfrac{1}{2}\left[\mathbf{T}_{x\,z}+\mathbf{T}_{z\,x}\pm i\left(\mathbf{T}_{y\,z}+\mathbf{T}_{z\,y}\right)\right]\\ \mathbf{T}_{2\,\pm2}&=\tfrac{1}{2}\left[\mathbf{T}_{x\,x}-\mathbf{T}_{y\,y}\pm i\left(\mathbf{T}_{x\,y}+\mathbf{T}_{y\,x}\right)\right] \qquad [16]\end{aligned}$$

in keeping with the standard definition of spherical tensors used in NMR (*3*, *4*, *6*, *20*, *21*). Explicitly the Cartesian basis is written

$$\mathbf{T}_{x\,x}=\begin{pmatrix}1&0&0\\0&0&0\\0&0&0\end{pmatrix}\qquad \mathbf{T}_{x\,y}=\begin{pmatrix}0&1&0\\0&0&0\\0&0&0\end{pmatrix}$$
$$\mathbf{T}_{x\,z}=\begin{pmatrix}0&0&1\\0&0&0\\0&0&0\end{pmatrix}$$
$$\mathbf{T}_{y\,x}=\begin{pmatrix}0&0&0\\1&0&0\\0&0&0\end{pmatrix}\qquad \mathbf{T}_{y\,y}=\begin{pmatrix}0&0&0\\0&1&0\\0&0&0\end{pmatrix}$$
$$\mathbf{T}_{y\,z}=\begin{pmatrix}0&0&0\\0&0&1\\0&0&0\end{pmatrix}$$
$$\mathbf{T}_{z\,x}=\begin{pmatrix}0&0&0\\0&0&0\\1&0&0\end{pmatrix}\qquad \mathbf{T}_{z\,y}=\begin{pmatrix}0&0&0\\0&0&0\\0&1&0\end{pmatrix}$$
$$\mathbf{T}_{z\,z}=\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix} \qquad [17]$$

and the spherical tensor basis is

$$\mathbf{T}_{0\,0}=-\frac{1}{\sqrt{3}}\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\quad \mathbf{T}_{1\,0}=-\frac{i}{\sqrt{2}}\begin{pmatrix}0&1&0\\-1&0&0\\0&0&0\end{pmatrix}$$
$$\mathbf{T}_{1\,\pm1}=-\frac{1}{2}\begin{pmatrix}0&0&-1\\0&0&\mp i\\1&\pm i&0\end{pmatrix}$$

$$\mathbf{T}_{2\,0} = \frac{1}{\sqrt{6}}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \mathbf{T}_{2\,\pm 1} = \mp\frac{1}{2}\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & \pm i \\ 1 & \pm i & 0 \end{pmatrix}$$

$$\mathbf{T}_{2\,\pm 2} = \frac{1}{2}\begin{pmatrix} 1 & \pm i & 0 \\ \pm i & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \qquad [18]$$

Both the CTB and STB are complete and satisfy the orthonormalization conditions

$$Tr\left\{\mathbf{T}^{\dagger}_{k\,l}\mathbf{T}_{m\,n}\right\} = \delta_{k\,m}\delta_{l\,n}. \qquad [19]$$

The coefficients, a_{kj}, for the expansion of an arbitrary Cartesian tensor, **A**, in the spherical basis,

$$\mathbf{A} = \sum_{k=0}^{2}\sum_{j=-k}^{k} a_{k\,j}\mathbf{T}_{k\,j} \qquad [20]$$

can be obtained by

$$a_{k\,j} = Tr\left\{\mathbf{T}^{\dagger}_{k\,j}\mathbf{A}\right\}. \qquad [21]$$

As the STB components are not Hermitian, the matrix trace is taken with the conjugate transpose of the corresponding basis component. The coefficients obtained by [21]

$$\begin{aligned}
a_{0\,0} &= -\frac{1}{\sqrt{3}}\left[a_{x\,x} + a_{y\,y} + a_{z\,z}\right] \\
a_{1\,0} &= \frac{i}{\sqrt{2}}\left[a_{x\,y} - a_{y\,x}\right] \\
a_{1\,\pm 1} &= -\frac{1}{2}\left[a_{z\,x} - a_{x\,z} \mp i\left(a_{z\,y} - a_{y\,z}\right)\right] \\
a_{2\,0} &= \frac{1}{\sqrt{6}}\left[3a_{z\,z} - \left(a_{x\,x} + a_{y\,y} + a_{z\,z}\right)\right] \\
a_{2\,\pm 1} &= \mp\frac{1}{2}\left[a_{x\,z} + a_{z\,x} \mp i\left(a_{y\,z} + a_{z\,y}\right)\right] \\
a_{2\,\pm 2} &= \frac{1}{2}\left[a_{x\,x} - a_{y\,y} \mp i\left(a_{x\,y} + a_{y\,x}\right)\right] \qquad [22]
\end{aligned}$$

can readily be shown to satisfy Eq. [20] by direct substitution.

The spherical tensor basis states transform under rotation analogously to the angular momentum basis kets, with the q^{th} basis component of a rank-k spherical tensor transforming into a combination of basis states of the same rank (*9–13*),

$$\mathbf{T}^{R}_{k\,q} = \mathbf{R}\;\mathbf{T}_{k\,q}\mathbf{R}^{-1} = \sum_{j=-k}^{k} D^{(k)}_{j\,q}(\Omega_R)\mathbf{T}_{k\,j}. \qquad [23]$$

This equation, which will be referred to as the *tensor component equation* (or *component equation* for short), can be verified by direct substitution of the Wigner rotation matrix elements and the Cartesian representations of **R** and $\mathbf{T}_{kq}$. It again highlights that $\mathbf{T}^{R}_{kq}$ is the transformation of the q^{th}-component of the rank-k tensor, not the q^{th}-component of the transformed tensor. Equation [23] also clarifies the meaning of equation [5], which should be interpreted as a scalar multiple of equation [23]. To transform the full tensor, **A** is first expanded and then rotated in the spherical tensor basis

$$\begin{aligned}
\mathbf{A}' = \mathbf{R}\;\mathbf{A}\mathbf{R}^{-1} & \\
&= \mathbf{R}\left(\sum_{k=0}^{2}\sum_{j=-k}^{k} a_{k\,j}\mathbf{T}_{k\,j}\right)\mathbf{R}^{-1} \\
&= \sum_{k=0}^{2}\sum_{j=-k}^{k} a_{k\,j}\sum_{q=-k}^{k} D^{(k)}_{q\,j}(\Omega_R)\;\mathbf{T}_{k\,q} \\
&= \sum_{k=0}^{2}\sum_{q=-k}^{k}\sum_{j=-k}^{k} D^{(k)}_{q\,j}(\Omega_R)\;a_{k\,j}\mathbf{T}_{k\,q} \qquad [24]
\end{aligned}$$

or explicitly in matrix form as

$$a'_{0\,0} = D^{(0)}_{0\,0}(\Omega_R)\;a_{0\,0}$$

$$\begin{pmatrix} a'_{1\,-1} \\ a'_{1\,0} \\ a'_{1\,1} \end{pmatrix} = \begin{pmatrix} D^{(1)}_{-1\,-1}(\Omega_R) & D^{(1)}_{-1\,0}(\Omega_R) & D^{(1)}_{-1\,1}(\Omega_R) \\ D^{(1)}_{0\,-1}(\Omega_R) & D^{(1)}_{0\,0}(\Omega_R) & D^{(1)}_{0\,1}(\Omega_R) \\ D^{(1)}_{1\,-1}(\Omega_R) & D^{(1)}_{1\,0}(\Omega_R) & D^{(1)}_{1\,1}(\Omega_R) \end{pmatrix} \begin{pmatrix} a_{1\,-1} \\ a_{1\,0} \\ a_{1\,1} \end{pmatrix}$$

$$\begin{pmatrix} a'_{2\,-2} \\ a'_{2\,-1} \\ a'_{2\,0} \\ a'_{2\,1} \\ a'_{2\,2} \end{pmatrix} = \begin{pmatrix} D^{(2)}_{-2\,-2}(\Omega_R) & D^{(2)}_{-2\,-1}(\Omega_R) & D^{(2)}_{-2\,0}(\Omega_R) & D^{(2)}_{-2\,1}(\Omega_R) & D^{(2)}_{-2\,2}(\Omega_R) \\ D^{(2)}_{-1\,-2}(\Omega_R) & D^{(2)}_{-1\,-1}(\Omega_R) & D^{(2)}_{-1\,0}(\Omega_R) & D^{(2)}_{-1\,1}(\Omega_R) & D^{(2)}_{-1\,2}(\Omega_R) \\ D^{(2)}_{0\,-2}(\Omega_R) & D^{(2)}_{0\,-1}(\Omega_R) & D^{(2)}_{0\,0}(\Omega_R) & D^{(2)}_{0\,1}(\Omega_R) & D^{(2)}_{0\,2}(\Omega_R) \\ D^{(2)}_{1\,-2}(\Omega_R) & D^{(2)}_{1\,-1}(\Omega_R) & D^{(2)}_{1\,0}(\Omega_R) & D^{(2)}_{1\,1}(\Omega_R) & D^{(2)}_{1\,2}(\Omega_R) \\ D^{(2)}_{2\,-2}(\Omega_R) & D^{(2)}_{2\,-1}(\Omega_R) & D^{(2)}_{2\,0}(\Omega_R) & D^{(2)}_{2\,1}(\Omega_R) & D^{(2)}_{2\,2}(\Omega_R) \end{pmatrix} \begin{pmatrix} a_{2\,-2} \\ a_{2\,-1} \\ a_{2\,0} \\ a_{2\,1} \\ a_{2\,2} \end{pmatrix}.$$

While Eqs. [24] and [25] describe the rotation of the full tensor, the theoretical treatment of NMR interactions often focuses on particular matrix elements of the Cartesian tensor for different orientations of the physical system (*3*, *4*). For example, due to truncation at high magnetic field, it is the matrix element associated with the secular component of a tensor that principally determines its spectrum, such as σ_{zz} (in the laboratory frame) of the chemical shielding tensor. From Eq. [24], the coefficient of the q^{th}-component of the rank–k, transformed tensor is

$$a'_{k\,q} = \sum_{j=-k}^{k} D^{(k)}_{q\,j}(\Omega_R)\; a_{k\,j}. \qquad [26]$$

We will refer to this as the *coefficient equation* to distinguish it from the component equation (Eq. [23]). The coefficient equation is strikingly similar in form to the tensor component equation, with just a switch in the order of the indices for the Wigner coefficient. Great care needs to be taken to distinguish these two equations as they express different physical situations. The component equation applies to the tensor basis components; it describes how a single tensor component transforms into a sum of the other components under rotation. The coefficient equation, however, gives the coefficient of a specific tensor component after the transformation of an arbitrary tensor.

Yet in the NMR literature, equations for the transformation of spherical tensor coefficients are ubiquitously written as if they were the same as the tensor component equation (*3*, *4*, *20*, *21*),

$$b'_{k\,q} \overset{?}{=} \sum_{j=-k}^{k} D^{(k)}_{j\,q}(\Omega_R)\; b_{k\,j} \qquad [27]$$

with coefficients, b_{kj}, defined to be the complex-conjugates of those in [22],

$$\begin{aligned}
b_{0\,0} &= a^{*}_{0\,0} = -\frac{1}{\sqrt{3}}\left[a_{x\,x} + a_{y\,y} + a_{z\,z}\right] \\
b_{1\,0} &= a^{*}_{1\,0} = -\frac{i}{\sqrt{2}}\left[a_{x\,y} - a_{y\,x}\right] \\
b_{1\,\pm1} &= a^{*}_{1\,\pm1} = -\frac{1}{2}\left[a_{z\,x} - a_{x\,z} \pm i\left(a_{z\,y} - a_{y\,z}\right)\right] \\
b_{2\,0} &= a^{*}_{2\,0} = \frac{1}{\sqrt{6}}\left[3a_{z\,z} - \left(a_{x\,x} + a_{y\,y} + a_{z\,z}\right)\right] \\
b_{2\,\pm1} &= a^{*}_{2\,\pm1} = \mp\frac{1}{2}\left[a_{x\,z} + a_{z\,x} \pm i\left(a_{y\,z} + a_{z\,y}\right)\right] \\
b_{2\,\pm2} &= a^{*}_{2\,\pm2} = \frac{1}{2}\left[a_{x\,x} - a_{y\,y} \pm i\left(a_{x\,y} + a_{y\,x}\right)\right] \qquad [28]
\end{aligned}$$

These two expressions seem to confuse the rotation of the coefficients and the rotation of the basis set components and, in light of the coefficient equation, should not be valid. In fact Eq. [27] is not correct in that it is inconsistent with the Cartesian transformation under rotation as written in Eq. [4]. Rather, Eq. [27] should be written with the inverse of the rotation matrix in the Wigner rotation elements,

$$b'_{k\,q} = \sum_{j=-k}^{k} D^{(k)}_{j\,q}(\Omega_{R^{-1}})\; b_{k\,j}. \qquad [29]$$

This can be shown by noting that the appropriate pairing of the b_{kj} coefficients with the basis components to form the full tensor is

$$\mathbf{A} = \sum_{k=0}^{2}\sum_{j=-k}^{k} b^{*}_{k\,j}\mathbf{T}_{k\,j}, \qquad [30]$$

and so the b^{*}_{kj} must satisfy the coefficient equation,

$$b'^{*}_{k\,q} = \sum_{j=-k}^{k} D^{(k)}_{q\,j}(\Omega_R)\; b^{*}_{k\,j}, \qquad [31]$$

which can be rewritten as Eq. [29] by taking the complex-conjugate of both sides and making use of the property that $D^{(k)}_{jq}(\Omega_{R^{-1}}) = D^{(k)*}_{qj}(\Omega_R)$.

The distinction between Eqs. [27] and [29] is fundamental and clarifies the apparent inconsistency between the rotation of second-rank Cartesian tensors in Cartesian and spherical tensor forms found in the NMR literature, where the rotation using Eq. [27] must be partnered with its inverse rotation in Cartesian form to produce equivalent transformations. One prominent example of this mispairing is Appendix B of Mehring's text (*4*), which couples the Cartesian rotation matrix from the passive perspective (the inverse of the active perspective) with the Wigner rotation matrix elements in the active form, an error that can be traced back to Rose's text (*10*). Others (*6*, *20*, *21*) have noted that this mispairing is necessary and directly link the representation of the rotation in spherical form with its inverse rotation in the Cartesian representation, but fail to note that the inverse rotation should be associated with the Wigner rotation matrix elements. The correct correspondence between the physical rotation of the system and its Cartesian and spherical tensor transformations is significant, particularly in structural studies where connections back to a molecular frame are made. As the spatial components of the NMR Hamiltonian are tied to the molecular frame of reference, they rotate

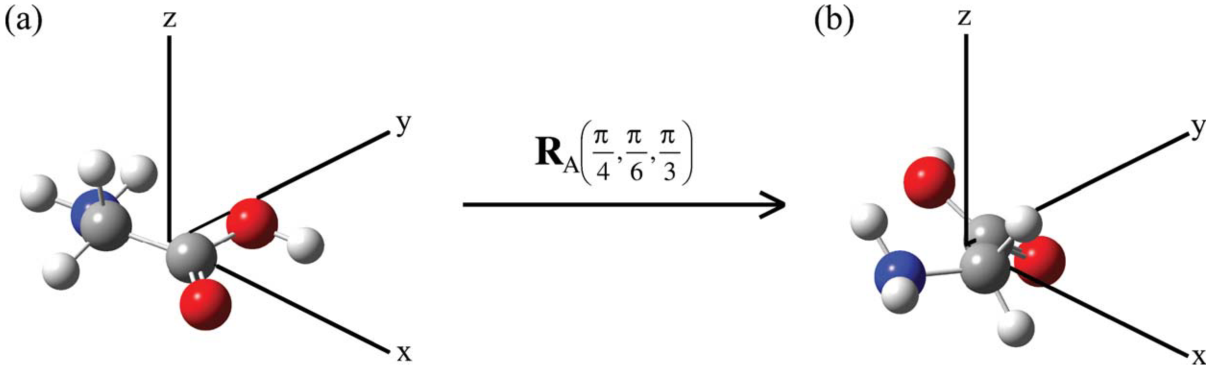

Figure 2 Two orientations of glycine in the laboratory frame related by an active rotation $\mathbf{R}_{\mathrm{A}}\left(\frac{\pi}{4},\frac{\pi}{6},\frac{\pi}{3}\right)$ of the molecular coordinates. The standard CPK scheme is used to designate the atom colors (H, white; C, gray; N, blue; O, red).

with the molecule. The result is that in many cases the transformation effected by the application of Eq. [27] has been the opposite of what was intended or expected. For example, Haeberlen (*3*) uses Eq. [27] with the Wigner matrix elements from the passive perspective, so is actually performing an active rotation of the tensors (and molecules). Mehring (*4*), as well as Spiess and Schmidt-Rohr (*20*), use the active Wigner rotation matrix elements and Eq. [27], so are actually performing a passive rotation.

EXAMPLE: THE TRANSFORMATION OF A CHEMICAL SHIELDING TENSOR

As a worked example, the transformation of the ab initio chemical shielding tensor for the alpha carbon of glycine in the gas phase is considered. This is done in three ways. In method I, the ab initio chemical shielding tensor is calculated directly using Gaussian03 (*22*) for an initial and rotated orientation. In method II, the transformed tensor is calculated from the initial tensor and the rotation matrix in Cartesian form (Eq. [4]). In method III, the transformation is effected using spherical tensors and the coefficient equation (Eq. [26]). To be consistent, all three of these must agree.

Figure 2(a) shows the geometry optimized structure of glycine in the gas phase calculated using Gaussian03 (B3LYP, 6311++G**), in which the molecular orientation in the laboratory (observer)-fixed coordinate frame is chosen by the program during refinement to be the standard nuclear orientation, with the principal axes of the moment of inertia tensor aligned along the three Cartesian axes. Figure 2(b) shows the same molecule in which the atomic Cartesian coordinates from Figure 2(a) have been rotated according to

$$\begin{pmatrix} x^b \\ y^b \\ z^b \end{pmatrix} = \mathbf{R}_{\mathrm{A}}\left(\frac{\pi}{4},\frac{\pi}{6},\frac{\pi}{3}\right)\begin{pmatrix} x^a \\ y^a \\ z^a \end{pmatrix}$$

$$= \begin{pmatrix} -\frac{1}{4}\sqrt{\frac{3}{2}} & -\frac{5}{4}\sqrt{\frac{1}{2}} & \frac{1}{2}\sqrt{\frac{1}{2}} \\ \frac{3}{4}\sqrt{\frac{3}{2}} & -\frac{1}{4}\sqrt{\frac{1}{2}} & \frac{1}{2}\sqrt{\frac{1}{2}} \\ -\frac{1}{4} & \frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{2} \end{pmatrix}\begin{pmatrix} x^a \\ y^a \\ z^a \end{pmatrix}, \qquad [32]$$

where the superscripts *a* and *b* refer to the initial and final molecular orientations, respectively, shown in the corresponding figures. In this expression, the new molecular orientation is considered to be the result of an active rotation with Euler angles $\Omega_{\mathrm{A}} = \left\{\alpha = \frac{\pi}{4}, \beta = \frac{\pi}{6}, \gamma = \frac{\pi}{3}\right\}$. However, the orientation in 2(b) could equally be considered the result of a passive rotation with Euler angles $\Omega_{\mathrm{P}} = \left\{\alpha = -\frac{\pi}{3}, \beta = -\frac{\pi}{6}, \gamma = -\frac{\pi}{4}\right\}$; either way, the numerical form of the rotation matrix and the orientations shown in Figure 2 would be the same.

For the alpha carbon, the calculated ab initio chemical shielding tensors (Gaussian03, B3LYP, 6311++G**) corresponding to the molecular orientations in Figure 2(a) and 2(b) are

$$\boldsymbol{\sigma}^{a} = \begin{pmatrix} 151.5 & -8.7 & 1.5 \\ -6.9 & 131.0 & -5.0 \\ 5.1 & -2.8 & 119.4 \end{pmatrix} \qquad [33]$$

and

$$\boldsymbol{\sigma}^{b,\mathrm{I}} = \begin{pmatrix} 129.0 & 1.2 & 0.1 \\ 0.6 & 152.0 & -10.9 \\ -3.1 & -7.7 & 120.9 \end{pmatrix} \qquad [34]$$

(in ppm). The additional superscript on the latter is meant to signify that it was calculated using method I.

The chemical shielding tensor for orientation *b* can also be directly calculated from the tensor for the initial orientation and the rotation matrix using method II, direct matrix multiplication in the Cartesian representation,

$$\boldsymbol{\sigma}^{b,\mathrm{II}} = \mathbf{R}_{\mathrm{A}}\left(\frac{\pi}{4},\frac{\pi}{6},\frac{\pi}{3}\right)\,\boldsymbol{\sigma}^{a}\,\mathbf{R}_{\mathrm{A}}^{-1}\left(\frac{\pi}{4},\frac{\pi}{6},\frac{\pi}{3}\right) = \begin{pmatrix} 129.0 & 1.2 & 0.2 \\ 0.6 & 152.0 & -10.9 \\ -3.1 & -7.8 & 120.9 \end{pmatrix}. \qquad [35]$$

This agrees with method I within the expected computational accuracy.

Finally, method III can be used, which employs the use of spherical tensors. First, the initial chemical shielding tensor is decomposed into its spherical components by calculating the coefficients (Eq. [21])

$$\sigma^{a}_{k\,j} = Tr\left\{\mathbf{T}^{\dagger}_{k\,j}\boldsymbol{\sigma}^{a}\right\}, \qquad [36]$$

for $k = \{0,1,2\}$ and $j = \{-k,\ldots,k\}$. These transform according to the coefficient equation (Eq. [26]) to give the coefficients for orientation *b*,

$$\sigma^{b}_{k\,q} = \sum_{j=-k}^{k} D^{(k)}_{q\,j}\left(\Omega_{R_{\mathrm{A}}\left(\frac{\pi}{4},\frac{\pi}{6},\frac{\pi}{3}\right)}\right)\,\sigma^{a}_{k\,j}. \qquad [37]$$

Here again, the Wigner rotation matrix elements will have the same numerical values whether we consider this an active rotation with Euler angles $\Omega_{\mathrm{A}} = \left\{\alpha = \frac{\pi}{4}, \beta = \frac{\pi}{6}, \gamma = \frac{\pi}{3}\right\}$ or a passive rotation with Euler angles $\Omega_{\mathrm{P}} = \left\{\alpha = -\frac{\pi}{3}, \beta = -\frac{\pi}{6}, \gamma = -\frac{\pi}{4}\right\}$. Once calculated, the full chemical shielding tensor for orientation *b* can be reconstituted according to Eq. [20] as

$$\boldsymbol{\sigma}^{b,\mathrm{III}} = \sum_{k=0}^{2}\sum_{j=-k}^{k}\sigma^{b}_{k\,j}\mathbf{T}_{k\,j} = \begin{pmatrix} 129.0 & 1.2 & 0.2 \\ 0.6 & 152.0 & -10.9 \\ -3.1 & -7.8 & 120.9 \end{pmatrix}, \qquad [38]$$

in agreement with both methods I and II.

Note that the molecular coordinates and the tensor transform together. This is reasonable, given that they both correspond to quantum mechanical observables that are tied to the molecular frame of reference. Molecular frame observables also rotate in the same sense as kets in state space, as Schmidt-Rohr and Spiess point out (*20*), with a transformed molecular ket

$$|\psi'\rangle = O|\psi\rangle \qquad [39]$$

and operator tied to the molecular frame

$$A' = O\,A\,O^{\dagger} \qquad [40]$$

having an expectation value that is invariant under molecular rotation

$$\langle\psi'|A'|\psi'\rangle = \langle\psi|A|\psi\rangle. \qquad [41]$$

DYADIC PRODUCTS, THE NMR HAMILTONIAN, AND REFERENCE FRAMES

The advantage of irreducible spherical tensors is that they isolate elements of second-rank Cartesian tensors that transform together under rotation. To construct the Hamiltonian directly in terms of spherical tensor components and take full advantage of these transformational properties, the Cartesian space, spin operator-containing components of the NMR Hamiltonian are first written as a dyadic product (*3*, *4*, *6*)

$$\mathbf{S}^{\lambda} = S^{\lambda} \otimes I = \begin{pmatrix} S^{\lambda}_{x}I_{x} & S^{\lambda}_{x}I_{y} & S^{\lambda}_{x}I_{z} \\ S^{\lambda}_{y}I_{x} & S^{\lambda}_{y}I_{y} & S^{\lambda}_{y}I_{z} \\ S^{\lambda}_{z}I_{x} & S^{\lambda}_{z}I_{y} & S^{\lambda}_{z}I_{z} \end{pmatrix}. \qquad [42]$$

and the NMR Hamiltonian as a trace over the product of the spatial and spin-containing Cartesian tensors

$$H^{\lambda} = c^{\lambda}\,I\cdot\mathbf{A}^{\lambda}\cdot S^{\lambda} = c^{\lambda}\,Tr\left\{\mathbf{A}^{\lambda}\,\mathbf{S}^{\lambda}\right\}. \qquad [43]$$

An analogous decomposition into the spherical tensor basis can be applied to the dyadic product with coefficients

$$\begin{aligned}
s_{0\,0} &= -\frac{1}{\sqrt{3}}\left[S_xI_x + S_yI_y + S_zI_z\right] \\
s_{1\,0} &= \frac{i}{\sqrt{2}}\left[S_xI_y - S_yI_x\right] \\
s_{1\,\pm1} &= -\frac{1}{2}\left[S_zI_x - S_xI_z \mp i\left(S_zI_y - S_yI_z\right)\right] \\
s_{2\,0} &= \frac{1}{\sqrt{6}}\left[3S_zI_z - \left(S_xI_x + S_yI_y + S_zI_z\right)\right] \\
s_{2\,\pm1} &= \mp\frac{1}{2}\left[S_xI_z + S_zI_x \mp i\left(S_yI_z + S_zI_y\right)\right] \\
s_{2\,\pm2} &= \frac{1}{2}\left[S_xI_x - S_yI_y \mp i\left(S_xI_y + S_yI_x\right)\right],
\end{aligned} \qquad [44]$$

allowing the Hamiltonian to be written

$$
\begin{aligned}
H^{\lambda} &= c^{\lambda}\,\mathrm{Tr}\left\{\,\mathbf{A}^{\lambda}\,\mathbf{S}^{\lambda}\right\}\\
&= c^{\lambda}\,\mathrm{Tr}\left\{\sum_{k=0}^{2}\sum_{j=-k}^{k} a_{k\,j}\mathbf{T}_{k\,j}\sum_{k'=0}^{2}\sum_{j'=-k'}^{k'} s_{k'\,j'}\mathbf{T}_{k'\,j'}\right\}\\
&= c^{\lambda}\,\sum_{k=0}^{2}\sum_{j=-k}^{k}(-1)^{j}a_{k\,j}s_{k\,-j}. \qquad [45]
\end{aligned}
$$

Here, the identity

$$\mathbf{T}_{k'\,j'} = (-1)^{j'}\mathbf{T}^{\dagger}_{k'\,-j'} \qquad [46]$$

has been used to simplify the trace. Note that the coefficients in the Cartesian dyadic product contain spin operators, which themselves may be treated using spherical tensors in spin space (*2*, *23–25*), a related but distinct issue from the representation of Cartesian tensors in real space treated here.

The transformation of the Hamiltonian under rotation in real space can now be written directly in terms of the rotation of the Cartesian tensor in Eq. [43] or through the transformation of the spherical tensor coefficients, a_{kj}, in Eq. [45]. For example, if the spatial tensor has known components in its principal axis system (the coordinate system in which the symmetric part of the spatial tensor is diagonal), then the tensor components in the laboratory frame can be calculated and combined with the spin-containing components to give the Hamiltonian as

$$
\begin{aligned}
H^{\lambda} &= c^{\lambda}\,Tr\left\{\,\mathbf{A}^{\mathrm{lab}}\,\mathbf{S}^{\mathrm{lab}}\right\}\\
&= c^{\lambda}\,Tr\left\{\,\mathbf{R}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right)\mathbf{A}^{\mathrm{PAS}}\,\mathbf{R}^{-1}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right)\mathbf{S}^{\mathrm{lab}}\right\} \qquad [47]
\end{aligned}
$$

and

$$
\begin{aligned}
H^{\lambda} = c^{\lambda}\,\sum_{k=0}^{2}\sum_{j=-k}^{k}(-1)^{j}a^{\mathrm{lab}}_{k\,j}s^{\mathrm{lab}}_{k\,-j} = c^{\lambda}\,\sum_{k=0}^{2}\sum_{j=-k}^{k}(-1)^{j}\\
\times\sum_{j'=-k}^{k}D^{(k)}_{j\,j'}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right)\,a^{\mathrm{PAS}}_{k\,j'}s^{\mathrm{lab}}_{k\,-j}, \qquad [48]
\end{aligned}
$$

respectively, in Cartesian and spherical tensor forms. Here $\Omega^{\mathrm{lab}}_{\mathrm{PAS}}$ is the set of Euler angles that parameterize the orientation of the principal axis system (PAS) as seen by an observer in the laboratory frame. The superscripts "lab" and "PAS" have been added to the tensors to indicate that the components are defined relative to an observer in those frames (and the λ dropped from the tensors for notational convenience). Both Eqs. [47] and [48] can be simplified considerably under the secular approximation (see Question 2).

The Hamiltonian in Eqs. [47] and [48] is written from the perspective of the laboratory frame, with the spatial tensor transformed to that frame before being combined with the spin components (also in the laboratory frame) to form the Hamiltonian. While the external magnetic field and spin operators associated with NMR observables are tied to the laboratory frame, making this an obvious choice for writing the tensor components of the Hamiltonian, the trace in Eq. [43] is invariant to a change in basis, so the spatial and spin tensors in the Hamiltonian may in fact be written in any arbitrary frame. For example, in some cases it may be convenient to consider the tensor components of the Hamiltonian from within the spatial tensor PAS frame,

$$H^{\lambda} = c^{\lambda}\,Tr\left\{\,\mathbf{A}^{\mathrm{PAS}}\,\mathbf{S}^{\mathrm{PAS}}\right\}. \qquad [49]$$

The spin tensor in the PAS must ultimately be related back to the spin tensor in the laboratory frame, as the latter contains the lab-frame angular momentum operators that direct the spin dynamics, but again the tensors are simply related by

$$\mathbf{S}^{\mathrm{PAS}} = \mathbf{R}\left(\Omega^{\mathrm{PAS}}_{\mathrm{lab}}\right)\mathbf{S}^{\mathrm{lab}}\,\mathbf{R}^{-1}\left(\Omega^{\mathrm{PAS}}_{\mathrm{lab}}\right), \qquad [50]$$

where now the Euler angles parameterize the orientation of the laboratory frame as seen by an observer in the PAS frame.

This leads to a potential source of confusion, as the Euler angles are defined relative to observers in different frames in Eqs. [47] and [49]. They are related, however, and by comparing Eqs. [47]–[50], and making use of the cyclic property of the trace,

$$
\begin{aligned}
H^{\lambda} &= c^{\lambda}\,Tr\left\{\,\mathbf{R}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right)\mathbf{A}^{\mathrm{PAS}}\,\mathbf{R}^{-1}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right)\mathbf{S}^{\mathrm{lab}}\right\}\\
&= c^{\lambda}\,Tr\left\{\,\mathbf{A}^{\mathrm{PAS}}\,\mathbf{R}^{-1}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right)\mathbf{S}^{\mathrm{lab}}\,\mathbf{R}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right)\right\}\\
&= c^{\lambda}\,Tr\left\{\,\mathbf{A}^{\mathrm{PAS}}\,\mathbf{R}\left(\Omega^{\mathrm{PAS}}_{\mathrm{lab}}\right)\mathbf{S}^{\mathrm{lab}}\,\mathbf{R}^{-1}\left(\Omega^{\mathrm{PAS}}_{\mathrm{lab}}\right)\right\}\\
&= c^{\lambda}\,Tr\left\{\,\mathbf{R}^{-1}\left(\Omega^{\mathrm{PAS}}_{\mathrm{lab}}\right)\mathbf{A}^{\mathrm{PAS}}\,\mathbf{R}\left(\Omega^{\mathrm{PAS}}_{\mathrm{lab}}\right)\mathbf{S}^{\mathrm{lab}}\right\}, \qquad [51]
\end{aligned}
$$

it is seen that

$$\mathbf{R}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right) = \mathbf{R}^{-1}\left(\Omega^{\mathrm{PAS}}_{\mathrm{lab}}\right) \qquad [52]$$

or

$$
\begin{aligned}
\mathbf{R}\left(\alpha^{\mathrm{lab}}_{\mathrm{PAS}},\beta^{\mathrm{lab}}_{\mathrm{PAS}},\lambda^{\mathrm{lab}}_{\mathrm{PAS}}\right) &= \mathbf{R}^{-1}\left(\alpha^{\mathrm{PAS}}_{\mathrm{lab}},\beta^{\mathrm{PAS}}_{\mathrm{lab}},\gamma^{\mathrm{PAS}}_{\mathrm{lab}}\right)\\
&= \mathbf{R}\left(-\gamma^{\mathrm{PAS}}_{\mathrm{lab}},-\beta^{\mathrm{PAS}}_{\mathrm{lab}},-\alpha^{\mathrm{PAS}}_{\mathrm{lab}}\right). \qquad [53]
\end{aligned}
$$

In other words, two observers in the lab and PAS frames have opposite views of the rotation that takes their frames from initial coincidence to their final orientation relative to each other, exactly as one would expect. Equation [51] also highlights that even for tensors written in the lab frame, the transformation of the spatial components of the Hamiltonian to that frame can be replaced by the application of the inverse transformation to the spin containing dyadic terms.

Finally, it is noted that in some cases a frame distinct from the lab or PAS may be more convenient to work in. For example, in their classic paper on sideband intensities under magic-angle spinning, Herzfeld and Berger (*26*) choose the MAS rotor as the frame of reference and then write both the lab frame magnetic field/spin operators (which are now time-dependent) and the chemical shift tensor in the rotor frame. Question 3 below presents an alternate derivation of the Hamiltonian used as the starting point in the Herzfeld-Berger analysis, writing the components in the laboratory frame and using a two-step transformation of the spatial tensor from the PAS to rotor and then rotor to lab frames.

CONCLUSIONS

The motivation behind the use of irreducible spherical tensors in NMR is that they allow the components of second-rank Cartesian tensors to be grouped according to their underlying rotational symmetry. In principal, this should simplify the treatment of anisotropic interactions in the NMR Hamiltonian. In practice, the inconsistent use of active and passive conventions and errors in several of the classic texts on angular momentum have kept these benefits from being fully realized and have led in many cases to transformations that correspond to the inverse of the stated rotation. In situations where spectroscopic observables are averaged over the full set of Euler angles or no connection is made back to a molecular frame of reference, this confusion in rotation is of little consequence. The calculated CSA powder line shape, for example, would be the same regardless of whether the molecular rotation was parameterized correctly or with an inverted sense. In cases where absolute connections between the spatial tensor and molecular or crystalline frames are desired, however, these discrepancies must be reconciled.

Here a consistent approach to the transformation of second-rank Cartesian tensors in Cartesian and spherical tensor forms has been shown. The introduction of an explicit spherical tensor basis for the decomposition of second-rank Cartesian tensors helps delineate the rotational properties of the basis states from those of the matrix elements. This provides a uniform approach to the rotation of the physical system and the corresponding transformation of the spatial components of the NMR Hamiltonian represented by either Cartesian or spherical tensors.

Questions and Answers

Question 1. There is considerable latitude in choosing either the active or passive convention for representing a transformation in NMR. For example, consider the transformation of a chemical shielding tensor under a change in coordinate frame of reference from the tensor PAS to the laboratory frame. Describe this transformation using the passive point of view and then recast the problem using the active point of view.

Answer:

The use of the passive point of view in this context is straight-forward. Letting the Euler angles ${}^{\mathrm{P}}\Omega^{\mathrm{lab}}_{\mathrm{PAS}}$ parameterize the rotation that would take the PAS frame into coincidence with the laboratory frame, the chemical shielding tensor in the lab frame would be written:

$$\sigma^{\,\mathrm{lab}} = \mathbf{R}_{\mathrm{P}}\left({}^{\mathrm{P}}\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right)\,\sigma^{\,\mathrm{PAS}}\,\mathbf{R}^{-1}_{\mathrm{P}}\left({}^{\mathrm{P}}\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right).$$

Alternatively, the coordinate frame transformation could be considered to result from an active rotation that takes the tensor PAS from initial alignment with the laboratory frame to its final orientation in the laboratory frame, parameterized by the Euler angles ${}^{\mathrm{A}}\Omega^{\mathrm{lab}}_{\mathrm{PAS}}$,

$$\sigma^{\,\mathrm{lab}} = \mathbf{R}_{\mathrm{A}}\left({}^{\mathrm{A}}\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right)\,\sigma^{\,\mathrm{PAS}}\,\mathbf{R}^{-1}_{\mathrm{A}}\left({}^{\mathrm{A}}\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right).$$

In this case, σ^{PAS} is both the initial tensor in the laboratory frame and the tensor in the PAS frame. ${}^{\mathrm{P}}\Omega^{\mathrm{lab}}_{\mathrm{PAS}}$ and ${}^{\mathrm{A}}\Omega^{\mathrm{lab}}_{\mathrm{PAS}}$ are of course related; if ${}^{\mathrm{P}}\Omega^{\mathrm{lab}}_{\mathrm{PAS}} = \{\alpha,\beta,\gamma\}$ then ${}^{\mathrm{A}}\Omega^{\mathrm{lab}}_{\mathrm{PAS}} = -\{\gamma,\beta,\alpha\}$.

Question 2. Write out the chemical shielding Hamiltonian under the secular approximation in terms of the PAS components, σ_{XX}, σ_{YY}, and σ_{ZZ}, and the Euler angles, $\Omega^{\mathrm{lab}}_{\mathrm{PAS}}$, that relate the PAS and laboratory frames. Use the active rotation convention.

Answer:

(a) Using Cartesian Tensors:

The starting point for this problem is Eq. [47]. First, the following associations are made for the chemical shielding interaction:

$$c^{\lambda} = \gamma,$$

$$\mathbf{A}^{\mathrm{PAS}} = \boldsymbol{\sigma}^{\,\mathrm{PAS}} = \begin{pmatrix} \sigma_{XX} & 0 & 0 \\ 0 & \sigma_{YY} & 0 \\ 0 & 0 & \sigma_{ZZ} \end{pmatrix}$$

(ignoring the antisymmetric terms),

and

$$\mathbf{S}^{\mathrm{lab}} = (B \otimes I)^{\mathrm{lab}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ B_z I_x & B_z I_y & B_z I_z \end{pmatrix},$$

for the static magnetic field aligned along the lab-frame z-axis. Under the secular approximation, $\mathbf{S}^{\mathrm{lab}}$ can be further simplified by dropping the I_x and I_y spin angular momentum terms, which do not commute with the Zeeman interaction, $H^{\mathrm{Zeeman}} = \gamma B_z I_z$, allowing the chemical shielding Hamiltonian to be written

$$H^{\mathrm{CS}} = \gamma \left\{ \mathbf{R}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right) \boldsymbol{\sigma}^{\mathrm{PAS}} \mathbf{R}^{-1}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right) \right\}_{zz} B_z I_z.$$

Using the active convention for writing the rotation matrix,

$$H^{\mathrm{CS}} = \gamma B_z I_z \Big(\sigma_{ZZ} \cos^2\beta + \sigma_{XX} \sin^2\beta \ \cos^2\gamma + \sigma_{YY} \sin^2\beta \ \sin^2\gamma \Big),$$

where $\Omega^{\mathrm{lab}}_{\mathrm{PAS}} = \{\alpha,\beta,\gamma\}$ are the Euler angles that would take the PAS frame from initial coincidence with the lab frame to its final orientation in the lab frame.

The Hamiltonian can be also be written in terms of the isotropic shift,

$$\sigma = \frac{1}{3}(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}),$$

anisotropy,

$$\delta = \sigma_{ZZ} - \sigma,$$

and asymmetry,

$$\eta = \frac{\sigma_{YY} - \sigma_{XX}}{\delta},$$

as,

$$H^{\mathrm{CS}} = \gamma B_z I_z \left[\sigma + \delta \left(\frac{3\cos^2\beta - 1}{2} - \frac{1}{2}\eta \sin^2\beta \ \cos 2\gamma \right) \right].$$

(b) Using Spherical Tensors:

The starting point here is Eq. [48], with the same associations given above and noting that

$$a^{\mathrm{PAS}}_{0\,0} = -\frac{1}{\sqrt{3}}[\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}] = -\sqrt{3}\,\sigma$$
$$a^{\mathrm{PAS}}_{1\,0} = 0$$
$$a^{\mathrm{PAS}}_{1\,\pm 1} = 0$$
$$a^{\mathrm{PAS}}_{2\,0} = \frac{1}{\sqrt{6}}[3\sigma_{ZZ} - (\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ})] = \sqrt{\frac{3}{2}}\,\delta$$
$$a^{\mathrm{PAS}}_{2\,\pm 1} = 0$$
$$a^{\mathrm{PAS}}_{2\,\pm 2} = \frac{1}{2}[\sigma_{XX} - \sigma_{YY}] = -\frac{1}{2}\eta\,\delta$$

and

$$s^{\mathrm{lab}}_{0\,0} = -\frac{1}{\sqrt{3}} B_z I_z$$
$$s^{\mathrm{lab}}_{1\,0} = 0$$
$$s^{\mathrm{lab}}_{1\,\pm 1} = -\frac{1}{2}\left[B_z I_x \mp i B_z I_y\right] \quad \overset{\mathrm{secular}}{\approx} \quad 0$$
$$s^{\mathrm{lab}}_{2\,0} = \sqrt{\frac{2}{3}} B_z I_z$$
$$s^{\mathrm{lab}}_{2\,\pm 1} = \mp\frac{1}{2}\left[B_z I_x \mp i B_z I_y\right] \quad \overset{\mathrm{secular}}{\approx} \quad 0$$
$$s^{\mathrm{lab}}_{2\,\pm 2} = 0$$

Equation [48] can then be written

$$\begin{aligned} H^{\mathrm{CS}} &= \gamma\, a^{\mathrm{lab}}_{0\,0} s^{\mathrm{lab}}_{0\,0} + \gamma\, a^{\mathrm{lab}}_{2\,0} s^{\mathrm{lab}}_{2\,0} \\ &= \gamma\, D^{(0)}_{0\,0}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right) a^{\mathrm{PAS}}_{0\,0} s^{\mathrm{lab}}_{0\,0} + \gamma \sum_{j'=-2}^{2} D^{(2)}_{0\,j'}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right) a^{\mathrm{PAS}}_{2\,j'} s^{\mathrm{lab}}_{2\,0} \\ &= \gamma\, B_z I_z \sigma + \gamma\, B_z I_z \left\{ -D^{(2)}_{0\,-2}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right) \sqrt{\frac{1}{6}}\eta\delta \right. \\ &\quad \left. + D^{(2)}_{0\,0}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right) \delta - D^{(2)}_{0\,2}\left(\Omega^{\mathrm{lab}}_{\mathrm{PAS}}\right) \sqrt{\frac{1}{6}}\eta\delta \right\} \\ &= \gamma\, B_z I_z \left[\sigma + \delta \left(\frac{3\cos^2\beta - 1}{2} - \frac{1}{2}\eta \sin^2\beta \ \cos 2\gamma \right) \right]. \end{aligned}$$

Question 3. In their classic paper on sideband intensities under magic-angle spinning, Herzfeld and Berger (*26*) write both the lab frame magnetic field/spin operators and the chemical shift tensor in the MAS rotor frame,

$$\begin{aligned} H^{\mathrm{cs}} &= -\gamma\, Tr\left\{ \boldsymbol{\sigma}^{\mathrm{rotor}} (B \otimes I)^{\mathrm{rotor}} \right\} \\ &= -\gamma\, Tr\Big\{ \mathbf{R}\left(\Omega^{\mathrm{rotor}}_{\mathrm{PAS}}\right) \boldsymbol{\sigma}^{\mathrm{PAS}} \mathbf{R}^{-1}\left(\Omega^{\mathrm{rotor}}_{\mathrm{PAS}}\right) \mathbf{R}\left(\Omega^{\mathrm{rotor}}_{\mathrm{lab}}\right) \\ &\qquad \times (B \otimes I)^{\mathrm{lab}} \mathbf{R}^{-1}\left(\Omega^{\mathrm{rotor}}_{\mathrm{lab}}\right) \Big\} \end{aligned}$$

Provide an alternate derivation of the Hamiltonian used as the starting point in the Herzfeld-Berger analysis (corresponding to the frequency given in Eq. [16] of their paper) by writing the components in the laboratory frame and using a two-step transformation of the spatial tensor from the PAS to rotor frame and then from the rotor to lab frames. Use spherical tensors and the passive rotation convention.

Answer: Under the secular approximation, the chemical shift Hamiltonian in spherical tensor form is

$$\begin{aligned}
H^{\text{cs}} &= -\gamma\, a_{0\,0}^{\text{lab}} s_{0\,0}^{\text{lab}} - \gamma\, a_{2\,0}^{\text{lab}} s_{2\,0}^{\text{lab}} \\
&= -\gamma\, D_{0\,0}^{(0)}\left(\Omega_{\text{rotor}}^{\text{lab}}\right)\, a_{0\,0}^{\text{rotor}} s_{0\,0}^{\text{lab}} \\
&\quad - \gamma \sum_{j'=-2}^{2} D_{0\,j'}^{(2)}\left(\Omega_{\text{rotor}}^{\text{lab}}\right)\, a_{2\,j'}^{\text{rotor}} s_{2\,0}^{\text{lab}} \\
&= -\gamma\, D_{0\,0}^{(0)}\left(\Omega_{\text{rotor}}^{\text{lab}}\right) D_{0\,0}^{(0)}\left(\Omega_{\text{PAS}}^{\text{rotor}}\right)\, a_{0\,0}^{\text{PAS}} s_{0\,0}^{\text{lab}} \\
&\quad - \gamma \sum_{j'=-2}^{2} \sum_{j''=-2}^{2} D_{0\,j'}^{(2)}\left(\Omega_{\text{rotor}}^{\text{lab}}\right) D_{j'\,j''}^{(2)}\left(\Omega_{\text{PAS}}^{\text{rotor}}\right)\, a_{2\,j''}^{\text{PAS}} s_{2\,0}^{\text{lab}} \\
&= -\gamma\, B_z I_z \sigma - \gamma \sum_{j'=-2}^{2} \sum_{j''=-2}^{2} D_{0\,j'}^{(2)}\left(\Omega_{\text{rotor}}^{\text{lab}}\right) \\
&\quad \times D_{j'\,j''}^{(2)}\left(\Omega_{\text{PAS}}^{\text{rotor}}\right)\, a_{2\,j''}^{\text{PAS}} s_{2\,0}^{\text{lab}} \\
&= -\gamma\, B_z I_z \sigma - \gamma\, B_z I_z \sum_{j'=-2}^{2} D_{0\,j'}^{(2)}\left(\Omega_{\text{rotor}}^{\text{lab}}\right) \\
&\quad \left\{ -D_{j'\,-2}^{(2)}\left(\Omega_{\text{PAS}}^{\text{rotor}}\right) \sqrt{\frac{1}{6}}\eta\delta + D_{j'\,0}^{(2)}\left(\Omega_{\text{PAS}}^{\text{rotor}}\right) \right. \\
&\qquad \left. \times \delta - D_{j'\,2}^{(2)}\left(\Omega_{\text{PAS}}^{\text{rotor}}\right) \sqrt{\frac{1}{6}}\eta\delta \right\}
\end{aligned}$$

Using the passive convention, the Euler angles that would take the rotor-fixed frame to the laboratory frame under MAS are

$$\Omega_{\text{rotor}}^{\text{lab}} = \{\omega_r t, \theta_m, 0\},$$

where

$$\theta_m = \cos^{-1}\left(\frac{1}{\sqrt{3}}\right).$$

(N.B., this is just one of the possible ways in which MAS can be parameterized). Substituting above and simplifying the expression gives

$$\begin{aligned}
H^{\text{cs}} = -\gamma\, B_z I_z \Bigg\{ & \sigma. \\
& + \delta\left[\frac{1}{2}\sin^2\beta - \frac{1}{4}\eta\cos 2\alpha \left(1 + \frac{1}{3}\cos 2\beta\right)\right] \\
& \qquad \times \cos(2\omega_r t + 2\gamma) \\
& + \frac{1}{3}\eta\delta\, \sin 2\alpha\, \cos\beta\, \sin(2\omega_r t + 2\gamma) \\
& - \frac{1}{\sqrt{2}}\delta \left(1 + \frac{1}{3}\eta\cos 2\alpha\right) \sin 2\beta\, \cos(\omega_r t + \gamma) \\
& + \frac{\sqrt{2}}{3}\eta\delta\, \sin 2\alpha \sin\beta\, \sin(\omega_r t + \gamma) \Bigg\}
\end{aligned}$$

where the Euler angles $\Omega_{\text{PAS}}^{\text{rotor}} = \{\alpha, \beta, \gamma\}$ parameterize the rotation that would take the PAS to the rotor frame. With some minor algebraic and trigonometric rearrangement, this can be reduced to Eq. [16] of their article.

ACKNOWLEDGMENTS

The author would like to thank Dr. Moreno Lelli for lively discussions on rotation matrices and Professor Alex Bain, Mr. Lingchao Zhu, and Mr. Chen Yang for a careful reading and comments on the text. This work was supported by NSF grant CHE0848607.

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BIOGRAPHY

Len Mueller is an Associate Professor in the Department of Chemistry at the University of California, Riverside. He received his B.S. in Chemistry from the University of Rochester (1988), C.P.G.S. in Natural Science (Chemistry) from the University of Cambridge (1989), and Ph.D. in Chemistry from the California Institute of Technology (1997). From 1996–1998 he was an American Cancer Society Postdoctoral Fellow at the Massachusetts Institute of Technology. Len's research interests include nuclear magnetic resonance spectroscopy as a probe of molecular and biological structure and dynamics.