Spherical Tensor Operators in NMR

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March 5, 2004

1. **Quick Review of Vector Operators**: Considering an infinitesimal rotation through δ about the axis $\hat{J}_u = \hat{\mathbf{J}}.\mathbf{u}$, the components of a vector operator $\mathbf{V}$, transform $\hat{V}_i \rightarrow \hat{V}_i'$ according to the following transformation rules:

$$\hat{V}_i \xrightarrow{\mathscr{D}(R)} \hat{V}_i' = \mathscr{D}(R)\hat{V}_i\mathscr{D}^\dagger(R) \quad (1a)$$

$$= \hat{V}_i - i\frac{\delta}{\hbar}[\hat{V}_i, \hat{J}_u] \quad (1b)$$

Moreover

$$\mathscr{D}^\dagger(R)\hat{V}_i\mathscr{D}(R) = \sum_j R_{ij}\hat{V}_j \quad (1c)$$

also

$$\mathscr{D}(R) = 1 - exp\,(-i\frac{\delta}{\hbar}\hat{J}_u) \quad (1d)$$

The equality in (1c) holds because of the following concepts:

(a) The expectation value of a component $\langle\alpha|\hat{V}_i|\alpha\rangle$ remains unchanged in the rotated frame (with respect to the transformed operator), i.e., $\langle\alpha'|\hat{V}_i'|\alpha'\rangle = \langle\alpha|\hat{V}_i|\alpha\rangle$ where $|\alpha\rangle \longrightarrow \mathscr{D}(R)|\alpha\rangle = |\alpha'\rangle$ and $\hat{V}_i'$ is the *operator transform*. The expectation value in the two bases must be the same, because we are assuming that space is isotropic, and all physical observables and physical laws must remain invariant under the rotation of the entire system, including the measuring apparatus. In such a scenario, $\hat{V}_i'|\alpha'\rangle = \hat{V}_i|\alpha\rangle$.

(b) The expectation value $\langle\alpha|\hat{V}_i|\alpha\rangle$ is unchanged with respect to transformed operator and kets, but with respect to the kets and operators in the un-rotated frame, it transforms like the components of a cartesian vector, i.e., $\langle\alpha|\hat{V}_i|\alpha\rangle \longrightarrow \sum_j R_{ij}\langle\alpha|\hat{V}_j|\alpha\rangle = \langle\alpha'|\hat{V}_i|\alpha'\rangle = \langle\alpha|\mathscr{D}^\dagger(R)\hat{V}_i\mathscr{D}(R)|\alpha\rangle$. This last equation is not to be confused with the equality $\langle\alpha'|\hat{V}_i'|\alpha'\rangle = \langle\alpha|\hat{V}_i|\alpha\rangle$, in which both the operator and the kets are transformed.

(c) Since the matrix with elements R_{ij} is orthogonal, i.e., $\sum_k R_{ik}R_{jk} = \delta_{ij}$, (1c) can also be written as:

$$\boxed{\mathscr{D}(R)\hat{V}_i\mathscr{D}^\dagger(R) = \sum_j \hat{V}_j R_{ji}} \quad (1e)$$

The above equation will be used as our starting point for defining *tensor operators*.

The defining transformation rule for vector operators can also be written in a more compact form:

$$[\hat{V}_i, \hat{J}_j] = i\hbar\epsilon_{ijk}\hat{V}_k \tag{1f}$$

We have observed that scalar and vector operators are defined through the behaviour under rotations. Likewise we can also define tensor operators by characterizing their behaviour under transformations — scalar and vector operators being particular cases of these tensor operators (ranks 0 and 1 respectively).

2. **Elaboration of point (b)** Rotations in Quantum Mechanics present some confusion because they involve a rotation of both the variables as well as the states. Another confusion arises because of the possibility of *active* and *passive* rotations. We shall be concerned with passive rotations, which involve a rotation of the co-ordinate axes – affording what is called a *basis transformation.* The active conceptualism is totally equivalent, however it pays to focus on just either of the two! Consider a state represented by a ket $|\psi\rangle$ in the Hilbert space. This state will be depend on a dynamic variable, like the position co-ordinate $\overrightarrow{\mathbf{r}}$. A complete description of the state is thus $|\psi(\overrightarrow{\mathbf{r}})\rangle$. Now we rotate the co-ordinate axes such that the position vector transforms as $\overrightarrow{\mathbf{r}} \mapsto \overrightarrow{\mathbf{r}}'$. We assume that this rotation in the physical space is represented by a rotation matrix $\mathscr{D}$, such that $\mathscr{D}\overrightarrow{\mathbf{r}} = \overrightarrow{\mathbf{r}}'$. In the new basis, the state will also have been modified. We **define** the transformation of the state $|\psi\rangle \mapsto |\psi'\rangle$, such that:

$$|\psi'(\overrightarrow{\mathbf{r}}')\rangle = |\psi(\overrightarrow{\mathbf{r}})\rangle \tag{2a}$$

(2a) would strictly be true upto some global phase $e^{i\phi}$. It expresses our intuition that all observables and spectra of eigenvalues remain unchanged when both the variable and the state are rotated: the same idea as has been expressed in [1b] as $\langle\alpha'|\hat{V}_i'|\alpha'\rangle$=$\langle\alpha|\hat{V}_i|\alpha\rangle$. From (2a), we continue:

$$|\psi'(\overrightarrow{\mathbf{r}}')\rangle = |\psi(\mathscr{D}^{-1}\overrightarrow{\mathbf{r}}')\rangle \tag{2b}$$

As $\overrightarrow{\mathbf{r}}'$ is just an arbitrary variable, we can replace it by $\overrightarrow{\mathbf{r}}$:

$$|\psi'(\overrightarrow{\mathbf{r}})\rangle = |\psi(\mathscr{D}^{-1}\overrightarrow{\mathbf{r}})\rangle = \mathscr{D}|\psi(\overrightarrow{\mathbf{r}})\rangle \tag{2c}$$

$\mathscr{D}$ is unitary because the norms of $\mathscr{D}|\psi\overrightarrow{\mathbf{r}}\rangle$ and $|\psi\overrightarrow{\mathbf{r}}\rangle$ are the same. Moreover from the last equality in (2c), note that we are using the same rotation matrix $\mathscr{D}$ for rotations of both the co-ordinates and the states. If we are considering rotations in the real, physical space, all elements of the matrix representing $\mathscr{D}$ are real and hence its representation is a symmetric matrix. In general Hilbert space, the matrix representation of an arbitrary rotation R is denoted as $\mathscr{D}(R)$.

3. **Cartesian Tensor Operator** Motivated by the definition of a vector operator presented in (1e) , we can define a tensor operator T with components $\{T_s\}$ which transforms according to the equation:

$$\boxed{T_i \longrightarrow T_i' = \mathscr{D}(R)\hat{T}_i\mathscr{D}^\dagger(R) = \sum_s T_s\mathscr{D}_{s,i}(R)} \tag{3}$$

Given two vector operators $\hat{\mathbf{V}}$ and $\hat{\mathbf{W}}$, we can form a cartesian tensor with 9 components $\hat{V}_i\hat{W}_j$ where $i, j = 1, 2, 3$. This cartesian tensor, however is not *irreducible* and it is not convenient to work with it. The component $\hat{V}_i\hat{W}_j$ can be reduced into a scalar, a tensor product (or antisymmetric tensor of rank 1) and a traceless, symmetric tensor of rank 2 as expressed below:

$$\hat{V}_i\hat{W}_j = \frac{\hat{\mathbf{V}}.\hat{\mathbf{W}}}{3}\delta_{ij} + \frac{(\hat{V}_i\hat{W}_j - \hat{W}_i\hat{V}_j)}{2} + \big(\frac{\hat{V}_i\hat{W}_j + \hat{W}_i\hat{V}_j}{2} - \frac{\hat{\mathbf{V}}.\hat{\mathbf{W}}}{3}\delta_{ij}\big) \tag{4}$$

The number of components corresponding to these tensors of ranks $0, 1$ and 2 are $1, 3$ and 5 respectively, which add up to 9. These numbers correspond well to $2l + 1$ components of the spherical harmonic functions Y_l^m of rank l where $l = 0, 1$ and 2. In fact the *irreducible tensor operators* transform just like the spherical harmonic functions and hence they are most often called the *spherical tensor operators.*

4. **Transformation of Spherical Harmonics under Rotations** The spherical harmonic function parametrically depends on the angles θ and ϕ in the spatial co-ordinate basis and is given by the wavefunction representation in space as:

$$Y_l^m(\theta, \phi) = \langle \hat{\mathbf{n}} | l, m\rangle \tag{5}$$

where $\hat{\mathbf{n}}$ is a unit vector that points in the θ,ϕ direction. Now consider the rotation $|\hat{\mathbf{n}}\rangle \longmapsto |\hat{\mathbf{n}}'\rangle = \mathscr{D}(R)|\hat{\mathbf{n}}\rangle$. Taking the inner product with the bra $\langle l, m|$, we arrive at the relationship:

$$\begin{aligned} \langle l, m|\hat{\mathbf{n}}'\rangle &= \langle l, m|\mathscr{D}(R)|\hat{\mathbf{n}}\rangle \\ \langle \hat{\mathbf{n}}'|l, m\rangle &= \langle \hat{\mathbf{n}}|\mathscr{D}(R)^\dagger|l, m\rangle \\ \Longrightarrow Y_l^m(\hat{\mathbf{n}}') &= \langle \hat{\mathbf{n}}|\mathscr{D}(R)^\dagger|l, m\rangle \\ &= \sum_{m'} \langle \hat{\mathbf{n}}|l, m'\rangle\langle l, m'|\mathscr{D}(R)|l, m\rangle \end{aligned} \tag{6a}$$

where in (6a), we have suppressed the sum over all possible values of l, because of the invariance of the $\mathscr{E}(l)$ sub-space. Finally (6a) can written in the more amenable form as:

$$Y_l^m(\hat{\mathbf{n}}') = \sum_{m'} Y_l^{m'}(\hat{\mathbf{n}})\mathscr{D}^l_{m',m}(R) \tag{6b}$$

5. **Definition of Spherical Tensor Operators** Being motivated by the transformation relations of tensors (3) and spherical harmonics (5), we can define a tensor operator of rank k as an operator whose $2k + 1$ components transform according to the relations given below:

$$\mathscr{D}^\dagger(R)T_q^k\mathscr{D}(R) = \sum_{q'=-k}^{k} \mathscr{D}^k_{q,q'}(R)T_{q'}^k \tag{7a}$$

If we write the transpose of (7a), we obtain the following definition of a tensor operator of rank k:

$$\boxed{\mathscr{D}(R)T_q^k\mathscr{D}^\dagger(R) = \sum_{q'=-k}^{k} T_{q'}^k\mathscr{D}^k_{q',q}(R)} \tag{7b}$$

Note the similarity of (7b) with (1e). The tensor operators T_q^k transform in a similar fashion to the spherical harmonic wavefunctions Y_l^m with $k = l$ and $q = m$. Some authors prefer to use the notation T_k^q, whereas I shall use the former. A more convenient operational definition of a spherical tensor operator, analogous to the relation given in (1f) is given by the following commutation rleations that must be satisfied by a tensor operator:

$$[\hat{J}_z, T_q^k] = \hbar q T_q^k \tag{8a}$$

and

$$[\hat{J}_\pm, T_q^k] = \hbar\sqrt{k(k+1) - m(m \pm 1)}\, T_{q\pm 1}^k \tag{8b}$$

6. **Spherical Tensor Operator Reduction of a Rank 1 Tensor (Vector)** A vector $\hat{\mathbf{A}}$ has components $\{\hat{A}_x, \hat{A}_y, \hat{A}_z\}$. These components do not form an irreducible representation. However, we can find the following so-called *standard* components of $\hat{\mathbf{A}}$ that transform like the components of a rank 1 tensor, $T_1^{0,\pm 1}$:

$$T_0^1 = \hat{A}_z \tag{9a}$$

$$T_1^1 = -\frac{1}{\sqrt{2}}(\hat{A}_x + i\hat{A}_y) \tag{9b}$$

$$T_{-1}^1 = \frac{1}{\sqrt{2}}(\hat{A}_x - i\hat{A}_y) \tag{9c}$$

It can be verified that this spherical tensor operator of rank 1 satisfies the commutation relations given in (8). A simple recipe for the formation of tensor operators is by using the the general forms of the spherical tensor operators, $Y_l^m(\theta, \phi) = Y_l^m(\hat{\mathbf{n}})$ that are generally presented in standard tables. The unit vector $\hat{\mathbf{n}}$ can be replaced by an arbitrary vector $\hat{\mathbf{V}}$, with components $\{\hat{V}_x, \hat{V}_y, \hat{V}_z\}$. The individual components of the unit vector are replaced according to the relations $(\hat{\mathbf{n}})_z = z/r \mapsto \hat{V}_z$, $(\hat{\mathbf{n}})_x = x/r \mapsto \hat{V}_x$ and $(\hat{\mathbf{n}})_y = y/r \mapsto \hat{V}_z$. We consider the example of the formation of the components of a rank 1 tensor operator from the spherical harmonics $Y_1^{0,\pm 1}$:

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} cos\,\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \quad\Longrightarrow\quad T_0^1 = a\hat{V}_z \tag{10a}$$

$$Y_1^{\pm 1} = \mp\sqrt{\frac{3}{8\pi}} e^{\pm i\phi} sin\,\theta = \mp\sqrt{\frac{3}{8\pi}}\frac{x \pm iy}{r} \quad\Longrightarrow\quad T_0^{\pm 1} = \mp b\,(\hat{V}_x \pm \hat{V}_y) \tag{10b}$$

In deriving (10), we have also made use of the substitutions commonplace in the spherical coordinate system, i.e., $x = r\,cos\,\phi\,sin\,\theta$, $y = r\,sin\,\phi\,sin\,\theta$ and $z = r\,cos\,\theta$. The coefficients a and b above will be determined by the normalization of the tensor operators. We need to re-normalize because we have replaced a unit vector $\hat{\mathbf{n}}$ by an arbitrary vector $\hat{\mathbf{V}}$.

7. A straightforward but useful point to remember is that the spherical tensor operators are irreducible in standard $\mathscr{E}(\alpha, \hat{\mathbf{J}})$ basis, where α represents the eigenvalues of the operator $\hat{H}$, such that $\{\hat{H}, \hat{\mathbf{J}}^2, \hat{J}_z\}$ form a C.S.C.O.

8. **Construction of Higher Rank Tensors** We can also extend the same technique to generate tensor of any higher rank, for example, we can consider the formation of the components

of a rank 2 tensor:

$$\begin{aligned} Y_2^{\pm 2} &= \sqrt{\frac{15}{32\pi}} e^{\pm 2i\phi} sin^2\theta \\ &= \sqrt{\frac{15}{32\pi}} \frac{x^2 - y^2 \pm 2ixy}{r^2} \\ \implies & T_2^{\pm 2} = c\,(\hat{V}_x \pm i\hat{V}_y)^2 \end{aligned} \tag{10c}$$

The following theorem helps generate an arbitrary tensor T_q^k of rank k from tensors $X_{q_1}^{k_1}$ and $Z_{q_2}^{k_2}$ with ranks k_1 and k_2 respectively:

$$T_q^k = \sum_{q_1} \sum_{q_2} \langle k_1, k_2; q_1, q_2 | k_1, k_2; k, q\rangle \, X_{q_1}^{k_1} \, Z_{q_2}^{k_2} \tag{11}$$

the indices q_1 and q_2 in (11) run from to $-k_1$ to k_1 and from $-k_2$ to k_2 respectively. Moreover the inner product $\langle k_1, k_2; q_1, q_2 | k_1, k_2; k, q\rangle$ can be recognized to be the Clebsch-Gordon coefficient $C(j_1, j_2, m_1, m_2, J, M)$ with $j_1 = k_1$, $j_2 = k_2$, $m_1 = q_1$, $m_2 = q_2$, $J = k$ and $M = q$. This co-efficient will be non-zero only if $q = q_1 + q_2$. The similarity of (11) with the relationship between the direct product and total angular momentum bases must be appreciated:

$$|J, M\rangle = \sum_{m_1} \sum_{m_2} \langle j_1, j_2; m_1, m_2 | j_1, j_2; J, M\rangle \, |j_1, j_2; m_1, m_2\rangle \tag{12}$$

It follows from (11) and (12), that higher rank tensors can be obtained by combining two low rank tensors in almost the same way in which two individual angular momenta are added. Both methods are essentially the same, employing the same C-G co-efficients.

9. **Spherical Tensor Operator Basis for NMR** Different operator bases for an NMR system can be constructed. Each basis provides its own set of merits and demerits. For an n-dimensional system we need $n^2 (= 4^N)$ operators in the operator space, where N is the number of spins, if we are only considering 1/2 spins. (See the document "Superoperators in NMR" for a discussion of operators and superoperators). One useful basis is the set of spherical tensor operators. For a system of spin with a single spin I, we shall obtain basis tensor operators of ranks $0, 1, \ldots, 2I$. For a single spin 1/2 the tensor operators in the Zeeman basis are simply:

$$\begin{aligned} T_0^0 &= \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2}\mathbb{1} = \mathbb{E} \\ T_0^1 &= \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = -I_z \\ T_1^1 &= \frac{1}{2}\begin{pmatrix} 0 & -1 \\ 0 & 0 \end{pmatrix} = -I_+ \\ T_{-1}^1 &= \frac{1}{2}\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = I_- \end{aligned} \tag{13}$$

While constructing spherical tensor operators, we make note of the fact that the operators must form an orthonormal set, defined as:

$$Tr(U_i^\dagger U_j) = \delta_{ij} \tag{14}$$

Moreover the following phase convention is respected for tensor operators, in accordance with the Condon-Shortley phase convention for spherical harmonics:

$$(T_q^k)^\dagger = (-1)^q T_{-q}^k \tag{15}$$

Equipped with the conditions set forth in (14) and (15), and the commutation relations given in (8), we can derive all spherical tensor basis operators. For example, a single spin 1 will have a set of 9 basis operators, explicitly written in the Zeeman eigenbasis as:

$$\begin{aligned}
T_0^0 &= \frac{1}{3}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \frac{1}{3}\mathbb{1} \\
T_1^1 &= -\frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} = -\frac{1}{2}\, I_+ \\
T_0^1 &= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \frac{1}{\sqrt{2}}\, I_z \\
T_{-1}^1 &= \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} = \frac{1}{2}\, I_-
\end{aligned} \tag{16}$$

Likewise we also have the following rank 2 operators:

$$\begin{aligned}
T_2^2 &= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
T_1^2 &= \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{pmatrix} \\
T_0^2 &= \frac{1}{\sqrt{6}}\begin{pmatrix} 0 & 1 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
T_{-1}^2 &= -\frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} = (-1)^{-1}\,(T_1^2)^\dagger \\
T_{-2}^2 &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} = (-1)^2\,(T_2^2)^\dagger
\end{aligned} \tag{16 contd.}$$

As an additional example, let us construct the spherical operators for the two-spin case, using (11). We need 16 tensor operators. Inspection shows that they will be of ranks $k = 0$, 1, 2 and 3.

References

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