Module II, Lecture 03: Formal Theory of Rotations

Rotation operators in physics

It stands to reason that in the absence of external fields and perturbations the result of an experiment on a physical system should not depend on the choice of coordinates. In other words, it is reasonable to assume that *space itself is uniform and isotropic*. In particular, the energy of a physical system should not be changed by static coordinate translations and rotations:

$$\begin{array}{llll} |\psi\rangle \to \hat{T}|\psi\rangle & \Rightarrow & \langle\psi|\hat{T}^\dagger\hat{H}\hat{T}|\psi\rangle = \langle\psi|\hat{H}|\psi\rangle \\ |\psi\rangle \to \hat{R}|\psi\rangle & \Rightarrow & \langle\psi|\hat{R}^\dagger\hat{H}\hat{R}|\psi\rangle = \langle\psi|\hat{H}|\psi\rangle \end{array} \tag{1}$$

where $\hat{T}$ is a unitary operator that performs coordinate system translation and $\hat{R}$ is the rotation operator, which is also unitary because it preserves norms and angles. Because the relations above hold for any wavefunction, they must hold for the corresponding operators. Therefore, both $\hat{T}$ and $\hat{R}$ commute with the Hamiltonian:

$$\begin{array}{lllll} \hat{T}^\dagger\hat{H}\hat{T} = \hat{H} & \Rightarrow & \hat{T}^{-1}\hat{H}\hat{T} = \hat{H} & \Rightarrow & \left[\hat{H},\hat{T}\right] = 0 \\ \hat{R}^\dagger\hat{H}\hat{R} = \hat{H} & \Rightarrow & \hat{R}^{-1}\hat{H}\hat{R} = \hat{H} & \Rightarrow & \left[\hat{H},\hat{R}\right] = 0 \end{array} \tag{2}$$

This leads to the conservation of the corresponding observables:

$$\begin{array}{l} \frac{d}{dt}\langle\psi|\hat{T}|\psi\rangle = \ldots = i\langle\psi|\left[\hat{H},\hat{T}\right]|\psi\rangle = 0 \\ \frac{d}{dt}\langle\psi|\hat{R}|\psi\rangle = \ldots = i\langle\psi|\left[\hat{H},\hat{R}\right]|\psi\rangle = 0 \end{array} \tag{3}$$

Emmy Noether proved in 1915 that any differentiable symmetry of a physical system leads to the conservation law for the generator of that symmetry. Differentiable symmetries are the subject of Lie group theory.

We will now find out what these observables are. Let us derive the operator performing a rotation by a small angle φ in the XY plane:

$$\begin{cases} \hat{R}(\varphi): x \to x\cos\varphi - y\sin\varphi \\ \hat{R}(\varphi): y \to x\sin\varphi + y\cos\varphi \\ \hat{R}(\varphi): z \to z \end{cases} \tag{4}$$

$$\hat{R}(\varphi)|\psi(x,y,z)\rangle = |\psi(x\cos\varphi - y\sin\varphi, x\sin\varphi + y\cos\varphi, z)\rangle$$

Because the angle φ is small, we can use a Taylor expansion to second term around $\varphi = 0$:

$$\hat{R}(\varphi)|\psi\rangle = \hat{R}(0)|\psi\rangle + \left[\frac{\partial}{\partial\varphi}\hat{R}(\varphi)|\psi\rangle\right]_{\varphi=0}\varphi + O(\varphi^2) \tag{5}$$

The derivative in brackets is computed using the composite function differentiation rule:

$$\left[\frac{\partial}{\partial\varphi}\hat{R}(\varphi)|\psi\rangle\right]_{\varphi=0} = \left[\frac{\partial}{\partial\varphi}|\psi(x\cos\varphi - y\sin\varphi, x\sin\varphi + y\cos\varphi, z)\rangle\right]_{\varphi=0} = \ldots = \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)|\psi\rangle \tag{6}$$

The angular momentum operator is instantly recognizable. We therefore find the following expression for the operator performing a rotation by an infinitesimal angle $d\varphi$ around the Z axis:

$$\hat{R}(d\varphi)|\psi\rangle = \left[1 - i\hat{L}_Z d\varphi\right]|\psi\rangle \qquad \hat{L}_Z = -i\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{7}$$

Similar treatment can demonstrate that small rotations in the YZ and XZ planes are performed by $\hat{L}_{\mathrm{X}}$ and $\hat{L}_{\mathrm{Y}}$ respectively. In the case of infinitesimal translation, linear momentum operators and the associated conservation laws appear in a similar fashion. Infinitesimal time evolution treatment leads to the conservation of energy. These are very profound results – all conservation laws stem from symmetries.

We can now obtain a differential equation for the rotation operator itself and solve it. The result explains the "rotating frame" name that is commonly given to the interaction representation:

$$\hat{R}(\varphi+d\varphi)=\hat{R}(d\varphi)\hat{R}(\varphi)=\left[1-i\hat{L}_{\mathrm{Z}}d\varphi\right]\hat{R}(\varphi) \quad \Rightarrow$$
$$\frac{\hat{R}(\varphi+d\varphi)-\hat{R}(\varphi)}{d\varphi}=-i\hat{L}_{\mathrm{Z}}\hat{R}(\varphi) \quad \Rightarrow \quad \frac{d\hat{R}(\varphi)}{d\varphi}=-i\hat{L}_{\mathrm{Z}}\hat{R}(\varphi) \quad \Rightarrow \quad \hat{R}(\varphi)=e^{-i\hat{L}_{\mathrm{Z}}\varphi} \tag{8}$$

The conclusion is that all rotation operators are exponentials of the angular momentum operators. Similar calculations for the other two axes lead to the very important result that the transformation of any continuous function under a coordinate system rotation in $\mathbb{R}^3$ is given by:

$$\hat{R}(\alpha,\beta,\gamma)f(x,y,z)=e^{i\hat{L}_{\mathrm{X}}\alpha}e^{i\hat{L}_{\mathrm{Y}}\beta}e^{i\hat{L}_{\mathrm{Z}}\gamma}f(x,y,z)$$
$$\hat{L}_{\mathrm{X}}=-i\left(\hat{y}\frac{\partial}{\partial z}-\hat{z}\frac{\partial}{\partial y}\right);\quad \hat{L}_{\mathrm{Y}}=-i\left(\hat{z}\frac{\partial}{\partial x}-\hat{x}\frac{\partial}{\partial z}\right);\quad \hat{L}_{\mathrm{Z}}=-i\left(\hat{x}\frac{\partial}{\partial y}-\hat{y}\frac{\partial}{\partial x}\right) \tag{9}$$

that is, the angular momentum operators are the basis of the Lie algebra corresponding to the Lie group of rotations. Our extensive knowledge of the properties of the angular momentum operators is now presented in a different light – the commutation relations between angular momentum operators

$$[\hat{L}_{\mathrm{X}},\hat{L}_{\mathrm{Y}}]=i\hat{L}_{\mathrm{Z}} \quad [\hat{L}_{\mathrm{Y}},\hat{L}_{\mathrm{Z}}]=i\hat{L}_{\mathrm{X}} \quad [\hat{L}_{\mathrm{Z}},\hat{L}_{\mathrm{X}}]=i\hat{L}_{\mathrm{Y}} \tag{10}$$

are now identified as structure relations of a Lie algebra. Their central role in the angular momentum theory is explained by the fact that they generate the rotation group. Note that the expressions for the angular momentum operators as well as the conservation laws for the corresponding observables are consequences of just one assumption – that physical space is isotropic.

Rotation group

The rotation group, known formally as $SO(3,\mathbb{R})$, the *special orthogonal group* in three dimensions, consists of all three-dimensional rotations – continuous linear transformations of $\mathbb{R}^3$ that leave the scalar product invariant and have a determinant of +1. It is a subgroup of the orthogonal group $O(3,\mathbb{R})$, which also includes inversions. The real field is often implicitly assumed and the group is referred to simply as $SO(3)$. Elements of $SO(3)$ are related by the exponential map $a\rightarrow\exp(ia)$ to their infinitesimal generators in $\mathfrak{so}(3)$, which is a Lie algebra of imaginary Hermitian 3×3 matrices. In the mathematics literature the exponential map is defined as $a\rightarrow\exp(a)$ and $\mathfrak{so}(3)$ is the algebra of real antisymmetric 3×3 matrices. Because any three-dimensional rotation can be decomposed into a combination of three rotations around the coordinate axes, $SO(3)$ is a triparametric Lie group.

Strictly speaking, only the commutator and the linear combination with real coefficients are defined in $\mathfrak{so}(3)$, and therefore operators like $\hat{L}_{+}=\hat{L}_{\mathrm{X}}+i\hat{L}_{\mathrm{Y}}$ and $\hat{L}_{\mathrm{X}}^{2}$ do not belong there – their exponentials do not correspond to rotations. They do, however, occur in physical reality and for that reason we should make space for them. A *universal enveloping algebra* $U(\mathfrak{a})$ of a Lie algebra $\mathfrak{a}$ is (for physics purposes, mathematicians again beg to differ) the associative algebra obtained from $\mathfrak{a}$ by allowing plain products and complex coefficients. It allows us to move from a non-associative structure of the original Lie algebra to an associative structure while preserving the representations. It also often contains many physically significant operators that are missing from $\mathfrak{a}$.

The total momentum operator $\hat{L}^2 = \hat{L}_X^2 + \hat{L}_Y^2 + \hat{L}_Z^2$, other powers of momentum projection operators as well as the raising and lowering operators belong to $U\left(\mathfrak{so}(3)\right)$. It is therefore clear that we are in most cases working with $U\left(\mathfrak{so}(3)\right)$ when we build angular momentum Hamiltonians. The total momentum operator $\hat{L}^2$ is also the *Casimir operator* (the sum of squares of all generators) of $\mathfrak{so}(3)$. It commutes with all elements of the algebra, but does not belong to it. Irreducible representations of $\hat{L}^2$ are always proportional to the unit matrix.

Group theory was introduced into quantum mechanics by Eugene Wigner (above) and Hermann Weyl. Irreducible matrix representations of the rotation group are presently known as Wigner matrices.

Parameterization of rotations

It is very important to understand that when a molecule rotates or undergoes rotational diffusion in three-dimensional space, spins *do not rotate*. They get translated in space, but their projections on the lab frame axes stay the same. The anisotropic interactions, however, do rotate, because in most cases they are determined by the electronic structure and the angles that the distance vectors make with the applied magnetic field.

It is easy to verify by direct inspection that the exponentials of the following complex Hermitian matrices give the rotation matrices around the three coordinate axes:

$$\begin{aligned}
J_1 &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix} \quad \Rightarrow \quad \exp\left(iJ_1\alpha\right) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{pmatrix} \\
J_2 &= \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix} \quad \Rightarrow \quad \exp\left(iJ_2\beta\right) = \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \\
J_3 &= \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \Rightarrow \quad \exp\left(iJ_3\gamma\right) = \begin{pmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}
\end{aligned} \tag{11}$$

These matrices are therefore a basis set of a representation of $\mathfrak{so}(3)$ in $\mathfrak{gl}(3,\mathbb{R})$ and a generator set for a representation of $SO(3)$ in $GL(3,\mathbb{R})$ with the rotation angles $\{\alpha,\beta,\gamma\}$ as continuous parameters. The generators can be recovered from their exponentials by a *tangent space transformation*:

$$J_1 = -i\frac{\partial}{\partial\alpha}\left[\exp\left(iJ_1\alpha\right)\right]_{\alpha=0} \qquad J_2 = -i\frac{\partial}{\partial\beta}\left[\exp\left(iJ_2\beta\right)\right]_{\beta=0} \qquad J_3 = -i\frac{\partial}{\partial\gamma}\left[\exp\left(iJ_3\gamma\right)\right]_{\gamma=0} \tag{12}$$

An infinite number of other generator sets and therefore parameterizations exist. Importantly, the three generators should not commute, otherwise the tangent space transformation becomes ill defined. The most popular parameterizations in the current use include:

- Euler angles convention A
  1. Rotate about the Z axis through an angle α $(0\ldots 2\pi)$
  2. Rotate about the new Y axis through an angle β $(0\ldots \pi)$
  3. Rotate about the new Z axis through an angle γ $(0\ldots 2\pi)$

  This is a very inconvenient sequence because the reference frame drifts with the object. It is only useful when the frame of reference is object-centred (*e.g.* for an aeroplane).

- Euler angles convention B
  1. Rotate about the Z axis through an angle γ $(0\ldots 2\pi)$
  2. Rotate about the Y axis through an angle β $(0\ldots \pi)$
  3. Rotate about the Z axis through an angle α $(0\ldots 2\pi)$

  This sequence is more convenient and easier to visualize in the spin dynamics context because the frame of reference remains the same throughout the transformation. The angles involved are the same and the two conventions A and B accomplish identical rotations.

  Euler angles are notoriously difficult to convert into because they are not a valid parameterization of $SO(3)$, since the generators corresponding to the three Euler angles do not obey the required commutation relations – it is easy to see that they do not commute in the right way:

$$J_1 = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \qquad J_2 = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \qquad J_3 = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{13}$$

  The commutator of the first and the last generator yields zero instead of the second generator. In practice this leads to nasty singularities: $\beta = 0$ and $\beta = \pi$ points are singular, meaning that the differential equations involving Euler angles run into analytical and numerical difficulties. In general, while it is always possible to translate Euler angles into more regular conventions (angle-axis, DCM, quaternions *etc.*), it is not easy to go back.

- Angle-axis parameterization

  Any rotation may be defined in terms of a unit vector and an angle of rotation around that vector. Given a vector $\vec{n}$ of unit length and a rotation angle φ, the rotation matrix is:

$$R = \begin{bmatrix} \cos\varphi + n_X^2(1-\cos\varphi) & n_X n_Y(1-\cos\varphi) - n_Z\sin\varphi & n_X n_Z(1-\cos\varphi) + n_Y\sin\varphi \\ n_Y n_X(1-\cos\varphi) + n_Z\sin\varphi & \cos\varphi + n_Y^2(1-\cos\varphi) & n_Y n_Z(1-\cos\theta) - n_X\sin\varphi \\ n_Z n_X(1-\cos\varphi) - n_Y\sin\varphi & n_Z n_Y(1-\cos\varphi) + n_X\sin\varphi & \cos\varphi + n_Z^2(1-\cos\varphi) \end{bmatrix} \tag{14}$$

  This may be shown to be a valid parameterization of the rotation group and all singularities associated with Euler angles disappear in this approach. Angle-axis parameterization also has the benefit of being easy to visualize.

- Quaternions

  Another valid parameterization of $SO(3)$ that has no singularities and in which a rotation is defined by four parameters $\{a,b,c,d\}$, such that $a^2+b^2+c^2+d^2=1$ and

$$\begin{pmatrix} a+di & b+ci \\ -b+ci & a-di \end{pmatrix} \tag{15}$$

is a family of generators of $SU(2)$. The quaternion representation is most easily obtained from angle-axis parameters:

$$\begin{array}{ll} a = n_X \sin(\varphi/2) & b = n_Y \sin(\varphi/2) \\ c = n_Z \sin(\varphi/2) & d = \cos(\varphi/2) \end{array} \tag{16}$$

Given a unit quaternion $\{w,x,y,z\}$, the rotation matrix is obtained as:

$$R = \begin{bmatrix} 1-2y^2-2z^2 & 2xy-2zw & 2xz+2yw \\ 2xy+2zw & 1-2x^2-2z^2 & 2yz-2xw \\ 2xz-2yw & 2yz+2xw & 1-2x^2-2y^2 \end{bmatrix} \tag{17}$$

- Directional cosine matrix

  An explicit 3x3 matrix performing the rotation in question, *i.e.* $R^{-1}AR$. Usually results from the instrumental readout or from the diagonalization of a tensor specified explicitly as a 3x3 matrix. In the latter case the DCM is the matrix of eigenvectors of the tensor, and its application to any vector or matrix would rotate them into the eigenframe of the tensor.

  It should be noted that the matrix of eigenvectors of an interaction tensor, if taken straight from the diagonalization procedure, is often a reflection away from the DCM due to randomness associated with eigenvector phases and labels. For this reason it is usually inadvisable to use diagonalization as a source of the directional cosine matrix.

In simple practical calculations, the ***rotation matrix*** treatment of spin interaction tensor rotations:

$$\hat{\hat{R}}\left[\hat{\vec{L}} \cdot A \cdot \hat{\vec{S}}\right] = \hat{\vec{L}} \cdot \left(R^{-1}AR\right) \cdot \hat{\vec{S}} \tag{18}$$

does often suffice. R is defined as a superposition of rotations around the three laboratory frame axes:

$$R(\alpha,\beta,\gamma) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\gamma & -\sin\gamma \\ 0 & \sin\gamma & \cos\gamma \end{pmatrix} \tag{19}$$

In complex spin systems, however, this approach quickly becomes cumbersome. In particular, it completely blocks all attempts at performing relaxation theory treatment. We do therefore need a more regular way of describing rotations using representation theory of $SO(3)$.

Irreducible representations of the rotation group

We will now consider representations of $SO(3)$ with operators acting on the Hilbert space of all well-behaved functions on $\mathbb{R}^3$. The complete basis set of that space is infinite and therefore any faithful matrix representation of $SO(3)$ would be infinite-dimensional – our task is to reduce it. $SO(3)$ is generated by the three angular momentum operators, and so the task of finding irreducible representations amounts to finding a transformation that simultaneously partitions $\hat{L}_X$, $\hat{L}_Y$ and $\hat{L}_Z$ into the smallest possible blocks. Because all three momentum projection operators commute with the Casimir operator $\hat{L}^2$, they share the invariant subspaces with it and it would therefore suffice to determine which families of functions are invariant under the total angular momentum operator. Skipping the well-known derivation, we will simply note here that eigenfunctions of $\hat{L}^2$ are known as spherical harmonics:

$$Y_{lm}(\theta,\varphi)=(-1)^{\frac{m+|m|}{2}}\left(\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right)^{1/2}P_l^m(\cos\theta)e^{im\varphi}\qquad l\in\mathbb{N},\ m=-l,-l+1,\ldots,l$$
$$P_l^m(x)=(1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_l(x)\qquad P_l(x)=\frac{1}{2^l l!}\frac{d^l}{dx^l}\left[(x^2-1)^l\right] \tag{20}$$

Sets of spherical harmonics of a given rank span the invariant subspaces of the total angular momentum operator as well as the three projection operators:

$$\hat{L}^2 Y_{lm}=l(l+1)Y_{lm}\qquad \hat{L}_{\mathrm{Z}}Y_{lm}=mY_{lm}$$
$$\hat{L}_{\mathrm{X}}Y_{lm}=\frac{1}{2}\left[\sqrt{l(l+1)-m(m+1)}Y_{l,m+1}+\sqrt{l(l+1)-m(m-1)}Y_{l,m-1}\right] \tag{21}$$
$$\hat{L}_{\mathrm{Y}}Y_{lm}=\frac{1}{2i}\left[\sqrt{l(l+1)-m(m+1)}Y_{l,m+1}-\sqrt{l(l+1)-m(m-1)}Y_{l,m-1}\right]$$

Therefore the spherical harmonics of different ranks form basis sets for different irreducible representations of $SO(3)$ – a spherical harmonic is transformed by any rotation into a linear combination of spherical harmonics of the same rank. Matrix elements of irreducible representations:

$$\mathfrak{D}_{m,m'}^{(l)}(\alpha,\beta,\gamma)=\left\langle Y_{l,m}\middle|\hat{R}(\alpha,\beta,\gamma)\middle|Y_{l,m'}\right\rangle \tag{22}$$

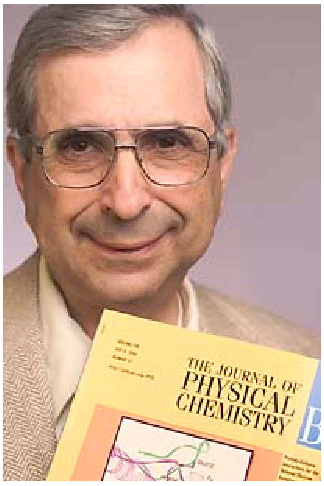
are known as *Wigner functions* and the corresponding matrices as *Wigner rotation matrices*. They will occur very often from now on, particularly in the context of spin relaxation theory.

Spherical harmonics may also be written *via* Cartesian coordinates:

l	m	$Y_{lm}(\theta,\varphi)$	$Y_{lm}(x,y,z)$	$\hat{T}_{lm}(L)$
0	0	$\sqrt{\frac{1}{4\pi}}$	$\sqrt{\frac{1}{4\pi}}$	$\hat{E}$
1	1	$-\sqrt{\frac{3}{8\pi}}e^{i\varphi}\sin\theta$	$-\sqrt{\frac{3}{8\pi}}\frac{x+iy}{r}$	$-\sqrt{\frac{1}{2}}\hat{L}_+$
1	0	$\sqrt{\frac{3}{4\pi}}\cos\theta$	$\sqrt{\frac{3}{4\pi}}\frac{z}{r}$	$\hat{L}_{\mathrm{Z}}$
1	−1	$\sqrt{\frac{3}{8\pi}}e^{-i\varphi}\sin\theta$	$\sqrt{\frac{3}{8\pi}}\frac{x-iy}{r}$	$\sqrt{\frac{1}{2}}\hat{L}_-$
2	2	$\sqrt{\frac{5}{32\pi}}e^{2i\varphi}\sin^2\theta$	$\sqrt{\frac{15}{32\pi}}\frac{(x+iy)^2}{r^2}$	$\frac{1}{2}\hat{L}_+^2$
2	1	$-\sqrt{\frac{5}{8\pi}}e^{i\varphi}\sin\theta\cos\theta$	$-\sqrt{\frac{5}{8\pi}}\frac{(x+iy)z}{r^2}$	$-\frac{1}{2}\left(\hat{L}_{\mathrm{Z}}\hat{L}_+ +\hat{L}_+\hat{L}_{\mathrm{Z}}\right)$
2	0	$\sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta-1\right)$	$\sqrt{\frac{5}{16\pi}}\frac{2z^2-x^2-y^2}{r^2}$	$\sqrt{\frac{2}{3}}\left(\hat{L}_{\mathrm{Z}}^2-\frac{1}{4}\left(\hat{L}_+\hat{L}_- +\hat{L}_-\hat{L}_+\right)\right)$
2	−1	$\sqrt{\frac{5}{8\pi}}e^{-i\varphi}\sin\theta\cos\theta$	$\sqrt{\frac{15}{8\pi}}\frac{(x-iy)z}{r^2}$	$\frac{1}{2}\left(\hat{L}_{\mathrm{Z}}\hat{L}_- +\hat{L}_-\hat{L}_{\mathrm{Z}}\right)$
2	−2	$\sqrt{\frac{5}{32\pi}}e^{-2i\varphi}\sin^2\theta$	$\sqrt{\frac{15}{32\pi}}\frac{(x-iy)^2}{r^2}$	$\frac{1}{2}\hat{L}_-^2$

The operators obtained by replacing the Cartesian coordinates with Cartesian spin operators are known as *irreducible spherical tensor operators* (IST). The table above gives single-spin irreducible spherical tensor operators. Their two-spin analogues:

$$\begin{aligned} \hat{T}^{(2)}_{\pm 2}(L,S) &= +\frac{1}{2}\hat{L}_{\pm}\hat{S}_{\pm} \\ \hat{T}^{(2)}_{\pm 1}(L,S) &= \mp\frac{1}{2}\left(\hat{L}_{Z}\hat{S}_{\pm}+\hat{L}_{\pm}\hat{S}_{Z}\right) \\ \hat{T}^{(2)}_{0}(L,S) &= +\sqrt{\frac{2}{3}}\left(\hat{L}_{Z}\hat{S}_{Z}-\frac{1}{4}\left(\hat{L}_{+}\hat{S}_{-}+\hat{L}_{-}\hat{S}_{+}\right)\right) \end{aligned} \qquad (23)$$



Spherical tensors were introduced into NMR by Jack Freed (above) and Bryan Sanctuary.

will be useful in setting up coupling tensor rotations. For linear interactions (such as Zeeman interaction) the $\hat{\vec{L}}$ operator vector is replaced by the magnetic field vector. For quadratic couplings both sets of operators refer to the same spin. Because of their common group-theoretical heritage, spherical harmonics and irreducible spherical tensors have common rotation properties:

$$\hat{\hat{R}}(\alpha,\beta,\gamma)\hat{T}^{(l)}_{m} = \sum_{m'=-l}^{l}\hat{T}^{(l)}_{m'}\mathfrak{D}^{(l)}_{m',m}(\alpha,\beta,\gamma) \qquad \hat{\hat{R}}(\alpha,\beta,\gamma)Y_{lm} = \sum_{m'=-l}^{l}Y_{lm'}\mathfrak{D}^{(l)}_{m',m}(\alpha,\beta,\gamma) \qquad (24)$$

The second-rank Wigner matrix, which occurs particularly often, is given in the table below.

	$d^{(2)}_{m,2}$	$d^{(2)}_{m,1}$	$d^{(2)}_{m,0}$	$d^{(2)}_{m,-1}$	$d^{(2)}_{m,-2}$
$d^{(2)}_{2,n}$	$\frac{(1+\cos\beta)^2}{4}$	$-\frac{(1+\cos\beta)\sin\beta}{2}$	$\sqrt{\frac{3}{8}}\sin^2\beta$	$-\frac{(1-\cos\beta)\sin\beta}{2}$	$\frac{(1-\cos\beta)^2}{4}$
$d^{(2)}_{1,n}$	$\frac{(1+\cos\beta)\sin\beta}{2}$	$\frac{\cos\beta-1}{2}+\cos^2\beta$	$-\sqrt{\frac{3}{8}}\sin 2\beta$	$\frac{\cos\beta+1}{2}-\cos^2\beta$	$-\frac{(1-\cos\beta)\sin\beta}{2}$
$d^{(2)}_{0,n}$	$\sqrt{\frac{3}{8}}\sin^2\beta$	$\sqrt{\frac{3}{8}}\sin 2\beta$	$\frac{3\cos^2\beta-1}{2}$	$-\sqrt{\frac{3}{8}}\sin 2\beta$	$\sqrt{\frac{3}{8}}\sin^2\beta$
$d^{(2)}_{-1,n}$	$\frac{(1-\cos\beta)\sin\beta}{2}$	$\frac{\cos\beta+1}{2}-\cos^2\beta$	$\sqrt{\frac{3}{8}}\sin 2\beta$	$\frac{\cos\beta-1}{2}+\cos^2\beta$	$-\frac{(1+\cos\beta)\sin\beta}{2}$
$d^{(2)}_{-2,n}$	$\frac{(1-\cos\beta)^2}{4}$	$\frac{(1-\cos\beta)\sin\beta}{2}$	$\sqrt{\frac{3}{8}}\sin^2\beta$	$\frac{(1+\cos\beta)\sin\beta}{2}$	$\frac{(1+\cos\beta)^2}{4}$

The full Wigner functions are defined in terms of the reduced functions given above as:

$$\mathfrak{D}^{(2)}_{m,n} = e^{-im\alpha}d^{(2)}_{m,n}(\beta)e^{-in\gamma} \qquad (25)$$

Because all spin interactions are at most second-rank, the following expansion in terms irreducible spherical tensor operators holds in all cases (extended as noted above to linear and quadratic cases):

$$\hat{\vec{L}}\cdot\mathbf{A}\cdot\hat{\vec{S}} = \sum_{\substack{k,n=\\ \{X,Y,Z\}}} a_{kn}\hat{L}_k\hat{S}_n = a^{(0)}_0\hat{T}^{(0)}_0 + \sum_{m=-1}^{1}a^{(1)}_m\hat{T}^{(1)}_m + \sum_{m=-2}^{2}a^{(2)}_m\hat{T}^{(2)}_m \qquad (26)$$

The first rank terms will henceforth be ignored – they are suspected to exist, but have never been observed because they are very small. The following table gives the coefficients required for the transformation between the standard 3x3 matrix representation and irreducible spherical tensors:

(l,m)	$a_m^{(l)}$	$\hat{T}_m^{(l)}$
$(0,0)$	$-\frac{1}{\sqrt{3}}\left(a_{XX}+a_{YY}+a_{ZZ}\right)$	$-\frac{1}{\sqrt{3}}\hat{\vec{L}}\cdot\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\cdot\hat{\vec{S}}$
$(1,1)$	$-\frac{1}{2}\left(a_{ZX}-a_{XZ}-i\left(a_{ZY}-a_{YZ}\right)\right)$	$-\frac{1}{2}\hat{\vec{L}}\cdot\begin{pmatrix}0&0&-1\\0&0&-i\\1&i&0\end{pmatrix}\cdot\hat{\vec{S}}$
$(1,0)$	$-\frac{i}{\sqrt{2}}\left(a_{XY}-a_{YX}\right)$	$-\frac{1}{\sqrt{2}}\hat{\vec{L}}\cdot\begin{pmatrix}0&-i&0\\i&0&0\\0&0&0\end{pmatrix}\cdot\hat{\vec{S}}$
$(1,-1)$	$-\frac{1}{2}\left(a_{ZX}-a_{XZ}+i\left(a_{ZY}-a_{YZ}\right)\right)$	$-\frac{1}{2}\hat{\vec{L}}\cdot\begin{pmatrix}0&0&-1\\0&0&i\\1&-i&0\end{pmatrix}\cdot\hat{\vec{S}}$
$(2,2)$	$+\frac{1}{2}\left(a_{XX}-a_{YY}-i\left(a_{XY}+a_{YX}\right)\right)$	$+\frac{1}{2}\hat{\vec{L}}\cdot\begin{pmatrix}1&i&0\\i&-1&0\\0&0&0\end{pmatrix}\cdot\hat{\vec{S}}$
$(2,1)$	$-\frac{1}{2}\left(a_{XZ}+a_{ZX}-i\left(a_{YZ}+a_{ZY}\right)\right)$	$-\frac{1}{2}\hat{\vec{L}}\cdot\begin{pmatrix}0&0&1\\0&0&i\\1&i&0\end{pmatrix}\cdot\hat{\vec{S}}$
$(2,0)$	$+\frac{1}{\sqrt{6}}\left(2a_{ZZ}-\left(a_{XX}+a_{YY}\right)\right)$	$+\frac{1}{\sqrt{6}}\hat{\vec{L}}\cdot\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&2\end{pmatrix}\cdot\hat{\vec{S}}$
$(2,-1)$	$+\frac{1}{2}\left(a_{XZ}+a_{ZX}+i\left(a_{YZ}+a_{ZY}\right)\right)$	$+\frac{1}{2}\hat{\vec{L}}\cdot\begin{pmatrix}0&0&1\\0&0&-i\\1&-i&0\end{pmatrix}\cdot\hat{\vec{S}}$
$(2,-2)$	$+\frac{1}{2}\left(a_{XX}-a_{YY}+i\left(a_{XY}+a_{YX}\right)\right)$	$+\frac{1}{2}\hat{\vec{L}}\cdot\begin{pmatrix}1&-i&0\\-i&-1&0\\0&0&0\end{pmatrix}\cdot\hat{\vec{S}}$

The ISTs in this table have been written out explicitly in matrix form to expose their symmetry. Coefficients and signs are determined by the requirement to preserve the rotation and commutation properties of the spherical tensor operators. If the interaction tensor is diagonal in the current reference frame, the transformation becomes particularly simple:

$$\begin{gathered}\hat{\vec{L}}\cdot\mathbf{A}\cdot\hat{\vec{S}}=a_{XX}\hat{L}_X\hat{S}_X+a_{YY}\hat{L}_Y\hat{S}_Y+a_{ZZ}\hat{L}_Z\hat{S}_Z=\\-\frac{a_{XX}+a_{YY}+a_{ZZ}}{\sqrt{3}}\hat{T}_0^{(0)}+\frac{2a_{ZZ}-\left(a_{XX}+a_{YY}\right)}{\sqrt{6}}\hat{T}_0^{(2)}+\frac{a_{XX}-a_{YY}}{2}\left[\hat{T}_{-2}^{(2)}+\hat{T}_2^{(2)}\right]\end{gathered} \tag{27}$$

Setting up rotations for complex spin systems

In rigid molecules, the simple rotational transformation rule derived above for the irreducible spherical tensors is inherited by the full spin system Hamiltonian:

$$\hat{H}(\alpha,\beta,\gamma)=\hat{H}_{\text{iso}}+\sum_{k,m=-2}^{2}\mathfrak{D}_{km}^{(2)}(\alpha,\beta,\gamma)\hat{Q}_{km} \tag{28}$$

where $\hat{Q}_{km}$ (called *rotational basis operators*) are linear combinations of irreducible spherical tensors corresponding to the interactions within the spin system. No matter how large and complicated the spin system, there are always just 25 rotational basis operators. To derive the expressions for $\hat{Q}_{km}$, we would note that for a multi-spin system in a rigid molecule, rotated by $\hat{\hat{R}}$, we have:

$$\begin{gathered}\hat{H}=\hat{H}_{\text{iso}}+\hat{\hat{R}}\sum_{L}\sum_{m=-2}^{2}a_m^{(2)}(L)\hat{T}_m^{(2)}(L)+\\+\hat{\hat{R}}\sum_{L,S}\sum_{m=-2}^{2}a_m^{(2)}(L,S)\hat{T}_m^{(2)}(L,S)+\hat{\hat{R}}\sum_{S}\sum_{m=-2}^{2}a_m^{(2)}(S,S)\hat{T}_m^{(2)}(S,S)\end{gathered} \tag{29}$$

where $\hat{H}_{\text{iso}}$ is the isotropic part of the Hamiltonian and the three terms in brackets correspond to linear, bilinear and quadratic couplings within the spin system. After we apply the rotation $\hat{\hat{R}}$, we get:

$$\begin{gathered}\hat{H}=\hat{H}_{\text{iso}}+\sum_{L}\sum_{k,m=-2}^{2}a_m^{(2)}(L)\hat{T}_k^{(2)}(L)\mathfrak{D}_{km}^{(2)}+\\+\sum_{L,S}\sum_{k,m=-2}^{2}a_m^{(2)}(L,S)\hat{T}_k^{(2)}(L,S)\mathfrak{D}_{km}^{(2)}+\sum_{S}\sum_{k,m=-2}^{2}a_m^{(2)}(S,S)\hat{T}_k^{(2)}(S,S)\mathfrak{D}_{km}^{(2)}\end{gathered} \tag{30}$$

Reordering the terms and taking Wigner functions out of the brackets yields:

$$\hat{H}=\hat{H}_{\text{iso}}+\sum_{k,m=-2}^{2}\mathfrak{D}_{km}^{(2)}\left[\sum_{L}a_m^{(2)}(L)\hat{T}_k^{(2)}(L)+\sum_{L,S}a_m^{(2)}(L,S)\hat{T}_k^{(2)}(L,S)+\sum_{S}a_m^{(2)}(S,S)\hat{T}_k^{(2)}(S,S)\right] \tag{31}$$

We can now define the terms in brackets as the rotational basis and conclude that all information about the amplitudes and internal orientations of all interactions has been packaged into just 25 operators:

$$\hat{Q}_{km}=\sum_{L}a_m^{(2)}(L)\hat{T}_k^{(2)}(L)+\sum_{L,S}a_m^{(2)}(L,S)\hat{T}_k^{(2)}(L,S)+\sum_{S}a_m^{(2)}(S,S)\hat{T}_k^{(2)}(S,S) \tag{32}$$

All required expressions for ISTs, spherical tensor coefficients and Wigner functions are tabulated above.

Setting up spin system rotations – a summary:

1. Get all interactions into 3x3 Cartesian matrix form.
2. Translate the interaction matrices into spherical tensor parameters $a_m^{(l)}$ using the relations given in the table above. Ignore the first-rank components.
3. Compute the isotropic Hamiltonian $\hat{H}_{\text{iso}}$ and the 25 rotational basis operators $\hat{Q}_{km}$. If at all possible, avoid using Euler angles to parameterize rotations.
4. The spin system Hamiltonian at any orientation relative to the frame of reference in which the original tensors were specified is given by Equation (28).

This is in practice the most consistent and straightforward way of setting up rotations in complicated spin systems. In particular, it avoids re-creating all coupling operators at every orientation when powder patterns are computed and also facilitates relaxation theory treatment.