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## 1 Coordinate Transformations

### 1.1 Coordinate Systems

Principal axes systems (PAS) are defined for various tensors and axes systems fixed to different objects:

name	axes system
S0	at site 1 (ONE). Equivalent sites related by symmetry transformations of the crystal are not counted.
Sc	single crystal
Ss	absorber/sample/scatterer
Sl	laboratory
Sg	polarized $\gamma$ -quanta
$Se_i$	PAS of the electric field gradient tensor (EFG at site i)
$Sx2_i$	PAS of the mean square displacement tensor (MSD at site i)
$Sx2_c$	PAS of the mean square displacement tensor (MSD of the crystal)
$Sd_i$	PAS of the zero field splitting tensor of the spin Hamiltonian at site i
SA	PAS of the A-tensor of the spin Hamiltonian
SG	PAS of the g-tensor of the spin Hamiltonian

## 1.2 Euler angles

Two coordinate systems  $Sa$  and  $Sb$  with unit vectors  $\mathbf{e}_i^a$  and  $\mathbf{e}_i^b$  ( $i=x,y,z$ ), respectively, are related to each other by a rotation matrix  $R^{ab}$ , such that

$$\mathbf{e}_i^b = \sum_k \mathbf{e}_k^a R_{ki}^{ab}(\phi^{ab}, \theta^{ab}, \psi^{ab}) \quad (1)$$

with the short notation

$$\mathbf{e}^b = \mathbf{e}^a R^{ab}. \quad (2)$$

The Cartesian vectors ( $i=x,y,z$ ) are expressed by spherical vectors ( $m = \pm 1, 0$ ) [1]:

$$\begin{aligned} \mathbf{e}_{+1}^a &= -\frac{1}{\sqrt{2}}(\mathbf{e}_x^a + i\mathbf{e}_y^a) \\ \mathbf{e}_0^a &= \mathbf{e}_z^a \\ \mathbf{e}_{-1}^a &= \frac{1}{\sqrt{2}}(\mathbf{e}_x^a - i\mathbf{e}_y^a) \end{aligned} \quad (3)$$

The spherical rotation matrix

$$D_{mn}^L(\phi, \theta, \psi) = e^{-im\phi} d_{mn}^L(\theta) e^{-in\psi} \quad (4)$$

transforms spherical unit vectors with  $L=1$

$$\mathbf{e}_n^b = \sum_m \mathbf{e}_m^a D_{mn}^1(\phi^{ab}, \theta^{ab}, \psi^{ab}) \quad (5)$$

Inserting the spherical vectors of eq.3 and the matrix elements of  $d^1$  according to the definition in [1]:

$$d^1 = \begin{pmatrix} +1 & \begin{pmatrix} \cos^2 \frac{\theta}{2} & -\frac{1}{\sqrt{2}} \sin \theta & \sin^2 \frac{\theta}{2} \\ +\frac{1}{\sqrt{2}} \sin \theta & \cos \theta & -\frac{1}{\sqrt{2}} \sin \theta \\ \sin^2 \frac{\theta}{2} & +\frac{1}{\sqrt{2}} \sin \theta & \cos^2 \frac{\theta}{2} \end{pmatrix} \\ 0 \\ -1 \end{pmatrix}$$

the following Cartesian vector equations are obtained:

$$\phi = \phi^{ab} \quad \theta = \theta^{ab} \quad \psi = \psi^{ab} \quad (6)$$

$$\begin{aligned} \mathbf{e}_x^b &= + [\cos^2(\theta/2) \cos(\phi + \psi) - \sin^2(\theta/2) \cos(\phi - \psi)] \mathbf{e}_x^a \\ &\quad + [\cos^2(\theta/2) \sin(\phi + \psi) - \sin^2(\theta/2) \sin(\phi - \psi)] \mathbf{e}_y^a - \sin \theta \cos \psi \mathbf{e}_z^a \\ \mathbf{e}_y^b &= - [\cos^2(\theta/2) \sin(\phi + \psi) + \sin^2(\theta/2) \sin(\phi - \psi)] \mathbf{e}_x^a \\ &\quad + [\cos^2(\theta/2) \cos(\phi + \psi) + \sin^2(\theta/2) \cos(\phi - \psi)] \mathbf{e}_y^a + \sin \theta \sin \psi \mathbf{e}_z^a \\ \mathbf{e}_z^b &= + \sin \theta \cos \phi \mathbf{e}_x^a + \sin \theta \sin \phi \mathbf{e}_y^a + \cos \theta \mathbf{e}_z^a \end{aligned}$$

The polar angle of the z-axis  $\mathbf{e}_z^a$  of system  $Sa$  with respect to system  $Sb$  and vice versa  $\mathbf{e}_z^b$  with respect to  $Sa$  are read from eq. 6

$$\mathbf{e}_z^b(\theta^{ab}, \phi^{ab}) \quad \mathbf{e}_z^a(\theta^{ab}, \pi - \psi^{ab}) \quad (7)$$

The transformation of eq.5 is a rotation of the unit vectors  $\mathbf{e}_m^a$  to new vectors  $\mathbf{e}_m^b$  which are expressed in the system  $Sa$ . Considering the rotation as an operation  $D$  acting on the vector  $\mathbf{e}_m^a$  and applying the property  $\mathbf{e}_{n'}^{a*} \mathbf{e}_n^a = \delta_{n'n}$  for orthonormal vectors

$$\begin{aligned} D\mathbf{e}_m^a &= \mathbf{e}_m^b \\ &= \sum_{n'} \mathbf{e}_{n'}^a D_{n'm} \\ \mathbf{e}_n^{a*} D\mathbf{e}_m^a &= D_{nm} \end{aligned} \quad (8)$$

the familiar definition of the elements of the rotation matrix is obtained. An arbitrary vector  $\mathbf{q}$  in space is rotated by  $D$  to a vector  $\mathbf{q}'$ . The matrix  $d^1$  has been defined to evaluate the vector components of the rotated vector  $\mathbf{q}' = D\mathbf{q}$ . The definition of [2] is opposite in the sense that the coordinate system is rotated and the vector (the field) is fixed in space, which leads to an inverse transformation and that way another meaning of the Euler angles.

The vector  $\mathbf{q}$  with respect to  $Sa$  has Cartesian components  $q_i^a$

$$\mathbf{q} = \sum_i q_i^a \mathbf{e}_i^a \quad (9)$$

which are expressed by the spherical components  $q_m, m = \pm, 0$

$$\begin{aligned} q_{+1}^a &= -\frac{1}{\sqrt{2}}(q_x^a + iq_y^a) \\ q_0^a &= q_z^a \\ q_{-1}^a &= \frac{1}{\sqrt{2}}(q_x^a - iq_y^a) \end{aligned} \quad (10)$$

so that eq. 9 is replaced by

$$\mathbf{q} = \sum_m q_m^{a*} \mathbf{e}_m^a \quad (11)$$

The rotation of  $\mathbf{q}$  reads step by step:

$$D\mathbf{q} = D \sum_m q_m^{a*} \mathbf{e}_m^a \quad (12)$$

$$\begin{aligned}
&= \sum_m q_m^{a*} D \mathbf{e}_m^a \\
&= \sum_m q_m^{a*} \sum_n \mathbf{e}_n^a D_{nm} \\
&= \sum_n \left[ \sum_m D_{nm} q_m^{a*} \right] \mathbf{e}_n^a \\
&= \sum_n q_n'^{a*} \mathbf{e}_n^a
\end{aligned}$$

The last equation defines the components  $q_n'^a$  of the rotated vector  $\mathbf{q}'$ .

$$q_n'^a = \sum_m q_m^a D_{mn}^\dagger \quad (13)$$

This equation 13 is used if an object, a tensor of any rank, is rotated in space. The transformation is given by the inverse rotation  $D^\dagger = D^{-1}$ .

The other task is to express tensor components  $q_m^a$  with respect to a coordinate system  $Sb$ , which axes  $\mathbf{e}_m^b$  are known with respect to  $Sa$  by eq.5. By the following equations this transformation is defined:

$$\mathbf{q} = \sum_m q_m^{a*} \mathbf{e}_m^a = \sum_n q_n^{b*} \mathbf{e}_n^b \quad (14)$$

The components  $q_m^a$  and  $q_n^b$  of a vector  $\mathbf{q}$  are expressed with respect to both systems.

Inserting  $\mathbf{e}_n^b$  from eq. 5 one obtains step by step

$$\begin{aligned}
\sum_m q_m^{a*} \mathbf{e}_m^a &= \sum_n q_n^{b*} \sum_m \mathbf{e}_m^a D(\Omega^{ab})_{mn} \\
q_m^{a*} &= \sum_n q_n^{b*} D(\Omega^{ab})_{mn} \\
q_m^a &= \sum_n q_n^b D(\Omega^{ab})_{nm}^\dagger
\end{aligned} \quad (15)$$

The same way  $q_m^b$  can be written by the  $q_m^a$ :

$$\begin{aligned}
\sum_m q_m^a D(\Omega^{ab})_{mn'} &= \sum_n q_n^b \delta_{nn'} \\
\sum_m q_m^a D(\Omega^{ab})_{mn'} &= q_{n'}^b
\end{aligned} \quad (16)$$

The invers transformation of  $D(\Omega^{ab})^\dagger$  (e.g. read from Eq. 4)

$$D(\phi^{ab}, \theta^{ab}, \psi^{ab})^\dagger = D(-\psi^{ab}, -\theta^{ab}, -\phi^{ab}) \quad (17)$$

shall be written as

$$\begin{aligned} D(\Omega^{ab})^\dagger &= D(\Omega^{ba}) \\ \Omega^{ba} &= (-\psi^{ab}, -\theta^{ab}, -\phi^{ab}) \end{aligned} \quad (18)$$

With this notation the results from above are summerized as follows:

$$\begin{aligned} \mathbf{e}^b &= \mathbf{e}^a D^1(\Omega^{ab}) \quad \text{with} \quad \mathbf{e}_z^b(\theta^{ab}, \phi^{ab}) \\ \mathbf{e}^a &= \mathbf{e}^b D^1(\Omega^{ba}) \quad \text{with} \quad \mathbf{e}_z^a(-\theta^{ab}, -\psi^{ab}) = \mathbf{e}_z^a(\theta^{ab}, \pi - \psi^{ab}) \end{aligned} \quad (19)$$

This way the polar angle of the unit vector  $\mathbf{e}_z^a$  of Eq. 7 are obtained back. For the components of tensors of any rank L the set of equations are according to Eqs. 15,16:

$$T_n^L(b) = \sum_m T_m^L(a) D_{mn}^L(\Omega^{ab}) \quad (20)$$

an the invers transformation

$$T_n^L(a) = \sum_m T_m^L(b) D_{mn}^L(\Omega^{ba}) \quad (21)$$

For the rotated tensor components  $T'$  (Eq. 13)

$$T_n'^L(a) = \sum_m T_m^L(a) D_{mn}^{L\dagger}(\Omega^{ab}) \quad (22)$$

the Euler angles are defined by  $\mathbf{e}^b$  of Eq. 19.

## 2 The tensor $V_M^L$

The amplitudes for electric and magnetic multi-pole transition  $a_p^{\alpha\beta}(e, m)$  with polarization  $p = \pm 1$  to the excited state  $|e_\alpha\rangle$  from the ground state  $|g_\beta\rangle$  are written as [3]:

$$\begin{aligned} a_p^{\alpha\beta}(e) &= 2\pi \left( \frac{\hbar c}{V k} \right) \sqrt{2I_e + 1} E_L i^{L+1} \sum_M V_{LM}^{\alpha\beta} D_{Mp}^L \\ a_p^{\alpha\beta}(m) &= 2\pi \left( \frac{\hbar c}{V k} \right) \sqrt{2I_e + 1} M_L i^L p \sum_M V_{LM}^{\alpha\beta} D_{Mp}^L \\ V_{LM}^{\alpha\beta} &= \left( \frac{2L + 1}{2I_e + 1} \right)^{1/2} \sum_{m_e m_g} e_{\alpha m_e}^* g_{\beta m_g} C(I_g L I_e, m_g M m_e) \end{aligned} \quad (23)$$

with the reduced matrix elements [4, 5]

$$\begin{aligned} E_L &= \langle I_e || \frac{1}{c} \sum_i \mathbf{j}(\mathbf{r}_i) \mathbf{A}_L(e) || I_g \rangle \\ M_L &= \langle I_e || \frac{1}{c} \sum_i \mathbf{j}(\mathbf{r}_i) \mathbf{A}_L(m) || I_g \rangle \end{aligned} \quad (24)$$

and the eigenstates of the ground state  $|g_\beta\rangle$  and excited state  $|e_\alpha\rangle$ :

$$\begin{aligned} |e_\alpha\rangle &= \sum_{m_e} e_{\alpha m_e} |I_e m_e\rangle \\ |g_\beta\rangle &= \sum_{m_g} g_{\beta m_g} |I_g m_g\rangle \end{aligned} \quad (25)$$

The reduced matrix elements are differently defined in the literature. The definition used here is that of Wigner [5] and Rose [4]. Edmonds [2] define reduced elements

$$\langle j' || T_{kq} || j \rangle_{Edmonds} = (-1)^{2k} \sqrt{2j'+1} \langle j' || T_{kq} || j \rangle_{Wigner} \quad (26)$$

Here the factor  $(-1)^{2k}$  plays no role since  $k=L$  is an integer.

If  $V_{LM}(a)$  is known in the system  $Sa$  the components of the rotated multipole (of an equivalent site) are according to Eq. 23

$$V_{LN}^{\alpha\beta}(b) = \sum_M V_{LM}^{\alpha\beta}(a) D_{MN}^L(\phi^{ab}, \theta^{ab}, \psi^{ab}) \quad (27)$$

and the components of the rotated multipole (of an equivalent site):

$$\begin{aligned} V_{LN}^{\alpha\beta}(a) &= \sum_M V_{LM}^{\alpha\beta}(a) D_{MN}^{L\dagger}(\phi^{ab}, \theta^{ab}, \psi^{ab}) \\ &= \sum_M V_{LM}^{\alpha\beta}(a) D_{MN}^L(-\psi^{ab}, -\theta^{ab}, -\phi^{ab}) \end{aligned} \quad (28)$$

A compact equation for intensities of nuclear transitions is obtained introducing the intensity matrices [3]

$$I_{MN}^L = V_{LM}^* V_{LN} \quad J_{MN}^{LL'} = V_{LM}^* V_{L'N} \quad (29)$$

which are transformed as

$$I^L(b) = D^{L\dagger} I^L(a) D^L \quad J^{LL'}(b) = D^{L\dagger} J^{LL'}(a) D^{L'} \quad (30)$$

The calculation of intensities of nuclear transitions is written in terms of the  $I^L$  and  $J^{LL'}$  [3], which leads to compact equations with clear transformation properties for the 2x2 matrix  $r_{pq}^{\alpha\beta}$  ( $p, q = \pm 1$ ) entering the index of refraction for nuclear scattering .

$$r_{pq}^{\alpha\beta} = \frac{1}{(1 + \delta^2)} \cdot \left[ (I^1)^{\alpha\beta}_{pq} + p \cdot q \delta^2 (I^2)^{\alpha\beta}_{pq} - \delta (p(J^{21})^{\alpha\beta}_{pq} + q(J^{12})^{\alpha\beta}_{pq}) \right] \quad (31)$$

The real number  $\delta = M_1/E_2$  is the ratio of the reduced matrix elements of Eq. 24. The powder average of  $r_{pq}^{\alpha\beta}(\phi, \theta, \psi)$  of a transition is given by the trace of the intensity matrices

$$\overline{r_{pp}^{\alpha\beta}} = \frac{1}{(1 + \delta^2)} \cdot [Tr(I^{1\alpha\beta}) + \delta^2 Tr(I^{2\alpha\beta})], \quad p = \pm 1 \quad (32)$$

The code for the calculation of  $r_{pq}^{\alpha\beta}$  offers the use of time inversion symmetry by which the relation of symmetry equivalent sites with an internal magnetic field is effectively calculated. The time inversion transformation  $\Theta$  applied to  $V_{LM}$  is derived from the transformation properties of the eigenstates (eq. 25) as defined by

$$\begin{aligned} \Theta|\alpha j m\rangle &= (-1)^{j-m} |\alpha j - m\rangle \quad [1] \\ \Theta|\alpha j m\rangle &= (-1)^{j+m} |\alpha j - m\rangle \quad [2] \end{aligned} \quad (33)$$

For both conventions eq. 33 is also satisfied for the vector addition state

$$|JM\rangle = \sum_{m_1 m_2} |j_1 m_1\rangle |j_2 m_2\rangle C(j_1 j_2 J, m_1 m_2 M) \quad (34)$$

Note that  $(-1)^{j+m}$  is not equal  $(-1)^{j-m}$  for have integer m.

Applying  $\Theta$  to the eigenstates gives

$$\begin{aligned} \Theta|e_\alpha\rangle &= \sum_{m_e} \Theta e_{\alpha m_e} |I_e m_e\rangle \\ &= \sum_{m_e} e_{\alpha m_e}^* \Theta |I_e m_e\rangle \\ &= \sum_{m_e} e_{\alpha m_e}^* (-1)^{I_e - m_e} |I_e - m_e\rangle \\ &= \sum_{m_e} e_{\alpha - m_e}^* (-1)^{I_e + m_e} |I_e m_e\rangle \end{aligned} \quad (35)$$

Inserting the time inverted eigen states the  $\Theta V_{LM}^{\alpha\beta}$  are deduced step by step:

$$\begin{aligned}
\Theta V_{LM}^{\alpha\beta} &\sim \sum_{m_e m_g} (-1)^{I_e+m_e} e_{\alpha-m_e} (-1)^{I_g+m_g} g_{\beta-m_g}^* C(I_g L I_e, m_g M m_e) \\
&\sim (-1)^{I_e+M} \sum_{m_e m_g} (-1)^{I_g+2m_g} e_{\alpha-m_e} g_{\beta-m_g}^* C(I_g L I_e, m_g M m_e) \\
\Theta V_{L-M}^{\alpha\beta} &\sim (-1)^{L-M} \sum_{m_e m_g} (-1)^{2(I_g-m_g)} e_{\alpha m_e} g_{\beta m_g}^* C(I_g L I_e, m_g M m_e) \\
&= (-1)^{L-M} V_{LM}^* \\
\Theta V_{LM}^{\alpha\beta} &= (-1)^{L+M} V_{L-M}^* \quad \text{Brink and Satchler} \\
&= (-1)^{L-M} V_{L-M}^* \quad \text{Edmonds}
\end{aligned} \tag{36}$$

Since L is an integer the two conventions give the same result.

### 3 Spherical and cartesian 2. rank tensors

Several 2. rank tensors are preferably expressed as cartesian tensors, as the electric field graient tensor  $V_{\alpha\beta}$  with  $\alpha\beta = xx, xy, xz, \dots, zz$ , the g-tensor, A-tensor, and others defined for ligand field theories, phonons in crystals etc. In order to use the Wigner rotation matrices the tensors have to be expressed in spherical coordinates. This task has been solved by A.J. Stone [6]. Some results for second rank tensors are collected here. The transformation is carraied out by Clebsch-Gordon like coefficients.

$$\begin{aligned}
T_{\alpha\beta} &= \sum_{\eta j m} T_{\eta j; m} \langle \eta j; m | \alpha \beta \rangle \\
T_{\eta j; m} &= \sum_{\alpha\beta} T_{\alpha\beta} \langle \alpha \beta | \eta j; m \rangle \\
\langle \alpha \beta | \eta j; m \rangle^* &= \langle \eta j; m | \alpha \beta \rangle
\end{aligned} \tag{37}$$

For vectors (irreducible tensors of 1. rank) the standard transformation reads:

$$A_{1; m} = \sum_{\alpha} A_{\alpha} \langle \alpha | 1; m \rangle \tag{38}$$



where the unitary matrix of coefficients  $\langle \alpha | 1; m \rangle$  is

$$U = \begin{matrix} & |1; 1\rangle & |1; 0\rangle & |1; -1\rangle \\ \begin{matrix} \langle x| \\ \langle y| \\ \langle z| \end{matrix} & \begin{pmatrix} -i\kappa\frac{1}{\sqrt{2}} & 0 & i\kappa\frac{1}{\sqrt{2}} \\ \kappa\frac{1}{\sqrt{2}} & 0 & \kappa\frac{1}{\sqrt{2}} \\ 0 & i\kappa & 0 \end{pmatrix} \end{matrix} \quad (39)$$

Condon and Shortley's phase convention  $\kappa = -i$  is used (taken over by [1, 2]).

The spherical vectors are coupled together with the Clebsch-Gordan coefficients. For a second rank tensor the coupling coefficients  $\langle \alpha\beta | 1j; m \rangle$  are derived step by step:

$$\begin{aligned} (AB)_{1j;m} &= \sum_{m',m''} A_{1;m'} B_{1;m''} \langle 11m'm'' | jm \rangle \\ &= \sum_{m',m''} \sum_{\alpha} A_{\alpha} \langle \alpha | 1; m' \rangle \sum_{\beta} A_{\beta} \langle \beta | 1; m'' \rangle \langle 11m'm'' | jm \rangle \\ &= \sum_{\alpha\beta} A_{\alpha} B_{\beta} \langle \alpha\beta | 1j; m \rangle \\ \langle \alpha\beta | 1j; m \rangle &= \sum_{m',m''} \langle \alpha | 1; m' \rangle \langle \beta | 1; m'' \rangle \langle 11m'm'' | jm \rangle \end{aligned} \quad (40)$$

The coefficients  $\langle \alpha\beta | 1j; m \rangle$  are called by A.J. Stone the cartesian-spherical transformation coefficients: CS coefficients. The CS for 2. rank tensors are tabulated in [6].

The 2. rank tensors  $A_{\alpha\beta}$ ,  $g_{\alpha\beta}$  of a Spin-hamiltonian are symmetric so that they can be split into two irreducible tensors, 1/3 of the trace times the unit matrix and an traceless symmetric tensor. In the PAS the tensor A can be written as

$$A = \frac{1}{3} \text{Tr}(A) \cdot \underline{\mathbf{1}} + (A_{zz} - \frac{1}{3} \text{Tr}(A)) \cdot \begin{pmatrix} -\frac{1}{2}(1-\eta) & 0 & 0 \\ 0 & -\frac{1}{2}(1+\eta) & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (41)$$

where the asymmetry  $\eta = (A_{xx} - A_{yy})/A_{zz}$  is introduced. The spherical tensor components are calculated according to Eq. 37.

$$\begin{aligned} A_{00} &= -\frac{1}{\sqrt{3}} \text{Tr}(A) \\ A_{22} &= \frac{1}{2}\eta & A_{21} &= 0 & A_{20} &= \sqrt{\frac{3}{2}} \\ A_{2-1} &= 0 & A_{2-2} &= \frac{1}{2}\eta \end{aligned} \quad (42)$$

The set up of the Spin-Hamiltonian requires the calculation of e.g. the effective magnetic field  $H_{eff,\alpha} = \sum_{\beta} g_{\alpha\beta} H_{\beta}$  acting on the spin from the applied field  $H$ . The equation written in spherical coordinates is given by Eqs. 2.9 and 2.14 in the paper [6]:

$$H_{eff,1m} = - \sum_l (-1)^l \left( \frac{2l+1}{3} \right)^{1/2} \sum_{m'm''} H_{m'} g_{lm''} \langle 1lm'm'' | 1m \rangle \quad (43)$$

Inserting the Clebsch-Gordan coefficients the following vector components are obtained.

$$\begin{aligned} H_{eff,1} &= \frac{1}{3} H_1 Tr(g) - H_{-1} g_{22} + \frac{1}{\sqrt{2}} H_0 g_{21} - \frac{1}{\sqrt{6}} H_1 g_{20} \\ H_{eff,0} &= \frac{1}{3} H_0 Tr(g) - \frac{1}{\sqrt{2}} H_1 g_{2-1} + \sqrt{\frac{2}{3}} H_0 g_{20} - \frac{1}{\sqrt{2}} H_{-1} g_{21} \\ H_{eff,-1} &= \frac{1}{3} H_{-1} Tr(g) - H_1 g_{2-2} + \frac{1}{\sqrt{2}} H_0 g_{2-1} - \frac{1}{\sqrt{6}} H_{-1} g_{20} \end{aligned} \quad (44)$$

Analog equations are obtained for the hyperfine field, the product of the A-tensor with the expectation value of the spin:  $A < \mathbf{S}_{eff} >$  (or the S-operators).

$$H_{eff,1m} = - \sum_l (-1)^l \left( \frac{2l+1}{3} \right)^{1/2} \sum_{m'm''} A_{lm'} \langle S_{m''} \rangle \langle l1m'm'' | 1m \rangle \quad (45)$$

Vector components of the same structure are obtained.

$$\begin{aligned} H_{eff,1} &= \frac{1}{3} Tr(A) \langle S_1 \rangle - A_{22} \langle S_{-1} \rangle + \frac{1}{\sqrt{2}} A_{21} \langle S_0 \rangle - \frac{1}{\sqrt{6}} A_{20} \langle S_1 \rangle \\ H_{eff,0} &= \frac{1}{3} Tr(A) \langle S_0 \rangle - \frac{1}{\sqrt{2}} A_{2-1} \langle S_1 \rangle + \sqrt{\frac{2}{3}} A_{20} \langle S_0 \rangle - \frac{1}{\sqrt{2}} A_{21} \langle S_{-1} \rangle \\ H_{eff,-1} &= \frac{1}{3} Tr(A) \langle S_{-1} \rangle - A_{2-2} \langle S_1 \rangle + \frac{1}{\sqrt{2}} A_{2-1} \langle S_0 \rangle - \frac{1}{\sqrt{6}} A_{20} \langle S_{-1} \rangle \end{aligned} \quad (46)$$

It shall be noted that the spherical vector operators  $\mathbf{S}_{\pm 1}$  are not the shift operators  $S_{\pm}$  but according to the matrix Eq. 39  $\mathbf{S}_{\pm 1} = \mp 1/\sqrt{2} S_{\pm}$ .

## 4 Application to experimental setups

The convention for the coordinates as used in the code of the sub-routines `th_hdeq(isubthe,icase,iput,iget,info)` and `th_hdeq()` in the file

th\_22nuclear.f shall be described in the following.

The sample, which contains one, several, or a powder of single crystal(s), is oriented with respect to the laboratory system Sl. Sl is fixed in space, the  $\gamma$ -direction is along the z-axis of the lab. system.

In order to assign the notation of 1.2 the system Sl is identified with Sa and the sample system Ss with Sb. The orientation of Sb given by the unit vectors  $\mathbf{e}_n^b$  of Eq. 5 determines the Euler angle  $\phi, \theta, \psi$ . The z-direction  $\mathbf{e}_z^b$  of the sample system Ss determines already  $\phi, \theta$ . The auxiliary routine **euler** in the directory *effi/help routines/euler* has an entry point in the list of functions for the calculation of the Euler angles.

All physical quantities (tensors of different rank) known with respect to the sample system have to be transformed to the lab. system. That means  $q_m^b$  are expressed with respect to the Sa system. The transformation is achieved by Eq. 16 (Eq. 20, resp. ).

With the following short notation, which is used in the Fortran code, the various transformations and Euler angles involved with the coordinate systems of Tab. 1.1 are easily identified:

$$\begin{aligned}
T(l) &= T(s) Dsl \quad \text{with} \quad \mathbf{e}_k^s(\Omega^{ls}) \\
T(s) &= T(c) Dcs \quad \text{with} \quad \mathbf{e}_k^c(\Omega^{sc}) \\
T(c) &= T(e) Dec \quad \text{with} \quad \mathbf{e}_k^e(\Omega^{ce}) \\
T(c) &= T(x2i) Dx2ic \quad \text{with} \quad \mathbf{e}_k^{x2i}(\Omega^{c,x2i}) \\
T(c) &= T(d) Ddc \quad \text{with} \quad \mathbf{e}_k^e(\Omega^{cd})
\end{aligned} \tag{47}$$

$Dab$  stands for  $D^L(\Omega^{ab})$  with L denoting the rank of tensors T(a) and T(b) of systems Sa and Sb, respectively.  $\mathbf{e}_k^a(\Omega^{ba})$  unequivocally defines the Euler angle by the unit vectors  $\mathbf{e}_k^a$  in the system Sb. In all cases of Eq. 47 the inverses of the Wigner rotation matrices are used as  $Dab = D(\Omega^{ab}) = D^\dagger(\Omega^{ba}) = Dba^\dagger$ .

The physical quantities are referred to the system Sc which shall be chosen with respect to symmetry axes of the crystal. The principal axes systems of Tab. 1.1 :  $Se_i$ ,  $Sx2_i$ ,  $Sx2_c$  and  $S_i$  are usually defined with respect to the crystal system. This gives the sequence of transformations of Eqs. 47.

If the sample is a single crystal the systems Sc of the crystal and Ss shall be the same. For the ideal powder a random distribution of crystal orientations implicates a random distribution of coordinate systems fixed to

the crystals. The subroutine `sphere()` provides an almost uniform distribution of grid points over the unit sphere. The directions  $\mathbf{p}(\theta, \phi)$  defined by the grid points (up to  $128 \cdot 48$ ) are considered as the z-direction of the system  $S_s$  of the sample. For a random orientation also a sufficient large number  $n_p$  of angles  $\psi$  increases the number of coordinate systems to maximal  $n_p \cdot 128 \cdot 48$ .

In this case the sample system  $S_s = S(\text{grid point})$  is oriented with respect to a single crystal by the Euler angles  $\mathbf{e}_k^s(\Omega^{cs})$  with  $\Omega^{cs} = (\phi, \theta, \psi)$ . The angle  $\psi$ , the rotation around  $\mathbf{p}(\theta, \phi)$  is arbitrarily fixed. For the transformation of the tensor components of the crystal system to the sample system

$$T(\text{grid point}) = T(c) Dcs \quad (48)$$

(where  $T(s) = T(\text{grid point})$ ) the Wigner rotation matrix  $Dcs = D^L(\phi, \theta, \psi)$  is used with the Euler angles as taken from the subroutine `sphere()`.

The last point concerns symmetry equivalent sites in the crystal (translational symmetry is disregarded). There are a small number of rotations/reflections (according to the point symmetry groups of the crystal C2, C3, D2, etc and the local symmetry at each site) which relate the equivalent sites. The rotations are defined in the crystal system  $S_c$ . The tensor fields in the PAS of site 1 are transformed to the crystal system  $S_c$  as described above. This tensor field is rotated by some Euler angle and the rotated field in the same system  $S$  are asked for. This problem is met by Eq. 13 (Eq. 22, resp.).

Some remarks to the average over the angle  $\psi$ , the integral  $\frac{1}{2\pi} \int e^{im\psi} d\psi$  which is replaced by a summation

$$I = \sum_{k=0}^n e^{im\psi_k} \quad (49)$$

The angular dependence of the intensities which in turn depend on tensor quantities of different rank and orientation could be developed in an expansion series of spherical harmonics  $Y_{lm}$ . This series ends at some value  $l$  determined by the sequence of direct products of the tensor quantities involved. The largest  $l$  value which is the largest  $m$  value in the sum Eq. 49 determines the  $n$  value for the sum to be zero as is required by the exact integral.

It is easily deduced that the sum  $I$  is zero for equidistant  $\psi_k = \frac{2\pi}{n+1} \cdot k$  and  $n \geq m$ . With  $a = e^{im2\pi/(n+1)}$  and the formula

$$\sum_{k=0}^n a^k = \frac{1 - a^{n+1}}{1 - a} \quad (50)$$

we have for  $a^{n+1} = e^{im2\pi} = 1$  and  $1 - e^{im2\pi/(n+1)} \neq 0$ .

As the choice of  $n_p = n$  depends on the largest  $m$  value in an expansion series of the intensities, which in case of a single site is already a 2. rank tensor for dipole and a 4. rank tensor for quadrupole transitions, the lowest value for  $n_p$  is 2 or even 4, respectively.

The subroutine `th_hdeq()` has no constant  $n_p = n\_psi\_powder$  for the case of an ideal powder in an external magnetic field. This routine does not transform the fields at the nuclear site but transforms the intensity tensor and diagonalizes the nuclear Hamiltonian only once for each direction (given by the grid points over the unit sphere) of the external field. The intensity matrices ( $V_{LM}$  tensors) are calculated for the  $\gamma$ -direction parallel to the field such that the angle  $\psi$  is a rotation of the crystal around the magnetic field. This rotation does not effect the energy eigen values of the Hamiltonian and the intensity matrices are calculated by the transformation  $I(\psi) = D(\psi, 0, 0)^\dagger I D(\psi, 0, 0)$ . The integration over  $\psi$  is readily performed with the result, that all off-diagonal elements  $\overline{I(\psi)_{MN}}^\psi$  ( $M \neq N$ ) vanish. As the full intensity tensor (3 tensors for mixed transition) is stored the  $r_{pq}$  matrices can be calculated for any  $\gamma$ -direction with respect to the field direction (only the  $\theta$ -angle is considered) This possibility requires the mean square displacement tensor (MSD-tensor) to be isotropic.

If there is no external magnetic field and by the choice of a grid point density by the constant  $iset \geq 0$  the subroutine `th_hdeq()` calculates the ideal powder intensities according to Eq. 32, the average of  $\overline{r_{pq}^{\alpha\beta}}$  for each transition  $(\alpha\beta)$ .

## 5 Appendix

The rotation matrices used are following the definition used by Brink and Satchler [1]:

$$d_{mn}^j(\beta) = \sum_t (-1)^t \frac{[(j+m)!(j-m)!(j+n)!(j-n)!]^{1/2}}{(j+m-t)!(j-n-t)!t!(t+n-m)!} \quad (51)$$

$$\left(\cos\frac{\beta}{2}\right)^{2j+m-n-2t}\left(\sin\frac{\beta}{2}\right)^{2t+n-m}$$

The equation given by Rose [4] on p. 52 is obtained by changing the sign of  $m, n$ , and  $\sin\beta/2$  inside the brackets. The tables given in both cases ( $j=1/2, 1$  in [4] and  $j=1/2, \dots, 2$  in [1]) are identical. The matrix elements are different from that used by Edmonds [2].

## References

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