C^{++}OPPS technical details on the model equations

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Contents

1 Definition of diffusive operator

The slowly relaxing local structure (SRLS) model describes the dynamics of the system as the coupled motion of two rigid rotator diffusors, called bodies. Coupling of the motions is due to an orienting potential that one body generates on the other.
Let's define the following reference systems (see Figure 1):

- LF is the laboratory inertial frame;
- M_iF is the frame where the diffusion tensor of the ith body is diagonal. The system is fixed on the ith body;
- VF is the frame fixed on the first body (the generator of the potential) in which is defined the orienting potential;
- OF is a frame fixed on the second body which "feels" the orientation effect;
- μF the reference frame where the magnetic tensor $\boldsymbol{\mu}$ is diagonal.

Let's introduce some sets of Euler angles that transform among the various frames:

- $\boldsymbol{\Omega}_{LM_1}$ to transform from LF to M_1F;
- $\boldsymbol{\Omega}_L$ to transform from LF to VF;
- $\boldsymbol{\Omega}_V$ to transform from M_1F to VF;
- $\boldsymbol{\Omega}_{M_1M_2}$ to transform from M_1F to M_2F;
- $\boldsymbol{\Omega}$ to transform from VF to OF;
- $\boldsymbol{\Omega}_O$ to transform from M_2F to OF.
- $\boldsymbol{\Omega}_{M_2\mu}$ to transform from B_2F to μF.

We need two stochastic variables and we make the choice $\boldsymbol{q} = (\boldsymbol{\Omega}_L, \boldsymbol{\Omega})$ so the Smoluchosky operator is

$$\begin{aligned}\hat{\Gamma} &= {}^O\hat{J}^\dagger(\boldsymbol{\Omega}){}^O\boldsymbol{D}_2 P_{eq}(\boldsymbol{q}){}^O\hat{J}(\boldsymbol{\Omega}) + \\ &+ \left[{}^V\hat{J}(\boldsymbol{\Omega}) - {}^V\hat{J}(\boldsymbol{\Omega}_L)\right]^\dagger {}^V\boldsymbol{D}_1 P_{eq}(\boldsymbol{q}) \left[{}^V\hat{J}(\boldsymbol{\Omega}) - {}^V\hat{J}(\boldsymbol{\Omega}_L)\right]\end{aligned} \tag{1}$$

where the right O and V apexes mean that an operator or a tensor are defined in OF or VF and $\boldsymbol{D}_1$ and $\boldsymbol{D}_2$ are the diffusion tensors of the two bodies. Both diffusion tensor are in general full tensors.
In eq. 1, $P_{eq}(\boldsymbol{q})$ is the distribution equilibrium of the system. We take the case of isotropic environment so the energy of the system is independent on $\boldsymbol{\Omega}_L$:

$$P_{eq}(\boldsymbol{q}) = P_{eq}(\boldsymbol{\Omega})/8\pi^2 = \mathcal{N}\exp\left[-V(\boldsymbol{\Omega})/k_BT\right] \tag{2}$$

For the orienting potential we choose

$$\begin{aligned}U(\boldsymbol{\Omega}) = V(\boldsymbol{\Omega})/k_BT &= c_0^2\mathcal{D}_{0,0}^2(\boldsymbol{\Omega}) + c_2^2\left[\mathcal{D}_{0,2}^2(\boldsymbol{\Omega}) + \mathcal{D}_{0,-2}^2(\boldsymbol{\Omega})\right] + \\ &+ c_0^4\mathcal{D}_{0,0}^4(\boldsymbol{\Omega}) + c_2^4\left[\mathcal{D}_{0,2}^4(\boldsymbol{\Omega}) + \mathcal{D}_{0,-2}^4(\boldsymbol{\Omega})\right] + \\ &+ c_4^4\left[\mathcal{D}_{0,4}^4(\boldsymbol{\Omega}) + \mathcal{D}_{0,-4}^4(\boldsymbol{\Omega})\right]\end{aligned} \tag{3}$$

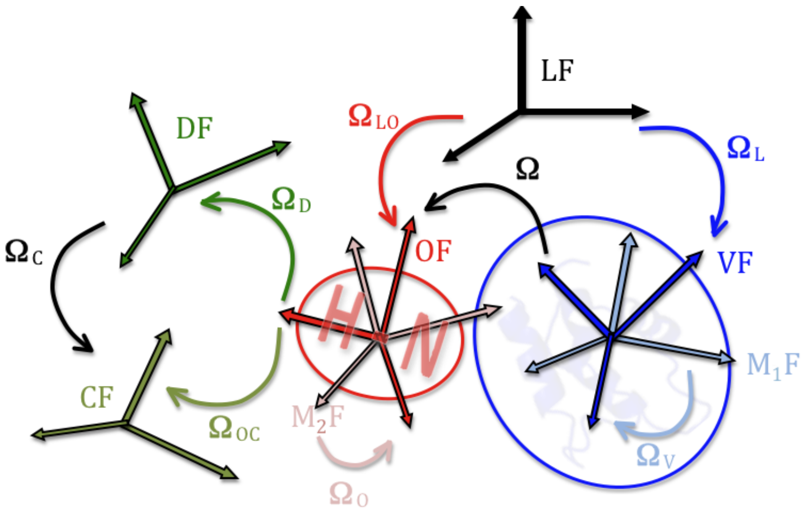

Figure 1: Representation of all the frames needed in the SRSL model.

and for more convenience let's write the potential as

$$U(\mathbf{\Omega}) = \sum_{\nu=0}^{4} \sum_{\mu=-\nu}^{\nu} \epsilon_{\mu}^{\nu} \mathcal{D}_{0,\mu}^{\nu}(\mathbf{\Omega}) \tag{4}$$

where both ν and μ take only even values and $\epsilon_{\mu}^{\nu} = (-)^{\mu} \epsilon_{-\mu}^{\nu\,*}$ to ensure that the potential is real. We symmetrize the diffusive operator to make it Hermitian:

$$\tilde{\Gamma} = P_{eq}(\mathbf{\Omega})^{-1/2} \hat{\Gamma} P_{eq}(\mathbf{\Omega})^{-1/2} \tag{5}$$

Now, we can interpret the operator as composed of a part independent on the potential and a function which depends on the interaction between the two bodies

$$\tilde{\Gamma} = \hat{\mathcal{J}} + F(\mathbf{\Omega}) \tag{6}$$

The first part is composed of terms of the type $\hat{\boldsymbol{J}}^{\dagger} \boldsymbol{D} \hat{\boldsymbol{J}}$, while the explicit form of the function is obtained by remembering that $\tilde{\Gamma} P_{eq}^{1/2} = 0$:

$$F(\mathbf{\Omega}) = -P_{eq}^{-1/2} \hat{\mathcal{J}} P_{eq}^{1/2} \tag{7}$$

The operator will be spanned on the space of rotations defined by

$$|\lambda_1, \lambda_2\rangle = |L_1 M_1 K_1\rangle \times |L_2 M_2 K_2\rangle \tag{8}$$

where

$$|L_1 M_1 K_1\rangle = \sqrt{\frac{[L_1]}{8\pi^2}} \mathcal{D}_{M_1,K_1}^{L_1}(\mathbf{\Omega}_L) \tag{9}$$

$$|L_2 M_2 K_2\rangle = \sqrt{\frac{[L_2]}{8\pi^2}} \mathcal{D}_{M_2,K_2}^{L_2}(\mathbf{\Omega}) \tag{10}$$

and $[L] = 2L + 1$.
In Appendix A are reported some properties of the Wigner matrices that will be useful in the calculation of matrix elements.

2 Potential independent part

The potential independent part of the diffusive operator is made of four terms

$$\hat{\mathcal{J}} = \hat{J}_a + \hat{J}_b + \hat{J}_c + \hat{J}_d \tag{11}$$

with

$$\begin{aligned}
\hat{J}_a &= {}^O\hat{\boldsymbol{J}}^\dagger(\boldsymbol{\Omega})\,{}^O\boldsymbol{D}_2\,{}^O\hat{\boldsymbol{J}}(\boldsymbol{\Omega}) & (12)\\
\hat{J}_b &= {}^V\hat{\boldsymbol{J}}^\dagger(\boldsymbol{\Omega})\,{}^V\boldsymbol{D}_1\,{}^V\hat{\boldsymbol{J}}(\boldsymbol{\Omega}) & (13)\\
\hat{J}_c &= {}^V\hat{\boldsymbol{J}}^\dagger(\boldsymbol{\Omega}_V)\,{}^V\boldsymbol{D}_1\,{}^V\hat{\boldsymbol{J}}(\boldsymbol{\Omega}_L) & (14)\\
\hat{J}_d &= -\left[{}^V\hat{\boldsymbol{J}}^\dagger(\boldsymbol{\Omega})\,{}^V\boldsymbol{D}_1\,{}^V\hat{\boldsymbol{J}}(\boldsymbol{\Omega}_L) + {}^V\hat{\boldsymbol{J}}^\dagger(\boldsymbol{\Omega}_L)\,{}^V\boldsymbol{D}_1\,{}^V\hat{\boldsymbol{J}}(\boldsymbol{\Omega})\right] & (15)
\end{aligned}$$

It is convenient to change from cartesian to spherical representation of the operator. In Appendix B it is shown how it is possible write the operator as:

$$\hat{\mathcal{J}} = \sum_{l=0,2}\sum_{m=-l}^{l} \hat{J}_a^{(l,m)} + \hat{J}_b^{(l,m)} + \hat{J}_c^{(l,m)} + \hat{J}_d^{(l,m)} \tag{16}$$

with

$$\begin{aligned}
\hat{J}_a^{(l,m)} &= {}^O D_2^{(l,m)}\;{}^O\hat{\mathcal{K}}_a^{(l,m)}(\boldsymbol{\Omega}) & (17)\\
\hat{J}_b^{(l,m)} &= {}^V D_1^{(l,m)}\;{}^V\hat{\mathcal{K}}_b^{(l,m)}(\boldsymbol{\Omega}) & (18)\\
\hat{J}_c^{(l,m)} &= {}^V D_1^{(l,m)}\;{}^V\hat{\mathcal{K}}_c^{(l,m)}(\boldsymbol{\Omega}_L) & (19)\\
\hat{J}_d^{(l,m)} &= -2\;{}^V D_1^{(l,m)}\;{}^V\hat{\mathcal{K}}_d^{(l,m)}(\boldsymbol{\Omega},\boldsymbol{\Omega}_L) & (20)
\end{aligned}$$

and the specific expressions for the components $D^{(l,m)}$ and the operators $\hat{\mathcal{K}}^{(l,m)}$ are given in Appendix B.
A first convenience in employing irreducible spherical tensors and tensorial operators is that the components of the diffusion tensors in OF and VF are easily found

$$\begin{aligned}
{}^V D_1^{(l,m)} &= \sum_{m'=-l}^{l} \mathcal{D}^l_{m,m'}(\boldsymbol{\Omega}_V)\;{}^{M_1}D_1^{(l,m')\,*} & (21)\\
{}^O D_2^{(l,m)} &= \sum_{m'=-l}^{l} \mathcal{D}^l_{m,m'}(\boldsymbol{\Omega}_O)\;{}^{M_2}D_2^{(l,m')\,*} & (22)
\end{aligned}$$

Secondly, we will make use of the Wigner-Eckart theorem to evaluate the matrix elements.

2.1 Operator $\hat{J}_a$

This operator acts only on λ_2 so matrix elements are diagonal in λ_1 and we have:
for $l = 0$

$$\langle\lambda_2(\boldsymbol{\Omega})|\,{}^O\hat{\mathcal{K}}_a^{(0,0)}(\boldsymbol{\Omega})|\lambda_2'(\boldsymbol{\Omega})\rangle = -\frac{1}{\sqrt{3}}\delta_{\lambda_2,\lambda_2'}L_2(L_2+1) \tag{23}$$

for $l=2$

$$\langle\lambda_2(\mathbf{\Omega})|^O\hat{\mathcal{K}}_a^{(2,m)}(\mathbf{\Omega})|\lambda_2'(\mathbf{\Omega})\rangle = \delta_{L_2,L_2'}\delta_{M_2,M_2'}(-)^{(L_2-K_2)}\sqrt{\frac{(2L_2+3)!}{24(2L_2-2)!}}\begin{pmatrix} L_2 & 2 & L_2 \\ -K_2 & m & K_2' \end{pmatrix} \quad (24)$$

In the last equation we made use of the Wigner-Eckart thorem, as explained in Appendix C. Now it is possible to write the matrix element:

$$\begin{aligned}\langle\lambda_1\lambda_2|\hat{J}_a|\lambda_1'\lambda_2'\rangle &= \delta_{\lambda_1,\lambda_1'}\delta_{L_2,L_2'}\delta_{M_2,M_2'}\Big[-\delta_{K_2,K_2'}\frac{1}{\sqrt{3}}\,{}^O D_2^{(0,0)}L_2(L_2+1)+ \\ &+(-)^{(L_2-K_2)}\,{}^O D_2^{(2,K_2-K_2')}\sqrt{\frac{(2L_2+3)!}{24(2L_2-2)!}}\times \\ &\times\begin{pmatrix} L_2 & 2 & L_2 \\ -K_2 & K_2-K_2' & K_2' \end{pmatrix}\Big] \end{aligned} \quad (25)$$

2.2 Operator $\hat{J}_b$

Also this operator acts only on λ_2 but it is defined in VF.
For $l=0$

$$\langle\lambda_2(\mathbf{\Omega})|^V\hat{\mathcal{K}}_b^{(0,0)}(\mathbf{\Omega})|\lambda_2'(\mathbf{\Omega})\rangle = -\frac{1}{\sqrt{3}}\delta_{\lambda_2,\lambda_2'}L_2(L_2+1) \quad (26)$$

for $l=2$

$$\langle\lambda_2(\mathbf{\Omega})|^V\hat{\mathcal{K}}_b^{(2,m)}(\mathbf{\Omega})|\lambda_2'(\mathbf{\Omega})\rangle = \delta_{L_2,L_2'}\delta_{K_2,K_2'}(-)^{(L_2-M_2)}\sqrt{\frac{(2L_2+3)!}{24(2L_2-2)!}}\begin{pmatrix} L_2 & 2 & L_2 \\ -M_2 & -m & M_2' \end{pmatrix} \quad (27)$$

In the last equation we made use of the Wigner-Eckart thorem, as explained in Appendix C. Now it is possible to write the matrix element:

$$\begin{aligned}\langle\lambda_1\lambda_2|\hat{J}_b|\lambda_1'\lambda_2'\rangle &= \delta_{\lambda_1,\lambda_1'}\delta_{L_2,L_2'}\delta_{K_2,K_2'}\Big[-\delta_{M_2,M_2'}\frac{1}{\sqrt{3}}\,{}^V D_1^{(0,0)}L_2(L_2+1)+ \\ &+(-)^{(L_2-M_2)}\,{}^V D_1^{(2,M_2'-M_2)}\sqrt{\frac{(2L_2+3)!}{24(2L_2-2)!}}\times \\ &\times\begin{pmatrix} L_2 & 2 & L_2 \\ -M_2 & M_2-M_2' & M_2' \end{pmatrix}\Big] \end{aligned} \quad (28)$$

2.3 Operator $\hat{J}_c$

This operator is analogous to $\hat{J}_a$, but acting only on λ_1 and defined in VF, so:
for $l=0$

$$\langle\lambda_1(\mathbf{\Omega}_L)|^V\hat{\mathcal{K}}_c^{(0,0)}(\mathbf{\Omega}_L)|\lambda_1'(\mathbf{\Omega}_L)\rangle = -\frac{1}{\sqrt{3}}\delta_{\lambda_1,\lambda_1'}L_1(L_1+1) \quad (29)$$

for $l=2$

$$\langle\lambda_1(\mathbf{\Omega}_L)|^V\hat{\mathcal{K}}_c^{(2,m)}(\mathbf{\Omega}_L)|\lambda_1'(\mathbf{\Omega}_L)\rangle=\delta_{L_1,L_1'}\delta_{M_1,M_1'}(-)^{(L_1-K_1)}\sqrt{\frac{(2L_1+3)!}{24(2L_1-2)!}}\begin{pmatrix} L_1 & 2 & L_1 \\ -K_1 & m & K_1' \end{pmatrix}\tag{30}$$

In the last equation we made use of the Wigner-Eckart thorem, as explained in Appendix C. Now it is possible to write the matrix element:

$$\begin{aligned}\langle\lambda_1\lambda_2|\hat{J}_c|\lambda_1'\lambda_2'\rangle &= \delta_{\lambda_2,\lambda_2'}\delta_{L_1,L_1'}\delta_{M_1,M_1'}\Big[-\delta_{K_1,K_1'}\frac{1}{\sqrt{3}}\,{}^VD_1^{(0,0)}L_1(L_1+1)+\\ &\quad+(-)^{(L_1-K_1)}\,{}^VD_1^{(2,K_1-K_1')}\sqrt{\frac{(2L_1+3)!}{24(2L_1-2)!}}\times\\ &\quad\times\begin{pmatrix} L_1 & 2 & L_1 \\ -K_1 & K_1-K_1' & K_1' \end{pmatrix}\Big]\end{aligned}\tag{31}$$

2.4 Operator $\hat{J}_d$

The spherical tensorial operator $\hat{\mathcal{K}}_d^{(2)}$ acts on both the sub-spaces of the rotations and the Wigner-Eckart theorem would be useful if we employed the coupled representation. Because we are working with the uncoupled representation, it is easier to use the explicit formulas:
for $l=0$:

$$\begin{aligned}\langle\lambda_1\lambda_2|^V\hat{\mathcal{K}}_d^{(0,0)}|\lambda_1'\lambda_2'\rangle &= -\frac{1}{\sqrt{3}}\delta_{L_1,L_1'}\delta_{M_1,M_1'}\delta_{L_2,L_2'}\delta_{K_2,K_2'}\times\\ &\quad\times\Big[\frac{1}{2}\Big(\delta_{K_1,K_1'-1}\delta_{M_2,M_2'-1}c^-_{L_1,K_1+1}c^-_{L_2,M_2+1}+\\ &\quad+\delta_{K_1,K_1'+1}\delta_{M_2,M_2'+1}c^+_{L_1,K_1-1}c^+_{L_2,M_2-1}\Big)+\delta_{K_1,K_1'}\delta_{M_2,M_2'}K_1M_2\Big]\end{aligned}\tag{32}$$

for $l=2$:

$$\begin{aligned}\langle\lambda_1\lambda_2|^V\hat{\mathcal{K}}_d^{(2,0)}|\lambda_1'\lambda_2'\rangle &= \frac{1}{\sqrt{6}}\delta_{L_1,L_1'}\delta_{M_1,M_1'}\delta_{L_2,L_2'}\delta_{K_2,K_2'}\times\\ &\quad\times\Big[-\frac{1}{2}\Big(\delta_{K_1,K_1'-1}\delta_{M_2,M_2'-1}c^-_{L_1,K_1+1}c^-_{L_2,M_2+1}+\\ &\quad+\delta_{K_1,K_1'+1}\delta_{M_2,M_2'+1}c^+_{L_1,K_1-1}c^+_{L_2,M_2-1}\Big)+\delta_{K_1,K_1'}\delta_{M_2,M_2'}2K_1M_2\Big]\end{aligned}\tag{33}$$

$$\begin{aligned}\langle\lambda_1\lambda_2|^V\hat{\mathcal{K}}_d^{(2,\pm1)}|\lambda_1'\lambda_2'\rangle &= \mp\frac{1}{2}\delta_{L_1,L_1'}\delta_{M_1,M_1'}\delta_{L_2,L_2'}\delta_{K_2,K_2'}\times\\ &\quad\times\Big(\delta_{K_1,K_1'\pm1}\delta_{M_2,M_2'}c^\pm_{L_1,K_1\mp1}M_2+\delta_{K_1,K_1'}\delta_{M_2,M_2'\mp1}K_1c^\mp_{L_2,M_2\pm1}\Big)\end{aligned}\tag{34}$$

$$\langle\lambda_1\lambda_2|^V\hat{\mathcal{K}}_d^{(2,\pm2)}|\lambda_1'\lambda_2'\rangle = \frac{1}{2}\delta_{L_1,L_1'}\delta_{M_1,M_1'}\delta_{L_2,L_2'}\delta_{K_2,K_2'}\delta_{K_1,K_1'\pm1}\delta_{M_2,M_2'\mp1}c^\pm_{L_1,K_1\mp1}c^\mp_{L_2,M_2\pm1}\tag{35}$$

and the matrix element will be

$$\langle\lambda_1\lambda_2|\hat{J}_d|\lambda_1'\lambda_2'\rangle=-2\sum_{l=0,2}\sum_{m=-l}^{l}{}^VD_1^{(l,m)}\langle\lambda_1\lambda_2|^V\hat{\mathcal{K}}_d^{(l,m)}|\lambda_1'\lambda_2'\rangle\tag{36}$$

3 Potential dependent part

To evaluate the potential dependent function it sufficient to remember that $\tilde{\Gamma} P_{eq}^{1/2} = 0$, so

$$\begin{aligned} F(\mathbf{\Omega}) &= -P_{eq}^{-1/2}(\mathbf{\Omega})\hat{\mathcal{J}}(\mathbf{\Omega},\mathbf{\Omega}_V)P_{eq}^{1/2}(\mathbf{\Omega}) = \\ &= -P_{eq}^{-1/2}(\mathbf{\Omega})\hat{J}_a(\mathbf{\Omega})P_{eq}^{1/2}(\mathbf{\Omega}) - P_{eq}^{-1/2}(\mathbf{\Omega})\hat{J}_b(\mathbf{\Omega})P_{eq}^{1/2}(\mathbf{\Omega}) = \\ &= F_a(\mathbf{\Omega}) + F_b(\mathbf{\Omega}) \end{aligned} \tag{37}$$

The operators $\hat{J}_c$ and $\hat{J}_d$ do not contribute to $F(\mathbf{\Omega})$ because they contain derivatives with respect to $\mathbf{\Omega}_L$ and the equilibrium distribution probability depends only on $\mathbf{\Omega}$.
To build $F(\mathbf{\Omega})$ it is useful to evaluate some derivatives (all operators act on $\mathbf{\Omega}$ so this dependence will be omitted):

$${}^O\hat{J}_Z U = -\sum_{\nu,\mu} \epsilon_{\nu,\mu}\mu\mathcal{D}^{\nu}_{0,\mu} \tag{38}$$

$${}^V\hat{J}_Z U = 0 \tag{39}$$

$${}^O\hat{J}_\pm U = -\sum_{\nu,\mu} \epsilon_{\nu,\mu}c^{\pm}_{\nu,\mu}\mathcal{D}^{\nu}_{0,\mu\pm1} \tag{40}$$

$${}^V\hat{J}_\pm U = -\sum_{\nu,\mu} \epsilon_{\nu,\mu}c^{\mp}_{\nu,0}\mathcal{D}^{\nu}_{\mp1,\mu} \tag{41}$$

where ν takes the even values from 0 to 4 and μ the even values from $-\nu$ to ν.
From these derivatives one obatins:

$${}^O\hat{J}^2_Z U = \sum_{\nu,\mu} \epsilon_{\nu,\mu}\mu^2\mathcal{D}^{\nu}_{0,\mu} \tag{42}$$

$${}^V\hat{J}^2_Z U = 0 \tag{43}$$

$${}^O\hat{J}^2_\pm U = \sum_{\nu,\mu} \epsilon_{\nu,\mu}c^{\pm}_{\nu,\mu}c^{\pm}_{\nu,\mu\pm1}\mathcal{D}^{\nu}_{0,\mu\pm2} \tag{44}$$

$${}^V\hat{J}^2_\pm U = \sum_{\nu,\mu} \epsilon_{\nu,\mu}c^{\mp}_{\nu,0}c^{\mp}_{\nu,\mp1}\mathcal{D}^{\nu}_{\mp2,\mu} \tag{45}$$

$${}^O\hat{J}_+ {}^O\hat{J}_- U = \sum_{\nu,\mu} \epsilon_{\nu,\mu}c^{-}_{\nu,\mu}c^{+}_{\nu,\mu-1}\mathcal{D}^{\nu}_{0,\mu} \tag{46}$$

$${}^O\hat{J}_- {}^O\hat{J}_+ U = \sum_{\nu,\mu} \epsilon_{\nu,\mu}c^{+}_{\nu,\mu}c^{-}_{\nu,\mu+1}\mathcal{D}^{\nu}_{0,\mu} \tag{47}$$

$${}^V\hat{J}_+ {}^V\hat{J}_- U = {}^V\hat{J}_- {}^V\hat{J}_+ U = \sum_{\nu,\mu} \epsilon_{\nu,\mu}\nu(\nu+1)\mathcal{D}^{\nu}_{0,\mu} \tag{48}$$

$${}^O\hat{J}_Z {}^O\hat{J}_\pm U = \sum_{\nu,\mu} \epsilon_{\nu,\mu}c^{\pm}_{\nu,\mu}(\mu\pm1)\mathcal{D}^{\nu}_{0,\mu\pm1} \tag{49}$$

$${}^O\hat{J}_\pm {}^O\hat{J}_Z U = \sum_{\nu,\mu} \epsilon_{\nu,\mu}c^{\pm}_{\nu,\mu}\mu\mathcal{D}^{\nu}_{0,\mu\pm1} \tag{50}$$

$${}^V\hat{J}_Z {}^V\hat{J}_\pm U = \mp\sum_{\nu,\mu} \epsilon_{\nu,\mu}c^{\mp}_{\nu,0}\mathcal{D}^{\nu}_{\mp1,\mu} \tag{51}$$

$$ {}^{V}\hat{J}_{\pm}{}^{V}\hat{J}_{Z}U = 0 \tag{52} $$

$$ \begin{aligned} \left({}^{O}\hat{J}_{Z}U\right)^2 &= \sum_{\nu,\mu}\sum_{\nu',\mu'}(-)^{\mu-\mu'}\epsilon_{\nu,\mu}\epsilon_{\nu',\mu'}\mu\mu'\sum_{j}[j]\begin{pmatrix} \nu & \nu' & j \\ 0 & 0 & 0 \end{pmatrix}\times \\ &\times\begin{pmatrix} \nu & \nu' & j \\ \mu & \mu' & -(\mu+\mu') \end{pmatrix}\mathcal{D}^{j}_{0,\mu+\mu'} \end{aligned} \tag{53} $$

$$ \left({}^{V}\hat{J}_{Z}U\right)^2 = 0 \tag{54} $$

$$ \begin{aligned} \left({}^{O}\hat{J}_{\pm}U\right)^2 &= \sum_{\nu,\mu}\sum_{\nu',\mu'}(-)^{\mu-\mu'}\epsilon_{\nu,\mu}\epsilon_{\nu',\mu'}c^{\pm}_{\nu,\mu}c^{\pm}_{\nu',\mu'}\sum_{j}[j]\begin{pmatrix} \nu & \nu' & j \\ 0 & 0 & 0 \end{pmatrix}\times \\ &\times\begin{pmatrix} \nu & \nu' & j \\ \mu\pm1 & \mu'\pm1 & -(\mu+\mu'\pm2) \end{pmatrix}\mathcal{D}^{j}_{0,\mu+\mu'\pm2} \end{aligned} \tag{55} $$

$$ \begin{aligned} \left({}^{V}\hat{J}_{\pm}U\right)^2 &= \sum_{\nu,\mu}\sum_{\nu',\mu'}(-)^{\mu-\mu'}\epsilon_{\nu,\mu}\epsilon_{\nu',\mu'}c^{\mp}_{\nu,0}c^{\mp}_{\nu',0}\sum_{j}[j]\begin{pmatrix} \nu & \nu' & j \\ \mp1 & \mp1 & \pm2 \end{pmatrix}\times \\ &\times\begin{pmatrix} \nu & \nu' & j \\ \mu & \mu' & -(\mu+\mu') \end{pmatrix}\mathcal{D}^{j}_{\mp2,\mu+\mu'} \end{aligned} \tag{56} $$

$$ \begin{aligned} ({}^{O}\hat{J}_{+}U)({}^{O}\hat{J}_{-}U) &= \sum_{\nu,\mu}\sum_{\nu',\mu'}(-)^{\mu-\mu'}\epsilon_{\nu,\mu}\epsilon_{\nu',\mu'}c^{+}_{\nu,\mu}c^{-}_{\nu',\mu'}\sum_{j}[j]\begin{pmatrix} \nu & \nu' & j \\ 0 & 0 & 0 \end{pmatrix}\times \\ &\times\begin{pmatrix} \nu & \nu' & j \\ \mu+1 & \mu'-1 & -(\mu+\mu') \end{pmatrix}\mathcal{D}^{j}_{0,\mu+\mu'} \end{aligned} \tag{57} $$

$$ \begin{aligned} ({}^{V}\hat{J}_{+}U)({}^{V}\hat{J}_{-}U) &= \sum_{\nu,\mu}\sum_{\nu',\mu'}(-)^{\mu-\mu'}\epsilon_{\nu,\mu}\epsilon_{\nu',\mu'}c^{-}_{\nu,0}c^{+}_{\nu',0}\sum_{j}[j]\begin{pmatrix} \nu & \nu' & j \\ -1 & 1 & 0 \end{pmatrix}\times \\ &\times\begin{pmatrix} \nu & \nu' & j \\ \mu & \mu' & -(\mu+\mu') \end{pmatrix}\mathcal{D}^{j}_{0,\mu+\mu'} \end{aligned} \tag{58} $$

$$ \begin{aligned} ({}^{O}\hat{J}_{Z}U)({}^{O}\hat{J}_{\pm}U) &= -\sum_{\nu,\mu}\sum_{\nu',\mu'}(-)^{\mu-\mu'}\epsilon_{\nu,\mu}\epsilon_{\nu',\mu'}\mu c^{\pm}_{\nu',\mu'}\sum_{j}[j]\begin{pmatrix} \nu & \nu' & j \\ 0 & 0 & 0 \end{pmatrix}\times \\ &\times\begin{pmatrix} \nu & \nu' & j \\ \mu & \mu'\pm1 & -(\mu+\mu'\pm1) \end{pmatrix}\mathcal{D}^{j}_{0,\mu+\mu'\pm1} \end{aligned} \tag{59} $$

$$ ({}^{V}\hat{J}_{Z}U)({}^{V}\hat{J}_{\pm}U) = 0 \tag{60} $$

where $c^{\pm}_{\nu,\mu} = \sqrt{\nu(\nu+1)-\mu(\mu\pm1)}$ and $[j] = (2j+1)$.
Finally let's recall that

$$ P_{eq}^{-1/2}\hat{J}_{\alpha}\hat{J}_{\beta}P_{eq}^{1/2} = \frac{1}{4}\left[\left(\hat{J}_{\alpha}U\right)\left(\hat{J}_{\beta}U\right) - 2\hat{J}_{\alpha}\hat{J}_{\beta}U\right] \tag{61} $$

with $\alpha, \beta = \pm, Z$.

3.1 Function $F_a(\mathbf{\Omega})$

The first addend of the function F is given by

$$F_a = -\sum_{l,m} {}^O D_2^{(l,m)} P_{eq}^{-1/2} \hat{\mathcal{K}}_a^{(l,m)} P_{eq}^{1/2} = -\sum_{l,m} {}^O D_2^{(l,m)} F_a^{(l,m)} \tag{62}$$

All the components can be written as

$$F_a^{(l,m)} = -\sum_{\mu,\mu'} \sum_j f_a^{(l,m)}(\mu, \mu', j) \mathcal{D}^j_{0,\mu+\mu'+m} \tag{63}$$

with

$$\begin{aligned}
f_a^{(0,0)}(\mu,\mu',j) &= -\frac{1}{4\sqrt{3}} \sum_\nu \left\{ (-)^{\mu-\mu'} [j] \sum_{\nu'} \epsilon_{\nu,\mu}\epsilon_{\nu',\mu'} \begin{pmatrix} \nu & \nu' & j \\ 0 & 0 & 0 \end{pmatrix} \times \right. \\
&\times \left[\begin{pmatrix} \nu & \nu' & j \\ \mu+1 & \mu'-1 & -(\mu+\mu') \end{pmatrix} c^+_{\nu,\mu} c^-_{\nu',\mu'} + \right. \\
&+ \left. \left. \begin{pmatrix} \nu & \nu' & j \\ \mu & \mu' & -(\mu+\mu') \end{pmatrix} \mu\mu' \right] \right\} - \delta_{j,\nu}\delta_{\mu',0} 2\epsilon_{\nu,\mu}\nu(\nu+1)
\end{aligned} \tag{64}$$

$$\begin{aligned}
f_a^{(2,0)}(\mu,\mu',j) &= \frac{1}{4\sqrt{6}} \sum_\nu \left\{ (-)^{\mu-\mu'} [j] \sum_{\nu'} \{ \epsilon_{\nu,\mu}\epsilon_{\nu',\mu'} \begin{pmatrix} \nu & \nu' & j \\ 0 & 0 & 0 \end{pmatrix} \times \right. \\
&\times \left[- \begin{pmatrix} \nu & \nu' & j \\ \mu+1 & \mu'-1 & -(\mu+\mu') \end{pmatrix} c^+_{\nu,\mu} c^-_{\nu',\mu'} + \right. \\
& \left. \left. \begin{pmatrix} \nu & \nu' & j \\ \mu & \mu' & -(\mu+\mu') \end{pmatrix} 2\mu\mu' \right] \right\} + \delta_{j,\nu}\delta_{\mu',0} 2\epsilon_{\nu,\mu} \left[\nu(\nu+1) - 3\mu^2 \right]
\end{aligned} \tag{65}$$

$$\begin{aligned}
f_a^{(2,\pm1)}(\mu,\mu',j) &= \pm\frac{1}{4} \sum_\nu \left[(-)^{\mu-\mu'} [j] \sum_{\nu'} \epsilon_{\nu,\mu}\epsilon_{\nu',\mu'} \mu \, c^\pm_{\nu',\mu'} \begin{pmatrix} \nu & \nu' & j \\ 0 & 0 & 0 \end{pmatrix} \times \right. \\
&\times \left. \begin{pmatrix} \nu & \nu' & j \\ \mu & \mu'\pm1 & -(\mu+\mu'\pm1) \end{pmatrix} \right] + \delta_{j,\nu}\delta_{\mu',0}\epsilon_{\nu,\mu} c^\pm_{\nu,\mu} (2\mu\pm1)
\end{aligned} \tag{66}$$

$$\begin{aligned}
f_a^{(2,\pm2)}(\mu,\mu',j) &= \frac{1}{8} \sum_\nu \left[(-)^{\mu-\mu'} [j] \sum_{\nu'} \epsilon_{\nu,\mu}\epsilon_{\nu',\mu'} c^\pm_{\nu,\mu} c^\pm_{\nu',\mu'} \begin{pmatrix} \nu & \nu' & j \\ 0 & 0 & 0 \end{pmatrix} \times \right. \\
&\times \left. \begin{pmatrix} \nu & \nu' & j \\ \mu\pm1 & \mu'\pm1 & -(\mu+\mu'\pm2) \end{pmatrix} \right] - \delta_{j,\nu}\delta_{\mu',0} 2\epsilon_{\nu,\mu} c^\pm_{\nu,\mu} c^\pm_{\nu,\mu\pm1}
\end{aligned} \tag{67}$$

As can be seen from the above equations, we have changed the "natural" order of the indexes, i.e. summation ordered as $\sum_\nu \sum_\mu \sum_{\nu'} \sum_{\mu'} \sum_j$, to the quite "non-natural" order $\sum_\mu \sum_{\mu'} \sum_j \sum_\nu \sum_{\nu'}$. This ordering permits us to write the matrix elements in such a way that the selection rules are evident and all the components $f_a^{(l,m)}$ can be calculated only once, speeding up the algorithm. The matrix element, diagonal in λ_1, is

$$\langle \lambda_2 | F_a | \lambda_2' \rangle = -\sum_{l,m} {}^O D_2^{(l,m)} \sum_{\mu,\mu',j} f_a^{(l,m)}(\mu,\mu',j) \langle \lambda_2 | \mathcal{D}^j_{0,\mu+\mu'+m} | \lambda_2' \rangle =$$

$$
\begin{aligned}
&= -\delta_{M_2,M_2'}(-)^{M_2-K_2}\sqrt{[L_2,L_2']}\sum_{l,m}{}^{O}D_2^{(l,m)}\sum_{\mu,\mu',j} f_a^{(l,m)}(\mu,\mu',j)\times\\
&\quad\times\begin{pmatrix} L_2 & j & L_2' \\ -M_2 & 0 & M_2 \end{pmatrix}\begin{pmatrix} L_2 & j & L_2' \\ -K_2 & \mu+\mu'+m & K_2' \end{pmatrix} =\\
&= -\delta_{M_2,M_2'}(-)^{M_2-K_2}\sqrt{[L_2,L_2']}\sum_{l}\sum_{\mu,\mu',j}{}^{O}D_2^{(l,K_2-K_2'-\mu-\mu')} f_a^{(l,K_2-K_2'-\mu-\mu')}(\mu,\mu',j)\times\\
&\quad\times\begin{pmatrix} L_2 & j & L_2' \\ -M_2 & 0 & M_2 \end{pmatrix}\begin{pmatrix} L_2 & j & L_2' \\ -K_2 & K_2-K_2' & K_2' \end{pmatrix}
\end{aligned}
\tag{68}
$$

and the variability of the indexes is

$$
\begin{cases}
-4 \le \mu \le 4\\
max\{-4,(K_2-K_2'-\mu+2)\} \le \mu' \le min\{4,(K_2-K_2'-\mu-2)\}\\
max\{0,|K_2-K_2'-\mu-\mu'|,|L_2-L_2'|\} \le j \le min\{8,(L_2+L_2')\}\\
|\mu| \le \nu \le 4\\
max\{|\mu'|,|\nu-j|\} \le \nu' \le min\{4,(\nu+j)\}
\end{cases}
\tag{69}
$$

which represent the ranges that avoid the explicit zeroes of the $3j$ symbols in the expressions.

3.2 Function $F_b(\mathbf{\Omega})$

Analogously, the second addend of the function F is given by

$$
F_b = -\sum_{l,m}{}^{V}D_1^{(l,m)}P_{eq}^{-1/2}\hat{\mathcal{K}}_b^{(l,m)}P_{eq}^{1/2} = -\sum_{l,m}{}^{V}D_1^{(l,m)}F_b^{(l,m)}
\tag{70}
$$

All the components can be written as

$$
F_b^{(l,m)} = -\sum_{\mu,\mu'}\sum_{j} f_b^{(l,m)}(\mu,\mu',j)\mathcal{D}^{j}_{-m,\mu+\mu'}
\tag{71}
$$

with

$$
\begin{aligned}
f_b^{(0,0)}(\mu,\mu',j) &= -\frac{1}{4\sqrt{3}}\sum_{\nu}\Bigg\{(-)^{\mu-\mu'}[j]\sum_{\nu'}\epsilon_{\nu,\mu}\epsilon_{\nu',\mu'}\begin{pmatrix} \nu & \nu' & j \\ 1 & 1 & 0 \end{pmatrix}\times\\
&\quad\times\begin{pmatrix} \nu & \nu' & j \\ \mu & \mu' & -(\mu+\mu') \end{pmatrix} c^{-}_{\nu,0}c^{+}_{\nu',0} - \delta_{j,\nu}\delta_{\mu',0}2\epsilon_{\nu,\mu}\nu(\nu+1)\\
f_b^{(2,0)}(\mu,\mu',j) &= \frac{1}{\sqrt{2}} f_b^{(0,0)}(\mu',0,j)\\
f_b^{(2,\pm1)}(\mu,\mu',j) &= -\frac{1}{4}\sum_{\nu}\delta_{j,\nu}\delta_{\mu',0}\epsilon_{\nu,\mu}c^{\mp}_{\nu,0}\\
f_b^{(2,\pm2)}(\mu,\mu',j) &= \frac{1}{8}\sum_{\nu}\Bigg[(-)^{\mu-\mu'}[j]\sum_{\nu'}\epsilon_{\nu,\mu}\epsilon_{\nu',\mu'}c^{\mp}_{\nu,0}c^{\mp}_{\nu',0}\begin{pmatrix} \nu & \nu' & j \\ \mp1 & \mp1 & \pm2 \end{pmatrix}\times\\
&\quad\times\begin{pmatrix} \nu & \nu' & j \\ \mu & \mu' & -(\mu+\mu') \end{pmatrix}\Bigg] - \delta_{j,\nu}\delta_{\mu,\mu'}2\epsilon_{\nu,\mu}c^{\mp}_{\nu,0}c^{\mp}_{\nu,\mp1}
\end{aligned}
\tag{72}
$$

As can be seen from the above equations, we have changed the "natural" order of the indexes, i.e. summation ordered as $\sum_{\nu}\sum_{\mu}\sum_{\nu'}\sum_{\mu'}\sum_{j}$, to the quite "non-natural" order $\sum_{\mu}\sum_{\mu'}\sum_{j}\sum_{\nu}\sum_{\nu'}$.

This ordering permits us to write the matrix elements in such a way that the selection rules are evident and all the components $f_b^{(l,m)}$ can be calculated only once, speeding up the algorithm. The matrix element, diagonal in λ_1, is

$$\begin{aligned}
\langle\lambda_2|F_b|\lambda_2'\rangle &= -\sum_{l,m} {}^V D_1^{(l,m)} \sum_{\mu,\mu',j} f_b^{(l,m)}(\mu,\mu',j)\langle\lambda_2|\mathcal{D}^j_{-m,\mu+\mu'}|\lambda_2'\rangle = \\
&= -(-)^{M_2-K_2}\sqrt{[L_2,L_2']}\sum_{l,m} {}^V D_1^{(l,m)} \sum_{\mu,\mu',j} f_b^{(l,m)}(\mu,\mu',j) \times \\
&\times \begin{pmatrix} L_2 & j & L_2' \\ -M_2 & -m & M_2' \end{pmatrix} \begin{pmatrix} L_2 & j & L_2' \\ -K_2 & \mu+\mu' & K_2' \end{pmatrix} = \\
&= -(-)^{M_2-K_2}\sum_{l}\sum_{\mu,\mu',j} {}^V D_1^{(l,M_2'-M_2)} f_b^{(l,M_2'-M_2)}(\mu,\mu',j) \times \\
&\times \begin{pmatrix} L_2 & j & L_2' \\ -M_2 & M_2-M_2' & M_2' \end{pmatrix} \begin{pmatrix} L_2 & j & L_2' \\ -K_2 & K_2-K_2' & K_2' \end{pmatrix}
\end{aligned} \tag{73}$$

and the variability of the indexes is

$$\begin{cases} -4 \leq \mu \leq 4 \\ max\{-4,(K_2-K_2'-\mu)\} \leq \mu' \leq min\{4,(K_2-K_2'-\mu)\} \\ max\{0,|K_2-K_2'-\mu-\mu'|,|L_2-L_2'|\} \leq j \leq min\{8,(L_2+L_2')\} \\ |\mu| \leq \nu \leq 4 \\ max\{|\mu'|,|\nu-j|\} \leq \nu' \leq min\{4,(\nu+j)\} \end{cases} \tag{74}$$

which represent the ranges that avoid the explicit zeroes of the $3j$ symbols in the expressions.

4 Symmetrization of diffusive operator

The diffusive operator $\tilde{\Gamma}$ is Hermitian and its associated matrix, with the basis set given in eq. (8), is Hermitian. It would be desirable to work with a real symmetric matrix in order to simplify the further operations to be done during the Lanczos tridiagonalization. Inspecting the matrix elements one observes that there is a symmetry for the concerted change in sign of the indexes K_1, M_2 and K_2. Precisely, if $\hat{\mathcal{T}}$ is an operator which changes the sign of the three indexes, we have:

$$\begin{aligned}
&\hat{\mathcal{T}}\langle L_1M_1K_1,L_2M_2K_2|\tilde{\Gamma}|L_1'M_1'K_1',L_2'M_2'K_2'\rangle = \\
&= \langle L_1M_1-K_1,L_2-M_2-K_2|\tilde{\Gamma}|L_1'M_1'-K_1',L_2'-M_2'-K_2'\rangle \\
&= (-)^{K_1+M_2+K_2}(-)^{K_1'+M_2'+K_2'}\langle L_1M_1K_1,L_2M_2K_2|\tilde{\Gamma}|L_1'M_1'K_1',L_2'M_2'K_2'\rangle^*
\end{aligned} \tag{75}$$

This symmetry permits to introduce a unitary transformation which transforms the Hermitian matrix into a real symmetric one. Instead of applying the transformation to the matrix associated to the diffusive operator we prefer to define a transformed basis. The matrix elements of the operator in the new basis are written as linear combinations of the elements in the original basis. This procedure complicates a little bit the formalism but saves a lot of computational time. The new basis set is

$$|\Lambda\rangle = \mathcal{N}e^{i\frac{\pi}{4}(j-1)}\left(|L_1M_1K_1,L_2M_2K_2\rangle + js|L_1M_1-K_1,L_2-M_2-K_2\rangle\right) \tag{76}$$

where the indexes L_1, M_1 and L_2 have the same variability of the old base, while for the other indexes we have

$$\left\{ \begin{array}{cccc} K_1 = 0 & K_2 = 0 & M_2 = 0 & j = (-)^{L_1+L_2} \\ K_1 = 0 & K_2 = 0 & 0 < M_2 \leq L_2 & j = \pm 1 \\ K_1 = 0 & 0 < K_2 \leq L_2 & -L_2 \leq M_2 \leq L_2 & j = \pm 1 \\ 0 < K_1 \leq L_1 & -L_2 \leq K_2 \leq L_2 & -L_2 \leq M_2 \leq L_2 & j = \pm 1 \end{array} \right. \tag{77}$$

The other two symbols to be defined are

$$s = (-)^{K_1+M_2+K_2} \tag{78}$$

and

$$\mathcal{N} = \left[2\left(1 + \delta_{K_1,0}\delta_{M_2,0}\delta_{K_2,0}\right)\right]^{-1/2} \tag{79}$$

It is straightforward to proof that in the new basis the matrix elements of the diffusive operator are

$$\begin{aligned} \langle \Lambda|\tilde{\Gamma}|\Lambda'\rangle &= 2\mathcal{N}\mathcal{N}'\left[\delta_{j,j'} Re\left\{\langle +|\tilde{\Gamma}|+\rangle + j's'\langle +|\tilde{\Gamma}|-\rangle\right\} + \right. \\ &\quad \left. + \delta_{j,-j'}\, j'\, Im\left\{\langle +|\tilde{\Gamma}|+\rangle + j's'\langle +|\tilde{\Gamma}|-\rangle\right\}\right] \end{aligned} \tag{80}$$

where $|+\rangle = |L_1M_1K_1, L_2M_2K_2\rangle$ and $|-\rangle = \hat{\mathcal{T}}|+\rangle$.

5 Starting vector

Let's recall that the diffusive operator is spanned over the following basis:

$$|\lambda\rangle = |L_1M_1K_1\rangle \otimes |L_2M_2K_2\rangle \tag{81}$$

with

$$|L_1M_1K_1\rangle = \sqrt{\frac{[L_1]}{8\pi^2}}\mathcal{D}^{L_1}_{M_1,K_1}(\mathbf{\Omega}_L) \tag{82}$$

$$|L_2M_2K_2\rangle = \sqrt{\frac{[L_2]}{8\pi^2}}\mathcal{D}^{L_2}_{M_2,K_2}(\mathbf{\Omega}) \tag{83}$$

The starting vector is defined by the physical observable:

$$|v\rangle = \sqrt{\frac{2[J]}{(1+\delta_{K,K'})}}C^J_{M,KK'}(\mathbf{\Omega}_O)P^{1/2}_{eq} \tag{84}$$

By use of properties of Wigner matrices

$$C^J_{M,KK'}(\mathbf{\Omega}_O) = \sum_{M'}\mathcal{D}^J_{M,M'}(\mathbf{\Omega}_L)C^J_{M',KK'}(\mathbf{\Omega}) = \frac{1}{2}\sum_{M'}\mathcal{D}^J_{M,M'}(\mathbf{\Omega}_L)\left[\mathcal{D}^J_{M',K}(\mathbf{\Omega}) + \mathcal{D}^J_{M',K'}(\mathbf{\Omega})\right] \tag{85}$$

Given:

$$P^{1/2}_{eq}(\mathbf{\Omega}_V, \mathbf{\Omega}) = \mathcal{N}e^{-U(\mathbf{\Omega})/2} \tag{86}$$

the starting vector can be rewritten as

$$|v\rangle = \sqrt{\frac{[J]}{2(1+\delta_{K,K'})}} \sum_{M'} \mathcal{D}^J_{M,M'}(\mathbf{\Omega}_L) \left[\mathcal{D}^J_{M',K}(\mathbf{\Omega}) + \mathcal{D}^J_{M',K'}(\mathbf{\Omega})\right] P_{eq}^{1/2}(\mathbf{\Omega}) \tag{87}$$

The projection of starting vector on basis is

$$\begin{aligned}
\langle v|\lambda\rangle &= \langle v|L_1M_1K_1, L_2M_2K_2\rangle = \\
&= \sqrt{\frac{[J]}{2(1+\delta_{K,K'})}} \sum_{M'} \langle \mathcal{D}^J_{M,M'}|L_1M_1K_1\rangle \times \\
&\quad \times \left[\langle \mathcal{D}^J_{M',K} P_{eq}^{1/2}|L_2M_2K_2\rangle + \langle \mathcal{D}^J_{M',K'} P_{eq}^{1/2}|L_2M_2K_2\rangle\right] = \\
&= \sqrt{\frac{[J]}{2(1+\delta_{K,K'})}} \sum_{M'} \sqrt{\frac{[L_1]}{8\pi^2}} \int d\mathbf{\Omega}_L \mathcal{D}^J_{M,M'} \mathcal{D}^{L_1}_{M_1,K_1} \times \\
&\quad \times \sqrt{\frac{[L_2]}{8\pi^2}} \left[\int d\mathbf{\Omega} \mathcal{D}^J_{M',K} \mathcal{D}^{L_2}_{M_2,K_2} P_{eq}^{1/2} + \int d\mathbf{\Omega} \mathcal{D}^J_{M',K'} \mathcal{D}^{L_2}_{M_2,K_2} P_{eq}^{1/2}\right] = \\
&= \mathcal{N} \sqrt{\frac{[L_2]}{2(1+\delta_{K,K'})}} \delta_{J,L_1} \delta_{M,M_1} \delta_{K_1,M_2} \times \\
&\quad \times \left[(-)^{M_2-K} \int_0^\pi d\beta \sin(\beta) d^{L_1}_{-K_1,-K}(\beta) d^{L_2}_{K_1,K_2}(\beta) \int_0^{2\pi} d\gamma e^{-i(K_2-K)\gamma} e^{-U(\beta,\gamma)/2} + \right. \\
&\quad \left. + (-)^{M_2-K'} \int_0^\pi d\beta \sin(\beta) d^{L_1}_{-K_1,-K'}(\beta) d^{L_2}_{K_1,K_2}(\beta) \int_0^{2\pi} d\gamma e^{-i(K_2-K')\gamma} e^{-U(\beta,\gamma)/2}\right]
\end{aligned} \tag{88}$$

The orienting potential is

$$U(\beta,\gamma) = c_{2,0}\mathcal{D}^2_{0,0} + c_{2,2}\left(\mathcal{D}^2_{0,2} + \mathcal{D}^2_{0,-2}\right) + c_{4,0}\mathcal{D}^4_{0,0} + c_{4,2}\left(\mathcal{D}^4_{0,2} + \mathcal{D}^4_{0,-2}\right) + c_{4,4}\left(\mathcal{D}^4_{0,4} + \mathcal{D}^4_{0,-4}\right) \tag{89}$$

and given that

$$d^2_{0,-2}(\beta) = d^2_{0,2}(\beta) \tag{90}$$

$$d^4_{0,-2}(\beta) = d^4_{0,2}(\beta) \tag{91}$$

$$d^4_{0,-4}(\beta) = d^4_{0,4}(\beta) \tag{92}$$

$$\tag{93}$$

the coefficients $c_{l,m}$ are real and the potential can be rewritten as

$$U(\beta,\gamma) = -2u_0(\beta) - 2u_2(\beta)\cos(2\gamma) - 2u_4(\beta)\cos(4\gamma) \tag{94}$$

with

$$u_0(\beta) = -\left[c_{2,0}d^2_{0,0}(\beta) + c_{4,0}d^4_{0,0}(\beta)\right]/2 \tag{95}$$

$$u_2 = -c_{2,2}d^2_{0,2}(\beta) - c_{4,2}d^4_{0,2}(\beta) \tag{96}$$

$$u_4 = -c_{4,4}d^4_{0,4}(\beta) \tag{97}$$

So we are left to evaluate the following integral:

$$\int_0^\pi d\beta \sin(\beta) d^{L_1}_{-K_1,-K}(\beta) d^{L_2}_{K_1,K_2}(\beta) e^{u_0(\beta)} \int_0^{2\pi} d\gamma e^{-i(K_2-K)\gamma} e^{u_2(\beta)\cos(2\gamma) + u_4(\beta)\cos(4\gamma)} \tag{98}$$

The idea is to try to evaluate analytically the integral in γ:

$$\begin{aligned}
A(\beta) &= \int_0^{2\pi} d\gamma e^{-i(K_2-K)\gamma} e^{u_2\cos(2\gamma)+u_4\cos(4\gamma)} = && (99)\\
&= \int_0^{2\pi} d\gamma \cos((K_2-K)\gamma) e^{u_2\cos(2\gamma)+u_4\cos(4\gamma)} = && (100)\\
&= \frac{1}{2}\int_0^{4\pi} d\theta \cos(n\theta) e^{u_2\cos(\theta)+u_4\cos(2\theta)} = && (101)\\
&= 2\int_0^{\pi} d\theta \cos(n\theta) e^{u_2\cos(\theta)+u_4\cos(2\theta)} && (102)
\end{aligned}$$

where $n = (K_2 - K)/2$ and the integral is non zero only for integer values of n.
It seems that it is not possible to give an analytical expression for $A(\beta)$, but it is possible to give an explicit evaluation. The modified Bessel functions of first kind represent the coefficients of the expansion of exponentials of trigonometric functions over cosines, so we can write:

$$e^{u_4 cos(2\theta)} = I_0(|u_4|) + 2\sum_{s=1}^{\infty}(-)^s I_s(|u_4|) cos(2s\theta) \tag{103}$$

with $I_n(z)$ a modified Bessel function of first kind of integer order n and argument z.
Substituting the last expression in $A(\beta)$ one obtains:

$$\begin{aligned}
A(\beta) &= 2\int_0^{\pi} d\theta \cos(n\theta) e^{u_2\cos(\theta)} e^{u_4\cos(2\theta)} =\\
&= 2\int_0^{\pi} d\theta \cos(n\theta) e^{u_2\cos(\theta)} \left[I_0(|u_4|) + 2\sum_{s=1}^{\infty}(-)^s I_s(|u_4|) cos(2s\theta)\right] =\\
&= 2\pi(-)^n I_0(|u_4|) I_n(|u_2|) + 4\sum_{s=1}^{\infty}(-)^s I_s(|u_4|)\int_0^{\pi} d\theta cos(n\theta) cos(2s\theta) e^{u_2 cos(\theta)} =\\
&= 2\pi(-)^n I_0(|u_4|) I_n(|u_2|) + 2\sum_{s=1}^{\infty}(-)^s I_s(|u_4|)\int_0^{\pi} d\theta \left[cos\left((n-2s)\theta\right) + cos\left((n+2s)\theta\right)\right] e^{u_2 cos(\theta)} =\\
&= 2\pi(-)^n I_0(|u_4|) I_n(|u_2|) + 2\pi(-)^n\sum_{s=1}^{\infty}(-)^s I_s(|u_4|)\left[I_{n-2s}(|u_2|) + I_{n+2s}(|u_2|)\right] && (104)
\end{aligned}$$

As can be seen if the potential does not depend on γ than the integral is $A(\beta) = 2\pi$, while in the case of only $u_4 = 0$ the integral has the explicit "simple" expression $A(\beta) = 2\pi(-)^n I_n(|u_2|)$. In the general case the integral is expressed as an infinite sum of products of modified Bessel functions of first kind.
Let's call $\Delta_n(|u_2|, |u_4|) = (-)^n\sum_{s=1}^{\infty}(-)^s I_s(|u_4|)\left[I_{n-2s}(|u_2|) + I_{n+2s}(|u_2|)\right]$ and $n^{(')} = |K_2 - K^{(')}|/2$, then the projection of the starting vector on the basis is:

$$\begin{aligned}
\langle v|\lambda\rangle &= \mathcal{N}\sqrt{\frac{[L_2]}{2(1+\delta_{K,K'})}}\delta_{J,L_1}\delta_{M,M_1}\delta_{K_1,M_2}\times\\
&\times\Bigg[(-)^{M_2-K+n}\int_0^{\pi} d\beta \sin(\beta) d^{L_1}_{-K_1,-K}(\beta) d^{L_2}_{K_1,K_2}(\beta) I_0(|u_4|) I_n(|u_2|) +\\
&+(-)^{M_2-K}\int_0^{\pi} d\beta \sin(\beta) d^{L_1}_{-K_1,-K}(\beta) d^{L_2}_{K_1,K_2}(\beta)\Delta_n(|u_2|,|u_4|) +
\end{aligned}$$

$$+(-)^{M_2-K'+n'}\int_0^\pi d\beta\sin(\beta)d^{L_1}_{-K_1,-K'}(\beta)d^{L_2}_{K_1,K_2}(\beta)I_0(u_4)I_{n'}(|u_2|)+$$
$$+(-)^{M_2-K'}\int_0^\pi d\beta\sin(\beta)d^{L_1}_{-K_1,-K'}(\beta)d^{L_2}_{K_1,K_2}(\beta)\Delta_{n'}(|u_|2,|u_4|)\Big] \tag{105}$$

The starting vector is non zero if $L_1 = J$, $M_1 = M$ and $K1 - M2 = 0$. Due to the global spatial rotational invariance, the two indexes L_1 and M_1 are diagonal in matrix elements, so once the physical observable has be chosen, they can be set equal to, respectively, J and M. Moreover, only functions with $J = 2$ and $M = 0$ will be employed so only basis functions with $L_1 = 2$ and $M_1 = 0$ will contribute to the determination of spectral densities.

By a simple substitution it is possible to change, in the matrix elements, the two indexes K_1 and M_2 with the two linear combinations $M_\pm = K_1 \pm M_2$. This substitution is useful in the case that $\mathbf{\Omega}_V = 0$ and the diffusion tenor ${}^V D_1$ is axial. In this case also M_- becomes diagonal and only basis functions with $M_- = 0$ are needed. Considering the transformation given in eq. (76), the representation of the starting vector on the new basis will be in general complex. It is easier to write the Lanczos algorithm is the vector is only real (or only complex), so we define the following observables

$$C^\pm_{K,K'} = C^2_{0,KK'} \pm C^{2\,*}_{0,KK'} = \left[\mathcal{D}^2_{0,K} \pm (-)^K\mathcal{D}^2_{0,-K}\right] + \left[\mathcal{D}^2_{0,K'} \pm (-)^{K'}\mathcal{D}^2_{0,-K'}\right] \tag{106}$$

The starting vector for the two observables is

$$|v^\pm\rangle = \mathcal{N}^\pm_{KK'}C^\pm_{KK'}P^{1/2}_{eq} \tag{107}$$

where the normalization constant is

$$\mathcal{N}^\pm_{KK'} = \frac{4(1+\delta_{K,K'}) \pm 2(\delta_{K,0}+\delta_{K',0}) \pm 4(-)^{K+K'}\delta_{K,-K'}}{[2]} \tag{108}$$

The representation on the basis is given by

$$\begin{aligned}\langle v^\pm|\Lambda\rangle \quad &\propto \quad \mathcal{N}^\pm_{KK'}\mathcal{N}e^{i\frac{\pi}{4}(j-1)}\Big(\langle C^\pm_{KK'}P^{1/2}_{eq}|L_1M_1K_1,L_2M_2K_2\rangle+ \\ &\qquad +js\langle C^\pm_{KK'}P^{1/2}_{eq}|L_1M_1-K_1,L_2-M_2-K_2\rangle\Big)\end{aligned} \tag{109}$$

With some boring passages it is possible to proof that

$$js\langle C^\pm_{KK'}P^{1/2}_{eq}|L_1M_1-K_1,L_2-M_2-K_2\rangle = \pm j\langle C^\pm_{KK'}P^{1/2}_{eq}|L_1M_1K_1,L_2M_2K_2\rangle^* \tag{110}$$

implying that

$$\begin{aligned}\langle v^\pm|\Lambda\rangle \quad &\propto \quad \mathcal{N}^\pm_{KK'}\mathcal{N}e^{i\frac{\pi}{4}(j-1)}\Big(\delta_{j,\pm1}Re\left\{\langle C^\pm_{KK'}P^{1/2}_{eq}|L_1M_1K_1,L_2M_2K_2\rangle\right\}+ \\ &\qquad +\delta_{j,\mp1}Im\left\{\langle C^\pm_{KK'}P^{1/2}_{eq}|L_1M_1K_1,L_2M_2K_2\rangle\right\}\Big)\end{aligned} \tag{111}$$

Due to the fact that the representation of the starting vector on the new basis is a linear combination of integrals (105) only the real part is non zero, i.e. the starting vector $|v^+\rangle$ is non-zero only for $j = 1$ (real vector) and $|v^-\rangle$ is non-zero only for $j = -1$ (immaginary vector):

$$\langle v^+|\Lambda\rangle \quad \propto \quad \mathcal{N}^+_{KK'}\mathcal{N}\delta_{j,1}\langle C^+_{KK'}P^{1/2}_{eq}|L_1M_1K_1,L_2M_2K_2\rangle \tag{112}$$
$$\langle v^-|\Lambda\rangle \quad \propto \quad \mathcal{N}^-_{KK'}\mathcal{N}\delta_{j,-1}\langle C^-_{KK'}P^{1/2}_{eq}|L_1M_1K_1,L_2M_2K_2\rangle \tag{113}$$

In the equation for $|v^-\rangle$ we omitted the complex i factor because before running the Lanczos tridiagonalization the starting vector is normalized. Being the complex i factor only a scaling constant it is removed in the normalization procedure and the vector, effectively, results to be real. In the case that D_{YZ} and D_{XY} for both the probe and the cage are zero in the OF and VF, respectively, than only matrix elements with $j = 1$ contribute to the spectral densities.

6 Spectral densities

We are interested in the calculation of spectral densities like

$$j^J_{M,KK'} = \langle \mathcal{D}^J_{M,K} P_{eq}^{1/2} | \left(i\omega - \tilde{\Gamma} \right)^{-1} | \mathcal{D}^J_{M,K'} P_{eq}^{1/2} \rangle \tag{114}$$

For our purposes we need only spectral densities for $J = 2$ and $M = 0$ and to have a light notation, J and M will be neglected in the symbols so we will indicate $j^2_{0,KK'}$ as $j_{KK'}$. These spectral densities are the Fourier-Laplace transforms of the correlation functions $g_{KK'}$

$$g_{KK'} = \langle \mathcal{D}^2_{0,K} P_{eq}^{1/2} | e^{-\tilde{\Gamma} t} | \mathcal{D}^2_{0,K'} P_{eq}^{1/2} \rangle \tag{115}$$

It is easier to calculate autocorrelation functions, which implies the employment of a symmetric Lanczos algorithm, so we introduced the "symmetrized" observables $C^{\pm}_{KK'}$ (eq. 106). It is easy to see that the spectral densities $j_{KK'}$ can be expressed as linear combinations of the symmetrized ones:

$$8 j_{KK'} = 4\mathcal{N}^+_{KK'} j^+_{KK'} + 4\mathcal{N}^-_{KK'} j^-_{KK'} - \mathcal{N}^+_{KK} j^+_{KK} - \mathcal{N}^-_{KK} j^-_{KK} - \mathcal{N}^+_{K'K'} j^+_{K'K'} - \mathcal{N}^-_{K'K'} j^-_{K'K'} \tag{116}$$

For both dipolar and CSA interactions, the spectral densities is given by

$$Re\left\{J^{\mu\mu}(\omega)\right\} = \sum_K |\mathcal{D}^2_{0,K}(\mathbf{\Omega}_\mu)|^2 Re\left\{j_{KK}(\omega)\right\} + 2 \sum_{K<K'} Re\left[\mathcal{D}^{2\,*}_{0,K}(\mathbf{\Omega}_\mu)\mathcal{D}^2_{0,K'}(\mathbf{\Omega}_\mu)\right] Re\left\{j_{KK'}(\omega)\right\} \tag{117}$$

where μ is "D" for dipolar and "C" for CSA interactions. The set of Euler angles $\mathbf{\Omega}_\mu$ is the one that transforms from OF to μF. So, on our choice of reference frames, we have, for the CSA,

$$\mathcal{D}^2_{K,0}(\mathbf{\Omega}_C) = \sum_{K'} \mathcal{D}^2_{K,K'}(\mathbf{\Omega}_D)\mathcal{D}^2_{K',0}(\mathbf{\Omega}_{CSA}) \tag{118}$$

The relaxation times T_1, T_2 and NOE are written, by standard arguments, as functions of the $J^{\mu\mu}(\omega)$ spectral densities.

Appendix A - Properties of Wigner matrices

In this appendix we report some useful properties of Wigner matrices.
Definition:
a Wigner matrix is a function of the set of Euler angles $\mathbf{\Omega}$:

$$\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) = e^{-iM\alpha} d^{L}_{M,K}\left(\beta\right) e^{-iK\gamma} \tag{A-1}$$

where $d^{L}_{M,K}\left(\beta\right)$ is the so called reduced Wigner matrix. A common formula to calculate its values is:

$$\begin{aligned} d^{L}_{M,K}\left(\beta\right) = \sum_{h} (-)^{h} \frac{[(L+M)!(L-M)!(L+K)!(L-K)!]^{1/2}}{(L+M-h)!(L-K-h)!h!(h+K-M)!} \times \\ \times (\cos\beta/2)^{2L+M-K-2h} (\sin\beta/2)^{2h+K-M} \end{aligned} \tag{A-2}$$

where the summation runs over all values of h for which the arguments of the factorials are non negative.
Symmetry:

$$\mathcal{D}^{L\,*}_{M,K}\left(\mathbf{\Omega}\right) = (-)^{M-K} \mathcal{D}^{L}_{-M,-K}\left(\mathbf{\Omega}\right) = \mathcal{D}^{L}_{K,M}(-\mathbf{\Omega}) \tag{A-3}$$

Product:

$$\begin{aligned} \mathcal{D}^{L_1}_{M_1,K_1}\left(\mathbf{\Omega}\right) \mathcal{D}^{L_2}_{M_2,K_2}\left(\mathbf{\Omega}\right) = \sum_{L_3} [L_3] \begin{pmatrix} L_1 & L_2 & L_3 \\ M_1 & M_2 & M_3 \end{pmatrix} \times \\ \times \begin{pmatrix} L_1 & L_2 & L_3 \\ K_1 & K_2 & K_3 \end{pmatrix} \mathcal{D}^{L_3\,*}_{M_3,K_3}\left(\mathbf{\Omega}\right) \end{aligned} \tag{A-4}$$

with $|L_1 - L_2| \le L_3 \le (L_1 + L_2)$, $M_3 = -\left(M_1 + M_2\right)$, $K_3 = -\left(K_1 + K_2\right)$ and $[L_3] = 2L_3 + 1$.
Internal product:
given *two* Wigner matrices ($\mathbf{\Omega}$ dependence will be omitted):

$$\int d\mathbf{\Omega} \mathcal{D}^{L_1\,*}_{M_1,K_1} \mathcal{D}^{L_2}_{M_2,K_2} = \frac{8\pi^2}{[L_1]} \delta_{L_1,L_2} \delta M_1, M_2 \delta_{K_1,K_2} \tag{A-5}$$

among *three* Wigner matrices:

$$\int d\mathbf{\Omega} \mathcal{D}^{L_1}_{M_1,K_1} \mathcal{D}^{L_2}_{M_2,K_2} \mathcal{D}^{L_3}_{M_3,K_3} = 8\pi^2 \begin{pmatrix} L_1 & L_2 & L_3 \\ M_1 & M_2 & M_3 \end{pmatrix} \begin{pmatrix} L_1 & L_2 & L_3 \\ K_1 & K_2 & K_3 \end{pmatrix} \tag{A-6}$$

Transformation by rotation:
give and irreducible spherical tensor $T^{(l,\,m)}_{a}$ defined in frame a, it's expression in frame b is given by:

$$T^{(l,m)}_{a} = \sum_{k} \mathcal{D}^{l}_{m,k}\left(\mathbf{\Omega}_{a\to b}\right) T^{(l,k)}_{b} \tag{A-7}$$

where $\mathbf{\Omega}_{a\to b}$ is the set of Euler angles transforming from a to b. The inverse transformation is:

$$T^{(l,k)}_{b} = \sum_{m} \mathcal{D}^{l\,*}_{m,k}\left(\mathbf{\Omega}_{b\to a}\right) T^{(l,m)}_{a} \tag{A-8}$$

Angular momentum operators:
a Wigner matrix which depends on a set of Euler angles $\mathbf{\Omega}$ transforming from a frame a to a frame b is an eigenfunction of the angular momentum operators defined on the two frames, and also of their z proiections.
In frame a:

$$\begin{cases} {}^{a}\hat{J}^{2}\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) = L\left(L+1\right)\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) \\ {}^{a}\hat{J}_{Z}\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) = -M\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) \\ {}^{a}\hat{J}_{\pm}\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) = -c^{\mp}_{L,M}\mathcal{D}^{L}_{M\mp1,K}\left(\mathbf{\Omega}\right) \end{cases} \tag{A-9}$$

In frame b:

$$\begin{cases} {}^{b}\hat{J}^{2}\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) = L\left(L+1\right)\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) \\ {}^{b}\hat{J}_{Z}\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) = -K\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) \\ {}^{b}\hat{J}_{\pm}\mathcal{D}^{L}_{M,K}\left(\mathbf{\Omega}\right) = -c^{\pm}_{L,K}\mathcal{D}^{L}_{M,K\pm1}\left(\mathbf{\Omega}\right) \end{cases} \tag{A-10}$$

with $c^{\pm}_{L,M} = \sqrt{L\left(L+1\right) - M\left(M \pm 1\right)}$.

Appendix B - Irreducible spherical tensor operator

The potential independent part of the diffusive operator is substantially a sum of terms of the type $\hat{\boldsymbol{J}}^{\dagger}\boldsymbol{D}\hat{\boldsymbol{J}}$. It is possible to write this operator, which is expressed in cartesian coordinates, as the contraction of rank zero of a spherical tensor of rank two, $\boldsymbol{D}^{(2)}$ and a spherical tensorial operator of rank two $\hat{\boldsymbol{\mathcal{K}}}^{(2)}$, i.e.

$$\hat{\boldsymbol{J}}^{\dagger}\boldsymbol{D}\hat{\boldsymbol{J}} = \left[\boldsymbol{D}^{(2)} \otimes \hat{\boldsymbol{\mathcal{K}}}^{(2)}\right]_0^0 \tag{B-1}$$

The contraction is the combination of three components

$$\left[\boldsymbol{D}^{(2)} \otimes \hat{\boldsymbol{\mathcal{K}}}^{(2)}\right]_0^0 = D^{(0)}\hat{\mathcal{K}}^{(0)} \oplus D^{(1)}\hat{\mathcal{K}}^{(1)} \oplus D^{(2)}\hat{\mathcal{K}}^{(2)} \tag{B-2}$$

The component of rank zero gives informations on the isotropic characteristics, the rank one part is linked to the asymmetry and the rank two component contains informations of the anisotropy. Because the diffusion tensor is symmetric then $D^{(1)} = 0$ so only the components of rank zero and two remain to be considered. Using the standard procedure it is possible to write:

$$D^{(0,0)} = -\frac{1}{\sqrt{3}}\left(D_{XX} + D_{YY} + D_{ZZ}\right) \tag{B-3}$$

$$D^{(2,0)} = \frac{1}{\sqrt{6}}\left(2D_{ZZ} - D_{XX} - D_{YY}\right) \tag{B-4}$$

$$D^{(2,\pm1)} = \mp\left(D_{XZ} \pm iD_{YZ}\right) \tag{B-5}$$

$$D^{(2,\pm2)} = \frac{D_{XX} - D_{YY}}{2} \pm iD_{XY} \tag{B-6}$$

and

$$\hat{\mathcal{K}}^{(0,0)} = -\frac{1}{\sqrt{3}}\left[\frac{1}{2}\left(\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+\right) + \hat{J}_Z^2\right] \tag{B-7}$$

$$\hat{\mathcal{K}}^{(2,0)} = \frac{1}{\sqrt{6}}\left(3\hat{J}_Z^2 + \sqrt{3}\hat{\mathcal{K}}^{(0,0)}\right) \tag{B-8}$$

$$\hat{\mathcal{K}}^{(2,\pm1)} = \mp\frac{1}{2}\left(\hat{J}_Z\hat{J}_\pm + \hat{J}_\pm\hat{J}_Z\right) \tag{B-9}$$

$$\hat{\mathcal{K}}^{(2,\pm2)} = \frac{1}{2}\hat{J}_\pm^2 \tag{B-10}$$

Operator $\hat{J}_d$ has a little different structure from the other three operators:

$$\hat{J}_d = -{}^V\hat{\boldsymbol{J}}^{\dagger}(\boldsymbol{\Omega}_L){}^V\boldsymbol{D}_1\hat{\boldsymbol{J}}(\boldsymbol{\Omega}) - {}^V\hat{\boldsymbol{J}}^{\dagger}(\boldsymbol{\Omega}){}^V\boldsymbol{D}_1\hat{\boldsymbol{J}}(\boldsymbol{\Omega}_L) \tag{B-11}$$

The two angular momentum operators ${}^V\hat{\boldsymbol{J}}(\boldsymbol{\Omega})$ and ${}^V\hat{\boldsymbol{J}}(\boldsymbol{\Omega}_L)$ act on two orthogonal sub-spaces, so they commute and it is possible to sum the two contributions. The spherical representation of $\hat{J}_d$ is the same of that given in equations B-7-B-10, multiplied by a factor of -2.

Appendix C - Application of Wigner-Eckart theorem

Let's consider two frames a and b, $\boldsymbol{\Omega}$ as the set of Euler angles that transforms from a to b. Thanks to the Wigner-Eckart theorem we can write, for the components of the operator $\hat{\mathcal{K}}_a^{(2,m)}$ defined in a:

$$\langle LMK|\hat{\mathcal{K}}_a^{(2,m)}|L'M'K'\rangle = (-)^{L-K} \begin{pmatrix} L & 2 & L' \\ -K & m & K' \end{pmatrix} \langle LM\|\hat{\mathcal{K}}_a^{(2)}\|L'M'\rangle \tag{C-1}$$

so if the reduced matrix element is known, the calculation of all the five matrix elements of the rank 2 tensorial operator simply reduces to the evaluation of five $3j$ symbols.
The calculation of the reduced matrix element is quite simple if one considers the $(2,2)$ component, for which:

$$\langle LMK|\hat{\mathcal{K}}_a^{(2,2)}|L'M'K'\rangle = \frac{1}{2}\delta_{LL'}\delta_{MM'}\delta_{K,K'+2}c^{+}_{L,K-1}c^{+}_{L,K-2} \tag{C-2}$$

From Wigner-Eckart theorem one can indipendently write:

$$\langle LMK|\hat{\mathcal{K}}_a^{(2,2)}|L'M'K'\rangle = (-)^{L-K} \begin{pmatrix} L & 2 & L' \\ -K & 2 & K' \end{pmatrix} \langle LM\|\hat{\mathcal{K}}_a^{(2)}\|L'M'\rangle \tag{C-3}$$

The last two equations must be equal and this is true only if $L = L'$ and $M = M'$ in the last equation, that is

$$\begin{aligned} \langle LMK|\hat{\mathcal{K}}_a^{(2,2)}|L'M'K'\rangle = \delta_{LL'}\delta_{MM'}\delta_{K,K'+2}(-)^{L-K} \begin{pmatrix} L & 2 & L \\ -K & 2 & K-2 \end{pmatrix} \times \\ \times\langle LM\|\hat{\mathcal{K}}_a^{(2)}\|L'M'\rangle \end{aligned} \tag{C-4}$$

Using the Racah formula for $3j$ symbols one can write

$$\begin{aligned} \begin{pmatrix} L & 2 & L \\ -K & 2 & K-2 \end{pmatrix} = \left[4!\,(L-K)!\,(L+K)!\,(L-K+2)!\,(L+K-2)!\right]^{1/2} \times \\ \times\sqrt{\Delta\,(L,2,L)}\sum_t \frac{(-)^{t+L-K}}{t!\,(2-t)!\,(L-2-K+t)!\,(4-t)!\,(L+K-t)!\,(t-2)!} \end{aligned} \tag{C-5}$$

where $\Delta\,(L,2,L) = 4(2L-2)!/(2L+3)!$ and the summation is over all integers t such that the arguments of the factorials are non-negative.
The formula is different from zero only for $t = 2$, so the $3j$ symbol can be expressed in a simple analytic form

$$\begin{pmatrix} L & 2 & L \\ -K & 2 & K-2 \end{pmatrix} = (-)^{L-K}\sqrt{\frac{3}{2}}\sqrt{\Delta\,(L,2,L)}\left[\frac{(L+K)!\,(L-K+2)!}{(L-K)!\,(L+K-2)!}\right] \tag{C-6}$$

and by expressing

$$\begin{aligned} (L+K)! &= (L+K-2)!\,(L+K-1)\,(L+K) \\ (L-K+2)! &= (L-K)!\,(L-K+1)\,(L-K+2) \end{aligned} \tag{C-7}$$

one obtains

$$\left(\begin{array}{ccc} L & 2 & L \\ -K & 2 & K-2 \end{array}\right) = (-)^{L-K}\sqrt{\frac{3}{2}}\sqrt{\Delta\left(L,2,L\right)}\times \\ \times\sqrt{\left(L+K-1\right)\left(L-K+1\right)\left(L-K+2\right)\left(L+K\right)} \tag{C-8}$$

With boring passages it can be proofed that

$$\sqrt{\left(L+K-1\right)\left(L-K+1\right)\left(L-K+2\right)\left(L+K\right)} = c^{+}_{L,K-1}c^{+}_{L,K-2} \tag{C-9}$$

so by comparison the reduced matrix element can be found to be

$$\langle LM\|\hat{\mathcal{K}}^{(2)}_{a}\|L'M'\rangle = \delta_{LL'}\delta_{MM'}\sqrt{\frac{(2L+3)!}{24\,(2L-2)!}} \tag{C-10}$$

For the operator defined in b, $\hat{\mathcal{K}}^{(2,m)}_{b}$, we can make analogous considerations. Remembering that the action of shift operators ${}^{b}\hat{J}_{\pm}$ have the opposite behavior of the shift operators in a, it can be found that

$$\langle LMK|\hat{\mathcal{K}}^{(2,m)}_{b}|L'M'K'\rangle = (-)^{L-M}\left(\begin{array}{ccc} L & 2 & L' \\ -M & -m & M' \end{array}\right)\langle LK\|\hat{\mathcal{K}}^{(2)}_{b}\|L'K'\rangle \tag{C-11}$$

with

$$\langle LK\|\hat{\mathcal{K}}^{(2)}_{b}\|L'K'\rangle = \delta_{LL'}\delta_{KK'}\sqrt{\frac{(2L+3)!}{24\,(2L-2)!}} \tag{C-12}$$