Supporting Information

to

Orientation order and rotation mobility of nitroxide biradicals determined by quantitative simulation of EPR spectra.

Matrix elements for rotation diffusion superoperator in the case of non-coincident orientation and rotation tensors.

The goal of this section is to determine the matrix elements of stochastic Liouville superoperator for the purpose of EPR spectra simulation in the situation, when the principal axes of rotation diffusion are not coincident with the principal axes of molecule orientation.

Let us consider Smoluchowski equation for rotation diffusion in orientation potential [1, 2]:

$$\frac{\partial P(\Omega,\mathrm{t}|\Omega_0,0)}{\partial t} = -\mathbf{\Gamma}P(\Omega,\mathrm{t}|\Omega_0,0)$$

$$= -\mathbf{LRL}P(\Omega,\mathrm{t}|\Omega_0,0) - \mathbf{LRL}\left(\frac{U(\Omega)}{k_B T}\right)P(\Omega,\mathrm{t}|\Omega_0,0) = \quad (1)$$

$$= -\sum_{i,j=x,y,z} R_{ij}\left[L_i L_j + L_i\left(L_j\mathcal{U}\right)\right]P(\Omega,\mathrm{t}|\Omega_0,0)$$

Here $\mathcal{P} = P(\Omega,\mathrm{t}|\Omega_0,0)$ is the probability density to find the molecule at moment t in the orientation given by Euler angles Ω, on the condition that at zero time the molecule had the orientaition Ω_0, $\mathbf{\Gamma}$ is the stationary Markovian operator defining correlation functions for rotation, diffusion tensor is assumed to be symmetric, $R_{ij} = R_{ji}$, $\mathbf{L}$ is the operator of infinitesimal rotation, identical to dimensionless quantum-mechanical angular momentum operator, $\mathcal{U} = \frac{U(\Omega)}{k_B T}$ is dimensionless mean-field potential.

Equation (1) defines stationary orientation distribution $P_0(\Omega)$, such that $\mathbf{\Gamma}P_0(\Omega) = 0$. Explicit expression for $P_0(\Omega)$ is given by Maxwell–Boltzmann distribution:

$$P_0(\Omega) = e^{-\mathcal{U}}$$

For calculation of EPR spectra, one should work with symmetrized superoperator

$$\hat{\mathbf{\Gamma}} = P_0(\Omega)^{-1/2}\mathbf{\Gamma}P_0(\Omega)^{1/2} \quad (2)$$

which is self-adjoint. By applying symmetrization transformation (2) to expression (1), one obtains:

$$\hat{\mathbf{\Gamma}} = e^{\mathcal{U}/2}\mathbf{\Gamma}e^{-\mathcal{U}/2} = e^{\mathcal{U}/2}\sum_{i,j=x,y,z} R_{ij}\left[L_iL_j + L_i\left(L_j\mathcal{U}\right)\right]e^{-\mathcal{U}/2}\mathcal{P} \tag{3}$$

Since the angular momentum operator is the first order differential operator, the following identities can be used:

$$\begin{aligned} &L_i\left(f\cdot g\right) = \left(L_if\right)\cdot g + f\cdot\left(L_ig\right) \\ &L_i\left(e^{-\mathcal{U}/2}\right) = \left(-\frac{1}{2}\right)e^{-\mathcal{U}/2}\left(L_i\mathcal{U}\right) \end{aligned} \tag{4}$$

By using expressions (4), equation (3) transforms into

$$\begin{aligned} \hat{\mathbf{\Gamma}} &= \sum_{i,j=x,y,z} R_{ij}\left[-\frac{1}{4}\left(L_i\mathcal{U}\right)\left(L_j\mathcal{U}\right)\mathcal{P} + \frac{1}{2}\left(L_iL_j\mathcal{U}\right)\mathcal{P} + \frac{1}{2}\left(L_i\mathcal{P}\right)\left(L_j\mathcal{U}\right) - \frac{1}{2}\left(L_i\mathcal{U}\right)\left(L_j\mathcal{P}\right) + \left(L_iL_j\mathcal{P}\right)\right] \\ &= \sum_{i,j=x,y,z} R_{ij}\left[-\frac{1}{4}\left(L_i\mathcal{U}\right)\left(L_j\mathcal{U}\right)\mathcal{P} + \frac{1}{2}\left(L_iL_j\mathcal{U}\right)\mathcal{P} + \left(L_iL_j\mathcal{P}\right)\right] \end{aligned} \tag{5}$$

The second equality in (5) follows from the symmetry of diffusion tensor, $D_{ij} = D_{ji}$. By expanding the sum in (5), one obtains:

$$\begin{aligned} \hat{\mathbf{\Gamma}} = &R_{xx}\left[-\frac{1}{4}\left(L_x\mathcal{U}\right)^2\mathcal{P} + \frac{1}{2}\left(L_x{}^2\mathcal{U}\right)\mathcal{P} + \left(L_x{}^2\mathcal{P}\right)\right] \\ &+R_{yy}\left[-\frac{1}{4}\left(L_y\mathcal{U}\right)^2\mathcal{P} + \frac{1}{2}\left(L_y{}^2\mathcal{U}\right)\mathcal{P} + \left(L_y{}^2\mathcal{P}\right)\right] \\ &+R_{zz}\left[-\frac{1}{4}\left(L_z\mathcal{U}\right)^2\mathcal{P} + \frac{1}{2}\left(L_z{}^2\mathcal{U}\right)\mathcal{P} + \left(L_z{}^2\mathcal{P}\right)\right] \\ &+R_{xy}\left[-\frac{1}{2}\left(L_x\mathcal{U}\right)\left(L_y\mathcal{U}\right)\mathcal{P} + \frac{1}{2}\left(\left(L_xL_y + L_yL_x\right)\mathcal{U}\right)\mathcal{P} + \left(L_xL_y + L_yL_x\right)\mathcal{P}\right] \\ &+R_{xz}\left[-\frac{1}{2}\left(L_x\mathcal{U}\right)\left(L_z\mathcal{U}\right)\mathcal{P} + \frac{1}{2}\left(\left(L_xL_z + L_zL_x\right)\mathcal{U}\right)\mathcal{P} + \left(L_xL_z + L_zL_x\right)\mathcal{P}\right] \\ &+R_{yz}\left[-\frac{1}{2}\left(L_y\mathcal{U}\right)\left(L_z\mathcal{U}\right)\mathcal{P} + \frac{1}{2}\left(\left(L_yL_z + L_zL_y\right)\mathcal{U}\right)\mathcal{P} + \left(L_yL_z + L_zL_y\right)\mathcal{P}\right] \end{aligned} \tag{6}$$

The expression (6) can be rewritten with the use of operators $\mathbf{L}^2, L_z, L_\pm \equiv L_x \pm iL_y$, for which the set of Wigner functions $\mathcal{D}^L_{MK}\left(\Omega\right)$ with constant L and M is closed. It is convenient to adopt the following notation for combinations of diffusion tensor components [2]:

$$\rho = \frac{R_{xx} + R_{yy}}{2}, \varepsilon = \frac{R_{xx} - R_{yy} + 2iR_{xy}}{R_{xx} + R_{yy}}, \eta = \frac{2R_{zz}}{R_{xx} + R_{yy}}, \kappa = \frac{2\left(R_{xz} + iR_{yz}\right)}{R_{xx} + R_{yy}} \tag{7}$$

Then the equation (6) transforms into:

$$\begin{aligned}
\hat{\mathbf{\Gamma}} = & -\frac{\varepsilon^{*}\rho}{8}\left(L_{+}\mathcal{U}\right)^{2}\mathcal{P} - \frac{\varepsilon\rho}{8}\left(L_{-}\mathcal{U}\right)^{2}\mathcal{P} - \frac{\rho}{4}\left(L_{+}\mathcal{U}\right)\left(L_{-}\mathcal{U}\right)\mathcal{P} - \frac{\eta\rho}{4}\left(L_{z}\mathcal{U}\right)^{2}\mathcal{P} \\
& + \frac{\varepsilon^{*}\rho}{4}\left(L_{+}^{2}\mathcal{U}\right)\mathcal{P} + \frac{\varepsilon\rho}{4}\left(L_{-}^{2}\mathcal{U}\right)\mathcal{P} + \frac{\rho}{2}\left(\mathbf{L}^{2}\mathcal{U}\right)\mathcal{P} + \frac{(\eta-1)\rho}{2}\left(L_{z}^{2}\mathcal{U}\right)\mathcal{P} \\
& + \frac{\varepsilon^{*}\rho}{2}L_{+}^{2}\mathcal{P} + \frac{\varepsilon\rho}{2}L_{-}^{2}\mathcal{P} + \rho\mathbf{L}^{2}\mathcal{P} + (\eta-1)\rho L_{z}^{2}\mathcal{P} \\
& - \frac{\kappa^{*}\rho}{4}\left(L_{+}\mathcal{U}\right)\left(L_{z}\mathcal{U}\right)\mathcal{P} - \frac{\kappa\rho}{4}\left(L_{-}\mathcal{U}\right)\left(L_{z}\mathcal{U}\right)\mathcal{P} \\
& + \frac{\kappa^{*}\rho}{4}\left[\left(L_{+}L_{z} + L_{z}L_{+}\right)\mathcal{U}\right]\mathcal{P} + \frac{\kappa\rho}{4}\left[\left(L_{-}L_{z} + L_{z}L_{-}\right)\mathcal{U}\right]\mathcal{P} \\
& + \frac{\kappa^{*}\rho}{2}\left(L_{+}L_{z} + L_{z}L_{+}\right)\mathcal{P} + \frac{\kappa\rho}{2}\left(L_{-}L_{z} + L_{z}L_{-}\right)\mathcal{P}
\end{aligned} \tag{8}$$

The items in (8) can be divided into two groups. The first group contains the terms, which are independent of the mean-field potential:

$$\begin{aligned}
\hat{\mathbf{\Gamma}}_{iso} = & \frac{\varepsilon^{*}\rho}{2}L_{+}^{2}\mathcal{P} + \frac{\varepsilon\rho}{2}L_{-}^{2}\mathcal{P} + \rho\mathbf{L}^{2}\mathcal{P} + (\eta-1)\rho L_{z}^{2}\mathcal{P} \\
& + \frac{\kappa^{*}\rho}{2}\left(L_{+}L_{z} + L_{z}L_{+}\right)\mathcal{P} + \frac{\kappa\rho}{2}\left(L_{-}L_{z} + L_{z}L_{-}\right)\mathcal{P}
\end{aligned} \tag{9}$$

The remaining terms, i. e. those depending on mean-field potential, comprise the second group:

$$\begin{aligned}
\hat{\mathbf{\Gamma}}_{U} = & -\frac{\varepsilon^{*}\rho}{8}\left(L_{+}\mathcal{U}\right)^{2}\mathcal{P} - \frac{\varepsilon\rho}{8}\left(L_{-}\mathcal{U}\right)^{2}\mathcal{P} - \frac{\rho}{4}\left(L_{+}\mathcal{U}\right)\left(L_{-}\mathcal{U}\right)\mathcal{P} - \frac{\eta\rho}{4}\left(L_{z}\mathcal{U}\right)^{2}\mathcal{P} \\
& + \frac{\varepsilon^{*}\rho}{4}\left(L_{+}^{2}\mathcal{U}\right)\mathcal{P} + \frac{\varepsilon\rho}{4}\left(L_{-}^{2}\mathcal{U}\right)\mathcal{P} + \frac{\rho}{2}\left(\mathbf{L}^{2}\mathcal{U}\right)\mathcal{P} + \frac{(\eta-1)\rho}{2}\left(L_{z}^{2}\mathcal{U}\right)\mathcal{P} \\
& - \frac{\kappa^{*}\rho}{4}\left(L_{+}\mathcal{U}\right)\left(L_{z}\mathcal{U}\right)\mathcal{P} - \frac{\kappa\rho}{4}\left(L_{-}\mathcal{U}\right)\left(L_{z}\mathcal{U}\right)\mathcal{P} \\
& + \frac{\kappa^{*}\rho}{4}\left[\left(L_{+}L_{z} + L_{z}L_{+}\right)\mathcal{U}\right]\mathcal{P} + \frac{\kappa\rho}{4}\left[\left(L_{-}L_{z} + L_{z}L_{-}\right)\mathcal{U}\right]\mathcal{P}
\end{aligned} \tag{10}$$

The operator $\hat{\mathbf{\Gamma}}$ will be calculated in the basis of normalized Wigner functions:

$$
\begin{aligned}
\left|LMK\right\rangle &= \sqrt{\frac{2L+1}{8\pi^2}}\mathcal{D}_{MK}^{L}(\Omega) \\
\left\langle LMK\right| &= \sqrt{\frac{2L+1}{8\pi^2}}\mathcal{D}_{MK}^{L}{}^{*}(\Omega)
\end{aligned} \tag{11}
$$

Then the corresponding matrix elements are given by

$$
\left\langle L_1M_1K_1\right|\hat{\mathbf{\Gamma}}\left|L_2M_2K_2\right\rangle = \frac{\sqrt{(2L_1+1)(2L_2+1)}}{8\pi^2}\int d\Omega \mathcal{D}_{M_1K_1}^{L_1}{}^{*}(\Omega)\hat{\mathbf{\Gamma}}\mathcal{D}_{M_2K_2}^{L_2}(\Omega) \tag{12}
$$

The following properties of the angular momentum operators are used for calculation of matrix elements:

$$
L_{\pm}{}^{2}\mathcal{D}_{MK}^{L}(\Omega) = \sqrt{\left[L(L+1)-K(K\pm1)\right]\left[L(L+1)-(K\pm1)(K\pm2)\right]}\mathcal{D}_{M\ K\pm2}^{L}(\Omega) \tag{13}
$$

$$
\begin{aligned}
L_{\pm}L_{z}\left[\mathcal{D}_{MK}^{L}(\Omega)\right] &= K\sqrt{L(L+1)-K(K\pm1)}\mathcal{D}_{M\ K\pm1}^{L}(\Omega) \\
L_{z}L_{\pm}\left[\mathcal{D}_{MK}^{L}(\Omega)\right] &= (K\pm1)\sqrt{L(L+1)-K(K\pm1)}\mathcal{D}_{M\ K\pm1}^{L}(\Omega)
\end{aligned} \tag{14}
$$

Also, the following notation is used for eigenvalues of ladder operators:

$$
M_{\pm}(L,K) \equiv \sqrt{L(L+1)-K(K\pm1)} \tag{15}
$$

By applying Eqs. (12), (13) and (14) to expression (9), one obtains the matrix elements of the superoperator $\hat{\mathbf{\Gamma}}_{iso}$:

$$
\begin{aligned}
&\left\langle L_1M_1K_1\right|\hat{\mathbf{\Gamma}}_{iso}\left|L_2M_2K_2\right\rangle = \\
&= \delta_{L_1L_2}\delta_{M_1M_2}\Bigg\{\delta_{K_1K_2}\left[\rho L_1(L_1+1)+(\eta-1)\rho K_1{}^2\right] \\
&\qquad + \delta_{K_1\ K_2+1}\left[\frac{\kappa^{*}\rho}{2}(2K_2+1)M_{+}(\mathrm{L}_1,K_2)\right] \\
&\qquad + \delta_{K_1\ K_2-1}\left[\frac{\kappa\rho}{2}(2K_2-1)M_{-}(\mathrm{L}_1,K_2)\right] \\
&\qquad + \delta_{K_1\ K_2+2}\left[\frac{\varepsilon^{*}\rho}{2}M_{+}(\mathrm{L}_1,K_2)M_{+}(\mathrm{L},K_2+1)\right] \\
&\qquad + \delta_{K_1\ K_2-2}\left[\frac{\varepsilon\rho}{2}M_{-}(\mathrm{L}_1,K_2)M_{-}(\mathrm{L},K_2-1)\right]\Bigg\}
\end{aligned} \tag{16}
$$

Let us now turn to calculating matrix elements for potential-dependent terms $\hat{\mathbf{\Gamma}}_{U}$. For the mean-field potential, the decomposition in Wigner functions is used

$$\mathcal{U} = -\sum_{J=0}^{\infty}\sum_{q=-J}^{J} a_q^J \cdot \mathcal{D}_{0q}^J(\Omega) \tag{17}$$

Only terms with even J are non-zero in (17), due to the fact that the mean-field potential is centrosymmetric. The superoperator $\hat{\mathbf{\Gamma}}_U$ can also be decomposed into the series in Wigner functions:

$$\hat{\mathbf{\Gamma}}_U = \sum_{J=0}^{\infty}\sum_{q=-J}^{J} \mathcal{X}_q^J \cdot \mathcal{D}_{0q}^J(\Omega) \tag{18}$$

For the components $\mathcal{X}_q^J$ the same selection rules hold as for the potential decomposition terms a_q^J.

The matrix elements, which correspond to equation (18), are given by

$$\begin{aligned} \langle L_1M_1K_1|\hat{\mathbf{\Gamma}}_U|L_2M_2K_2\rangle &= \sum_{L=0}^{\infty}\sum_{K=-L}^{L}\frac{\sqrt{(2L_1+1)(2L_2+1)}}{8\pi^2}\mathcal{X}_K^L \\ &\quad\times\int d\Omega\left[\mathcal{D}_{M_1K_1}^{L_1}{}^*(\Omega)\hat{\mathbf{\Gamma}}\mathcal{D}_{M_2K_2}^{L_2}(\Omega)\mathcal{D}_{0K}^{L}(\Omega)\right] \\ &= \sum_{L=0}^{\infty}\sqrt{(2L_1+1)(2L_2+1)}\mathcal{X}_{K_1-K_2}^L \\ &\quad\times(-1)^{M_1+K_1}\begin{pmatrix} L_2 & L & L_1 \\ M_2 & 0 & -M_1\end{pmatrix}\begin{pmatrix} L_2 & L & L_1 \\ K_2 & K_1-K_2 & -K_1\end{pmatrix} \end{aligned} \tag{19}$$

The last equality in (19) was obtained with the use of Clebsch-Gordan decomposition:

$$\begin{aligned} &\mathcal{D}_{M_1N_1}^{J_1}(\Omega)\cdot\mathcal{D}_{M_2N_2}^{J_2}(\Omega) = \\ &= \sum_{J=|J_1-J_2|}^{J_1+J_2}\sum_{M,N=-J}^{J}(-1)^{M+N}(2J+1)\begin{pmatrix} J_1 & J & J_2 \\ M_1 & -M & M_2\end{pmatrix}\begin{pmatrix} J_1 & J & J_2 \\ N_1 & -N & N_2\end{pmatrix}\mathcal{D}_{MN}^J(\Omega) \end{aligned} \tag{20}$$

For calculating the terms $\mathcal{X}_K^L$, individual terms in (10) should be expanded in series in Wigner functions, as follows:

$$L_{\pm}\mathcal{U} = -\sum_{J=0}^{\infty}\sum_{q=-J}^{J} a_q^J \cdot M_{\pm}(J,q)\mathscr{D}_{0q\pm1}^{J}(\Omega)$$

$$\mathbf{L}^2\mathcal{U} = -\sum_{Jq} a_q^J \cdot J(J+1)\mathscr{D}_{0q}^{J}(\Omega)$$

$$\begin{aligned}(L_{\pm}\mathcal{U})^2 &= \sum_{J_1q_1J_2q_2} a_{q_1}^{J_1}a_{q_2}^{J_2} \cdot M_{\pm}(J_1,q_1)M_{\pm}(J_2,q_2)\mathscr{D}_{0q_1\pm1}^{J_1}(\Omega)\mathscr{D}_{0q_2\pm1}^{J_2}(\Omega) \\ &= \sum_{J,q}(-1)^q(2J+1)\mathscr{D}_{0q}^{J}(\Omega)\sum_{J_1q_1J_2q_2} a_{q_1}^{J_1}a_{q_2}^{J_2} \cdot M_{\pm}(J_1,q_1)M_{\pm}(J_2,q_2) \\ &\times\begin{pmatrix} J_1 & J & J_2 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} J_1 & J & J_2 \\ q_1\pm1 & -q & q_2\pm1\end{pmatrix}\end{aligned} \tag{21}$$

$$\begin{aligned}(L_{+}\mathcal{U})(L_{-}\mathcal{U}) &= \sum_{J_1q_1J_2q_2} a_{q_1}^{J_1}a_{q_2}^{J_2} \cdot M_{+}(J_1,q_1)M_{-}(J_1,q_1)\mathscr{D}_{0q_1+1}^{J_1}(\Omega)\mathscr{D}_{0q_2-1}^{J_2}(\Omega) \\ &= \sum_{J,q}(-1)^q(2J+1)\mathscr{D}_{0q}^{J}(\Omega)\sum_{J_1q_1J_2q_2} a_{q_1}^{J_1}a_{q_2}^{J_2} \cdot M_{+}(J_1,q_1)M_{-}(J_1,q_2) \\ &\times\begin{pmatrix} J_1 & J & J_2 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} J_1 & J & J_2 \\ q_1+1 & -q & q_2-1\end{pmatrix}\end{aligned} \tag{22}$$

$$L_z\mathcal{U} = -\sum_{J=0}^{\infty}\sum_{q=-J}^{J} a_q^J \cdot q\mathscr{D}_{0q}^{J}(\Omega)$$

$$L_z{}^2\mathcal{U} = -\sum_{J=0}^{\infty}\sum_{q=-J}^{J} a_q^J \cdot q^2\mathscr{D}_{0q}^{J}(\Omega)$$

$$\begin{aligned}(L_z\mathcal{U})^2 &= \sum_{J_1q_1J_2q_2} a_{q_1}^{J_1}a_{q_2}^{J_2} \cdot q_1 \cdot q_2\mathscr{D}_{0q_1}^{J_1}(\Omega)\mathscr{D}_{0q_2}^{J_2}(\Omega) \\ &= \sum_{J,q}(-1)^q(2J+1)\mathscr{D}_{0q}^{J}(\Omega)\sum_{J_1q_1J_2q_2} a_{q_1}^{J_1}a_{q_2}^{J_2} \cdot q_1 \cdot q_2 \\ &\times\begin{pmatrix} J_1 & J & J_2 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} J_1 & J & J_2 \\ q_1 & -q & q_2\end{pmatrix}\end{aligned} \tag{23}$$

$$
\begin{aligned}
\left(L_{+}\mathcal{U}\right)\left(L_{z}\mathcal{U}\right) &= \sum_{J_1 q_1 J_2 q_2} a_{q_1}^{J_1} a_{q_2}^{J_2} \cdot M_{+}\left(J_1, q_1\right) \cdot q_2 \mathcal{D}_{0 q_1+1}^{J_1}\left(\Omega\right) \mathcal{D}_{0 q_2}^{J_2}\left(\Omega\right) \\
&= \sum_{J,q} \left(-1\right)^{q} \left(2J+1\right) \mathcal{D}_{0q}^{J}\left(\Omega\right) \sum_{J_1 q_1 J_2 q_2} a_{q_1}^{J_1} a_{q_2}^{J_2} \cdot M_{+}\left(J_1, q_1\right) \cdot q_2 \\
&\quad \times \begin{pmatrix} J_1 & J & J_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J_1 & J & J_2 \\ q_1+1 & -q & q_2 \end{pmatrix} \\
\left(L_{-}\mathcal{U}\right)\left(L_{z}\mathcal{U}\right) &= \sum_{J_1 q_1 J_2 q_2} a_{q_1}^{J_1} a_{q_2}^{J_2} \cdot M_{-}\left(J_1, q_1\right) \cdot q_2 \mathcal{D}_{0 q_1-1}^{J_1}\left(\Omega\right) \mathcal{D}_{0 q_2}^{J_2}\left(\Omega\right) \\
&= \sum_{J,q} \left(-1\right)^{q} \left(2J+1\right) \mathcal{D}_{0q}^{J}\left(\Omega\right) \sum_{J_1 q_1 J_2 q_2} a_{q_1}^{J_1} a_{q_2}^{J_2} \cdot M_{-}\left(J_1, q_1\right) \cdot q_2 \\
&\quad \times \begin{pmatrix} J_1 & J & J_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J_1 & J & J_2 \\ q_1-1 & -q & q_2 \end{pmatrix}
\end{aligned} \qquad (24)
$$

$$
\begin{aligned}
L_{\pm}{}^{2}\mathcal{U} &= -\sum_{Jq} a_{q}^{J} \cdot M_{\pm}\left(J,q\right) M_{\pm}\left(J,q+1\right) \mathcal{D}_{0q\pm 2}^{J}\left(\Omega\right) \\
&= -\sum_{Jq} a_{q\mp 2}^{J} \cdot M_{\pm}\left(J,q\mp 2\right) M_{\pm}\left(J,q\mp 1\right) \mathcal{D}_{0q}^{J}\left(\Omega\right)
\end{aligned} \qquad (25)
$$

$$
\begin{aligned}
\left(L_{\pm}L_{z} + L_{z}L_{\pm}\right)\mathcal{U} &= -\sum_{Jq} a_{q}^{J} \cdot M_{\pm}\left(J,q\right) \left(2q \pm 1\right) \mathcal{D}_{0q\pm 1}^{J}\left(\Omega\right) \\
&= -\sum_{Jq} a_{q\mp 1}^{J} \cdot M_{\pm}\left(J,q\mp 1\right) \left(2q \mp 1\right) \mathcal{D}_{0q}^{J}\left(\Omega\right)
\end{aligned} \qquad (26)
$$

Then, by combining expressions (10), (21)–(26), the overall value of $\mathcal{X}_{K}^{L}$ can be written as:

$$
\begin{aligned}
\mathcal{X}_K^L &= -a_q^J \cdot \frac{\rho}{2}\left[J(J+1)+(\eta-1)q^2\right] \\
&-\frac{\varepsilon^*\rho}{4}a_{q-2}^J \cdot M_+(J,q-2)M_+(J,q-1) \\
&-\frac{\varepsilon\rho}{4}a_{q+2}^J \cdot M_-(J,q+2)M_-(J,q+1) \\
&-\frac{\kappa^*\rho}{4}a_{q-1}^J \cdot M_+(J,q-1)(2q-1) \\
&-\frac{\kappa\rho}{4}a_{q+1}^J \cdot M_-(J,q+1)(2q+1) \\
&-(-1)^q(2J+1)\sum_{J_1q_1J_2q_2} a_{q_1}^{J_1}a_{q_2}^{J_2}\begin{pmatrix} J_1 & J & J_2 \\ 0 & 0 & 0 \end{pmatrix}\times \\
&\times\left[\frac{\varepsilon^*\rho}{8}M_+(J_1,q_1)M_+(J_2,q_2)\begin{pmatrix} J_1 & J & J_2 \\ q_1+1 & -q & q_2+1 \end{pmatrix}\right. \\
&+\frac{\varepsilon\rho}{8}M_-(J_1,q_1)M_-(J_2,q_2)\begin{pmatrix} J_1 & J & J_2 \\ q_1-1 & -q & q_2-1 \end{pmatrix} \\
&+\frac{\rho}{4}M_+(J_1,q_1)M_-(J_1,q_2)\begin{pmatrix} J_1 & J & J_2 \\ q_1+1 & -q & q_2-1 \end{pmatrix} \\
&+\frac{\eta\rho}{4}\cdot q_1 \cdot q_2\begin{pmatrix} J_1 & J & J_2 \\ q_1 & -q & q_2 \end{pmatrix} \\
&+\frac{\kappa^*\rho}{4}M_+(J_1,q_1)\cdot q_2\begin{pmatrix} J_1 & J & J_2 \\ q_1+1 & -q & q_2 \end{pmatrix} \\
&\left.+\frac{\kappa\rho}{4}M_-(J_1,q_1)\cdot q_2\begin{pmatrix} J_1 & J & J_2 \\ q_1-1 & -q & q_2 \end{pmatrix}\right]
\end{aligned}
\tag{27}
$$

Now one can return to designations D_{ij} for the rotation diffusion tensor components. For the matrix elements of superoperator $\hat{\mathbf{\Gamma}}_{iso}$, one obtains:

$$
\begin{aligned}
&\langle L_1M_1K_1|\hat{\mathbf{\Gamma}}_{iso}|L_2M_2K_2\rangle = \\
&=\delta_{L_1L_2}\delta_{M_1M_2}\left\{\delta_{K_1K_2}\left[\frac{R_{xx}+R_{yy}}{2}\left[L_1\left(L_1+1\right)-K_1{}^2\right]+R_{zz}K_1{}^2\right]\right. \\
&\qquad+\delta_{K_1\ K_2+1}\left[\frac{R_{xz}-iR_{yz}}{2}\left(2K_2+1\right)M_+(\mathrm{L}_1,K_2)\right] \\
&\qquad+\delta_{K_1\ K_2-1}\left[\frac{R_{xz}+iR_{yz}}{2}\left(2K_2-1\right)M_-(\mathrm{L}_1,K_2)\right] \\
&\qquad+\delta_{K_1\ K_2+2}\left[\frac{R_{xx}-R_{yy}-2iR_{xy}}{4}M_+(\mathrm{L}_1,K_2)M_+(\mathrm{L},K_2+1)\right] \\
&\qquad\left.+\delta_{K_1\ K_2-2}\left[\frac{R_{xx}-R_{yy}+2iR_{xy}}{4}M_-(\mathrm{L}_1,K_2)M_-(\mathrm{L},K_2-1)\right]\right\}
\end{aligned}
\tag{28}
$$

Following the ideas of Refs. [1, 3, 4], for rendering of stochastic Liouville superoperator in the complex symmetric form, the following modified basis should be used:

$$
\left|LMK'j^K\right\rangle=\sqrt{\frac{j^K}{2\left(1+\delta_{K0}\right)}}\left(\left|LM\left|K\right|\right\rangle+j^K\left(-1\right)^{L+K}\left|LM-\left|K\right|\right\rangle\right) \tag{29}
$$

where

$$
\begin{aligned}
&j^K=\mathrm{sgn}(K),\ if\ \mathrm{K}\neq 0 \\
&j^K=\left(-1\right)^L,\ if\ \mathrm{K}=0
\end{aligned}
\tag{30}
$$

It can be shown that in the modified basis, the matrix elements of superoperator $\hat{\mathbf{\Gamma}}_{iso}$ are given by the following equations:

if $K_1 = K_2,\ j^K{}_1 = j^K{}_2$

$$\left\langle L_1 M_1 K_1 j^K{}_1 \middle| \hat{\boldsymbol{\Gamma}}_{iso} \middle| L_2 M_2 K_2 j^K{}_2 \right\rangle = \mathrm{Re}\left\langle L_1 M_1 \left|K_1\right| \middle\| \hat{\boldsymbol{\Gamma}}_{iso} \middle| L_2 M_2 \left|K_2\right| \right\rangle \\ - \delta_{\left|K_1\right|,1} \cdot j^K{}_1 (-1)^{L_1} \mathrm{Re}\left\langle L_1 M_1 - \left|K_1\right| \middle\| \hat{\boldsymbol{\Gamma}}_{iso} \middle| L_2 M_2 \left|K_2\right| \right\rangle \tag{31}$$

if $K_1 = K_2,\ j^K{}_1 \neq j^K{}_2$

$$\left\langle L_1 M_1 K_1 j^K{}_1 \middle| \hat{\boldsymbol{\Gamma}}_{iso} \middle| L_2 M_2 K_2 j^K{}_2 \right\rangle = \delta_{\left|K_1\right|,1} \cdot (-1)^{L_1} \mathrm{Im}\left\langle L_1 M_1 - \left|K_1\right| \middle\| \hat{\boldsymbol{\Gamma}}_{iso} \middle| L_2 M_2 \left|K_2\right| \right\rangle \tag{32}$$

if $K_1 \neq K_2,\ j^K{}_1 = j^K{}_2$

$$\left\langle L_1 M_1 K_1 j^K{}_1 \middle| \hat{\boldsymbol{\Gamma}}_{iso} \middle| L_2 M_2 K_2 j^K{}_2 \right\rangle = \left[\left(1+\delta_{K_1 0}\right)\left(1+\delta_{K_2 0}\right)\right]^{1/2} \mathrm{Re}\left\langle L_1 M_1 \left|K_1\right| \middle\| \hat{\boldsymbol{\Gamma}}_{iso} \middle| L_2 M_2 \left|K_2\right| \right\rangle \tag{33}$$

if $K_1 \neq K_2,\ j^K{}_1 \neq j^K{}_2$

$$\left\langle L_1 M_1 K_1 j^K{}_1 \middle| \hat{\boldsymbol{\Gamma}}_{iso} \middle| L_2 M_2 K_2 j^K{}_2 \right\rangle = -j^K{}_1 \left[\left(1+\delta_{K_1 0}\right)\left(1+\delta_{K_2 0}\right)\right]^{1/2} \\ \times \mathrm{Im}\left\langle L_1 M_1 \left|K_1\right| \middle\| \hat{\boldsymbol{\Gamma}}_{iso} \middle| L_2 M_2 \left|K_2\right| \right\rangle \tag{34}$$

where

$$\left\langle L_1 M_1 K_1 \middle| \hat{\boldsymbol{\Gamma}}_{iso} \middle| L_2 M_2 K_2 \right\rangle = \\ = \delta_{L_1 L_2} \delta_{M_1 M_2} \left\{ \delta_{K_1 K_2} \left[\frac{R_{xx} + R_{yy}}{2} \left[L_1 (L_1 + 1) - K_1{}^2 \right] + R_{zz} K_1{}^2 \right] \right. \\ + \delta_{K_1\ K_2+1} \left[\frac{R_{xz} - iR_{yz}}{2} (2K_2 + 1) M_+(\mathrm{L}_1, K_2) \right] \\ + \delta_{K_1\ K_2-1} \left[\frac{R_{xz} + iR_{yz}}{2} (2K_2 - 1) M_-(\mathrm{L}_1, K_2) \right] \\ + \delta_{K_1\ K_2+2} \left[\frac{R_{xx} - R_{yy} - 2iR_{xy}}{4} M_+(\mathrm{L}_1, K_2) M_+(\mathrm{L}, K_2 + 1) \right] \\ \left. + \delta_{K_1\ K_2-2} \left[\frac{R_{xx} - R_{yy} + 2iR_{xy}}{4} M_-(\mathrm{L}_1, K_2) M_-(\mathrm{L}, K_2 - 1) \right] \right\}$$

One can see that in the case of diagonal diffusion tensor, equations (31)–(34) are identical to the equation (B33) in Ref. [3]:

$$
\left\langle L_1 M_1 K_1 j^K{}_1 \left| \hat{\mathbf{\Gamma}}_{iso} \right| L_2 M_2 K_2 j^K{}_2 \right\rangle =
$$

$$
= \delta_{L_1 L_2} \delta_{M_1 M_2} \delta_{j^K{}_1 j^K{}_2} \left\{ \delta_{K_1 K_2} \left[\frac{R_{xx} + R_{yy}}{2} \left[L_1 (L_1 + 1) - K_1{}^2 \right] + R_{zz} K_1{}^2 \right] \right. \tag{35}
$$

$$
\left. + \left[\delta_{K_1 - 2\, K_2} N_+ (\mathrm{L}_1, K_2) + \delta_{K_1 + 2\, K_2} N_- (\mathrm{L}_1, K_2) \right] \frac{R_{xx} - R_{yy}}{4} \left[\left(1 + \delta_{K_1 0}\right) \left(1 + \delta_{K_2 0}\right) \right]^{1/2} \right\}
$$

where $N_\pm (L, K) = M_\pm (L, K) M_\pm (L, K \pm 1)$.

By returning to designations D_{ij} for the rotation diffusion tensor components, the following expression for the spherical components of superoperator $\hat{\mathbf{\Gamma}}_U$ are obtained:

$$
\begin{aligned}
\mathcal{X}_q^J = & -\frac{a_q^J}{2} \cdot \left(\frac{R_{xx} + R_{yy}}{2} \left[J (J + 1) - q^2 \right] + R_{zz} q^2 \right) \\
& - \frac{R_{xx} - R_{yy} - 2 i R_{xy}}{4} \frac{a_{q-2}^J}{2} \cdot M_+ (J, q - 2) M_+ (J, q - 1) \\
& - \frac{R_{xx} - R_{yy} + 2 i R_{xy}}{4} \frac{a_{q+2}^J}{2} \cdot M_- (J, q + 2) M_- (J, q + 1) \\
& - \frac{R_{xz} - i R_{yz}}{2} \frac{a_{q-1}^J}{2} \cdot M_+ (J, q - 1)(2q - 1) \\
& - \frac{R_{xz} + i R_{yz}}{2} \frac{a_{q+1}^J}{2} \cdot M_- (J, q + 1)(2q + 1) \\
& - (-1)^q \frac{2J + 1}{4} \sum_{J_1 q_1 J_2 q_2} a_{q_1}^{J_1} a_{q_2}^{J_2} \begin{pmatrix} J_1 & J & J_2 \\ 0 & 0 & 0 \end{pmatrix} \times \\
& \times \left[\frac{R_{xx} - R_{yy} - 2 i R_{xy}}{4} M_+ (J_1, q_1) M_+ (J_2, q_2) \begin{pmatrix} J_1 & J & J_2 \\ q_1 + 1 & -q & q_2 + 1 \end{pmatrix} \right. \\
& + \frac{R_{xx} - R_{yy} + 2 i R_{xy}}{4} M_- (J_1, q_1) M_- (J_2, q_2) \begin{pmatrix} J_1 & J & J_2 \\ q_1 - 1 & -q & q_2 - 1 \end{pmatrix} \\
& + \frac{R_{xx} + R_{yy}}{2} M_+ (J_1, q_1) M_- (J_1, q_2) \begin{pmatrix} J_1 & J & J_2 \\ q_1 + 1 & -q & q_2 - 1 \end{pmatrix} \\
& + R_z \cdot q_1 \cdot q_2 \begin{pmatrix} J_1 & J & J_2 \\ q_1 & -q & q_2 \end{pmatrix} \\
& + \left(R_{xz} - i R_{yz} \right) M_+ (J_1, q_1) \cdot q_2 \begin{pmatrix} J_1 & J & J_2 \\ q_1 + 1 & -q & q_2 \end{pmatrix} \\
& \left. + \left(R_{xz} + i R_{yz} \right) M_- (J_1, q_1) \cdot q_2 \begin{pmatrix} J_1 & J & J_2 \\ q_1 - 1 & -q & q_2 \end{pmatrix} \right]
\end{aligned} \tag{36}
$$

One can see that in the case of diagonal rotation diffusion tensor, the equation (36) reduces to Eq, (B6) in Ref. [3]:

$$
\begin{aligned}
\mathcal{X}_q^J &= -\frac{1}{2}\Bigg(\left(a_{q-2}^J \cdot N_+(J,q-2) + a_{q+2}^J \cdot N_-(J,q+2)\right)\frac{R_{xx}-R_{yy}}{4} + \\
&\quad + a_q^J\left(\frac{R_{xx}+R_{yy}}{2}\left[J(J+1)-q^2\right] + R_{zz}q^2\right)\Bigg) - \\
&\quad -\frac{2J+1}{4}\sum_{J_1 q_1 J_2 q_2} a_{q_1}^{J_1} a_{q_2}^{J_2}\begin{pmatrix} J_1 & J & J_2 \\ 0 & 0 & 0 \end{pmatrix} \times \\
&\quad \times\Bigg[\frac{R_{xx}-R_{yy}}{4}\Bigg(M_+(J_1,q_1)M_+(J_2,q_2)\begin{pmatrix} J_1 & J & J_2 \\ q_1+1 & -q & q_2+1 \end{pmatrix} + \\
&\qquad + M_-(J_1,q_1)M_-(J_2,q_2)\begin{pmatrix} J_1 & J & J_2 \\ q_1-1 & -q & q_2-1 \end{pmatrix}\Bigg) + \\
&\quad + \frac{R_{xx}+R_{yy}}{2} M_+(J_1,q_1)M_-(J_1,q_2)\begin{pmatrix} J_1 & J & J_2 \\ q_1+1 & -q & q_2-1 \end{pmatrix} + \\
&\quad + R_{zz}\cdot q_1 \cdot q_2 \begin{pmatrix} J_1 & J & J_2 \\ q_1 & -q & q_2 \end{pmatrix}\Bigg]
\end{aligned}
$$

For calculation of matrix elements of superoperator $\hat{\mathbf{\Gamma}}_U$ in the modified basis (29), the expression (19) should be modified. For this, the following symmetry relation for $\mathcal{X}_K^L$ should be noted:

$$\mathcal{X}_{-q}^J = (-1)^q \left(\mathcal{X}_q^J\right)^* \tag{37}$$

which follows from the symmetry property of the mean-field potential:

$$a_{-q}^J = (-1)^q \left(a_q^J\right)^* \tag{38}$$

This entails the symmetry property for the matrix element:

$$\langle L_1 M_1 - K_1 | \hat{\mathbf{\Gamma}}_U | L_2 M_2 - K_2 \rangle = (-1)^{L_1+L_2+K_1+K_2} \langle L_1 M_1 K_1 | \hat{\mathbf{\Gamma}}_U | L_2 M_2 K_2 \rangle^*$$

Thus, any matrix element in symmetrized basis (29), can be calculated from the matrix elements in the original basis (11):

$$\left\langle L_1 M_1 K_1 j^K{}_1 \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 K_2 j^K{}_2 \right\rangle = \frac{1}{2}\left(\sqrt{j^K{}_1}\right)^* \sqrt{j^K{}_2}\left[\left(1+\delta_{K_1 0}\right)\left(1+\delta_{K_2 0}\right)\right]^{-1/2} \times$$
$$\times\Big(\left\langle L_1 M_1 |K_1| \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 |K_2| \right\rangle + j^K{}_1 j^K{}_2 \left\langle L_1 M_1 |K_1| \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 |K_2| \right\rangle^*$$
$$+ j^K{}_2 (-1)^{L_2+K_2}\left(\left\langle L_1 M_1 |K_1| \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 -|K_2| \right\rangle + j^K{}_1 j^K{}_2 \left\langle L_1 M_1 |K_1| \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 -|K_2| \right\rangle^*\right)\Big)$$

if $j^K{}_1 = j^K{}_2$

$$\left\langle L_1 M_1 K_1 j^K{}_1 \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 K_2 j^K{}_2 \right\rangle = \left[\left(1+\delta_{K_1 0}\right)\left(1+\delta_{K_2 0}\right)\right]^{-1/2} \times$$
$$\times\left(\mathrm{Re}\left\langle L_1 M_1 |K_1| \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 |K_2| \right\rangle + j^K{}_2 (-1)^{L_2+K_2}\,\mathrm{Re}\left\langle L_1 M_1 |K_1| \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 -|K_2| \right\rangle\right) \quad (39)$$

if $j^K{}_1 \neq j^K{}_2$

$$\left\langle L_1 M_1 K_1 j^K{}_1 \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 K_2 j^K{}_2 \right\rangle = j^K{}_2\left[\left(1+\delta_{K_1 0}\right)\left(1+\delta_{K_2 0}\right)\right]^{-1/2} \times$$
$$\times\left(\mathrm{Im}\left\langle L_1 M_1 |K_1| \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 |K_2| \right\rangle + j^K{}_2 (-1)^{L_2+K_2}\left(\mathrm{Im}\left\langle L_1 M_1 |K_1| \middle| \hat{\mathbf{\Gamma}} \middle| L_2 M_2 -|K_2| \right\rangle\right) \quad (40)$$

In the explicit form, if $j^K{}_1 = j^K{}_2$

$$\left\langle L_1 M_1 K_1 j^K{}_1 \middle| \hat{\mathbf{\Gamma}}_U \middle| L_2 M_2 K_2 j^K{}_2 \right\rangle = \left[\left(1+\delta_{K_1 0}\right)\left(1+\delta_{K_2 0}\right)\right]^{-1/2}$$
$$\times \sum_{L=0}^{\infty}\sqrt{(2L_1+1)(2L_2+1)}\,(-1)^{M_1+K_1}\begin{pmatrix} L_2 & L & L_1 \\ M_2 & 0 & -M_1 \end{pmatrix}$$
$$\times\left[\mathrm{Re}\,\mathcal{X}^L_{K_1-K_2}\begin{pmatrix} L_2 & L & L_1 \\ K_2 & K_1-K_2 & -K_1 \end{pmatrix}\right.$$
$$\left. + j^K{}_2 (-1)^{L_2+K_2}\,\mathrm{Re}\,\mathcal{X}^L_{K_1+K_2}\begin{pmatrix} L_2 & L & L_1 \\ -K_2 & K_1+K_2 & -K_1 \end{pmatrix}\right] \quad (41)$$

if $j^K{}_1 \neq j^K{}_2$

$$
\begin{aligned}
&\left\langle L_1 M_1 K_1 j^K{}_1 \middle| \hat{\boldsymbol{\Gamma}}_U \middle| L_2 M_2 K_2 j^K{}_2 \right\rangle = j^K{}_2 \left[\left(1+\delta_{K_1 0}\right)\left(1+\delta_{K_2 0}\right) \right]^{-1/2} \\
&\quad \times \sum_{L=0}^{\infty} \sqrt{\left(2L_1+1\right)\left(2L_2+1\right)} \left(-1\right)^{M_1+K_1} \begin{pmatrix} L_2 & L & L_1 \\ M_2 & 0 & -M_1 \end{pmatrix} \\
&\quad \times \Bigg[\operatorname{Im} \mathcal{X}^L_{K_1-K_2} \begin{pmatrix} L_2 & L & L_1 \\ K_2 & K_1-K_2 & -K_1 \end{pmatrix} \\
&\qquad + j^K{}_2 \left(-1\right)^{L_2+K_2} \operatorname{Im} \mathcal{X}^L_{K_1+K_2} \begin{pmatrix} L_2 & L & L_1 \\ -K_2 & K_1+K_2 & -K_1 \end{pmatrix} \Bigg]
\end{aligned} \tag{42}
$$

The equation (41) is identical to Eq. (B7) from Ref. [3]. That means, that for diagonal rotation diffusion tensor, and orthorhombic potential, expressions (41)–(42) reduce to those known in literature.

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