Homework #2 (2020-2021), Q2 only, extended to work out rotational Brownian motion as a model for rotational diffusion.

The setup is a fluorescent tag tethered to a protein that is tumbling. Irradiating the tag with a laser will preferentially excite dipoles that are aligned with the polarization of the laser. When the molecule tumbles and later fluoresces, the emitted light will be less-polarized because of the tumbling. The physics (see https://en.wikipedia.org/wiki/Fluorescence_anisotropy) is that the polarization of $\left\langle \cos^2 \beta \right\rangle$, where β is the angle between the polarization vector of the light, and the dipole at the time of emission. This polarization can be measured as a function of time. To relate this timecourse to the rotational tumbling of the molecule, we want to understand how a population of unit vectors that is, say, vertical at time 0, evolves, given a model for the tumbling of the coordinate frame.
For unit vectors that are initially aligned on the x_1-axis, $\cos^2\beta = x_1^2$. To see how $\left\langle x_1^2 \right\rangle$ evolves, it suffices to look at how $s = \frac{1}{\sqrt{3}}\left(x_1^2 - \frac{1}{2}x_2^2 - \frac{1}{2}x_3^2\right)$ evolves, since $x_1^2 + x_2^2 + x_3^2 = 1$. The key observation is that $s = \frac{1}{\sqrt{3}}\left(x_1^2 - \frac{1}{2}x_2^2 - \frac{1}{2}x_3^2\right)$ is a function on the sphere that is entirely contained in the 5-dimensional representation analyzed in LTGR homework #2, Q2. So it suffices to see how the vector $\begin{pmatrix}1\\0\\0\\0\\0\end{pmatrix}$ evolves under rotations. We consider small rotations around each axis by an angle θ.

In the 5-d space, $R_1(\theta)$ becomes:

$$\begin{pmatrix} s' \\ t' \\ u' \\ v' \\ w' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & \cos 2\theta & 0 & 0 & \sin 2\theta \\ 0 & 0 & \cos\theta & \sin\theta & 0 \\ 0 & 0 & -\sin\theta & \cos\theta & 0 \\ 0 & -\sin 2\theta & 0 & 0 & \cos 2\theta \end{pmatrix} \begin{pmatrix} s \\ t \\ u \\ v \\ w \end{pmatrix}.$$

In the 5-d space, $R_2(\theta)$ becomes:

$$\begin{pmatrix} s' \\ t' \\ u' \\ v' \\ w' \end{pmatrix} = \begin{pmatrix} \frac{1}{4} + \frac{3}{4}\cos 2\theta & -\frac{\sqrt{3}}{4}(1-\cos 2\theta) & 0 & -\frac{\sqrt{3}}{2}\sin 2\theta & 0 \\ -\frac{\sqrt{3}}{4}(1-\cos 2\theta) & \frac{3}{4} + \frac{1}{4}\cos 2\theta & 0 & -\frac{1}{2}\sin 2\theta & 0 \\ 0 & 0 & \cos\theta & 0 & -\sin\theta \\ \frac{\sqrt{3}}{2}\sin 2\theta & \frac{1}{2}\sin 2\theta & 0 & \cos 2\theta & 0 \\ 0 & 0 & \sin\theta & 0 & \cos\theta \end{pmatrix} \begin{pmatrix} s \\ t \\ u \\ v \\ w \end{pmatrix}.$$

In the 5-d space, $R_3(\theta)$ becomes:

$$\begin{pmatrix} s' \\ t' \\ u' \\ v' \\ w' \end{pmatrix} = \begin{pmatrix} \frac{1}{4}+\frac{3}{4}\cos 2\theta & \frac{\sqrt{3}}{4}(1-\cos 2\theta) & -\frac{\sqrt{3}}{2}\sin 2\theta & 0 & 0 \\ \frac{\sqrt{3}}{4}(1-\cos 2\theta) & \frac{3}{4}+\frac{1}{4}\cos 2\theta & \frac{1}{2}\sin 2\theta & 0 & 0 \\ \frac{\sqrt{3}}{2}\sin 2\theta & -\frac{1}{2}\sin 2\theta & \cos 2\theta & 0 & 0 \\ 0 & 0 & 0 & \cos\theta & -\sin\theta \\ 0 & 0 & 0 & \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} s \\ t \\ u \\ v \\ w \end{pmatrix}.$$

For short times, let's say that the molecule is equally likely to make small rotations around each axis of rotation, but the sizes of the rotations may differ: $\langle \theta^2 \rangle = a_i \Delta T$. Compute the effect of rotation around each axis, compared to no rotation at all:

$$\frac{1}{2}\left(R_1(\theta)+R_1(-\theta)\right)-I \text{ corresponds to } -\begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 2\theta^2 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2}\theta^2 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}\theta^2 & 0 \\ 0 & 0 & 0 & 0 & 2\theta^2 \end{pmatrix}.$$

$$\frac{1}{2}\left(R_2(\theta)+R_2(-\theta)\right)-I \text{ corresponds to } -\begin{pmatrix} \frac{3}{2}\theta^2 & \frac{\sqrt{3}}{2}\theta^2 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2}\theta^2 & \frac{1}{2}\theta^2 & 0 & 0 & 0 \\ 0 & 0 & \frac{\theta^2}{2} & 0 & 0 \\ 0 & 0 & 0 & 2\theta^2 & 0 \\ 0 & 0 & 0 & 0 & \frac{\theta^2}{2} \end{pmatrix}$$

$$\frac{1}{2}\left(R_3(\theta)+R_3(-\theta)\right)-I \text{ corresponds to} -\begin{pmatrix} \frac{3}{2}\theta^2 & -\frac{\sqrt{3}}{2}\theta^2 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2}\theta^2 & \frac{1}{2}\theta^2 & 0 & 0 & 0 \\ 0 & 0 & 2\theta^2 & 0 & 0 \\ 0 & 0 & 0 & \frac{\theta^2}{2} & 0 \\ 0 & 0 & 0 & 0 & \frac{\theta^2}{2} \end{pmatrix}$$

So after a time ΔT , a vector $\vec{z}$ in the 5-D space is transformed to a vector $(I - M\Delta T)\vec{z}$, where

$$M=\frac{1}{6}\begin{pmatrix} 3a_2+3a_3 & \sqrt{3}(a_2-a_3) & 0 & 0 & 0 \\ \sqrt{3}(a_2-a_3) & 4a_1+a_2+a_3 & 0 & 0 & 0 \\ 0 & 0 & a_1+a_2+4a_3 & 0 & 0 \\ 0 & 0 & 0 & a_1+4a_2+a_3 & 0 \\ 0 & 0 & 0 & 0 & 4a_1+a_2+a_3 \end{pmatrix}.$$

So the expected evolution in time is $\vec{z}(t)=\exp(-Mt)\vec{z}(0)=\sum_{m=1}^{5}c_m e^{-\lambda_m t}$, where the λ_m's are the eigenvalues of M. Note that M is block-diagonal, with a 2×2 part and three diagonal elements. So three of the eigenvalues are those diagonal elements, namely, $\lambda_i=\frac{1}{2}\left(a+a_i\right)$, where $a=\frac{1}{3}(a_1+a_2+a_3)$.

The eigenvalues for the 2×2 part, $M=\frac{1}{6}\begin{pmatrix} 3a_2+3a_3 & \sqrt{3}(a_2-a_3) \\ \sqrt{3}(a_2-a_3) & 4a_1+a_2+a_3 \end{pmatrix}$: trace is $\frac{2}{3}(a_1+a_2+a_3)=2a$.

Determinant is $\frac{1}{3}\left(a_1a_2+a_1a_3+a_2a_3\right)$. So the last two eigenvalues are given by

$$\lambda_{\pm}=a\pm\sqrt{a^2-\frac{1}{3}\left(a_1a_2+a_1a_3+a_2a_3\right)}.$$

Thus, measurement of the fluorescence depolarization, and resolving it into a sum of exponentials, can determine the parameters of the rotational diffusion – as well as the adequacy of the model.