1 Molecule Hamiltonian

We first consider the combination of the Zeeman and molecular Hamiltonian with the molecular z axis deviating from the lab z axis: (in the basis of $|S, m_{Q_1} = -1, 0, 1\rangle$)

$$\begin{aligned} H_{Zee}/\gamma\hbar =& \mathbf{B} \cdot \mathbf{S} = B_x S_x + B_y S_y + B_z S_z \\ =& \begin{pmatrix} -B_0 \cos\theta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & B_0 \cos\theta \end{pmatrix} + \frac{B_0 \sin\theta \cos\chi}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \\ &+ \frac{B_0 \sin\theta \sin\chi}{\sqrt{2}} \begin{pmatrix} 0 & i & 0 \\ -i & 0 & i \\ 0 & -i & 0 \end{pmatrix} \\ =& \begin{pmatrix} -B_0 \cos\theta & \frac{B_0 \sin\theta e^{i\chi}}{\sqrt{2}} & 0 \\ \frac{B_0 \sin\theta e^{-i\chi}}{\sqrt{2}} & 0 & \frac{B_0 \sin\theta e^{i\chi}}{\sqrt{2}} \\ 0 & \frac{B_0 \sin\theta e^{-i\chi}}{\sqrt{2}} & B_0 \cos\theta \end{pmatrix}, \end{aligned} \tag{1}$$

where the rotational transformation from lab to molecule frame (Z-Y-Z rotation) is applied to the magnetic field:

$$D_{rot}(\Omega) = \begin{pmatrix} -\sin\phi\sin\chi + \cos\theta\cos\phi\cos\chi & -\cos\chi\sin\phi - \cos\theta\cos\phi\sin\chi & \sin\theta\cos\phi \\ \cos\phi\sin\chi + \cos\theta\sin\phi\cos\chi & \cos\phi\cos\chi - \cos\theta\sin\phi\sin\chi & \sin\phi\sin\theta \\ -\sin\theta\cos\chi & \sin\theta\sin\chi & \cos\theta \end{pmatrix}. \tag{2}$$

The total Hamiltonian reads:

$$\begin{aligned} H_0 =& H_{Zee} + H_{mol} \\ =& \begin{pmatrix} -\gamma B_0 \cos\theta + \frac{D_0}{3} & \frac{e^{i\chi}\gamma B_0}{\sqrt{2}} \sin\theta & E_0 \\ \frac{e^{-i\chi}\gamma B_0}{\sqrt{2}} \sin\theta & -\frac{2}{3} D_0 & \frac{e^{i\chi}\gamma B_0}{\sqrt{2}} \sin\theta \\ E_0 & \frac{e^{-i\chi}\gamma B_0}{\sqrt{2}} \sin\theta & \gamma B_0 \cos\theta + \frac{D_0}{3} \end{pmatrix}, \end{aligned} \tag{3}$$

where $\Omega = (\phi, \theta, \chi)$ denotes the Euler angle of the transformation from the lab frame to the protein frame. The energies of the Hamiltonian H_0 can be calculated by solving the secular equation $\det(H_0 - \lambda I) = 0$, where λ are the eigenvalues and I is the identity matrix. This leads to the characteristic equation:

$$\det \begin{pmatrix} a + \frac{1}{3} D_0 - \lambda & b & E_0 \\ b^* & -\frac{2}{3} D_0 - \lambda & b \\ E_0 & b^* & -a + \frac{1}{3} D_0 - \lambda \end{pmatrix} = 0, \tag{4}$$

here we have denoted $a = \gamma B_0 \cos\theta$ and $b = \frac{e^{i\chi}\gamma B_0}{\sqrt{2}} \sin\theta$. The determinant can be expanded as follows:

$$\begin{aligned}
\det(H_0 - \lambda I) &= \left(a + \frac{1}{3}D_0 - \lambda\right)\left(-\frac{2}{3}D_0 - \lambda\right)\left(-a + \frac{1}{3}D_0 - \lambda\right) \\
&\quad + [(b^2 + (b^*)^2]E_0 - 2|b|^2\left(\frac{1}{3}D_0 - \lambda\right) - E_0^2\left(-\frac{2}{3}D_0 - \lambda\right) \\
&= \left(-\frac{2}{3}D_0 - \lambda\right)\left(\lambda^2 - \frac{2}{3}D_0\lambda + \frac{1}{9}D_0^2 - a^2\right) \\
&\quad + (2|b|^2 + E_0^2)\lambda + [(b^2 + (b^*)^2]E_0 - \frac{2}{3}|b|^2 D_0 + \frac{2}{3}E_0^2 D_0 \\
&= \left(-\lambda^3 + \frac{1}{3}D_0^2\lambda + a^2\lambda + \frac{2}{3}D_0 a^2 - \frac{2}{27}D_0^3\right) \\
&\quad + (2|b|^2 + E_0^2)\lambda + [(b^2 + (b^*)^2]E_0 - \frac{2}{3}|b|^2 D_0 + \frac{2}{3}E_0^2 D_0 \\
&= -\lambda^3 + \left(\frac{1}{3}D_0^2 + a^2 + 2|b|^2 + E_0^2\right)\lambda + [(b^2 + (b^*)^2]E_0 \\
&\quad - \frac{2}{3}|b|^2 D_0 + \frac{2}{3}E_0^2 D_0 + \frac{2}{3}D_0 a^2 - \frac{2}{27}D_0^3 = 0,
\end{aligned} \tag{5}$$

This cubic equation of λ can be rewritten as

$$\lambda^3 + p\lambda + q = 0, \tag{6}$$

where

$$p = -\left(a^2 + 2|b|^2 + E_0^2 + \frac{D_0^2}{3}\right) = -\left(\gamma^2 B_0^2 + E_0^2 + \frac{D_0^2}{3}\right) < 0, \tag{7}$$

$$\begin{aligned}
q &= \frac{2D_0^3}{27} - \frac{2D_0E_0^2}{3} - \frac{2(a^2 - |b|^2)}{3}D_0 - [b^2 + (b^*)^2]E_0 \\
&= \frac{2D_0^3}{27} - \frac{2D_0E_0^2}{3} - \frac{2\gamma^2 B_0^2 D_0}{3}\frac{3\cos^2\theta - 1}{2} - \gamma^2 B_0^2 E_0 \cos(2\chi)\sin^2\theta.
\end{aligned} \tag{8}$$

Given that the Hamiltonian matrix has three real eigenvalues (the three energy levels), we can apply the trigonometric solution for the three real roots of λ, that is:

$$\lambda_k = 2\sqrt{\frac{-p}{3}}\cos\left[\frac{1}{3}\arccos\left(\frac{3q}{2p}\sqrt{\frac{-3}{p}}\right) + \frac{2\pi k}{3}\right], k = 1, 2, 3. \tag{9}$$

With calculations by our custom program, we found that $\lambda_3 > \lambda_2 > \lambda_1$. The transition frequency of $T_{z-x} = T_x - T_z$, for example, can be expressed as follows:

$$T_{z-x} = \lambda_3 - \lambda_1 = 2\sqrt{-p}\sin\left[\frac{1}{3}\arccos\left(\frac{3q}{2p}\sqrt{\frac{-3}{p}}\right) + \frac{\pi}{3}\right]. \tag{10}$$

2 The change of triplet state population induced by the external field

To start, we first consider the case without external field. The state preparation of $T_{x,y,z}$ states is governed by the intersystem crossing. Here we can use the perturbation theory to analyze the transition rate. By defining the intersystem-crossing operator as H_{ISC}, the transition amplitude is $\langle S_1|H_{ISC}|T'_x\rangle$, and the transition rate is (Christel M. Marian, Annu. Rev. Phys. Chem. 2021. 72:617–40),

$$k_{S_1\to T_1} \propto \frac{2\pi}{\hbar}|\langle S_1|H_{ISC}|T_1\rangle|^2, \tag{11}$$

and, in Condon approximation, the intersystem crossing rate is

$$k^{FC}_{S_1\to T_1} = \frac{2\pi}{\hbar}|\langle S_1|H_{ISC}|T_1\rangle|^2 \times \sum_{\nu_i,\nu_j}|\langle \nu_i|\nu_j\rangle|^2\delta[E(S_1,\nu_i) - E(T_1,\nu_j)], \tag{12}$$

where the ν_i and ν_j are the vibrational state of the $S_1$and T_i states, respectively, and the summation after the square of the transition amplitude is known as the Franck–Condon weighted density. Given that the energy gap in between the $T_{x,y,z}$ states (in unit of GHz) are very small compared to the vibrational levels (usually in unit of cm^{-1}), we can assume the Franck-Condon weighted densities of $|T_{x,y,z}\rangle$ states at the energy of the initial state $|S_1\rangle$ are the same. Therefore, we can assume that the intersystem crossing rates to different triplet substates share the same coefficient k_0 and can be described as follows:

$$k_{S_1\to T_i} = k_0|\langle S_1|H_{ISC}|T_i\rangle|^2, i = x, y, z. \tag{13}$$

By taking the integration over time, we can see that the population on T_i states is proportional to the square of the transition amplitude $|\langle S_1|H_{ISC}|T_i\rangle|^2$. Hence, we know that the relative population ratio of each triplet substate is

$$n_i = \frac{|\langle S_1|H_{ISC}|T_i\rangle|^2}{\sum_{j=x,y,z}|\langle S_1|H_{ISC}|T_j\rangle|^2} = \frac{|\langle S_1|H_{ISC}|T_i\rangle|^2}{|\langle S_1|H_{ISC}|T_1\rangle|^2}, i = x, y, z. \tag{14}$$

Here we make use of the fact that the total transition rate from S_1 to T_1 is the sum of the transition rates from S_1 to the triplet substates $T_{x,y,z}$.

When an external magnetic field B_0 is applied, we can assume that the total intersystem crossing rate $\langle S_1|H_{ISC}|T_1\rangle$ is not affected by the external magnetic field with the field strength that we can apply in the experiment. To distinguish the the substates in this case, we describe the substates of the triplet states as $T'_{x,y,z}$ states. Therefore, the population ratios of each substate is

$$\begin{aligned} n'_i =& \frac{|\langle S_1|H_{ISC}|T'_i\rangle|^2}{|\langle S_1|H_{ISC}|T_1\rangle|^2} \\ =& \frac{\sum_{j=x,y,z}|\langle S_1|H_{ISC}|T_j\rangle|^2|\langle T_j|T'_i\rangle|^2}{|\langle S_1|H_{ISC}|T_1\rangle|^2} \\ =& \sum_{j=x,y,z} n_j|\langle T_j|T'_i\rangle|^2, i = x, y, z. \end{aligned} \tag{15}$$

By measuring the population distribution under the case without external field and calculating the eigen-state vectors of the two cases, we can compute the population of the triplet substates under B_0.

3 Magnetic dipole transition probabilities calculation

The transition amplitude in between the triplet states is determined by the molecular orientation, microwave power and frequency, and transition magnetic moment. The magnetic dipole transition is arising from the coupling of the oscillating magnetic field with the electron spin magnetic moment, i.e.,

$$H(t) = g_s\mu_B \mathbf{B_1}(t) \cdot \mathbf{S} = g_s\mu_B \mathrm{T}^1(\mathbf{B}_1(t)) \cdot \mathrm{T}^1(\mathbf{S}). \tag{16}$$

In experiment, B_1 is applied with a waveguide placed horizontally in a cryostat, while the static magnetic field B_0 is applied with two magnets (each magnet is placed on either side of the cryostat); hence, we can assume B_1 perpendicular to B_0. Without the loss of generality, we set $\mathbf{B_1}(t) = B_1(t)\hat{x}_0$, i.e.,

$$\mathrm{T}^1_{p=-1}(\mathbf{B_1}(t)) = \frac{B_1(t)}{\sqrt{2}}, \mathrm{T}^1_{p=0}(\mathbf{B_1}(t)) = 0, \mathrm{T}^1_{p=1}(\mathbf{B_1}(t)) = -\frac{B_1(t)}{\sqrt{2}}. \tag{17}$$

When $B_0 = 0$, the transition matrix element between T_x and T_z states is

$$\begin{aligned}\langle T_x|H(t)|T_z\rangle =& g_s\mu_B\sqrt{\frac{1}{2}}\langle m_S = 1|\mathrm{T}^1(\mathbf{B}_1(t)) \cdot \mathrm{T}^1(\mathbf{S})|m_S = 0\rangle \\ &+ g_s\mu_B\sqrt{\frac{1}{2}}\langle m_S = -1|\mathrm{T}^1(\mathbf{B}_1(t)) \cdot \mathrm{T}^1(\mathbf{S})|m_S = 0\rangle,\end{aligned} \tag{18}$$

the tensor product in the molecular frame is

$$\begin{aligned}\mathrm{T}^1(\mathbf{B}_1(t)) \cdot \mathrm{T}^1(\mathbf{S}) &= \sum_{q=-1}^{1}(-1)^q \mathrm{T}^1_q(\mathbf{B}_1(t))\mathrm{T}^1_{-q}(\mathbf{S}) \\ &= \sum_{q=-1}^{1}\sum_{p=-1,1}(-1)^q \mathfrak{D}^{(1)}_{pq}(\Omega)\mathrm{T}^1_p(\mathbf{B}_1(t))\mathrm{T}^1_{-q}(\mathbf{S}) \\ &= \frac{B_1(t)}{\sqrt{2}}\sum_{q=-1}^{1}(-1)^q[\mathfrak{D}^{(1)}_{-1,q}(\Omega) - \mathfrak{D}^{(1)}_{1,q}(\Omega)]\mathrm{T}^1_{-q}(\mathbf{S}),\end{aligned} \tag{19}$$

Therefore, the rabi frequency Ω_1 can be expressed as a function of the Euler angles Ω as follows:

$$
\begin{aligned}
\hbar\Omega_1 =&\langle T_x|H(t)|T_z\rangle \\
=&g_s\mu_B\frac{B_1(t)}{2}\sum_{q=-1}^{1}(-1)^q[\mathfrak{D}^{(1)}_{-1,q}(\Omega)-\mathfrak{D}^{(1)}_{1,q}(\Omega)]\langle m_S=1|\mathrm{T}^1_{-q}(\mathbf{S})|m_S=0\rangle \\
&+g_s\mu_B\frac{B_1(t)}{2}\sum_{q=-1}^{1}(-1)^q[\mathfrak{D}^{(1)}_{-1,q}(\Omega)-\mathfrak{D}^{(1)}_{1,q}(\Omega)]\langle m_S=-1|\mathrm{T}^1_{-q}(\mathbf{S})|m_S=0\rangle \\
=&g_s\mu_B\frac{B_1(t)}{2}[\mathfrak{D}^{(1)}_{-1,-1}(\Omega)-\mathfrak{D}^{(1)}_{1,-1}(\Omega)-\mathfrak{D}^{(1)}_{-1,1}(\Omega)+\mathfrak{D}^{(1)}_{1,1}(\Omega)] \\
=&g_s\mu_B\frac{B_1(t)}{2}[(1+\cos\theta)\cos(\phi+\chi)-(1-\cos\theta)\cos(\phi-\chi)] \\
=&g_s\mu_B\frac{B_1(t)}{2}[\cos(\phi+\chi)-\cos(\phi-\chi)+\cos\theta(\cos(\phi-\chi)+\cos(\phi+\chi))] \\
=&g_s\mu_B B_1(t)(-\sin\phi\sin\chi+\cos\theta\cos\phi\cos\chi).
\end{aligned}
\tag{20}
$$

We can take a look at the microwave transition on the target spin S_t, for comparison. Given that the spin is polarized in lab frame, we have

$$
\begin{aligned}
H(t) =&\hbar\Omega_2 S_{t,x} = g_s\mu_B\mathrm{T}^1(\mathbf{B}_1(t))\cdot\mathrm{T}^1(\mathbf{S_t}) \\
=&g_s\mu_B\sum_{p=-1}^{1}(-1)^p\mathrm{T}^1_p(\mathbf{B}_1(t))\mathrm{T}^1_{-p}(\mathbf{S_t}) \\
=&\frac{g_s\mu_B B_1(t)}{\sqrt{2}}(\mathrm{T}^1_{-1}(\mathbf{S_t})-\mathrm{T}^1_1(\mathbf{S_t}))=g_s\mu_B B_1(t)S_{t,x}.
\end{aligned}
\tag{21}
$$

This result is consistent with the definition we have taken in the last section, in which the driving field is proportional to $S_{t,x}$. For convenience, we define $\Omega_2 = g_s\mu_B B_1/\hbar = \gamma_B B_1$ when $B_1(t)$ (the amplitude of the microwave driving field) remains constant during the time of applying the magnetic field, i.e., $B_1(t) = B_1$. Hence, when $B_0 = 0$, we have

$$
\Omega_1(\Omega, B_0=0) = \gamma_B B_1(-\sin\phi\sin\chi+\cos\theta\cos\phi\cos\chi). \tag{22}
$$

$B_0 \neq 0$ **situation.** For the general case with the presence of the external static magnetic field, the eigen-states will be affected by the Zeeman effect. In the previous sections, we have derived the eigenstates $|T_i'\rangle, i = x, y, z$ by diagonalizing the Hamiltonian matrix. Therefore, we can express the Rabi frequency Ω_1 in the new basis of $|T_i'\rangle$ as follows:

$$
\begin{aligned}
\Omega_1 =& \frac{1}{\hbar}\langle T_x'|H(t)|T_z'\rangle \\
=& \frac{g_s\mu_B B_1}{\sqrt{2}\hbar}\sum_{q=-1}^{1}(-1)^q\langle T_x'|[\mathfrak{D}^{(1)}_{-1,q}(\Omega)-\mathfrak{D}^{(1)}_{1,q}(\Omega)]\mathrm{T}^1_{-q}(\mathbf{S})|T_z'\rangle \\
=& \frac{1}{\sqrt{2}}\gamma_B B_1\sum_{q=-1}^{1}(-1)^q[\mathfrak{D}^{(1)}_{-1,q}(\Omega)-\mathfrak{D}^{(1)}_{1,q}(\Omega)]\langle T_x'|\mathrm{T}^1_{-q}(\mathbf{S})|T_z'\rangle \\
=& \frac{e^{i\chi}}{\sqrt{2}}\gamma_B B_1(-i\sin\phi-\cos\phi\cos\theta)\langle T_x'|\mathrm{T}^1_1(\mathbf{S})|T_z'\rangle \\
& -\gamma_B B_1\sin\theta\cos\phi\langle T_x'|\mathrm{T}^1_0(\mathbf{S})|T_z'\rangle \\
& \frac{e^{-i\chi}}{\sqrt{2}}\gamma_B B_1(-i\sin\phi+\cos\phi\cos\theta)\langle T_x'|\mathrm{T}^1_{-1}(\mathbf{S})|T_z'\rangle.
\end{aligned}
\tag{23}
$$

One may notice that, when $\Omega=(0,0,0)$ in the strong B_0 field approximation, the Rabi frequency of $|m=1\rangle$ to $|m=0\rangle$ transition is $\sqrt{2}\gamma_B B_1/2$, which is consistent with the result that $\langle m=1|\gamma_B B_1 S_x|m=0\rangle=\sqrt{S(S+1)-m(m+1)}\gamma_B B_1/2=\sqrt{2}\gamma_B B_1/2$.

In experiment, given that ϕ (the rotation angle about the lab-z axis) has no affect on the energy levels, we can take an average of the $|\Omega_1|^2$ over ϕ, represented as $\langle|\Omega_1|^2\rangle_\phi$, and take its squared root as the rabi frequency of the system. We have

$$
\begin{aligned}
&|\Omega_1|^2 \\
=&|C_1e^{i\chi}(-i\sin\phi-\cos\phi\cos\theta)+C_2\sin\theta\cos\phi \\
&+C_3e^{-i\chi}(-i\sin\phi+\cos\phi\cos\theta)|^2 \\
=&|C_1|^2(\sin^2\phi+\cos^2\phi\cos^2\theta)+|C_2|^2\sin^2\theta\cos^2\phi \\
&+|C_3|^2(\sin^2\phi+\cos^2\phi\cos^2\theta) \\
&+C_1C_2^*e^{i\chi}(-i\sin\phi-\cos\phi\cos\theta)\sin\theta\cos\phi \\
&+C_1C_3^*e^{2i\chi}(-1)(-i\sin\phi-\cos\phi\cos\theta)^2 \\
&+C_2C_1^*e^{-i\chi}(i\sin\phi-\cos\phi\cos\theta)\sin\theta\cos\phi \\
&+C_2C_3^*e^{i\chi}(i\sin\phi+\cos\phi\cos\theta)\sin\theta\cos\phi \\
&+C_3C_1^*e^{-2i\chi}(-1)(-i\sin\phi+\cos\phi\cos\theta)^2 \\
&+C_3C_2^*e^{-i\chi}(-i\sin\phi+\cos\phi\cos\theta)\sin\theta\cos\phi,
\end{aligned}
\tag{24}
$$

where

$$C_1=\frac{\gamma_B B_1}{\sqrt{2}}\langle T_x'|\mathrm{T}^1_1(\mathbf{S})|T_z'\rangle, \tag{25}$$

$$C_2=-\gamma_B B_1\langle T_x'|\mathrm{T}^1_0(\mathbf{S})|T_z'\rangle, \tag{26}$$

and

$$C_3=\frac{\gamma_B B_1}{\sqrt{2}}\langle T_x'|\mathrm{T}^1_{-1}(\mathbf{S})|T_z'\rangle. \tag{27}$$