Spin-dynamics and relaxation in Posner Molecules

A dissertation submitted in partial satisfaction
of the requirements for the degree
Bachelor of Science
in
Physics

by

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June 2020
The Dissertation of Vincent Hou is approved.

[Signature]

Professor Matthew P.A. Fisher, Committee Chair

March 2020
Acknowledgements

I’m very grateful for the opportunity to work as part of the Quantum Brain Project. I would like first to thank Professor Matthew P.A. Fisher for allowing me to join this fascinating research journey. His instinctive insight has always surprised me. The most precious thing I learnt from him is the way to to ask good questions, which is essential to any scientific research.

I would also like to thank my graduate mentor Yaodong Li, for all his help and patience during the past year. He guided me through the whole research process and encouraged me to explore hard concepts on my own, which truly builds up my ability. Apart from the subject, he also enlightened me on the understanding of the philosophy of physics research, which will always be kept with me to the future.

I really appreciate all the members in the group, specifically Joshua Straub who offered great suggestions on my project. Additionally, I would also like to thank Wayne Weng and Farzan Vafa for their kind help and inspiring discussions.
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Chapter 1

Introduction

1.1 Possibility of quantum processing in the brain

It has long been presumed that quantum mechanics cannot play a functional role in the brain, since maintaining quantum coherence on macroscopic time scales (seconds up to hours) is unlikely in its environment \[1, 2\]. Small molecules and individual ions go through environmental decoherence very quickly, which causes a rapid de-phasing of any quantum coherent phenomena. However, one exception is the nuclear spins. They are weakly coupled to the environmental degrees of freedom. Past research has shown that, under some circumstances, phase coherence times of five minutes or perhaps longer are possible \[3, 4\]. Putative quantum processing with nuclear spins in the brain has been proposed \[5\]. One of its fundamental requirement is a common biological element with a long nuclear spin coherence time to serve as a qubit, the standard unit of quantum information.
1.2 Quantum processing with Posner molecules

In 2015, M.P.A. Fisher identified the phosphorus nucleus, with nuclear spin $I = \frac{1}{2}$, as a possible biological element to serve as a neural qubit \[6\]. Phosphorus populates biological systems in the form of phosphate ion $\text{PO}_4^{3-}$. If another biological cation with nuclear spin $I = 0$ can displace the proton in binding to the phosphate ions, longer spin coherence times might be possible \[6\]. Fisher then proposed that a stable calcium-phosphate molecule $\text{Ca}_9(\text{PO}_4)_6$ would serve well for this purpose. The phosphorus spins in a Posner molecule are expected to have long coherence times \[6\].

Decent amount of experiments provided evidence that Posner clusters are stable in solution \[7, 8, 9, 10\]. Quantum chemistry calculations were also performed to examine the arrangement of the ions in a Posner molecule. The basic form consists of eight calcium ions situated on the corners of a cube, with the ninth located at the center, while six phosphate ions reside on the six faces of the cube. One of the most stable configurations was found to have $S_6$ symmetry, with a 3-fold rotational symmetry axis that is aligned along one of the cube diagonals \[11\]. Because of that, Fisher introduced a special quantum number called the “pseudo-spin”, and accordingly conjectured that the nuclear spin and rotational states are thus quantum entanglement in the Posner molecule \[6\]. It then led to a remarkable argument, that the binding reaction of two Posner molecules induces a “projective measurement” onto a state with zero total pseudo-spin, that ultimately could induce an impact neuron firing \[6\].

All these putative quantum processes essentially require a long spin/pseudospin coherence time. Therefore, in this thesis, we examine both spin and pseudospin relaxation times of a Posner molecule by mainly considering the influence from its rotational dynamics. We confirm a universal scaling form with numerical simulations (Ch. \[4\]), and provide an estimation for both relaxation times. Our estimations for spin relaxation time
and pseudospin relaxation time are $T_{(S_z)} \approx 2.5 \sim 25$ hrs and $T_{\tau} \approx 1.7 \sim 17$ hrs.
Chapter 2

Basics of a Posner molecule

2.1 Geometry of a Posner molecule

The Posner molecule, Ca_9(PO_4)_6, is a nanometer calcium-phosphate cluster that is conjectured to be stable in human body fluids, assumed to play an important role in bone-formation, etc. In a Posner molecule, both oxygen and calcium ions have nuclear-spin \( I = 0 \). They contribute only electronic degrees of freedom, which does not fall into the focus of this Thesis. We therefore ignore both ions, and focus on the phosphorus nuclei only.

Assuming the molecule’s stability (Sec. 1.2), its structure has been calculated with ab-initio methods, and is shown to have the shape of a distorted cube (Fig. 2.1a). Tetrahedral phosphate ions (PO_4^{3–}) are located at each center of all six cube faces. The distortion is an elongation along the [1, 1, 1] direction, which breaks the cubic symmetry group down to \( S_6 \). The group \( S_6 \) contains the three-fold rotation along the [1, 1, 1] cube diagonal, \( C_3 \).

\footnote{While here we are not considering the calcium and oxygen ions, it turns out that inclusion of them does not change the space group.}
We choose a reference frame where the $[1, 1, 1]$ direction coincides with the $z$-axis; this choice of reference frame will turn out to be convenient, since we will be mostly considering the rotational motions of the molecule, rather than its translational motions. It is referred as the *internal frame*. A demonstration of the molecule with the $z$-axis highlighted is shown in Fig. 2.1b. We choose the other cube diagonal in $[-1, 0, 1]$ direction, that is perpendicular to the $z$-axis, to be the $x$-axis; and that the $x - y$ plane intersects with the $z$-axis at its midpoint, denoted as the origin. Phosphorus nuclei are located at the vertices of two triangles that are perpendicular to the $z$-axis. The black triangle and the grey triangle represent the planes at $z = h_+$ and at $z = h_-$ respectively, where $h_{\pm}$ are their $z$-coordinates. The relative angle between the black triangle and the grey triangle is $\pi/3$. $\phi$ denotes the molecule’s orientation relative to the $z$-axis. Let $\varphi_i$ be the angular coordinate of the $i$-th nuclei, we note that $\varphi_i$’s of the black triangle are $\phi$, $\phi + 2\pi/3$ and $\phi + 4\pi/3$, while the nuclei of the grey triangle has orientations of $\phi + \pi/3$, $\phi + \pi$ and $\phi + 5\pi/3$.

### 2.2 Quantum mechanics of a single Posner molecule

*(static)*

Inside a single Posner molecule, every phosphorus nucleus has spin $s = \frac{1}{2}$. A Hilbert space $\mathcal{H}_{\text{nuc}}^{\text{spin}} = \mathbb{C}^2$ is associated to each nuclear spin-$\frac{1}{2}$ degrees of freedom. Since there are a total of 6 nuclei, the Posner molecule’s Hilbert space $(\mathcal{H}_{\text{nuc}}^{\text{spin}})^\otimes 6$ has $2^6 = 64$ dimensions. A convenient computational basis for the Hilbert space is the set of tensor products of $\sigma^z$ eigenstates: $B_{\text{comp}} = \{|00\ldots0\rangle, \ldots, |11\ldots1\rangle\}$.

Consider a counterclockwise rotation of $2\pi/3$ about the geometric symmetry axis $z$ (Fig. 2.1). The nuclear spins undergo a counterclockwise permutation after the rotation.
Figure 2.1: Geometry of Posner molecule. Each phosphate ion resides on the center of a cube face. The threefold symmetry axis is chosen to be the $z$-axis, and highlighted as the black arrow in Fig. 2.1a. The cube diagonal in $[-1,0,1]$ direction is picked to be the $x$-axis of the internal frame and $y$-axis is then determined with right-hand rule. Two equilateral triangular planes ($h_+$ and $h_-$) each formed by three phosphate ions are perpendicular to the $z$-axis. The initial position of the triangles each has one vertex with $x$-coordinate being zero and the corresponding opposite side parallel to the $y$-axis. Both triangle pairs are invariant under rotations by $2\pi/3$ around the symmetry axis, a consequence of the $C_3$ symmetry. In Fig. 2.1b, the molecule is rotated by angle $\phi$ from its initial position. The long dashed line indicates a rotation of $2\pi/3$ such that the triangle pair remains invariant.

We denote this permutation by operator $C_3$, such that it transforms the $B_{\text{comp}}$ elements as

$$C_3 |m_1m_2m_3m_4m_5m_6\rangle = |m_3m_1m_2m_6m_4m_5\rangle.$$  

(2.1)

label the vertices from 1...6 in Fig. 2.1. Since $(C_3)^3 = 1$, $C_3$ has eigenstates with eigenvalues $\omega^\tau$ where $\omega = e^{i2\pi/3}$ and $\tau = 0, \pm 1$. We define $\tau$ as the pseudospin quantum number. The Posner dynamics conserve $C_3$. We therefore seek for $C_3$ eigenstates to be the states that store quantum information [13]. Our convention of choosing eigenstates is
somewhat arbitrary, but convenient. We choose $C_3$, $S_{1\ldots6}^{z_{\text{lab}}}$, and $S_{1\ldots6}^2$ to be the complete set of commuting observables that fully breaks the degeneracies \[11\]. The eigenspaces $\mathcal{H}_\tau$ have 24-, 20-, and 20-fold degeneracies for $\tau = 0, 1$ and -1 respectively. Hence we classify the 64 eigenstates into 3 sectors depending on $\tau$.

Here we present a detailed demonstration of this analysis within a simple, fictitious molecule of three phosphorous nuclear spins residing on the vertices of a perfect triangle, say the one on the $h_+$ plane in Fig. 2.1a. The triple-spin plane corresponds to an 8-dimensional Hilbert space $\mathbb{C}^8$. $C_3$, $S_{123}^{z_{\text{lab}}}$, and $S_{123}^2$ share a total of 8 eigenstates in Table 2.1.

<table>
<thead>
<tr>
<th>State</th>
<th>Decomposition</th>
<th>$S_{123}$</th>
<th>$S_{z_{\text{lab}}}$</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$</td>
<td>000\rangle$</td>
<td>$3/2$</td>
<td>$3/2$</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{1}{\sqrt{3}}(</td>
<td>011\rangle +</td>
<td>101\rangle +</td>
<td>110\rangle)$</td>
</tr>
<tr>
<td>3</td>
<td>$\frac{1}{\sqrt{3}}(</td>
<td>100\rangle +</td>
<td>010\rangle +</td>
<td>001\rangle)$</td>
</tr>
<tr>
<td>4</td>
<td>$</td>
<td>111\rangle$</td>
<td>$3/2$</td>
<td>$-3/2$</td>
</tr>
<tr>
<td>5</td>
<td>$\frac{1}{\sqrt{3}}(</td>
<td>011\rangle + \omega^2</td>
<td>101\rangle + \omega</td>
<td>110\rangle)$</td>
</tr>
<tr>
<td>6</td>
<td>$\frac{1}{\sqrt{3}}(</td>
<td>100\rangle + \omega^2</td>
<td>010\rangle + \omega</td>
<td>001\rangle)$</td>
</tr>
<tr>
<td>7</td>
<td>$\frac{1}{\sqrt{3}}(</td>
<td>011\rangle + \omega</td>
<td>101\rangle + \omega^2</td>
<td>110\rangle)$</td>
</tr>
<tr>
<td>8</td>
<td>$\frac{1}{\sqrt{3}}(</td>
<td>100\rangle + \omega</td>
<td>010\rangle + \omega^2</td>
<td>001\rangle)$</td>
</tr>
</tbody>
</table>

Table 2.1: The three nuclear spins correspond to an 8-dimensional Hilbert space. A convenient choice of eigenstates is the eigenbasis shared by $S_{123}^2$, $S_{123}^{z_{\text{lab}}}$ and $C_3$. All states’ eigenvalues of each operator are listed in sequence in the table.

Coupling between phosphorus nuclear spins arises due to two factors: J-coupling, which is an indirect interaction between two nuclear spins; and the magnetic dipole-dipole interaction. The Hamiltonian of the J-coupling has an effective Heisenberg-like

---

1The internal frame rotates relative to the lab frame denoted by the subscript $\text{lab}$. Measurements of spins is conducted under this reference frame. So we define operator $S_{123}^{z_{\text{lab}}} = \sum_{i=1}^6 1 \otimes (i-1) \otimes S_i^{z_{\text{lab}}} \otimes 1 \otimes (6-i)$, where $1$ is the 2-by-2 identity matrix.

2The total-spin operator is defined as follows: $S_{1\ldots6}^2 = (S_1 + S_2 + \cdots + S_6)^2 = (\sum_{i=1}^6 1 \otimes (i-1) \otimes S_i \otimes 1 \otimes (6-i))^2$. 

---

7
form of \[\text{(11)}\]

\[H_J = \sum_{\langle i,j \rangle} J_{ij} \cdot S_i \cdot S_j. \quad (2.2)\]

The pair-dependent interaction strength is denoted by \(J_{ij}\). \(H_J\) encompasses \(C_3\) symmetry, \(SU(2)\) symmetry, and time-reversal symmetry. It is also time-independent, such that the total-spin \(S_{1\cdots6}\), \(z\) component of total-spin \(s_{1\cdots6}^{z_{lab}}\) and pseudospin \(\tau\) are all conserved. Hence we express the eigenstates using four quantum numbers,

\[|\alpha\rangle = |E, S_{1\cdots6}, s_{1\cdots6}^{z_{lab}}, \tau\rangle, \quad (2.3)\]

where \(E\) is the J-coupling energy (in Hz) and \(\alpha = 1, 2, \ldots, 64\). The Hamiltonian of dipole-dipole interaction is given by,

\[H_D = \sum_{\langle i,j \rangle} J_{D,ij} \cdot [S_i \cdot S_j - 3(S_i \cdot \hat{r}_{ij})(S_j \cdot \hat{r}_{ij})], \quad (2.4)\]

with \(J_{D,ij} = \frac{\mu_0 \gamma_i^2 \hbar}{4\pi r_{ij}^3}\) denoting the dipolar coupling strength. \(H_D\) has time-reversal symmetry only, and conserves neither spin nor pseudospin. We therefore consider \(H_D\) to be responsible for both spin and pseudospin relaxations of the initial/eigenstates. \(H_D\) is also orientation-dependent, which is therefore also time-dependent when the molecule undergoes rotational dynamics. The dynamics is therefore “stochastic”. For that reason, we do not expect oscillations/revivals in observables (spin and pseudospin). Rather, we expect exponential decay/relaxation of these observables to their values in equilibrium. It is therefore possible to define a “relaxation time” for these observables.

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\(^4\)Here we neglected dipolar interactions contributed by surrounding molecules/ions mainly because they have larger inter-particle distances with the phosphorus nuclei. Coupling strength \(J_{D,ij}\) is inversely proportional to the inter-particle distances by a power of three. Therefore, dipolar interactions induced by particles outside the Posner molecule is expected to be unimportant compared to intra-molecular dipolar interactions. The relaxation time can be as long as 21 days \[\text{(11)},\] much larger than our estimation (Sec. 4.3, indicating its insignificance in the relaxation process.
Chapter 3

Dynamical model of a single rotating Posner molecule

3.1 Rotational motion of the molecule (time-dependence of $H_D$)

In a microscopic view, the motion of the molecule is composed of segments of ballistic rotation, where the angular speed depends on the thermal energy of the Posner molecule; and the change of directions between consecutive ballistic “duration”s, attributed to collisions with the surrounding particles (e.g. water molecules). These can be summarized as a discrete-time stochastic process made up by ballistic “hop”s (Fig. 3.1).

Let $p$ be a phosphorus nucleus’ positional vector in the internal frame. At $t = 0$, the internal frame is the same as the lab frame. Then the internal frame starts to rotate randomly relative to the lab frame around its origin being a fixed point. It is convenient to construct a random rotation matrix $R$ that acts on $p$ to determine its coordinate in the lab frame. The random rotation matrix consists two parts: pick a random rotational
axis, and perform the rotation by a random angle $\theta$, generating a total of three degrees of freedom: two from the selection of rotational axis and one from the random angle rotated.

The selection of random rotational axis is done by performing a random SO(3) matrix $Q$ (App. A.2). This rotational axis is treated as the $z$-axis, such that an angle of $\Delta \theta$ is rotated around this axis in the clockwise direction. Let $A$ denote the rotation matrix around $z$-axis,

$$A = \begin{bmatrix}
\cos \theta & \sin \theta & 0 \\
-\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{bmatrix}. \quad (3.1)
$$

Performing a linear transformation such that this rotation is performed around the random $z$-axis picked by the random SO(3) matrix, we end up with

$$R = Q^T AQ. \quad (3.2)$$

We further refine this model with several parameters describing the stochastic ballistic angle, the angular velocity, and time duration for each discrete hop. Stochastic ballistic angle $\Delta \theta$ is a random variable with probability distribution of $Uniform(-\theta_b, \theta_b)$, where $\theta_b$ notates the largest possible ballistic angle swept by the molecule before it changes rotational direction. The stochastic ballistic angle $\Delta \theta$ is swept by a continuous rotation (Fig. 3.1) at angular speed $\omega_T$ determined by thermal energy, such that,

$$\frac{1}{2} I \omega_T^2 = \frac{3}{2} k_B T. \quad (3.3)$$

The stochastic ballistic time $\Delta t$ taken by each hop is given by $\Delta \theta / \omega_T$. For clarity we also introduce the ballistic time constant $t_b = |\theta_b| / \omega_T$. We conclude that $\Delta t \sim$
Uniform(0, t_b).

Figure 3.1: Here we present a simplified 2-dimensional demonstration of the rotational motion model. The arrowed vectors represent the orientations of the Posner molecule at $t_0$, $t_1$, and $t_2$, where $t_{i+1} = t_i + \Delta t_{i+1}$. The tail/beginning of the orientation-vector is fixed at the center of a unit sphere, and the head/end of the vector lands on the surface of the sphere. Each stochastic hop sweeps an angle of $\Delta \theta_i \sim \text{Uniform}(-\theta_b, \theta_b)$. Each hop is a continuous rotational motion with angular speed $\omega_T$, as demonstrated in Fig. 3.1b. Stochastic ballistic time $\Delta t$ has probability distribution $|\text{Uniform}(-\theta_b, \theta_b)|/\omega_T \equiv \text{Uniform}(0, t_b)$.

When viewed in the long-time limit, there are three limiting cases of $\theta_b$:

- When $\theta_b \rightarrow 0$, the model turns into a Brownian motion/rotational diffusion.

- When $\theta_b \rightarrow \pi$, the model turns into a discrete jump where the landing points of the orientation-vector’s head are distributed uniformly on the surface of a unit sphere.

- When $\theta_b \rightarrow \infty$, the model turns into a ballistic motion.

However, we notice that the limits of this motion are not directly related to pseudospin/spin dynamics (Sec. 3.2).
3.2 Pseudospin/spin dynamics

In this thesis, all Hamiltonians are written in units of Hz, such that $\hbar$ does not appear in time evolution operators. The strengths of the two interactions described in Sec. 3.1 depends on constants $J$ and $J_D$ respectively. The total Hamiltonian $H(t)$ that acts on the initial state is

$$H(t) = H_J + H_D(t), \quad (3.4)$$

such that the time-evolution operator has the form

$$U(t, t_0) = T e^{-i \int_{t_0}^t dt' H(t')} . \quad (3.5)$$

The time-ordering operator in Equation 3.5 is essential because $[H_D(t_i), H_D(t_j)] \neq 0$. There are no simple ways in which to handle the time-ordered exponentials given the complexity of $H_D$’s dependence on time. So we go for the form of direct numerical integration which evaluates the propagation of a wavefunction over a time period $t$ by discretizing time into $n$ small steps of width $\delta t = t/n$, assuming the change of the system is small in each step. The time-evolution operator is then simplified with the approximation,

$$U(t + \delta t, t) = e^{-i \int_{t}^{t+\delta t} dt' H(t')} \approx e^{-i \delta t H(t)} . \quad (3.6)$$

\(^1\)For the Posner molecule, the dipolar coupling strength $J_D (\approx 988.8 \text{ Hz}, \text{ shown in Sec. 4.3})$ is several orders of magnitude greater than the J-coupling strength $J$ (computation by Swift shows $J_1 = 0.178 \text{ Hz}$, $J_2 = 0.145 \text{ Hz}$ and $J_3 = -0.003 \text{ Hz}$, each representing J-coupling strength of nearest-neighbor, second-nearest-neighbor and third-nearest-neighbor) \[^{[1]}\]. We therefore neglect the influence from J-couplings on the initial states in the numerical simulations.
Such that the time operator over time $t$ can be written as a product of $n$ operators over the small intervals,

$$ U(t, t_0) = \lim_{\delta t \to 0} [U_n \cdots U_2 U_1] = \lim_{n \to \infty} \prod_{k=1}^{n} U_k, \quad (3.7) $$

where time propagation over the $k$th step/interval is

$$ U_k = e^{-i\delta t H(t_{k-1})}; \quad t_k = k \delta t. \quad (3.8) $$

The final state after an evolution of time $t$ is

$$ |\alpha, t_0; t \rangle = U(t, t_0) |\alpha, t_0 \rangle = \lim_{n \to \infty} \prod_{k=1}^{n} e^{-iH(t_{k-1})\delta t} |\alpha, t_0 \rangle. \quad (3.9) $$

For a single ballistic motion that sweeps an angle of $\Delta \theta$ (Fig. 3.1), the time taken is $\Delta t = \Delta \theta / \omega_T$. Hence in numerical integration form, the total steps/interval $n = \Delta t / \delta t$, such that

$$ |\alpha, t_0; t_0 + \Delta t \rangle = \lim_{\delta t \to 0} \prod_{k=1}^{\Delta t / \delta t} e^{-iH(t_{k-1})\delta t} |\alpha, t_0 \rangle. \quad (3.10) $$

Suppose the stochastic process runs for a total of $m$ steps, and denote $\Delta \theta_1, \Delta \theta_2, \ldots \Delta \theta_m \overset{i.i.d.}{\sim} \text{Uniform}(\theta_b, \theta)$ as the sizes of the hops, while $\Delta t_j = \Delta \theta_j / \omega_T$. Then we arrive at a full expression of the time propagation with the defined model (Sec. 3.1),

$$ |\alpha, t_0; t_0 + \sum_{j=1}^{m} \Delta t_j \rangle = \lim_{\delta t \to 0} \left( \prod_{k=1}^{\Delta t / \delta t} e^{-iH(t_{k-1})\delta t} \right) \cdots \left( \prod_{k=1}^{\Delta t_1 / \delta t} e^{-iH(t_{k-1})\delta t} \right) |\alpha, t_0 \rangle, \quad (3.11) $$

It is unrealistic to push $\delta t$ to the infinitely-near-zero regime in numerical simulations due to both obstacles coming from the highest precision a numerical quantity may have and
3.3 Heuristic picture of spin/pseudospin dynamics

Consider a spin on a Bloch sphere, where the north and south poles are chosen to be the spin-up $|0\rangle$ and spin-down $|1\rangle$ states. First consider placing this spin in an external field that continues to be turned on and off frequently, each time pointing towards a random direction in 3-dimensional space. Then consider a single phosphorus spin in a Posner molecule, which continues to rotate randomly, also, in 3-dimensional space. Since both cases have stochastic Hamiltonian changing with time - one is an external field, on is the dipolar coupling, we can draw an analogy between both cases. We provide the single spin analysis of the simple model (random field) and reach a scaling relation which we hope to also be valid for the original model (random rotational dynamics of the Posner molecule). The spin state then will precess an angle of $\varphi$ on the Bloch sphere, towards around the direction of the field, by an angle of

$$\varphi \sim J_D \tau_c,$$

where $\tau_c$ is the time that the field stays on in this direction. The Bloch vector of the spin performs a random walk on the surface of a unit sphere as the field is turned on and off in random directions. The spin state can be recognized as completely relaxed when its spin direction is flipped (a total precession of $\pi$). Following the random walk argument, it takes an average of $(\pi/\varphi)^2$ steps for the spin state to flip entirely (e.g. from $|0\rangle$ to $|1\rangle$), where each step consumes a time of $\tau_c$. Therefore the average time needed for a complete relaxation is $(\frac{\pi}{J_D \tau_c})^2 \tau_c$, suggesting that the spin and pseudospin relaxation time
has scaling form

\[ T_{\langle S_z \rangle} \sim J_D^{-2} \tau_c^{-1}; \quad T_\tau \sim J_D^{-2} \tau_c^{-1}, \]  

(3.13)

where this result is consistent with the Solomon-Bloembergen equation \[14\].

The definition for \( \tau_c \) can be arbitrary. The only significance is its dependence on \( \theta_b \) and \( t_b \), coming from our rotational dynamics model. We define \( \tau_c \) to be the rotational correlation time of the Posner molecule, the average time it takes for it to rotate \( \phi \) radians \footnote{\( \phi \) can be defined arbitrarily, but usually taken as 1}. We establish a rough relationship between \( \tau_c \) and \( \{\theta_b, t_b\} \). Begin with describing the stochastic process described in Sec. 3.1. Let \( \theta_n \) denote the mean-square angular deviation of the rotational diffusion,

\[ \langle \theta_n^2 \rangle = n \langle \Delta \theta^2 \rangle, \]  

(3.14)

where \( n \) denotes the number of stochastic steps (Sec. 3.1). The probability distribution of \( \Delta \theta \) is Uniform\((-\theta_b, \theta_b)\), such that

\[ \langle \Delta \theta^2 \rangle = \text{Var}(\Delta \theta) + \langle \Delta \theta \rangle^2 = \frac{\theta_b^2 - (-\theta_b)^2}{12} + 0 = \frac{\theta_b^2}{3}. \]  

(3.15)

Each hop takes time \( \Delta t \) to finish. Since \( \Delta t \sim \text{Uniform}(0, t_b) \), the average duration of \( n \) stochastic steps is

\[ n \langle \Delta t \rangle = nt_b/2, \]  

(3.16)

Now suppose

\[ \langle \theta_n^2 \rangle = \phi^2, \]  

(3.17)

where \( \phi \) is a constant number. Then the time to reach a mean-square angular deviation of \( \phi^2 \) is

\[ n \langle \Delta t \rangle = \frac{3\phi^2}{\theta_b^2} \cdot \frac{t_b}{2} = \frac{3\phi^2}{2} \cdot \frac{t_b}{\theta_b^2}. \]  

(3.18)
For $\phi$ being a small number (the mean-square angular deviation is small), the orientation of the molecule is approximately not changed, which is equivalent to the field being on in one direction for time $\tau_c$. Hence we conclude that

$$\tau_c = K t_b \theta_b^2 = \frac{K}{\omega_T \theta_b},$$

with $K$ being a tunable order-one constant that depends on the exact choice of $\phi$’s magnitude. The scaling form is

$$\tau_c \sim \omega_T^{-1} \theta_b^{-1}.$$ (3.20)

Define scaling parameters $C_{\langle S_z \rangle}$ and $C_\tau$. Combining with Equation 3.13, we arrive at a universal scaling form of

$$T_{\langle S_z \rangle} = \frac{C_{\langle S_z \rangle} \theta_b \omega_T}{J_D^2}; \quad T_\tau = \frac{C_\tau \theta_b \omega_T}{J_D^2}.$$ (3.21)

For this Bloch sphere picture to be valid, we require

$$\Delta \varphi \sim \frac{J_D}{\theta_b \omega_T} << 1,$$ (3.22)

which corresponds to certain regimes of $\theta_b$, $\omega_T$ and $J_D$ in numerical simulations. The constraint equation is

$$\theta_b >> J_D/\omega_T.$$ (3.23)

This condition (Equation 3.22) is supposed to be satisfied by the real Posner molecule. We expect common values of $\theta_b$ to fall in the range of $\pi/10 \sim \pi$. Based on that, with parameters $J_D \approx 988.8$ Hz and $\omega_T = 3.2 \times 10^{11}$ rad s$^{-1}$ (details in Sec. 4.3), $\Delta \varphi$ has a range of $10^{-9}$ to $10^{-8}$ that is much less than 1.

Our approach in this paper is to confirm the universal scaling form above (with
numerically accessible sets of parameters constrained by Equation 3.23, and extrapolate to parameters for a real Posner molecule (these parameters are dramatic/impossible to simulate numerically), thereby getting a semi-quantitative estimation of $T_{\langle S_z \rangle}$ and $T_\tau$. 

$T_{\langle S_z \rangle}$ can, in principle, be directly measured in NMR experiments, whereas one can infer the other ($T_\tau$).
Chapter 4

Results of numerical simulations

4.1 Results on spin relaxation

We choose the initial spin states in similarly as the initial pseudospin states (Sec. 2.2), except that spin states are not necessarily the eigenstates of $C_3$, therefore

$$|s_{\alpha}\rangle = |E, S_{1...6}, S_{1...6}^{\text{lab}}\rangle. \quad (4.1)$$

In principle, each initial state would have a decaying rate (Fig. 4.1a). As mentioned in Sec. 2.2, we expect observable $\langle S_{z}^{\text{lab}} \rangle$ (denoted as $\langle S_z \rangle$ in this chapter for simplicity) to perform exponential relaxation, therefore,

$$\langle S_z \rangle(t) = e^{-t/T_{\langle S_z \rangle}} \langle S_z \rangle(t = 0). \quad (4.2)$$

This statement is supported by numerical simulations as shown in Fig. 4.1b. Despite some noisy peaks around the equilibrium value, which is $\langle S_z \rangle = 0$, the simulated data is linear on the log-linear scale.

There are 64 initial spin states in total. Listing the decaying rates for all initial states
Figure 4.1: $\langle S_z \rangle(t)$ of different initial spin states, presented in linear-linear scale and log-linear scale. The numerical inputs are $\omega_T = 1000\pi$ rad $s^{-1}$, $J_D = 200$ Hz, and $\theta_b = \pi$ rad. In Fig. 4.1(a), absolute values are taken in order to present the negative $S_z$ data. Spin states with initial $\langle S_z \rangle(t = 0) = 0$ performs no relaxation, so are excluded in the log-linear plot (Fig. 4.1(b)). Results of numerical simulations provide a strong support on our assumption on the relaxation being exponential. The equilibrium value is shown to be $\langle S_z \rangle = 0$. When the relaxation approach the equilibrium value, our simulation becomes less accurate. It is not possible for the computer to output values that are infinitely close to 0. Hence peaks of noise/fluctuation occur at the tail in Fig. 4.1(b).

is not very helpful. However, we can define a “total”/“effective” rate, when starting from a mixed state of all 64 eigenstates. For concreteness, we choose a state as prepared by applying a magnetic field at finite temperature, and the canonical-ensemble partition function is

$$Z = \sum_{\alpha=1}^{64} e^{-\beta h s^z_{\alpha}}.$$  \hfill (4.3)
The probability of the mixed state is in state $|s_\alpha\rangle$ is

$$p_\alpha = \frac{e^{-\beta hs^z_\alpha}}{Z}.$$  \hfill(4.4)

The net magnetization in $z$-direction of the mixed state at time $t$ is

$$M_z(t) = \sum_\alpha p_\alpha e^{-t/t_\alpha} s^z_\alpha,$$  \hfill(4.5)

where $t_\alpha$ is the spin lifetime of the state $|s_\alpha\rangle$. By Taylor expansion in the small parameter $\beta h \ll 1$, $e^{-\beta hs^z_\alpha} \approx 1 - \beta hs^z_\alpha$, we have

$$M_z(t) \approx -\frac{\beta h}{64} \sum_\alpha (s^z_\alpha)^2 e^{-t/t_\alpha}.$$  \hfill(4.6)

For $t \ll t_\alpha$, before the state is fully relaxed, we can also Taylor expand the $e^{-t/t_\alpha}$ term,

$$M_z(t) = -\frac{\beta h}{64} \sum_\alpha (s^z_\alpha)^2 \left(1 - \frac{t}{t_\alpha} + \cdots\right);$$  \hfill(4.7)

in particular, $M_z(0) = -\frac{\beta h}{64} \sum_\alpha (s^z_\alpha)^2$. We also expect that

$$M_z(t) = M_z(0)e^{-t/T_{\langle S_z \rangle}} = -\frac{\beta h}{64} \left(\sum_\alpha (s^z_\alpha)^2\right) \cdot \left[1 - \frac{t}{T_{\langle S_z \rangle}} + \cdots\right].$$  \hfill(4.8)

By Equation 4.7 and 4.8, the total/effective rate is given by

$$\frac{1}{T_{\langle S_z \rangle}} = \frac{\sum_\alpha 64 \frac{(s^z_\alpha)^2}{t_\alpha}}{\sum_\alpha 64 (s^z_\alpha)^2}. \hfill(4.9)$$

We acquired data by time propagating all 64 spin states respectively with fixed parameter $\omega_T = 1000\pi \text{ rad s}^{-1}$, inputing different sets of $J_D$ and $\theta_b$ within the regime indicated in
Sec. 3.3 (Equation 3.22). We collect data of individual relaxation times \( t_\alpha \) from numerical simulations and then compute \( T\langle S_z \rangle \) with Equation 4.9.

![Diagram](image)

Figure 4.2: Data-collapse of relaxation time \( T\langle S_z \rangle \). Angular velocity \( \omega_T \) is fixed at 1000\( \pi \) rad s\(^{-1} \). Sets of \( J_D \) and \( \theta_b \) values are marked distinctively in shape-keys and color-keys. Individual relaxation times \( t_\alpha \) are estimated by the best fit slopes of the in the log-linear scale (presented in Fig. 4.1b). Collections of \( t_\alpha \)'s are used to compute the total/effective relaxation time \( T\langle S_z \rangle(J_D, \theta_b) \) by Equation 4.9 marked by colored shapes in both figures. Scaling parameter \( C \) is weakly dependent on \( \theta_b \) (Fig. 4.2a). The parameter \( C \) falls in the range [0.07, 0.12]. The representative scaling parameter is \( C = 0.09 \).

We pick 6 values for \( J_D \) ranging from 50 Hz to 500 Hz, and 10 values for \( \theta_b \) from a range of \( \pi/10 \) to \( \pi \). In Fig. 4.2a, we plot \( T\langle S_z \rangle \) against \( \theta_b \omega_T / J_D^2 \) and fit each group of data with the same \( \theta_b \). All the fitted lines are straight lines passing through the origin, declaring the linear relationship as expected. The slopes are weakly dependent on \( \theta_b \). Within the range we choose for \( \theta_b \), the slope rates do not differ from each other much. Therefore we can still structure a data-collapse that uses all data for the linear regression, presented

\footnote{Equation 3.19 which we use to obtain the universal scaling form (Equation 3.21) is based on the assumption that the rotational dynamical is approximately diffusive, meaning that \( \theta_b \to 0 \). When \( \theta_b \) gets larger in magnitude, Equation 3.19 may not necessarily hold. Hence it is reasonable to see such dependency.}
in Fig. 4.2b, on a log-log scale. The slope in Fig. 4.2b is 1, indicating the linearity, while the offset demonstrates the size of scaling parameter $C$. The rough confidence interval of $C$ is $[0.07, 0.12]$. Representative rate $C = 0.09$ gives an approximation of the scaling parameter $C_{\langle S_z \rangle}$ in Equation 3.23.

### 4.2 Results on pseudospin relaxation

Pseudospin $\tau$ is not a directly measurable observable. However, pseudospin relaxation of an initial state can be measured by the probability amplitude of it being in its initial $\tau$-sector. Suppose the ensemble is in a mixed state such that each of the pure states $\alpha$ occurs with probability $p_\alpha$. Then the corresponding density operator has form

$$\rho = \sum_\alpha p_\alpha |\alpha\rangle \langle \alpha|.$$  \hfill (4.10)

Denote the projection operator in $\tau$-sector as $\hat{P}_\tau$ and $|m; \tau\rangle$ as the eigenstate in the sector,

$$\hat{P}_\tau = \sum_m |m; \tau\rangle \langle m; \tau|.$$  \hfill (4.11)

The expectation value of this measurement can be calculated by

$$p_\tau = Tr[\hat{P}_\tau \rho].$$  \hfill (4.12)

The sectors have 24, 20, and 20 states for $\tau = 0, 1$ and $-1$ respectively (Sec. 2.2). Therefore, a completely relaxed state (defined by $p_\alpha = 1/64$ for all $\alpha$) has $p_{\tau=0} = 24/64$ and $p_{\tau=\pm1} = 20/64$.

We choose initial states to be maximally mixed within the sector for numerical simulation - that is, $p_\alpha = 1/24$ for $\alpha$ in the $\tau = 0$ sector, and $p_\alpha = 1/20$ for $\alpha$ in the $\tau = \pm1$.
Figure 4.3: $P_{\tau}(t)$ of different initial pseudospin states, presented in linear-linear scale and log-linear scale. The numerical inputs are $\omega_T = 1000\pi$ rad s$^{-1}$, $J_D = 200$ Hz, and $\theta_b = \pi$ rad. Initial states are maximally mixed within each $\tau$-sector. The probability functions are shifted exponential decays. The eigenspaces have 24-, 20-, and 20-fold degeneracies for $\tau = 0$, 1 and -1 respectively (Sec. 2.2). Therefore, theoretical equilibrium values of $P_{\tau}$ are $P_0(t \to \infty) = 24/64$ and $P_{\pm 1}(t \to \infty) = 20/64$. In Fig. 4.3b, the theoretical equilibrium values are subtracted in order to reveal the linearity. Results of numerical simulations provide a strong support on our assumption on the relaxation being exponential. Similar to $\langle S_z \rangle$ data (Fig. 4.1b), when the relaxation approaches the equilibrium value, our simulation becomes less accurate. Hence larger noise/fluctuations occur at the tail in Fig. 4.3b.
sector. Time propagating density matrix of $\tau$-sector initial state is

$$\rho_{\tau}(t) = U(t, t_0) \left[ \sum_{\alpha} p_{\alpha} \left| \alpha; \tau \right\rangle \left\langle \alpha; \tau \right| \right] U(t, t_0)^\dagger. \quad (4.13)$$

Hence we numerically evaluate

$$p_{\tau}(t) = \text{Tr}[\hat{P}_{\tau} \rho_{\tau}(t)]. \quad (4.14)$$

We expect $p_{\tau}$ to be a shifted exponential decay (Sec. 2.2),

$$p_{\tau}(t) = p_{\tau}(t \to \infty) + (1 - p_{\tau}(t \to \infty)) e^{-t/T_{\tau}}, \quad (4.15)$$

where $p_{\tau}(t \to \infty)$ is the equilibrium probability amplitude. This statement is supported by numerical simulations as shown in Fig. 4.4. Despite some noisy peaks around the equilibrium value, the modified simulated data is linear on the log-linear scale (Fig. 4.4b).

A data-collapse of 0-sector state is presented in Fig. 4.4. Similar to $\langle S_z \rangle$ data, we pick 6 values for $J_D$ ranging from 50 Hz to 500 Hz, and 10 values for $\theta_b$ from a range of $\pi/10$ to $\pi$. The linearity presented by the numerical results significantly support our universal scaling form (Equation 3.23). In Fig. 4.4a, we plot $T_{\tau}$ against $\theta_b \omega_T / J_D^2$ and fit each group of data with the same $\theta_b$. Like $T_{\langle S_z \rangle}$ data, all the fitted lines are straight lines passing through the origin, declaring the linear relationship as expected. The slopes are weakly dependent on $\theta_b$. The rough confidence interval of $C$ is [0.04, 0.08]. Representative rate $C = 0.06$ gives an approximation of the scaling parameter $C_{\tau}$ in Equation 3.23. Notably, $C_{\tau}$ scales similarly as $C_{\langle S_z \rangle}$. This conclusion implies the possibility of using experimentally measurable spin relaxation time to predict unmeasurable pseudospin relaxation time.

\[2\] See Appendix A.3 for $\pm1$-sectors.
Figure 4.4: Data-collapse of relaxation time $T_{\tau=0}$. Angular velocity $\omega_T$ is fixed at $1000\pi$ rad s$^{-1}$. Sets of $J_D$ and $\theta_b$ values are marked distinctively in shape-keys and color-keys. Each data point $T_\tau(J_D, \theta_b)$ is computed by Equation 4.9. Individual relaxation time (data point) is estimated by the best fit slope in the log-linear scale (presented in Fig. 4.3b). Scaling parameter $C$ is weakly dependent on $\theta_b$ (Fig. 4.4a). The parameter $C$ falls in the range [0.04, 0.08]. The representative scaling parameter is $C = 0.06$.

### 4.3 Extrapolation towards the reality

We define dipolar coupling strength $J_D$ (Sec. 2.2) as

$$J_{D,ij} = \frac{\mu_0 \gamma^2 \hbar}{4\pi r_{ij}^3}.$$  \hspace{1cm} (4.16)
Results of numerical simulations

Exact values of parameters and constants are as follows:

\[ \mu_0 = 4\pi \cdot 10^{-7}[\text{H m}^{-1}] \] \[ (4.17) \]

\[ \hbar = 1.05457 \cdot 10^{-34}[\text{J s}] \] \[ (4.18) \]

\[ r_{ij} \approx 4.75 \cdot 10^{-10} \sim 5.65 \cdot 10^{-10}[\text{m}] \] \[ (4.19) \]

\[ \gamma_P = 108.291 \cdot 10^6[\text{rad s}^{-1} \text{ T}^{-1}] \] \[ (4.20) \]

Hence we compute \( J_D \approx 988.8 \text{ Hz} \). By Equation \ref{eq:3.3} with a moment of inertia \( 1.22 \times 10^{-43} \text{ kg m}^2 \), \( \omega_T = 3.2 \times 10^{11} \text{ rad s}^{-1} \) at 300 K. \( \theta_b \) is a parameter remains unknown, which we believe should fall in the regimes of \( \pi/10 \) to \( \pi \). By Equation \ref{eq:3.21} substituting the scaling parameters estimated from the numerical simulations, we arrive at spin relaxation time \( T_{\langle S_z \rangle} \approx 2.5 \sim 25 \text{ hrs} \) and pseudospin relaxation time \( T_{\tau} \approx 1.7 \sim 17 \text{ hrs} \). The extrapolated numbers show that the spin/pseudospin relaxation times of a Posner molecule is in the scale of hours, which is a fairly long time comparing to the long believed assumption that quantum coherence is short-lived. The long-lived spin/pseudospin states in the Posner molecule surely can play a key role in the “quantum brain” idea \cite{6}.
Appendix A

Numerical simulation method

A.1 Numerical integration

We choose time interval $\delta t = t_b/10$ for the numerical integration. A great advantage of doing this is that the average computation time of one integration over a hop is the same for all $t_b$, as we do not want to have the total running time for $\theta_b = \pi$ to be 10 times as long as the $\theta_b = \pi/10$ data.

Computer works only with an integer number of intervals in the numerical integration. Since $\Delta t$ is a random variable with distribution $Uniform(0,t_b)$, we are not guaranteed that $\Delta t/\delta t$ always ends up as an integer. So we generate random integers $n$, which is the total number of $\delta t$’s that a hop lasts. Since $n = \Delta t/\delta t$, it should have a theoretical distribution of $Uniform(0,t_b/\delta t) \equiv Uniform(0,10)$. Hence we randomly draw a number from 0 to 10 at each time for the value of $n$. We first pick a random rotational axis and then propagate $n$ steps with angular step-size of $\theta_b/10$ and time step-size $t_b/10$. The iteration function is

$$|\alpha, t_i\rangle = e^{-iH(t_i-1)\delta t} |\alpha, t_{i-1}\rangle,$$

(A.1)
for $i = 1, 2, \ldots$. When $i$ reaches $n$, we pick again a random rotational axis and propagate with a new $n$ steps, drawn from 0 to 10, and so on. Each step we measure the spin and pseudospin expectation $\langle S_z \rangle$ and $P_\tau$. The iteration functions are

$$\langle S_z \rangle(t_i) = \langle \alpha, t_{i-1} | e^{iH(t_{i-1})\delta t}S_z e^{-iH(t_{i-1})\delta t} | \alpha, t_{i-1} \rangle, \quad (A.2)$$

$$P_\tau(t_i) = \sum_m |\langle m; \tau | \alpha, t_i \rangle|^2 = \sum_m |\langle m; \tau | e^{-iH(t_{i-1})\delta t} | \alpha, t_{i-1} \rangle|^2, \quad (A.3)$$

where $|m\rangle$ represents all states in that specific $\tau$ sector.

### A.2 Uniform random rotation matrix

In order to find random orientations for the Posner, we need to construct a uniform random rotation matrix $R$ such that rotates the initial $z$-axis of the lab frame into a random direction, such that it can serve as the new rotational axis for the molecule. There are many ways to generate such a matrix, here we will introduce one approach. Suppose we have a distribution $X$ such that

$$X = [X_1, X_2, \cdots, X_n] \text{ i.i.d. } \sim N(0, 1), \quad (A.4)$$

then,

$$X \sim N(0, I_n), \quad (A.5)$$

which is a multivariate normal distribution with mean being 0 and identity covariance matrix. Then for any rotation matrix $Q$ which is by definition orthogonal,

$$\|QX\|^2 = X^T Q^T Q X = \|X\|^2, \quad (A.6)$$
such that the magnitude of the mean is conserved. The covariance of $QX$ is just $QI_nQ^T = I_n$, which is also conserved. Hence we conclude that,

$$QX \sim N(0, I_n).$$ \hspace{1cm} (A.7)

Hence the distribution of $X$ is invariant under rotations. Now let $Y = X/\|X\|^2$,

$$QY = QX/\|QX\|^2 = QX/\|X\|^2,$$ \hspace{1cm} (A.8)

for any rotation matrix $Q$. From that we can conclude that $Y$ is also invariant to rotations and $\|Y\|^2 = 1$. The only one probability distribution for $Y$ that it satisfies both conditions at the same time is the uniform distribution on a unit sphere. With this in mind, we can construct a uniform random rotation matrix by picking out 3 uniformly distributed vectors at random and let them be $v_1, v_2$ and $v_3$. Then apply the Gram–Schmidt process to construct the orthonormal basis,

$$u_1 = v_1,$$ $$e_1 = u_1/\|u_1\|,$$ \hspace{1cm} (A.9)

$$u_2 = v_2 - \frac{v_2 \cdot u_1}{u_1 \cdot u_1},$$ $$e_2 = u_2/\|u_2\|,$$ \hspace{1cm} (A.10)

$$u_3 = v_3 - \frac{v_3 \cdot u_1}{u_1 \cdot u_1} - \frac{v_3 \cdot u_2}{u_2 \cdot u_2},$$ $$e_3 = u_3/\|u_3\|.$$ \hspace{1cm} (A.11)

Finally, let each component of the orthonormal basis $e_1, e_2$ and $e_3$ be a column of the matrix $R$,

$$R = [e_1, e_2, e_3],$$ \hspace{1cm} (A.12)

and we have obtained a uniform random rotation matrix. The very final step is to check the determinant of $R$, which will be either 1 or -1. If the determinant is -1 then interchange two of its columns. For an $SO(3)$ matrix, we have a simple standard criterion
for uniformity, namely that the distribution be unchanged when composed with any arbitrary rotation. Let $O$ be an arbitrary orthogonal matrix, then matrix $OR$ has columns of $Oe_1$, $Oe_2$ and $Oe_3$. As shown earlier, we know that $v_1$, $v_2$ and $v_3$ are all invariant to rotations. Thus,

$$Oe_1 = \frac{Ov_1}{\|Ov_1\|} = \frac{Ov_1}{\|v_1\|},$$  \hspace{1cm} (A.13)$$

$$Oe_2 = \frac{Ou_2}{\|Ou_2\|} = \frac{Ov_2 - \frac{Ov_2 \cdot Ov_1}{Ov_1 \cdot Ov_1}}{\|Ov_2 - \frac{Ov_2 \cdot Ov_1}{Ov_1 \cdot Ov_1}\|} = \frac{Ov_2 - \frac{v_2 \cdot v_1}{v_1 \cdot v_1}}{\|v_2 - \frac{v_2 \cdot v_1}{v_1 \cdot v_1}\|},$$  \hspace{1cm} (A.14)$$

and same reasoning for $e_3$. Therefore we conclude that $e_1$, $e_2$ and $e_3$ are invariant to rotations and hence also matrix $R$, meaning that $OR$ has the same distribution as $R$. Hence shown $R$ to be a uniform random rotation matrix.
A.3 Simulation results on pseudopin $\tau = \pm 1$ sectors

Figure A.1: Data-collapse of relaxation time $T_{\tau=1}$. Angular velocity $\omega_T$ is fixed at $1000\pi$ rad s$^{-1}$. Sets of $J_D$ and $\theta_b$ values are marked distinctively in shape-keys and color-keys. Individual relaxation time (data point) is estimated by the slope of the best fit line in the log-linear scale (presented in Fig. 4.3b). Scaling parameter $C$ is weakly dependent on $\theta_b$ (Fig. A.1a). The parameter $C$ falls in the range $[0.04, 0.06]$. The representative scaling parameter is $C = 0.05$, which differed from the scaling parameter of $T_{\tau=0}$ by a small amount.
Figure A.2: Data-collapse of relaxation time $T_{\tau=-1}$. Angular velocity $\omega_T$ is fixed at $1000\pi$ rad s$^{-1}$. Sets of $J_D$ and $\theta_b$ values are marked distinctively in shape-keys and color-keys. Individual relaxation time (data point) is estimated by the slope of the best fit line in the log-linear scale (presented in Fig. 4.3b). Scaling parameter $C$ is weakly dependent on $\theta_b$ (Fig. A.2a). The parameter $C$ falls in the range $[0.03, 0.07]$. The representative scaling parameter is $C = 0.05$, which is similar to the scaling parameter of $T_{\tau=1}$. 
Appendix B

Special features of triangular 3-spin system

B.1 Non-decaying states under planar rotation around \( C_3 \) symmetry axis

Suppose the molecule rotates around the internal \( z \)-axis (defined in Sec. 2.2) in the counterclockwise direction, with a constant angular speed \( \omega \) (see the demonstration in Fig. 2.1b). The time-dependent position vectors are

\[
\begin{align*}
\mathbf{r}_1(t) &= (r, \omega t), \\
\mathbf{r}_2(t) &= (r, \frac{2\pi}{3} + \omega t), \\
\mathbf{r}_3(t) &= (r, \frac{4\pi}{3} + \omega t)).
\end{align*}
\]

Let \( \phi_i \) be the initial polar angles of the nucleus with label \( i \), e.g. \( \phi_2 = \frac{2\pi}{3} \). We rewrite the Hamiltonian of dipole-dipole interaction (see Equation 2.4) using \( S^z, S^+ \) and \( S^- \).
operators,

\[ H_D = J_D \sum_{\langle i,j \rangle} [S_i^x S_j^x - \frac{1}{4} (S_i^+ S_j^- + S_i^- S_j^+) + \frac{3}{4} S_i^+ S_j^+ e^{-i(\phi_i + \phi_j + 2\omega t)} + \frac{3}{4} S_i^- S_j^- e^{i(\phi_i + \phi_j + 2\omega t)}]. \]  

(B.4)

Now define modified ladder operators,

\[ \tilde{S}_i^\pm = S_i^\pm e^{-i\omega t}, \]  

(B.5)

we can then write down a unitary operator \( \mathcal{U}_i \), such that for any states \( |a\rangle \) and \( |b\rangle \),

\[ \langle a | \mathcal{U}_i^{\dagger} S_i^\pm \mathcal{U}_i | b \rangle = \langle a | \tilde{S}_i^\pm | b \rangle, \]  

(B.6)

\[ \langle a | \mathcal{U}_i^{\dagger} S_i^z \mathcal{U}_i | b \rangle = \langle a | S_i^z | b \rangle. \]  

(B.7)

By the fact that

\[ S_i^\pm e^{-i\omega t} = e^{-i\omega t S_i^z} S_i^\pm e^{i\omega t S_i^z}, \]  

(B.8)

and

\[ e^{-i\omega t S_i^z} S_i^z e^{i\omega t S_i^z} = e^{-i\omega t S_i^z} e^{i\omega t S_i^z} S_i^z = S_i^z, \]  

(B.9)

we find

\[ \mathcal{U}_i = e^{i\omega t S_i^z / \hbar}. \]  

(B.10)

Define \( U = \prod_i \mathcal{U}_i \). In the 3-spin case,

\[ U(t) = \mathcal{U}_1 \mathcal{U}_2 \mathcal{U}_3 = e^{i\omega t (S_1^z + S_2^z + S_3^z)} = e^{i\omega t S_{123}^z} \]  

(B.11)
Hence we have found a unitary transformation that describes the planar rotation around $z$-axis. We are able to define time independent Hamiltonian $H'_D$

$$H'_D = J_D \sum_{\langle i,j \rangle} [S^z_i S^z_j - \frac{1}{4} (S^+_i S^-_j + S^-_i S^+_j) + \frac{3}{4} S^+_i S^+_j e^{-i(\phi_i+\phi_j)} + \frac{3}{4} S^-_i S^-_j e^{i(\phi_i+\phi_j)}]. \quad (B.12)$$

such that after the unitary transformation,

$$H_D(t) = U^\dagger(t) H'_D U(t), \quad (B.13)$$

while time independent J-coupling Hamiltonian is invariant under the transformation,

$$H_J = U^\dagger(t) H_J U(t). \quad (B.14)$$

The total Hamiltonian of the system is

$$H(t) = H_J + H_D(t) = U^\dagger(t) (H_J + H'_D) U(t). \quad (B.15)$$

Its discretized form is

$$H(\delta t) = H_J + H_D(\delta t) = U^\dagger(\delta t) (H_J + H'_D) U(\delta t). \quad (B.16)$$

In Sec. 3.2, we have defined the time-evolution operator such that the final state after time $t$ has form (Equation 3.9),

$$|\alpha, t_0; t \rangle = \lim_{n \to \infty} \prod_{k=1}^n e^{-i H(t_{k-1}) \delta t} |\alpha, t_0 \rangle. \quad (B.17)$$
Let $U_k$ denote $U(k\delta t)$. Substituting Equation [B.16]

\[ |\alpha, t_0; t\rangle = \lim_{n \to \infty} \prod_{k=1}^{n} e^{-iH(t_{k-1})\delta t} |\alpha, t_0\rangle \]  

(B.18)

\[ = \lim_{n \to \infty} \left[ U_n^\dagger e^{-i(H_J + H'_D)\delta t} U_n e^{-i(H_J + H'_D)\delta t} \cdots e^{-i(H_J + H'_D)\delta t} U_0 \right] |\alpha, t_0\rangle . \]  

(B.19)

For any $k$ in \{0, 1, \ldots, n\},

\[ U_k U_k^\dagger = e^{i\omega k\delta t S^z_{123}} e^{-i\omega(k-1)\delta t S^z_{123}} = e^{i\omega \delta t S^z_{123}}, \]  

(B.20)

Therefore\[ |\alpha, t_0; t\rangle = \lim_{n \to \infty} \left[ U_n e^{-i(H_J + H'_D)\delta t} e^{i\omega \delta t S^z_{123}} \cdots e^{-i(H_J + H'_D)\delta t} \right] |\alpha, t_0\rangle \]  

(B.21)

\[ = \lim_{n \to \infty} \left[ U_n e^{-i\delta t(H_J + H'_D - \omega S^z_{123})} \cdots e^{-i\delta t(H_J + H'_D - \omega S^z_{123})} \right] |\alpha, t_0\rangle \]  

(B.22)

\[ = U_n e^{-i \int (H_J + H'_D - \omega S^z_{123}) dt} |\alpha, t_0\rangle . \]  

(B.23)

Since $H_J, H'_D$, and $S^z_{123}$ are time-independent operators, while

\[ U_n = e^{i\omega \delta t S^z_{123}} = e^{i\omega t S^z_{123}}, \]  

(B.24)

we can therefore conclude that

\[ |\alpha, t_0; t\rangle = e^{-i(H_J + H'_D - 2\omega S^z_{123})t} |\alpha, t_0\rangle . \]  

(B.25)

\[ U_0 = e^{i\omega \Delta \delta t} = 1, \text{ hence is not marked out in Equation [B.21]} \]
Define time independent effective hamiltonian $\mathcal{H} = H_J + H'_D - 2\omega S_{123}^z$,

$$P_\tau(t) = \sum_m |\langle m; \tau | e^{-i\mathcal{H}t} |\alpha, t_{i-1}\rangle|^2.$$  

(B.26)

Initial states of the triple-spin plane are listed in Table 2.1. Notably, states $|2\rangle$, $|3\rangle$, $|5\rangle$, $|7\rangle$ happen to be the eigenstates of $\mathcal{H}$, therefore $P_\tau(t) = 1$ for them. These states experience no decay under planar rotation around the $C_3$ symmetry axis (Fig. B.1).

Figure B.1: $P_\tau(t)$ of initial pseudospin states listed in Table 2.1 that undergoes planar rotation around the internal $z$-axis in counterclockwise direction. The numerical inputs are $\omega = 1$ rad s$^{-1}$, $J_D = 1$ Hz, and $J = 0.1$ Hz. Notably, states $|2\rangle$, $|3\rangle$, $|5\rangle$, $|7\rangle$ are the four non-decaying states in this case. States $\{1, 8\}$ and $\{4, 6\}$ share similar oscillatory behavior within each pair.
Bibliography


