MAGNETIZATION DYNAMICS OF SINGLE MOLECULE MAGNETS

BY

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DISsertation

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Abstract

Molecular magnets are a class of magneto-organic material which behave at low temperatures like a single quantum spin of large angular momentum. In this thesis we will be concerned with the spin dynamics of these molecular magnets, occurring both in isolation, and in contact with external environments and with other molecular magnets. We begin by addressing the possibility of non-Abelian adiabatic transport in molecules of half-integer spin, under slow rotations of the molecule. Next we analyze the process of dissipative spin tunneling for a single molecule interacting with a phonon bath. Finally we attend to the problem of collective magnetization in a lattice of spins coupled by dipole-dipole interactions.
To friends and family
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Chapter 1

Review of Molecular Magnetism

In this chapter we briefly outline the basic foundation of molecular magnetism. We also visit the hallmark theoretical and experimental developments in the field, with emphasis on those topics which will be relevant to the rest of the thesis. Finally we review the spin path integral, and summarize the instanton solutions.

1.1 Introduction

Single molecule magnets are a twenty-year old class of magnetic materials, consisting of a metallic core surrounded by organic ligands that form organic solids. Interest in these materials stemmed from the realization that molecular magnets serve as ideal candidates for the observation of mesoscopic quantum effects. This is due to the properties of the metallic cores, whose unpaired electrons “lock” together at low temperatures to form a single large spin of $j \gg \frac{1}{2}$. Conceptually the $j \to \infty$ limit corresponds to a completely classical spin, while $j = 1/2$ is the purely quantum regime. Most molecular magnets have an effective spin value of approximately 5 to 10, and so sit at the interface between quantum and classical physics.

The best studied families are the Mn12, Fe8, and Mn4 clusters, for which $j = 10, 10, \text{ and } 9/2$ respectively. The nomenclature focuses on the magnetic atoms in the core of the molecule; Mn12, for example is shorthand for $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4$, and Fe8 stands for $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]\text{Br}_8(\text{H}_2\text{O})_9$. There are many variations to these molecules, both in core elements and in the surrounding organic ligands, but generically they are engineered such that the spin magnetization is bistable in its preferred orientation, separated by a large energy barrier. At low temperatures then only the $m = \pm j$ Zeeman levels are occupied, and spin transitions primarily take place through tunneling, analogous to that of a particle in a double well. Direct measurements of the tunneling frequency were performed on Fe8 by Wernsdorfer and Sessoli [46] through a clever application of the Landau-Zener-Stueckelberg protocol; similar (though indirect) evidence of resonant tunneling was previously obtained in Mn12 [39].

From a mathematical perspective, single molecule magnets have been a motivating force in the devel-
The development and understanding of spin path integrals, itself already a topic rich in geometry. One of the most striking examples is due to Garg [10] and others [26, 44], who demonstrated that the tunnel splitting of Fe8 could be understood in terms of the solid angle traced out by solutions to the corresponding classical problem. It is found that the tunneling frequency vanishes for specific values of the applied external field. These points behave like monopoles in parameter space, in the sense that a state adiabatically transported in a closed loop about such a point exhibits non-trivial holonomy, a.k.a. the well known Berry’s phase. Finally, Mead [29] has raised the possibility of such molecular systems exhibiting non-Abelian holonomy, in which the adiabatically transported state differs from the initial one by more than just a phase.

The field of molecular magnetism is an interdisciplinary confluence of chemistry, physics, and mathematics, and we can only hope to visit the most salient aspects of its varied history. In this chapter, we begin in section 1.2 with the single spin molecule, building up to more complicated interactions with the environment. In section 1.3 we examine important developments which provide unambiguous evidence of the quantum mechanical nature of these spins. Finally we conclude with a tutorial on the semiclassical path integral, and provide calculations for the instantons, including details not addressed in previously published work.

The rest of the thesis is based my dissertation work, and outlined as follows. Chapter 2 explores the idea of non-Abelian holonomy in molecular magnetism, and is based on [25]. Chapter 3 calculates the phononassisted spin tunneling rate, and builds on [24]. Finally, chapter 4 calculates the collective magnetization dynamics of molecular solids. The work in chapter 2 is done under the guidance of prof. Michael Stone. The work in chapters 3 and 4 is done under the guidance of prof. Anupam Garg (Northwestern University).

### 1.2 Spin Hamiltonian and Interactions

**Magnetic Centers and Single Molecule Magnets**

The basic building block of the single molecule magnets are the core magnetic centers, typically transition metal ions. For a center containing \( n \) unpaired electrons, the most relevant multiplet is that with the largest total spin, \( s = n/2 \). Fe8, for example, comprises eight Fe\(^{3+} \) ions, each with 5 unpaired electrons\(^1 \) yielding \( s = 5/2 \) per ion. At this level each magnetic center is essentially a single spin=\( s \) particle. Several magnetic centers now comprise a cluster, and their interaction is described by the exchange Hamiltonian,

\[
\mathcal{H}_{ei} = -\frac{1}{2} \sum_{a,b} J_{ab} \mathbf{S}_a \cdot \mathbf{S}_b,
\]

---

\(^1\)This follows from the Aufbau principle, which states generically states that the orbitals are filled as 4s then 3d then 4p; and from Hund’s rule, which states that each orbital is singly occupied before any orbital becomes doubly occupied.
Figure 1.1: Schematic of Fe8 along with the spin orientation of each center. (Figure modified from online slides by J. Slageren, *Introduction to Molecular Magnetism*, Physikalisches Institut, Universität Stuttgart).

(more generally a pair of spins interact via the tensor $\mathbf{S}_a \cdot \mathbf{M}_{ab} \cdot \mathbf{S}_b$, but typically the trace part of the matrix $\mathbf{M}$, aka the isotropic term, is dominant). Note that unlike the magnetic centers whose constituents are all spin 1/2, here the spins of each center need not be equal. Mn4, for example, is composed of one Mn$^{4+}$ ion ($s = 3/2$) and three Mn$^{3+}$ ions ($s = 2$). Continuing the exercise in addition of angular momenta, the resulting ground state will be a multiplet of some total angular momentum $j$, where $j$ need not be maximal. Here, the energetics depend on how the exchange coupling $J_{ab}$, i.e. the configuration of the magnetic centers and organic ligands, are engineered. For both Fe8 and Mn12 the ground state multiplet is of total spin $j = 10$, while Mn4 is that of $j = 9/2$. A schematic of Fe8 is depicted in (fig. 1.1). Roughly speaking, the $j = 10$ can be thought of as arising from $6 \times +5/2$ spin ups and $2 \times -5/2$ spin downs.

Within the ground-state multiplet, the crystal field splitting can be described by a Hamiltonian that, due to time reversal invariance, must be even in the angular momenta. Often it is sufficient to approximate the Hamiltonian with only quadratic and quartic terms. By working in the principle axes and subtracting off constants, the spin Hamiltonian of a single molecule magnet in the ground state multiplet and basked in an external field can be summarized by,

$$
\mathcal{H}_s = -D J_3^2 + E(J_1^2 - J_2^2) + C(J_4^4 + J_4^-) - g\mu_B \mathbf{H} \cdot \mathbf{J},
$$

(1.2)

where $0 < E < D$. Here $\mu_B$ is the Bohr magneton, $\mathbf{H}$ is the external field, and $g \approx 2$ is the Landé g-factor. The $\pm \mathbf{e}_3$, $\pm \mathbf{e}_2$, and $\pm \mathbf{e}_1$ directions are called the “easy”, “medium”, and “hard” axes, respectively,
corresponding to the semiclassical energy along those axes. More generally, the quartic (or higher order) terms can be described by a set of what are known as the Steven’s operators, of which $J_4^4 + J_4^2$ corresponds to $O_4^4$. For Fe8 (eq. 1.2) serves as a good description.

**Environmental Factors**

Next we consider the interaction of a single molecular spin with that of an environment. Specifically we will consider two sources of environmental baths: that of the dipolar interaction between the molecular spin (due to the core unpaired electrons) and the nuclear spins; and that of the molecular spin with the lattice. The former is analyzed by [42] whose results we will briefly summarize, and the latter is the subject of chapter 3.

Assuming that the nuclear spins have spin 1/2, the molecular-nuclear spin interaction can be described by the Hamiltonian,

$$H_{\text{nuc}} = \sum_i E_{dn} a^3 \{ J_3 \sigma_i, 3 - 3(J_3 \hat{e}_3 \cdot \hat{r}_i)(\sigma_i \cdot \hat{r}_i) \}, \quad (1.3)$$

where $\sigma_i$ is the sigma matrix describing the $i$-th nuclear spin, $a \sim 1-2\AA$, $E_{dn} \sim 1\text{mK}$, and $r_i$ is the displacement vector from the molecular spin to the nuclear spin. If we restrict ourselves to the lowest lying states, then $J_3$ can be further reduced to $j\sigma_3$. The transition rate $\Gamma_{\text{nuc}}$ between these two low-lying states, in the presence of an external bias, is computed in [42]. The effect of the nuclear spins is to render incoherent the original coherent flip-flop transitions of an isolated molecular magnet. It effectively introduces a linewidth broadening of approximately $10E_{dn} \sim 10^{-2}\text{K}$. By contrast, the tunnel splitting between the lowest levels is of order $\Delta \sim 10^{-8}\text{K}$, and the separation between the lowest doublet and the first excited doublet is approximately $E_{j-1} - E_j \approx 5\text{K}$.

In typical magnetization experiments the applied field introduces a bias that is well within $E_{j-1} - E_j$, but is nevertheless more than what the nuclear bath can soak up, i.e. several times greater than $W$. The excess energy must be absorbed elsewhere, and the simplest mechanism is that the remaining energy gets converted into lattice vibrations. This spin-phonon interaction may be given as

$$H_{\text{sp}}^{\text{pp}} = \frac{1}{2} \sum_{a,b,c,d=1}^3 \Lambda_{abcd}(\partial_a u_b(0) + \partial_b u_a(0)) \{ J_c, J_d \}, \quad (1.4)$$

where $u(x)$ is the displacement field at position $x$, and $\partial_a u_b + \partial_b u_a$ is the local strain.
Molecular-Molecular Interactions

Zooming out to the level of the entire solid, the interactions between each molecule must be considered. The dominant effect is that of dipole-dipole coupling, given by,

\[
\mathcal{H}_{ab} = \frac{\mu_0 g^2 \mu_B^2}{4\pi r_{ab}} \{\mathbf{J}_a \cdot \mathbf{J}_b - 3(\mathbf{J}_a \cdot \mathbf{r}_{ab})(\mathbf{J}_b \cdot \mathbf{r}_{ab})\},
\]  

(1.5)

where \(r_{ab}\) is the displacement vector between spin \(a\) and spin \(b\). At sufficiently low temperatures it suffices to approximate each molecule as a two-level spin-1/2 system, i.e. \(\mathbf{J} \rightarrow j \sigma\). Furthermore we may replace the isotropic interaction \(\mathbf{J}_a \cdot \mathbf{J}_b\) by an Ising-like coupling, i.e., \(J_{a,3} J_{b,3}\), etc. The low-temperature description therefore simplifies to,

\[
\mathcal{H}_{ab} = K_{ab} \sigma_{a,3} \sigma_{b,3}, \quad K_{ab} = j^2 \frac{\mu_0 g^2 \mu_B^2}{4\pi r_{ab}^3} \{1 - 3 \frac{z_{ab}^2}{r_{ab}^2}\}.
\]  

(1.6)

Despite this truncation the problem remains that of a many-body system with long-range interaction, which is difficult to treat. In [42] the authors overcome this by considering singling out a “central spin”, and replacing the dipole contributions of the other spins with that of a statistical distribution of biases. This essentially treats the rest of the spins as an external bath, much like in the previous case with nuclear spins. They then proceed to calculate the influence functional to second order in the tunnel splitting, obtaining,

\[
\mathcal{P}(t) = \frac{\Delta^2}{4} \int_0^t dt_1 \int_0^t dt_2 \exp \{i\varepsilon(t_1 - t_2) - \gamma_m \Delta |t_1 - t_2|\}.
\]  

(1.7)

Finally, by combining the influence functions of both the original nuclear spin bath as well as this molecular dipole-dipole “bath”, they obtain a transition rate

\[
\Gamma(\varepsilon) = \frac{\sqrt{2\pi}}{4W} \Delta^2 \exp \left\{-\frac{\varepsilon^2}{2W^2}\right\},
\]  

(1.8)

where \(\varepsilon\) is the total bias experienced by the spin.

1.3 Quantum Effects and Magnetization Dynamics

Quantum Behavior in Hysteresis

Direct evidence of macroscopic quantum phenomenon can be observed in the hysteresis curves of molecular magnets. At low temperatures, magnetization transition by thermal barrier hopping is suppressed, so the
magnetization can only flip via spin tunneling. Since the width of each level is much smaller than the separation between levels, tunneling between two levels can only occur if they are brought into approximate resonance by the external field. Intuitively, a spin localized in the lowest level of the metastable well (excited levels will not be significantly populated at low temperatures) will remain there most of the time, until it is brought into resonance with one of the levels of the stable well. When that happens, some percent of the population will tunnel into the level of the stable well and, if that level is not the lowest, drop down via phonon emission or some other relaxation mechanism (fig. 1.2). The corresponding picture in terms of the magnetization is that it remains static most of the time until two levels reach resonance, during which the magnetization jumps significantly. Field sweep experiments on both Mn12 [39] and Fe8 [13] reflect this step-like behavior (fig. 1.3).

Since the external field is explicitly time-dependent, the transition probability between two levels is given by Landau-Zener-Stueckelberg formula,

\[ P_{m_2, m_1} = 1 - \exp\left\{ -\frac{\pi \Delta^2_{m_1, m_2}}{2|\varepsilon|} \right\}, \tag{1.9} \]

where it is supposed that the approximate two-level description between \( m_1 \) and \( m_2 \) is given by \( \mathcal{H} = (\Delta_{m_1, m_2}/2)\sigma_1 + (\varepsilon/2)\sigma_3 \). (In fact, as argued in [22] the more appropriate quantity should be that given by Kayanuma [19],

\[ P_{m_2, m_1} = \frac{1}{2} - \frac{1}{2} \exp\left\{ -\pi \Delta^2_{m_1, m_2}/|\varepsilon| \right\}, \tag{1.10} \]

which applies when the bias field incorporates fluctuations arising from inter-molecular coupling, i.e. when the single-spin two-level description is given by \( \mathcal{H} = -(\Delta/2)\sigma_1 + (\varepsilon t/2 + \eta(t)/2)\sigma_3 \), where \( \eta(t) \) is a Gaussian random process. In practice both (1.9 and 1.10) agree in the experimentally relevant fast sweep limit of
Vanishing Splitting and Diabolical Points

By tuning the strength of the longitudinal field $H_z$ so that two energy levels become exactly degenerate, we can completely suppress tunneling between these levels. The same effect can be observed, rather unexpectedly, if we set $H_z$ to zero and tune the value of an applied transverse field $H_x$ instead. In that case the tunnel splitting is found to exhibit oscillatory behavior along $H_x$, displaying a total of $2j$ oscillations before rising monotonically with the applied field strength. Such oscillations can be observed in Fe8 [46] (fig. 1.4).

The locations of these minima are called Diabolical Points\(^2\), and in general they are found to exist along in the $xz$ plane (an applied field along the $y$ direction will actually lift the degeneracy. In practice it is difficult to avoid slight misalignment in the applied field, which is why the minima of the tunnel splitting in fig. 1.4) does not vanish completely, but rather seems to rise linearly).

In (fig. 1.5) we plot the locations of the diabolical points for a toy model with $j = 3/2$ to illustrate its lattice-like structure. We note the existence of a diabolical point at $H_x = H_z = 0$, confirming Kramers'\footnote{The name derives from conic shape of the spectrum near a crossing, resembling the ancient toy diabolo. Alternatively, “A point of the parameter space where degeneracy occurs without symmetry reasons is called a diabolic point, probably because it is an unexpected phenomenon which can only be an effect of the Devil” [14]}

\( \dot{\varepsilon} \gg \Delta \). At faster sweep rates the probability of transitioning is smaller, and so the change in magnetization will be smaller, as can be seen in (fig. 1.3).
Theorem. For systems with integer values of spin the lattice of Diabolical points is offset by half a period.

The vanishing of $\Delta$ along the $H_x$ axis has an elegant geometric interpretation due to Garg [10], who explained the oscillatory behavior as arising from interference of semiclassical instanton solutions analogous to that in a double-slit experiment. Here we briefly reproduce his argument, deferring to the appendix (A) all but the most salient aspects. Recall that the transition amplitude $A$ from an initial spin state $s_i$ to a final spin state $s_f$ can be represented by a Feynman integral over all paths,

$$A = \int_{s_i}^{s_f} Ds \exp \{ iS[s] \}, \quad (1.11)$$

where $S[s]$ is the action and the integral is over all possible paths which start and end at the specified states. Due to the rapid oscillatory nature of the integrand, the value of $A$ will be dominated by paths which stationarize the action. These paths are precisely the solution to the classical problem, and in the context of tunneling they are also called “instantons”. Working in the semiclassical approximation then, it can be shown that the tunnel splitting goes as,

$$\Delta \sim \sum_{s_c} \exp \{ iS[s_c] \}, \quad (1.12)$$
Figure 1.5: Locations of the diabolical points of the spin Hamiltonian $\mathcal{H} = -\frac{j}{2} \cosh \rho S_z^3 + \frac{j}{2} \sinh \rho (S_z^1 - S_z^2) - jX_1S_1 - jX_3S_3$, for $j = 3/2$. Here we plot the contours of the discriminant of the characteristic polynomial of $\mathcal{H}$, as a function of $X_1$ and $X_3$. The location of the zeros of the discriminant are precisely where two or more eigenvalues coincide.
where the summation is over all classical trajectories. For Fe8-like systems there will be two distinct trajectories $s_{c, \pm}$, and the action evaluated along these two trajectories will have the same real part but conjugate imaginary parts, i.e. $S[s_{c, \pm}] = S_R \pm i S_I$. Therefore the tunnel splitting goes as,

$$\Delta \sim \cos(S_I).$$

(1.13)

Tuning $H_x$ also tunes the instanton trajectories, and hence the value of $S_I$; each time $S_I$ reaches a half-integer multiple of $\pi$, the splitting vanishes. The success of the instanton method relies on the fact that for $H_z = 0$ the instantons can be solved exactly or approximately. For $H_z \neq 0$ the instantons are not known, and thus far methods for locating the other diabolical points have relied on WKB or high-order perturbation [3].

**Non-Exponential Relaxation**

At high temperatures where spin transitions take place mostly by thermal over-barrier hopping, the time-dependence of the sample magnetization behaves like an exponential, i.e. $M(t) - M(\infty) = A \exp(-t/\tau)$, where $\tau$ is a temperature dependent relaxation time that is expected to be described by an Arrhenius law, $\tau = \tau_0 \exp(\beta/\beta_0)$. In experiments, the Arrhenius behavior is observed up to a certain cross-over temperature, below which $\tau$ is found to be insensitive to temperature. In Mn12 this cross-over temperature is approximately 2K, and in Fe8 it is 0.5K.

The deviation of $\tau$ from the Arrhenius behavior is precisely a reflection of spin-flip mechanism transitioning from thermal-hopping to quantum-tunneling. In the latter case, a spin cannot flip unless the local field it experiences falls within a specified range — which is another way of stating the resonance criterion responsible for the step-like hysteresis curves in (sec. 1.3) — and this “window mechanism” leads to non-exponential time-dependence in the magnetization. In experiments on Fe8 [38,45], the magnetization is instead found to satisfy,

$$M(t) - M(0) = A\sqrt{t},$$

(1.14)

see figures 1.6 and 1.7. This initial power-law behavior persists for some short duration, eventually switching to asymptotic behavior.

Despite being mathematically similar, the issue of demagnetization is well understood, while that of magnetization has been much more controversial. One question is whether or not the initial saturation is essential; this was required in previous theoretical justifications [34,43], despite not being the case in magnetization experiments. Another issue is whether or not the exponent of 1/2 was truly universal [8]. In chapter 4 we will address magnetization and demagnetization in Fe8 by numerically solving for the population
Figure 1.6: Short time demagnetization of Fe8 from an initially saturated state, at low temperatures, for various values of the final magnetic field. Figure from [38].

Figure 1.7: Short time magnetization of Fe8 from an initially unsaturated state, at low temperatures. Figure from [45].
\[ \alpha = E/D, \]
\[ \Omega_0 = \frac{2j+1}{\alpha} \sqrt{D^2 - E^2}, \]
\[ \cosh(\rho) = 1/\sqrt{1 - \alpha^2}, \]
\[ \sinh(\rho) = \alpha/\sqrt{1 - \alpha^2}, \]
\[ X = \mu_B H \left\{ \frac{(2j-1)(j)}{D \sqrt{1 - \alpha^2}} \right\}^{-1}, \]
\[ \gamma \equiv \frac{C D (2j)(2j-1)(2j-2)(2j-3)}{(j)^{j(j-1)}/(1 - \alpha^2)}, \]
\[ u = \Omega_0 t, \]
\[ S_a = J_a/\sqrt{j}, \]
\[ S_a S_b = J_a J_b/((j)^{(j-1)/2}), \]
\[ S_4^\pm = J_\pm/((2j)(2j-1)(2j-2)(2j-3)), \]

<table>
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<tr>
<th>\text{Table 1.1: Table of dimensionless variables and j-rescaled angular momenta.}</th>
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1.4 Instantons of the Fe8 Hamiltonian

In this section we calculate the instanton trajectories which start and end at the minima of the semiclassical Hamiltonian. Since we are concerned only with the case where the bias \( \varepsilon \) is small, we can perturbatively incorporate the easy axis external field term; and so it suffices to restrict ourselves to the spin Hamiltonian \( \mathcal{H}_s \) with \( X_3 = 0 \). This way, the local minima of the semiclassical Hamiltonian become classically degenerate in energy, and the problem is considerably simplified.

To begin let us rescale our Hamiltonian according to (tab. 1.1), so that the Hamiltonian reads,

\[ \mathcal{H}_s = j \left\{ -\frac{1}{2} \cosh(\rho) S_3^2 + \frac{1}{2} \sinh(\rho) S_1^2 S_2^2 + \gamma (S_4^2 + S_4^2) - X_1 S_1 \right\}, \tag{1.15} \]

The reason for the curious \( j \) scaling in the definitions for higher powers of \( \mathcal{J} \) is that the Q-symbol for these higher powers do not go like \( j^2, j^3 \), etc., but are instead more complicated combinatorial factors. The rescaling in (tab. 1.1) compensates for this, so that the corresponding semiclassical terms become,

\[ S_a \rightarrow s_a(z, \bar{z}), \]
\[ S_a S_b \rightarrow s_a(z, \bar{z}) s_b(z, \bar{z}) + \frac{1}{2j-1} \delta_{ab} + \frac{1}{j} \epsilon_{abc} s_c(z, \bar{z}); \]
\[ S_4^\pm \rightarrow z^4 \left( 1 + z \bar{z} \right)^4 \tag{1.16} \]

The semiclassical Hamiltonian is then given, up to an additive constant, by

\[ h_0(z, \bar{z}) = j \left\{ -\frac{1}{2} \cosh(\rho) (s_3^2(z, \bar{z}) - 1) + \frac{1}{2} \sinh(\rho) (s_1^2(z, \bar{z}) - s_2^2(z, \bar{z})) + \gamma \frac{z^4 + \bar{z}^4}{(1 + z \bar{z})^4} - X_1 s_1(z, \bar{z}) \right\} \tag{1.17} \]

The semiclassical trajectory is found by stationarizing the action, which leads to the equations of motion
that \[12\],
\[
\frac{d\bar{z}}{du} = -\frac{i}{2j} (1 + z\bar{z}) \partial h \partial z, \quad \frac{dz}{du} = \frac{i}{2j} (1 + z\bar{z})^2 \partial h \partial \bar{z}.
\] (1.18)

Alternatively, instead of \( z \) and \( \bar{z} \) it may be more convenient to work in Archimedean cylindrical coordinates \( s_3 \) and \( \phi \), defined as,
\[
z = \sqrt{\frac{1 + s_3}{1 - s_3}} e^{i\phi}, \quad s_1 = \sqrt{1 - s_3^2} \cos \phi,
\]
\[
\bar{z} = \sqrt{\frac{1 + s_3}{1 - s_3}} e^{-i\phi}, \quad s_2 = \sqrt{1 - s_3^2} \sin \phi.
\] (1.19)

Now, strictly speaking the instanton trajectories exist only in Euclidean time \( \tau = iu \), and so the above equations (eq. 1.18, eq. 1.19) must be modified appropriately; and in doing so, it is also helpful to redefine the coordinate \( \varphi = i\phi \), so that,
\[
s_1(\tau) = \sqrt{1 - s_3^2} \cosh \varphi, \quad s_2(\tau) = -i \sqrt{1 - s_3^2} \sinh \varphi,
\] (1.20)

and the equations of motion read,
\[
\frac{ds_3}{d\tau} = -\frac{1}{j} \partial h \partial \varphi, \quad \frac{d\varphi}{d\tau} = \frac{1}{j} \partial h \partial s_3.
\] (1.21)

Suppose we neglect the hard-axis and fourth-order anisotropy terms for now. The inclusion of these terms can lead to non-trivial corrections to the tunnel splitting \( \Delta \) (despite the fourth-order anisotropy typically being small), but otherwise will not qualitatively change the nature of the solution. In addition it has the advantage of being exactly solvable. Therefore, it serves to be both a good approximation of the physics, and a clear illustration of the calculations involved.

Continuing, under our simplifications the semiclassical Hamiltonian reads,
\[
h_0 = j(1 - s_3^2)\left\{ \frac{1}{2} \cosh \rho + \frac{1}{2} \sinh \rho \cosh(2\varphi) \right\}.
\] (1.22)

The value of minimal energy is \( h = 0 \), occurring at \( s = \pm \hat{e}_3 \); and the enforcement of energy conservation leads to the two non-tunneling solutions \( s_3(\tau) = \pm 1 \), as well as the tunneling solution,
\[
\cosh(2\varphi(\tau)) = -\frac{\cosh \rho}{\sinh \rho} = -\frac{1}{\alpha}.
\] (1.23)
Along this solution, the equation of motion becomes,

\[ \frac{ds_3}{d\tau} = \pm (1 - s_3(\tau)^2), \]  

(1.24)

(where the + sign indicates a solution going from \( s_3 = -1 \to s_3 = +1 \), and the - sign indicates the opposite direction). Solving for the + direction, we find,

\[ s_3(\tau) = s_3(\tau|\tau_c) = \tanh(\tau - \tau_c), \]  

(1.25)

where \( \tau_c \) is an arbitrary real degree of freedom (we will address this subtlety further when we discuss the case for nonzero \( X_1 \)) and is interpreted as the “tunneling epoch”. Finally, using that,

\[ \cosh^2(\varphi) = \frac{1}{2}(\cosh(2\varphi) + 1) = \frac{1}{2}(\frac{1}{\alpha} - 1 + 1), \]  

(1.26)

it is seen that the two windings of the instanton, \( p = \pm 1 \), correspond to the two roots of the above equation, i.e.,

\[ \cosh \varphi = p \sqrt{-\frac{1}{2}(\frac{1}{\alpha} - 1)} \equiv p \cosh(\varphi_\alpha), \]
\[ \sinh \varphi = p \sqrt{-\frac{1}{2}(\frac{1}{\alpha} + 1)} \equiv p \sinh(\varphi_\alpha). \]  

(1.27)

Therefore, for the tunneling trajectory going from \( s_3 = -1 \) to \( s_3 = +1 \), there are two distinct instanton trajectories, given by,

\[ s_1(\tau|\tau_c,p) = +p \cosh(\varphi_\alpha)\text{sech}(\tau - \tau_c), \]
\[ s_2(\tau|\tau_c,p) = -i p \sinh(\varphi_\alpha)\text{sech}(\tau - \tau_c), \]  

(1.28)

\[ s_3(\tau|\tau_c) = + \tanh(\tau - \tau_c), \]

for \( p = \pm 1 \). That there are multiple distinct classical curves which satisfy the same boundary conditions, is a feature special to the spin Hamiltonian, and is not observed in typical one-dimensional double-well systems such as the quartic potential. It is precisely the interference of these multiple trajectories can give rise to the vanishing of the tunneling frequency \( \Delta \), as explained in [10] and observed in experiment [46].

Let us now relax the condition that \( \gamma = 0 \). Recall that \( \gamma \) corresponds to fourth order spin terms \( O(J^4) \), which if included become the highest order term in the spin Hamiltonian; without it, the highest order term is \( O(J^2) \). Therefore \( \gamma \) is a singular perturbation, and thus one would expect it to make non-trivial corrections.\(^3\)

\(^3\)One way to think about this is in terms of differential operators, which takes the form \( \gamma O(\partial^4) + \alpha O(\partial^2) \)
Now the semiclassical Hamiltonian reads,

\[
h_0 = j(1 - s_3^2) \left\{ \frac{1}{8} \gamma (1 - s_3^2) \cosh(4\varphi) + \frac{1}{2} \cosh(\rho) + \frac{1}{2} \sinh(\rho) \cosh(2\varphi) \right\},
\]

and continuing as before, the \( h = 0 \) tunneling solution satisfies,

\[
\cosh(2\varphi) = -\frac{\sinh \rho \pm \sqrt{\sinh^2 \rho - \frac{\gamma}{2} (1 - s_3^2)(4 \cosh \rho - \gamma (1 - s_3^2))}}{\gamma (1 - s_3^2)}.
\]

Of these two solutions, we must choose the one with the relative “−” sign, since in that case,

\[
\lim_{s_3 \to \pm 1} \cosh(2\varphi) = -1/\alpha,
\]

and because this is a finite quantity, \( s_1 \) and \( s_2 \) will vanish as \( s_3 \to \pm 1 \), thus assuring the endpoints of the trajectory lie on the real sphere. If we had taken the solution with the other sign, then \( \cosh(2\varphi) \) approaches infinity, and the trajectory endpoints are no longer guaranteed to remain on the real sphere\(^4\). These solutions are non-interfering, and are called jump instantons. As explained in [20], these solutions are the reason for the disappearance of Diabolical points at higher fields; but for our purposes we will not need to consider them.

Continuing, let us define \( C(s_3; \gamma, \rho) \) as the solution in (eq. 1.30) with the relative negative sign. The equation for \( s_3 \) then reads,

\[
\frac{ds_3}{d\tau} = \pm(1 - s_3^2) \times \sqrt{C^2(s_3; \gamma, \rho) - 1}\gamma (1 - s_3^2)C(s_3; \gamma, \rho) + \sinh \rho},
\]

\[\equiv \pm(1 - s_3^2) \times \Omega(s_3; \gamma, \rho),\]

where \( \delta \Omega \) satisfies the properties that, 1) \( \Omega(-s_3; \gamma, \rho) = \Omega(s_3; \gamma, \rho) \), 2) \( \lim_{s_3 \to \pm 1} \Omega(s_3; \gamma, \rho) = 1 \), 3) \( \lim_{\gamma \to 0} \Omega(s_3; \gamma, \rho) = 1 \), and 4) \( \Omega(s_3; \gamma, \rho) \) is purely real for \(-1 \leq s_3 \leq 1 \). As before, the “±” prefactor in (eq. 1.32) indicates the direction of tunneling. By choosing the boundary conditions such that \( \lim_{\tau \to -\infty} s_3 = -1 \), \( \lim_{\tau \to +\infty} s_3 = +1 \), the “+” sign in the differential equation, and taking the instanton to be centered at \( \tau = 0 \), we arrive at an instanton from \(-1 \to +1 \) which satisfies \( s_3(-\tau) = -s_3(\tau) \). Therefore one needs only consider the alternative initial condition that \( s_3(0) = 0 \); this form is amenable to numerical methods, since one no longer needs to worry about asymptotic initial conditions.

For small \( \alpha \) and \( \gamma \), it is possible to arrive at an approximate solution for \( s_3 \) by expanding \( \Omega(s_3) \approx \)

\[^4\text{Another way to think about this is to take the limit } \gamma \to 0 \text{, since the term } (1 - s_3^2) \text{ is always paired up with } \gamma. \text{ Again, the solution with the relative “−” is the continuation of the } \gamma = 0 \text{ case, whereas the “+” solution diverges as } \gamma \to 0 \text{, and reveals the singular nature of the fourth-order perturbation.} \]
Ω(0) + O(s^2_3), in which case (eq. 1.32) reads,
\[
\frac{ds_3}{d\tau} \approx \pm \Omega(0; \gamma, \rho)(1 - s^2_3),
\]
(1.33)
and the solution is once again a hyperbolic tangent, but with a frequency Ω(0) > 1.

In (fig. 1.8) we plot the numerically computed non-zero γ instanton trajectory (using values for Fe8), and compare to the analytically solvable trajectory for γ = 0. We can see that the two curves are qualitatively similar, and the effect of a non-zero γ is to decrease the characteristic instanton width. We also plot the approximate solution \( s_3(\tau) = \tanh(\Omega(0)\tau) \), and we see that it is quite close to the numerical solution.

![Figure 1.8: Comparison of plots of the \( s_3 \) component of the instanton trajectory, using the Fe8 values of \( \alpha = 0.157 \), and \( \gamma = -0.0615 \), computed numerically (blue, solid); \( \gamma = -0.0615 \) using the \( \tanh(\Omega(0)\tau) \) approximation (pink dashed); and \( \gamma = 0 \) (red).](image)

Finally, we address the case of \( \gamma = 0 \), and \( X_1 \neq 0 \), for which the instantons are once again exactly solvable. Here it will be easier to work in the original stereographic coordinates \( z \) and \( \bar{z} \). We shall restrict ourselves to small enough values of \( X_1 \) such that \( h_0 \) still exhibits 6 critical points on the sphere; if \(|X_1|\) surpasses \( 2\alpha/\sqrt{1 - \alpha^2} \), the two saddle points merge into the maxima; and for \(|X_1|\) further surpassing \( \sqrt{(1 + \alpha)/(1 - \alpha)} \) the two minima will merge toward the maxima as well (see fig. 1.9). We shall restrict ourselves to \(|X_1| < 2\alpha/\sqrt{1 - \alpha^2}\). Continuing, let us define for convenience,
\[
\lambda \equiv \sqrt{\frac{1 - \alpha}{1 + \alpha}}, \quad Y_1 \equiv X_1\lambda,
\]
(1.34)
so that the Hamiltonian reads,

$$h_0(z, \bar{z}) = \frac{j}{2\lambda} \frac{(z + \bar{z})(z + \bar{z} - 2Y_1(1 + z\bar{z})) - (z - \bar{z})^2\lambda^2}{(1 + z\bar{z})^2}. \quad (1.35)$$

The value of the energy minima is $h_{0,m} = -\frac{jY_1^2}{2\lambda}$, and equating that to $h_0(z, \bar{z})$ gives us the tunneling trajectory,

$$z = \frac{Y_1 - \bar{z}(1 \pm \lambda)}{(1 \pm \lambda) - Y_1 \bar{z}} \quad (1.36)$$

as well as the two non-tunneling trajectories, i.e. the critical points $(z, \bar{z}) = (z_\pm, \bar{z}_\pm)$, where

$$z_\pm = \bar{z}_\pm = \frac{1}{Y_1}(1 \pm \sqrt{1-Y_1^2}). \quad (1.37)$$

Putting the solution (eq. 1.36) for $z = z(\bar{z})$ back into the differential equation for $\bar{z}$ gives us finally,

$$\frac{d\bar{z}}{dr} = \mp \frac{1}{2} Y_1 (\bar{z} - \bar{z}_+)(\bar{z} - \bar{z}_-). \quad (1.38)$$

For the solution which tunnels from the “southern” minima to the “northern” minima we must invoke the solution (eq. 1.36) with $(1 + \lambda)$ in the numerator, leading to the overall “$-$” in the differential equation.
Solving for $\bar{z}$ and putting the trajectory back into $z = z(\bar{z})$, we obtain

$$
\bar{z}(\tau; \tau_c, \theta) = \frac{1}{Y_1} + \frac{i}{Y_1} \sqrt{1 - Y_1^2} \tanh \left\{ \frac{1}{2} \sqrt{1 - Y_1^2} (\tau - \tau_c) + i\theta \right\},
$$

$$
z(\tau; \tau_c, \theta) = \frac{1}{Y_1} + \frac{i}{Y_1} \sqrt{1 - Y_1^2} \tanh \left\{ \frac{1}{2} \sqrt{1 - Y_1^2} (\tau - \tau_c) + \tau_0 + i\theta \right\},
$$

(1.39)

where $\tau_0$ is a material constant defined by $\tanh(\tau_0) = \sqrt{1 - Y_1^2}/\lambda$. The variables $\tau_c$ and $\theta$, on the other hand, are related to the real and imaginary parts of the arbitrary constant which arises when solving (eq. 1.38).

Note that this constant cannot be pinned down by our asymptotic boundary conditions $\lim_{\tau \to \pm \infty} \bar{z} = \bar{z}_{\pm}$, etc, since any choice of the constant will satisfy this constraint.\(^5\) Physically, the $\tau_c$ variable corresponds to the tunneling epoch, just as in the previous cases. The $\theta$ variable (which we can take modulo $\pi$ due to the $\tanh$ function) labels a continuous family of windings, of which $\theta$ and $\theta + \pi/2$ form a winding pair. For our purposes we take the winding pair given by $\theta = \pi/4$ and $\theta = 3\pi/4 \equiv -\pi/4$. This choice was made tacitly in the previous two cases as well, and it has the advantage that $s_3$ is bounded over all $\tau$, and is antisymmetric in $\tau$. For $X_1 = 0$, the $s_3$ coordinate is pure real, but for nonzero $X_1$ the $s_3$ trajectory will carry a nonzero imaginary part as well. By contrast, [12] makes the choice that $\theta = 0, \pi/2$. In that case $s_3$ remains pure real, even for non-zero $X_1$; but it has the disadvantage that $s_3$ diverges at the tunneling epoch (fig. 1.10).

For physical calculations, the instanton trajectory with $\theta$ will yield the same result as that with $\theta' = \theta + \Delta \theta$, for $0 < \Delta \theta < \pi/4$.

### 1.4.1 Instantons and the Tunnel Splitting

The rest of this section is a review of path-integral calculus. The instanton solutions discussed previously in (sec. 1.4) are known as the “one-instanton” solutions, and For large enough transition time $T$, one could also chain together multiple instanton solutions which tunnel once, thrice, five times, etc.\(^6\) Furthermore, each tunneling event can be along one of two windings. Therefore each instanton is specified by $n$ tunneling epochs $-T/2 < \tau_1 \leq \tau_2 \leq \ldots \leq \tau_n < T/2$ and $n$ windings $p_1, p_2, \ldots, p_n$. In the semiclassical approximation (see appendix, sec. A), the transition amplitude in time $T$ is given by,

$$
\mathcal{K} \approx \frac{1}{T \to \infty} \mathcal{N}_{0f}^{-1} \sum_{n=1,3,5,\ldots} \sum_{p_1} F^n \cdots \sum_{p_n} \int_{-T/2}^{T/2} d\tau_1 \int_{-T/2}^{\tau_1} d\tau_2 \cdots \int_{-T/2}^{\tau_n} d\tau_n \exp \left\{ iS[\tau_1, \ldots, \tau_n; p_1, \ldots, p_n] \right\},
$$

(1.40)

where $\mathcal{N}_{0f}^{-1}$ is a normalization prefactor, $F$ is the fluctuation determinant, and $S$ is evaluated along the specified classical trajectory. Generally speaking $S$ decomposes into the sum of the action along each

\(^5\)Unlike initial-valued problems, boundary-valued problems guarantee neither existence nor uniqueness of solutions.

\(^6\)This assumes that the initial and final points are distinct. If they are the same, then the number of times that it tunnels must be even.
Figure 1.10: The real part (solid line) and imaginary part (dashed line) of $s_3$ for an instanton of nonzero $X_1$, using the convention $\theta = 0$ (red), and $\theta = \pi/4$ (blue).

individual instanton. Furthermore $S$ is translationally invariant, i.e. does not depend on $\tau$’s. In other words,

$$S[\tau_1, \ldots, \tau_n; p_1, \ldots, p_n] = S[p_1] + S[p_2] + \ldots S[p_n],$$

and (eq. 1.40) simplifies to,

$$K \approx \frac{\mathcal{N}_0^{-1}}{T \to \infty} \sum_{n=1,3,5, \ldots} \left( \frac{FT}{n!} \right)^n \left( \sum_p e^{iS[p]} \right)^n. \quad (1.42)$$

On the other hand, for a two-level system one expects that transition amplitudes goes like $K \propto \sin(\Delta T/2)$. Comparing the two expressions we arrive at the following result for the tunnel splitting,

$$\frac{\Delta}{2} = \mathcal{N}_0^{-1} F \sum_p \exp \{ iS[p] \}. \quad (1.43)$$

That is to say, the one-instanton approximation gives the solution to first order in $\Delta$.

The maneuver of chaining together multiple one-instanton solutions is known as the *dilute instanton gas approximation*, and is valid only if the characteristic separation between two instantons is much greater than the width of the instanton. The former quantity is given by $1/\Delta$, and the latter is given by $1/\Omega_0$, where $\Omega_0$ is the frequency of small oscillations about the classical minima. This results in the self-consistency
requirement that,
\[
\Delta \ll \Omega_0. \quad (1.44)
\]

To evaluate the action along the instanton we must first Wick-rotate to Euclidean time, i.e. \(iS \rightarrow S^E\). In general the real and the imaginary parts of the semiclassical trajectory \(z\) and \(\bar{z}\) decomposes as \(z = z_R + ipz_I\) and \(\bar{z} = \bar{z}_R + p\bar{z}_I\), where \(p = \pm 1\) is the winding, so the Euclidean semiclassical action for \(\mathcal{H}_s\) evaluated along the instanton is of the form
\[
S^E_s[p] = S_R + ipS_I, \quad (1.45)
\]
i.e. the real parts of the action is the same for each winding, while the imaginary parts differ by a sign.

Summing over \(p\), we have,
\[
N_{0j}^{-1} \sum_p pFe^{S^E_s[p]} = 2iF\bar{N}_0^{-1}e^{S_R} \sin(S_I),
\]
\[
N_{0j}^{-1} \sum_p Fe^{S^E_s[p]} = 2F\bar{N}_0^{-1}e^{S_R} \cos(S_I) \equiv \Delta/2. \quad (1.46)
\]

For the instantons in absence of external fields, the imaginary part is precisely \(S_I = -j\pi\), and so,
\[
\text{integer } j : \quad \cos(S_I) = \pm 1, \quad \sin(S_I) = 0,
\]
\[
\text{half-integer } j : \quad \cos(S_I) = 0, \quad \sin(S_I) = \pm 1. \quad (1.47)
\]

The vanishing of the splitting (due to \(\cos(S_I)\)) at half-integer \(j\) is precisely the manifestation of Kramers’ theorem that each level is doubly-degenerate.
Chapter 2

Adiabatic Dynamics and Non-Abelian Berry’s Phase

We consider the adiabatic evolution of Kramers-degenerate pairs of spin states of a half-integer quadrupole spin Hamiltonian undergoing slow rotation. Two methods are explored — equations of motion of the state via the Majorana parametrization, and via spin path integrals. As an illustration, we consider molecular magnets of the $j = 9/2$ Mn4 family, and demonstrate the intricate motion exhibited by the Majorana points under rigid axis rotation.

2.1 Introduction

Geometric phases in physics continue to be an active topic of research since its initial discovery by Berry [2], who considered the evolution of a slowly time-dependent system. In its original incarnation the Berry’s phase is thought of as an Abelian phase, and in the same year Wilczek and Zee [48] considered the non-Abelian generalization. Though of the same mathematical origin, systems capable of non-Abelian geometric phases are more difficult to construct, since they require the persistence of degenerate energy levels, and in nature such degeneracies rarely occur unless its existence is “protected” by some mathematical symmetry.

One possibility for exhibiting non-Abelian geometric phases was proposed by Mead [28,29], who suggested exploiting time-reversal invariance in molecular systems with an odd number of electrons. The spin states of these systems must therefore be of half-integer angular momentum, and Kramers theorem then guarantees the existence of double degeneracy for all levels. A minimal model which realizes this symmetry is given by the quadrupole Hamiltonian,

$$\mathcal{H}(Q) = \sum_{k,l} Q_{kl} J_k J_l,$$

where the total spin\(^1\) must satisfy $j \geq 3/2$. Here $Q$ is a real $3 \times 3$ symmetric traceless matrix, and as

\(^1\)it can be verified that for $j = 1/2$ (eq. 2.1) vanishes
explained in [1] the set of all such $Q$, after modding\(^2\) by the rotation group $SO(3)$, can be reduced to

$$Q_\theta = \begin{pmatrix}
\cos(\theta + \frac{2\pi}{3}) \\
\cos(\theta - \frac{2\pi}{3}) \\
\cos(\theta)
\end{pmatrix}.$$  \hfill (2.2)

After rescaling and adding constants, $\mathcal{H}(Q_\theta)$ reproduces\(^3\) precisely the Fe8 Hamiltonian (eq. 1.15).

The set of all transforms preserving the quadratic form (eq. 2.1) therefore decomposes into that of rotations and that of changing the $\theta$ value. Note that only the latter transform perturbs the energy eigenvalues. Since adiabatically tuning $\theta$ would correspond to the experimentally infeasible task of continuously changing the crystal field values $D$ and $E$, we will restrict our considerations to the adiabatic rotations. For a non-degenerate level $n$, the magnetization $\langle \psi, n | \mathcal{J} | \psi, n \rangle$ will simply co-rotate with the molecule, so that in the body frame of the molecule the magnetization will simply remain stationary. When the level is degenerate however, the evolution will be described by the non-Abelian Berry transport \([1, 48]\) so that even in the body frame, the magnetization can exhibit slow dynamical behavior, with observable consequences.

The aim of this chapter is to explore how a degenerate eigenstate of the quadrupole Hamiltonian evolves under slow rotations. In section 2.2 we review Kato’s equation for adiabatic dynamics and apply it to the specific case of rotations. In section 2.3 we introduce the Majorana parametrization of a general spin-$j$ state and develop the equations of motion for these points under adiabatic transforms, focusing on simplifications which arise when we restrict to Kramers-degenerate pairs of states. In section 2.4 we provide an alternative characterization via the semiclassical spin path-integral. And finally in section 2.5 we provide illustrations using the molecular magnet Mn4 to show how even simple anisotropies can give rise to intricate state evolutions.

### 2.2 Adiabatic Dynamics and Kato’s Equation

We begin with a brief review of adiabatic Berry-transport. Suppose our system is characterized by a parameter-dependent Hamiltonian $\mathcal{H}(\mathbf{Y})$, and that $\mathcal{H}$ possesses $N$ distinct eigenvalues, which remain distinct over all values of $\mathbf{Y}$ under consideration.\(^4\) For a particular eigenvalue $E_n(\mathbf{Y})$ ($n = 1, 2, \ldots, N$) and its associated eigenspace $V_n(\mathbf{Y})$, consider a state $|\Psi(0)\rangle$ initially in $V_n(\mathbf{Y})$. Now suppose $\mathbf{Y} = \mathbf{Y}(\epsilon t)$ were varied slowly in time ("slow" here means that the frequency $\epsilon$ is such that $\hbar \epsilon$ is much smaller than the

\(^2\)In the sense that two quadrupole matrices $Q$ and $Q'$ are identified if there exists a rotation $\mathcal{R}$ such that $Q = \mathcal{R}Q\mathcal{R}^{-1}$

\(^3\)Explicitly, this is given by $\cosh(\rho) = -3 \cos(\theta) / \sqrt{3 + 6 \cos(2\theta)}$

\(^4\)Note we do not require that $N$ be the same as the dimension of the full vector space; in fact, our interest is precisely for those eigenvalues which are degenerate. We instead require that the degeneracy of each eigenvalue does not change over $\mathbf{Y}$
energy gap between $E_n$ and any other levels, at all time). Then the evolution of $|\Psi(t)\rangle$ is such that it always remains in the eigenspace $V_n(Y(\epsilon t))$. But if $Y(\epsilon t)$ were taken to be a closed circuit so that $Y(0) = Y(\epsilon T)$, then the naïve conclusion that $|\Psi(T)\rangle$ simply differs from $|\Psi(0)\rangle$ by a dynamical phase, would be incorrect [2]. The actual evolution is given instead by the Berry-transport condition,

$$|\Psi(T)\rangle = e^{i\phi_{\text{dyn}}} U_{\text{ad}}(\epsilon T) |\Psi(0)\rangle,$$

(2.3)

where $U_{\text{ad}}(\epsilon T)$ is the Adiabatic Propagator, and is in general not equal to the identity. To calculate $U_{\text{ad}}$, it can be shown [48] that the adiabatic evolution of such a state $|\Psi\rangle$ satisfies the parallel transport condition,

$$\mathcal{P}(Y) dY |\Psi\rangle = 0.$$

(2.4)

Working in the “slow” time variable $s = \epsilon t$, we can interpret the propagator to $U_{\text{ad}}$ as the formal limit,

$$U_{\text{ad}} = \lim_{N \to \infty} \mathcal{P}(s_N) \mathcal{P}(s_{N-1}) \cdots \mathcal{P}(s_1) \mathcal{P}(s_0),$$

(2.5)

where we’ve discretized $s_k = k\epsilon T/N$. Note that while $\mathcal{P}$ is not unitary, in the infinitesimal limit it does become norm preserving. Intuitively then, the Berry condition says that we keep projecting the state down into the evolving eigenspace. The evolution (eq. 2.5) may alternatively be written as the solution to what is known as Kato’s Equation,

$$i \frac{d}{ds} |\Psi\rangle = [i \frac{d}{ds} \mathcal{P}, |\Psi\rangle],$$

(2.6)

named after Tosio Kato who first obtained it in 1950 [18]. We can think of Kato’s equation as an effective Schrödinger’s equation in slow time, with $[i \frac{d}{ds} \mathcal{P}, |\Psi\rangle]$ as the effective Hamiltonian.

When $E_n$ is non-degenerate, $U_{\text{ad}}$ is simply a U(1) phase, and was shown to depend on the shape of the trajectory $Y$ takes in parameter space (hence the name “geometric phase”). More generally the level could be $d$-degenerate, in which case $U_{\text{ad}}$ is a U($d$) element that could transform the initial state by more than just a phase, leading to a physically distinct state.

Our interest is in the evolution of spin for a molecule that is rotating in space. For a fixed orientation of the molecule, the spin Hamiltonian is a polynomial in the spin operators $\mathcal{J}_1$, $\mathcal{J}_2$, $\mathcal{J}_3$, and the effect of a spatial rotation $R$ is to change $\mathcal{J}_a \to R^{-1}_{ab} \mathcal{J}_b$, and corresponding transformation on the Hamiltonian may be
written,
\begin{align*}
\mathcal{H}(t) &= \mathcal{R}(ct)\mathcal{H}(0)\mathcal{R}^{-1}(ct).
\end{align*}
(2.7)

The same operator also evolves the projection,
\begin{align*}
\mathcal{P}(s) &= \mathcal{R}(s)\mathcal{P}(0)\mathcal{R}^{-1}(s),
\end{align*}
(2.8)

and we can work in a frame rotating with the molecule (the body frame) by setting \(|\Psi(s)\rangle \equiv \mathcal{R}(s)|\Phi(s)\rangle\).

In this frame, Kato’s equation becomes,
\begin{align*}
\frac{d}{ds}|\Phi(s)\rangle &= -\mathcal{P}(0)\mathcal{K}(s)\mathcal{P}(0)|\Phi(s)\rangle,
\end{align*}
(2.9)

where we have defined the Maurer-Cartan form (multiplied by \(ds\)),
\begin{align*}
\mathcal{K}(s) &\equiv \mathcal{R}^{-1}\frac{d\mathcal{R}}{ds} = i\sum_{a} Y_{a}(s)J_{a},
\end{align*}
(2.10)

(the second definition in eq. 2.10 is always possible because the Maurer-Cartan form is an element of the Lie algebra, which in this case is spanned by the \(J_{i}\)’s). For reference, a generic rotation \(\mathcal{R}\) written in the ZYZ Euler angle convention as
\begin{align*}
\mathcal{R}(s) &= \exp\{-i\phi(s)J_{3}\}\exp\{-i\theta(s)J_{2}\}\exp\{-i\psi(s)J_{3}\},
\end{align*}
(2.11)

leads to the components,
\begin{align*}
Y_{1} &= -\sin \psi \frac{d\theta}{ds} + \sin \theta \cos \psi \frac{d\phi}{ds}, \\
Y_{2} &= -\cos \psi \frac{d\theta}{ds} - \sin \theta \sin \psi \frac{d\phi}{ds}, \\
Y_{3} &= -\cos \theta \frac{d\phi}{ds} - \frac{d\psi}{ds}.
\end{align*}
(2.12)

The above parametrization is particularly convenient because it takes \(J_{3}\) to \(\mathcal{R}J_{3}\mathcal{R}^{-1} = \sin \theta \cos \phi \mathcal{J}_{1} + \sin \theta \sin \phi \mathcal{J}_{2} + \cos \theta \mathcal{J}_{3}\), with which we can identify the components of the external field for the usual Zeeman coupling.

Continuing, the evolution given by (eq. 2.9) now takes place entirely within the initial eigenspace \(V(0)\), and the (body-frame) adiabatic propagator, \(|\Phi(s)\rangle = \mathcal{U}_{\text{id}}^{b}(s)|\Phi(0)\rangle\), may be given by the time-ordered

\footnote{We are using \(\mathcal{R}\) as the notation for a rotation matrix (which is an element of SO(3)), and \(\mathcal{R}\) for the corresponding unitary operator (which is an linear operator in the spin-\(j\) representation of SU(2)).}
exponential (with $\delta s = \epsilon T/N$),

$$U_{ad}^b(s) = \lim_{N \to \infty} \mathcal{P}(0)(1 - \delta s K(s_N))\mathcal{P}(0)(1 - \delta s K(s_{N-1}))\mathcal{P}(0) \cdots \mathcal{P}(0)(1 - \delta s K(0))\mathcal{P}(0), \quad (2.13)$$

which we may interpret as the quantum evolution generated by the effective Hamiltonian $\mathcal{H}_{\text{eff}} = -i K$, and restricted via $\mathcal{P}(0)$ to the $V(0)$ subspace.

### 2.3 Kato’s Equation and the Majorana Points

In general Kato’s equation gives us a set of $2j + 1$ equations for the coefficients of the state $|\Psi\rangle$ in some basis. Of these, one degree of freedom encodes information regarding the overall phase of the state which, though important in its own right, is irrelevant when trying to distinguish between two physically distinct states. An alternative parametrization is to characterize the state by a set of $2j$ points on the sphere, called Majorana Points, after its discoverer. It can be thought of as the spin-$j$ analogue of the Bloch sphere for a spin-$1/2$ state. This revealing parametrization happens to discard phase information, and so any two distinct configurations of points corresponds also to physically distinct states. Therefore it is the perfect tool for exploring non-Abelian holonomy under adiabatic propagation, and our goal in this section to translate Kato’s equation into a set of equations for the Majorana points.

#### 2.3.1 Coherent States and Majorana Polynomial

We begin by briefly reviewing the construction of spin coherent states. A complete treatment of coherent states in general can be found in [31]. Let $\mathcal{J} = (\mathcal{J}_1, \mathcal{J}_2, \mathcal{J}_3)$ be the spin-$j$ angular momentum operators, and let $|j, m\rangle$ be the usual eigenstate of $\mathcal{J}_z$. The coherent state $|\bar{z}\rangle$ and its Hermitian conjugate $|z\rangle$ are then given by,

$$|\bar{z}\rangle = \exp(\bar{z}\mathcal{J}_+) |j, -j\rangle, \quad |z\rangle = \langle j, -j | \exp(z \mathcal{J}_-), \quad \text{ (2.14)}$$

where $\mathcal{J}_\pm \equiv \mathcal{J}_1 \mp i \mathcal{J}_2$ are the ladder operators, and $|j, -j\rangle$ is the lowest weight state. Here $z$ is a point on the Riemann sphere expressed as a complex number via stereographic coordinates, and corresponds to the direction pointed by the unit vector $s$. This correspondence may be given exactly by,

$$z = \frac{s_1 + i s_2}{1 - s_3} = \sqrt{\frac{1 + s_3}{1 - s_3}} e^{i \phi}, \quad \bar{z} = \frac{s_1 - i s_2}{1 - s_3} = \sqrt{\frac{1 + s_3}{1 - s_3}} e^{-i \phi}. \quad (2.15)$$
The spin coherent states $|\tilde{z}\rangle$ are not orthonormal but instead have an inner product given by,

$$(z|\tilde{z}') = (1 + z\tilde{z}')^{2j}, \quad (2.16)$$

so in particular the coherent state along the direction of $-\frac{1}{z}$ is orthogonal to the state along $z^6$. The geometric interpretation of this fact becomes clear once we note that $-\frac{1}{z}$ is precisely the point anti-podal to $z$. Finally, we can use (2.16) to define normalized spin coherent states,

$$|\tilde{z}\rangle = (1 + z\tilde{z})^{-j} |\tilde{z}\rangle, \quad (z| = (1 + z\tilde{z})^{-j} (z|. \quad (2.17)$$

Calculations of physical quantities must be performed using the normalized states (2.17), but mathematically the unnormalized states $|\tilde{z}\rangle$ and $(z|$ are more natural, as they are holomorphic (depending only on $z$ or $\tilde{z}$ but not both) and better capture the underlying algebraic structure of the representation.

Now, any spin-$j$ state $|\Psi\rangle$ may be written as a linear combination of $|j,m\rangle$ basis states,

$$|\Psi\rangle = \sum_{m=-j}^{j} a_m |j,m\rangle. \quad (2.18)$$

It turns out that the inner product of each $|j,m\rangle$ with $(z|$ yields a monomial in $z$ of degree $j + m$,

$$(z|j,m\rangle = \sqrt{\frac{(2j)!}{(j-m)!(j+m)!}} z^{j+m} \equiv c_m z^{j+m}. \quad (2.19)$$

In the second equation we have absorbed into $c_m$ all of the combinatorial factors. Using (2.19), we can identify with each state $|\Psi\rangle$ a unique polynomial of degree (at most) $2j$, by simply taking its inner product with $(z|$. That is,

$$P_\Psi(z) \equiv (z|\Psi) = \sum_{m=-j}^{j} a_m c_m z^{j+m}. \quad (2.20)$$

The quantity $P_\Psi$ is the Majorana Polynomial of the state $|\Psi\rangle$. By normalizing $(z|$, which simply tacks on a factor of $(1 + z\tilde{z})^{-j}$, we arrive at the Coherent State Wavefunction $\Psi(z,\tilde{z})$, defined as

$$\Psi(z,\tilde{z}) \equiv (z|\Psi) = (1 + z\tilde{z})^{-j} P_\Psi(z). \quad (2.21)$$

Let us turn our attention to the zeros of the wavefunction $\Psi$ over the Riemann sphere, and let us label these zeros by $\zeta_k$. From (2.21), if $\zeta_k$ is a zero of the polynomial $P_\Psi$, then so too will $\Psi$ vanish there. And

---

\[\text{This is a feature unique to the spin coherent states. By contrast, the overlap of two harmonic-oscillator coherent states can never be completely vanishing.}\]
since $P_{\Psi}$ is generically a polynomial of degree $2j$, we expect $\Psi$ to have $2j$ zeros. What if $P_{\Psi}$ is of degree smaller than $2j$? This could happen if the coefficient of leading $m = j$ term in the expansion (2.18) is zero, in which case the $P_{\Psi}$ is of degree at most $2j - 1$; or if both the $m = j$ and $m = j - 1$ terms are zero, in which case $P_{\Psi}$ is of degree at most $2j - 2$, etc, and consequently will no longer fully furnish $2j$ zeros. It turns out, however, that the wavefunction still maintains a complete set of $2j$ zeros, with the rest of these zeros having moved to the point at infinity, i.e. $z = \infty$, or the “north” pole. These zeros are picked up by the normalization factor $(1 + z \bar{z})^{-j}$, and the multiplicity of the zeros at $\infty$ is a result of the balance between the power of $-j$ appearing in the normalization, and the degree of the leading term in the polynomial.

2.3.2 Majorana Decomposition and Equations of Motion

There is an elegant connection between these $\zeta_k$'s and with what is known as the Majorana Decomposition. In general, it is known that when a collection of $2j$ spin-$1/2$ states are combined, the spin-$j$ irreducible representation of SU(2) resides in the space of total symmetric tensors, where an element $|\Psi\rangle$ of the symmetric tensor space $\text{Sym}[V_{1/2}^{\otimes 2j}]$ is a sum of the form

$$|\Psi\rangle = \sum_{i_1, i_2, \ldots, i_{2j}} A^{i_1 \ldots i_{2j}} |e_{i_1}\rangle \otimes |e_{i_2}\rangle \otimes \cdots \otimes |e_{i_{2j}}\rangle,$$

(2.22)

where the $|e_i\rangle$ are the basis vectors for $V_{1/2}$, i.e. $|e_1\rangle = |\uparrow\rangle$ and $|e_2\rangle = |\downarrow\rangle$, and where the symmetric tensor product $\otimes$ is defined to be the totally symmetrized linear product,

$$|e_1\rangle \otimes \cdots \otimes |e_{2j}\rangle = \frac{1}{(2j)!} \sum_{\pi \in S_{2j}} |e_{\pi(1)}\rangle \otimes |e_{\pi(2)}\rangle \cdots \otimes |e_{\pi(2j)}\rangle,$$

(2.23)

so that, for example,

$$|e_1\rangle \otimes |e_2\rangle \otimes |e_3\rangle = \frac{1}{6} (|e_1\rangle |e_2\rangle |e_3\rangle + |e_1\rangle |e_3\rangle |e_2\rangle + |e_2\rangle |e_1\rangle |e_3\rangle + |e_2\rangle |e_3\rangle |e_1\rangle + |e_3\rangle |e_1\rangle |e_2\rangle + |e_3\rangle |e_2\rangle |e_1\rangle).$$

(2.24)

Though (eq. 2.22) is well known result of the general theory of representation, Majorana showed [27] that an arbitrary spin-$j$ state can be decomposed as a single symmetrized tensor product of $2j$ spin-$1/2$ states. More precisely, it was shown that for any $|\Psi\rangle$ there exists $|\chi_k\rangle \in V_{1/2}$, for $k = 1, 2, \ldots, 2j$, such that,

$$|\Psi\rangle = |\chi_1\rangle \otimes |\chi_2\rangle \otimes \cdots \otimes |\chi_{2j}\rangle,$$

(2.25)
and we reproduce his arguments in the appendix. Now, it is known that any spin-1/2 state $|\chi\rangle$ is representable as a point on the Bloch sphere, and in fact this statement is equivalent to writing that the spinor $|\chi\rangle$ is proportional to a spin-1/2 coherent state, i.e. that there exists $\alpha \in \mathbb{C}$, and $w \in S^2$, such that,

$$|\chi\rangle = \alpha |\bar{w}\rangle_{1/2}.$$  \hspace{1cm} (2.26)

As such, our generic spin-$j$ state $|\Psi\rangle$ may be characterized by $2j$ points $w_k$ and an overall scaling $A = (\prod_{k=1}^{2j} \alpha_k)$, such that,

$$|\Psi\rangle = A |\bar{w}_1\rangle_{1/2} \odot |\bar{w}_2\rangle_{1/2} \odot \cdots \odot |\bar{w}_{2j}\rangle_{1/2}.$$  \hspace{1cm} (2.27)

Now, it can be shown that the inner product between the $2j$ symmetrized spinors and a spin-$j$ coherent state $|\bar{z}\rangle_j$ is given by [25]

$$\langle \bar{z} | \bar{\Psi} \rangle = \prod_{k=1}^{2j} (1 + z\bar{w}_k).$$  \hspace{1cm} (2.28)

As such, we see that the zeros $\zeta$ of our Majorana polynomial are precisely anti-podal to the directions of the state’s constituent spinors, i.e. $\zeta_k = -1/\bar{w}_k$. The points $w$ are called the Majorana Points of the state, and they offer geometric insight. For example, from (eq. 2.16) we see that the Majorana polynomial of a coherent state $|\bar{a}\rangle_2$ has all of $2j$ of its zeros located at $-1/\bar{a}$, meaning that all of its Majorana points are coalesced at $a$, thus giving an alternative illustration of why such a state is “coherent” (see fig. 2.1). Similarly, a $\mathcal{J}_3$ eigenstate $|j, m\rangle$ is a state with $j + m$ of its Majorana points located at the north pole and $j - m$ points located at the south pole.
Since the Majorana points carry information about the quantum state, it helps to translate the time evolution of the state into a set of $2j$ coupled equations of motions for its Majorana points. Following [7], let $\psi(z,t)$ be the coherent state wavefunction at time $t$, and let $\zeta = \zeta(t)$ be a zero of $\psi$ at $t$. By evolving infinitesimally forwards in time and demanding that $\zeta$ remain a zero, we arrive at,

$$\psi(\zeta + \delta\zeta, t + \delta t) = 0.$$ (2.29)

Then, expanding to first order and using that $\psi$ satisfies Schrödinger’s equation, we obtain the equation of motion,

$$\frac{d\zeta}{dt} = i\hat{H}_z \psi \left. \frac{\partial\psi}{\partial z} \right|_{z=\zeta}. $$ (2.30)

Here, $\hat{H}_z$ is the differential operator corresponding to the spin Hamiltonian $\mathcal{H}$. To translate to the Majorana points, we recall that $\zeta = -1/\bar{w}$, and that $\psi(z,t) = N(w,\bar{w})^{-1} \prod_{l=1}^{2j} (1 + z\bar{w}_l)$, so that,

$$\frac{d\bar{w}_k}{dt} = i\bar{w}_k^{-2j} \prod_{l \neq k} (\bar{w}_k - \bar{w}_l)^{-1} \hat{H}_z \left. \left( \prod_{i}^{2j} (1 + z\bar{w}_i) \right) \right|_{z=-1/\bar{w}_k},$$ (2.31)

$$= i\bar{w}_k^{-2j} \{(1/\bar{w}_k|_{j} \mathcal{H} |\bar{w}_1)_{1/2} \otimes \cdots \otimes |\bar{w}_{2j})_{1/2}\} \prod_{l \neq k} (\bar{w}_k - \bar{w}_l)^{-1}. $$

Though it is no less difficult to solve (eq. 2.31) than it is the original Schrödinger’s equation, this alternative parametrization can be revealing. Majorana himself used it to arrive at an independent derivation [27] of the non-adiabatic level-crossing probability that is traditionally attributed to Landau, Stueckelberg and Zener, and along the way he showed that if the Hamiltonian were linear in the generators, then the above system decouple simply into that of $2j$ sets of independently evolving $w$’s, all obeying the same differential equation.

### 2.3.3 Equations of Motion from Action Principle

Though not obvious, the equations of motion for the Majorana points are in fact symplectic, and in the following we will show that (eq. 2.31) can alternatively be derived from a set of Euler-Lagrange equations. To start, let us construct the Lagrangian for a spin path integral in the $2j$ Majorana points,

$$i\mathcal{L} = \left( \frac{d}{dt} (N^{-1} |\bar{w}_1, \ldots, \bar{w}_{2j}), N^{-1} |\bar{w}_1, \ldots, \bar{w}_{2j} \right) - iN^{-2} (w_1, \ldots, w_{2j} | \mathcal{H} |\bar{w}_1, \ldots, \bar{w}_{2j}), $$ (2.32)
where for simplicity of notation we have defined,
\[ |\tilde{w}_1, \ldots, \tilde{w}_{2j}\rangle \equiv |\tilde{w}_1\rangle_{1/2} \odot \cdots \odot |\tilde{w}_{2j}\rangle_{1/2}, \quad \mathcal{N}^2 \equiv ||\tilde{w}_1, \ldots, \tilde{w}_{2j}||^2. \]  
(2.33)

The explicit form of the normalization \(\mathcal{N}\) is given in the appendix. The first term in (eq. 2.32) is analogous to the Wess-Zumino term \(\langle z | d | \bar{z} \rangle\) in the usual spin-\(j\) action; taking one more exterior derivative yields the corresponding symplectic form \(\Omega\) on the \(w\)'s,
\[ \Omega = d \left( d(\mathcal{N}^{-1} |\tilde{w}_1, \ldots, \tilde{w}_{2j}\rangle), \mathcal{N}^{-1} |\tilde{w}_1, \ldots, \tilde{w}_{2j}\rangle \right). \]  
(2.34)

The second term in (eq. 2.32) is analogous to the semiclassical \(Q\)-symbol of Hamiltonian. At this point the Lagrangian is a function of the \(w\)'s and \(\tilde{w}\)'s, as well as \(\dot{w}\)'s and \(\dot{\tilde{w}}\)'s. After a straightforward but tedious derivation the corresponding Euler-Lagrange equations may be obtained as,
\[ \sum_{l=1}^{2j} \left[ \left( \sum_{\rho \in \mathcal{S}} \Lambda_{\rho} \right)^{-2} \sum_{\pi \in \mathcal{S}} \bar{A}_{\pi} \bar{\lambda}^{-1}_{\pi,l} w_{\pi(l)} \sum_{\sigma \in \mathcal{S}} \Lambda_{\sigma} \lambda^{-1}_{\sigma,i} \tilde{w}_{\sigma(i)} \right. \]
\[ - \left. \left( \sum_{\rho \in \mathcal{S}} \Lambda_{\rho} \right)^{-1} \sum_{\sigma \in \mathcal{S}} \Lambda_{\sigma} \lambda^{-1}_{\sigma,i} \bar{\lambda}^{-1}_{\sigma,l} (\delta_{l,\sigma(i)} + w_{\sigma(i)} \tilde{w}_{\sigma(i)}) \right] \dot{w}_l = i \frac{\partial}{\partial w_l} \{ \mathcal{N}^{-2} (w_1, \ldots, w_{2j}) | \mathcal{H} (w_1, \ldots, w_{2j}) \}, \]
(2.35)

where \(\mathcal{S}\) is the symmetric group of order \((2j)!\), \(\pi, \rho, \sigma\) are permutations, \(\bar{\pi}\) denotes the inverse permutation of \(\pi\), and,
\[ \lambda_{\sigma,i} \equiv 1 + w_l \tilde{w}_{\sigma(i)}, \quad \bar{\lambda}_{\sigma,i} \equiv 1 + \tilde{w}_l w_{\sigma(i)}, \quad \Lambda_{\sigma} \equiv \prod_{i=1}^{2j} \lambda_{\sigma,i}, \quad \bar{\Lambda}_{\sigma} \equiv \prod_{i=1}^{2j} \bar{\lambda}_{\sigma,i}. \]  
(2.36)

In particular we note that \(\sum_{\sigma \in \mathcal{S}} \Lambda_{\sigma} = (2j)! \mathcal{N}^2\), and also that \(\bar{\Lambda}_{\sigma} = \Lambda_{\sigma}\). To complete the derivation we show that the solution to (eq. 2.35) is given by the equations of motion (eq. 2.31). Noting that this equality is to hold regardless of the form of \(\mathcal{H}\), The left hand side yields, after substitution for \(\dot{w}\), that,
\[ l.h.s. = \sum_{l=1}^{2j} \left[ \left( \sum_{\rho \in \mathcal{S}} \Lambda_{\rho} \right)^{-2} \sum_{\pi \in \mathcal{S}} \bar{A}_{\pi} \bar{\lambda}^{-1}_{\pi,l} w_{\pi(l)} \sum_{\sigma \in \mathcal{S}} \Lambda_{\sigma} \lambda^{-1}_{\sigma,i} \tilde{w}_{\sigma(i)} \right. \]
\[ - \left. \left( \sum_{\rho \in \mathcal{S}} \Lambda_{\rho} \right)^{-1} \sum_{\sigma \in \mathcal{S}} \Lambda_{\sigma} \lambda^{-1}_{\sigma,i} \bar{\lambda}^{-1}_{\sigma,l} (\delta_{l,\sigma(i)} + w_{\sigma(i)} \tilde{w}_{\sigma(i)}) \right] i^{2j} \prod_{k \neq l} (\tilde{w}_l - \tilde{w}_k)^{-1} (-1/\tilde{w}_k), \]
(2.37)
while the right hand side reads,

\[ \text{r.h.s.} = (2j)! \sum_{\sigma \in \mathcal{S}} \left( \frac{\partial}{\partial w_i} (w_1, \ldots, w_{2j}) \right) - (2j)! \sum_{\sigma \in \mathcal{S}} \Lambda_{\sigma} \lambda_{\sigma,i}^{-1} \bar{w}_{\sigma(i)} (w_1, \ldots, w_{2j}). \]  

Finally, equality may be demonstrated by acting on both sides by \(|\bar{z}\rangle_j\) from the right, and showing that the resulting polynomials in \(\bar{z}\) are the same. This is assisted by the identities that,

\[ \sum_{\sigma \in \mathcal{S}} \prod_{k \neq l} (1 + \bar{w}_{\sigma(k)} w_k) \left( \bar{w}_{\sigma(l)} - \bar{w}_{\sigma(k)}^{-1} \right) = (2j - 1)! \prod_{i \neq l} (1 + \bar{z}w_i), \]  

and

\[ \sum_{\sigma \in \mathcal{S}} \sum_{i=1}^{2j} \left\{ \prod_{k \neq i} (1 + w_k \bar{w}_{\sigma(k)}) \prod_{k \neq l} \frac{1 + w_{\sigma(k)} w_k}{\bar{w}_{\sigma(l)} - \bar{w}_{\sigma(k)}} \right\} \times (1 + w_{\sigma(l)} \bar{w}_l)^{-1} [(1 + \bar{z}w_{\sigma(l)}) \bar{w}_{\sigma(i)} + \delta_{l,\sigma(i)} (\bar{z} - \bar{w}_l)] = (2j)! \bar{z} \prod_{k \neq i} (1 + \bar{z}w_k). \]  

### 2.3.4 Majorana Points and Doubly-Degenerate Kramers Pairs

Let us specialize our equations of motion to the case where the evolution takes place within the subspace \(V(0)\) spanned by an eigenspace and its time-reversal partner. Given an initial state \(|\Phi(0)\rangle\), the projection operator \(\mathcal{P}(0)\) can be given by,

\[ \mathcal{P}(0) = |\Phi(0)\rangle \langle \Phi(0)| + |\Theta \Phi(0)\rangle \langle \Theta \Phi(0)|, \]  

where \(\Theta = \exp \{-i\pi J_2\}^*\) is the time-reversal operator, with \(^*\) being the anti-linear complex-conjugation operator whose action in the \(|j, m\rangle\) basis is given by \(^*\) : \(a |j, m\rangle \mapsto \bar{a} |j, m\rangle\). Recall that angular momentum is odd under time-reversal, i.e., \(\Theta J = -J \Theta\). Furthermore, \(\Theta\) satisfies \(\Theta^2 = (-1)^2\), a crucial component of Kramers theorem.

Since Kato’s equation (eq. 2.9) describes the propagation in terms of an effective Hamiltonian \(\mathcal{H} = -i\mathcal{P}(0) \mathcal{K}(s) \mathcal{P}(0)\), one could in theory apply (eq. 2.31) to obtain the adiabatic evolution. Doing so however would necessitate writing down the differential operator \(\hat{\mathcal{P}}\) corresponding to the projection, and this is difficult to find in general. Motivated by the path integral construction, however, and the fact that \(V(0)\) is two-dimensional, we set out to find an effective spin-1/2 path integral.

To start, we let \(\lambda \in S^2\) be the stereographic complex coordinate of a point on the Riemann sphere, and
| = (1 + λ|^ )^{-1/2} |Φ(0)⟩ + λ |Φ(0)⟩, \]

|λ⟩ ≡ (1 + λ|^ )^{-1/2} ⟨ΘΦ(0)| + λ ⟨Φ(0)|. \]

These are analogous to the spin-1/2 coherent states in which |ΘΦ(0)⟩ and |Φ(0)⟩ are playing the roles of the spin-down and spin-up states respectively; and as such we recognize that the projection operator \( P(0) \) as the (over-complete) resolution

\[ P(0) = \frac{2}{4\pi} \int_{S^2} \frac{2}{1 + (1 + \lambda|^ )^2} |λ⟩⟨λ|. \]

This is in accordance with our intuition that the projection \( P(0) \) acts as the identity operator on the subspace \( V(0) \). Proceeding via time-slicing as usual, we obtain what is essentially the adiabatic path integral

\[ S_{ad} [λ, \bar{λ}] = \int_0^T ds \left( \frac{1}{2} \frac{dλ}{ds} - \frac{d\bar{λ}}{ds} \right) \left( \frac{1}{1 + \lambda|^ } - A(λ, \bar{λ}) \right), \]

with \( A = ⟨λ|K|λ⟩ \).

Now, when the Hamiltonian term is linear in the Lie algebra generators, then we know that the semiclassical equations of motion give the exact quantum evolution [36], [15]. In this case, since the "Hamiltonian" \( K \) corresponds to the Maurer-Cartan form of an SU(2) element, it is necessarily an element of the Lie algebra. (Alternatively, since this is effectively a spin-1/2 representation, we can always reduce it to a linear combination of the Pauli sigma matrices).

Continuing, these equations of motion are given by,

\[ \frac{dλ}{ds} = (1 + λ|^ )^2 \frac{∂A}{∂λ}, \quad \frac{d\bar{λ}}{ds} = -(1 + λ|^ )^2 \frac{∂A}{∂λ}. \]

But from the construction of |λ⟩, we can write

\[ (1 + λ|^ ) \frac{∂}{∂λ} (λ|O|λ⟩) = -⟨λ|OΘ|λ⟩, \]

for any operator \( O \). Defining \( B = ⟨λ|KΘ|λ⟩ \), we can rewrite the above equations of motion as,

\[ \frac{dλ}{ds} = -(1 + λ|^ )B, \quad \frac{d\bar{λ}}{ds} = -(1 + λ|^ )\bar{B}. \]

We now know the time evolution of \( λ(t) \), and hence that of |Φ(t)⟩. Finally, for \( \frac{dw}{dt} = \frac{dw}{dλ} \frac{dλ}{ds} \), it remains to
see how changes in $\lambda$ relate to changes in the Majorana points. To this end, observe that we may write,

$$|\bar{\lambda}\rangle = e^{i\gamma}N^{-1} |\bar{\psi}_1\rangle_{1/2} \otimes \cdots \otimes |\bar{\psi}_{2j}\rangle_{1/2}, \quad (2.48)$$

where as before $N = N(\{w\}, \{\bar{w}\})$ is the normalization of $|\bar{\psi}_1\rangle_{1/2} \otimes \cdots \otimes |\bar{\psi}_{2j}\rangle_{1/2}$ (noting that it is a function of both $w$'s and $\bar{w}$'s), and $\gamma$ is some phase factor which will drop out of the subsequent derivations. Next, we repeat the same derivations in (sec. 2.3.2), i.e. by constructing the wavefunction $|\lambda\rangle$ and considering how its zeros are perturbed by changes in $\lambda$. After some lengthy algebra, we obtain,

$$\frac{d\psi_k}{d\lambda} = -e^{2i\gamma}(1 + \psi_k\bar{\psi}_k) \prod_{l \neq k} \frac{1 + \bar{\psi}_l\psi_k}{\psi_k - \bar{\psi}_l}, \quad (2.49)$$

and similarly for $\bar{\psi}_k$. Putting everything together, we are left with,

$$\frac{d\psi_k}{ds} = -B(w_1, \ldots, \bar{w}_{2j})(1 + \psi_k\bar{\psi}_k) \prod_{l \neq k} \frac{1 + \bar{\psi}_l\psi_k}{\psi_k - \bar{\psi}_l}, \quad (2.50)$$

where we've defined,

$$B(w_1, \ldots, \bar{w}_{2j}) \equiv N(w_1, \ldots, \bar{w}_{2j})^{-2} (w_1|_{1/2} \otimes \cdots \otimes |w_{2j}|_{1/2} \mathcal{R}^{-1} \frac{d\mathcal{R}}{ds} \Theta\{|\bar{\psi}_1\rangle_{1/2} \otimes \cdots \otimes |\bar{\psi}_{2j}\rangle_{1/2}\}, \quad (2.51)$$

(note that this differs in definition of $B$ precisely by the phase factor $e^{2i\gamma}$). Here, the action of time-reversal $\Theta$ on the symmetrized product of the spin-1/2 kets is

$$\Theta\{|\bar{\psi}_1\rangle_{1/2} \otimes \cdots \otimes |\bar{\psi}_{2j}\rangle_{1/2}\} = (w_1w_2 \cdots w_{2j}) |-1/w_1\rangle_{1/2} \otimes \cdots \otimes |-1/w_{2j}\rangle_{1/2}. \quad (2.52)$$

Observe that $\Theta$ takes the Majorana points their anti-podes.

In (fig. 2.2) we demonstrate graphically the equivalence of (eq. 2.50) with that of Kato’s equation. First a set of $2j$ initial majorana points are chosen randomly, and from that its corresponding state and time reversed partner are constructed. Then the points are propagated by numerically solving (eq. 2.50), while the state is evolved via numerical matrix propagation of Kato’s equation (eq. 2.9), for an arbitrarily chosen rotation parametrized by $\theta$, $\phi$, and $\psi$. We can see that the trajectories resulting from both methods are identical.

At this point one should pause and ask what exactly it is we have gained by switching to such an intricate
Figure 2.2: Comparison of the Majorana-Point trajectory, calculated both by (red trajectory) numerical matrix holonomy, and (blue trajectory) by numerical propagation of the equations of motions (eq. 2.50). The location of the initial points are emphasized.

set of coupled equations of motions. To gain some insight, let us consider the fixed points of (eq. 2.50). If \( w_k \) is to be static, then there are two possibilities: either the factor \( B \) must vanish, or the product,

\[
\prod_{i \neq k} \frac{1 + \bar{w}_i w_k}{w_k - w_i} = 0. \tag{2.53}
\]

The former will depend on the details of the actual rotation, but the latter depends on the details of the degenerate subspace itself, and it is on this latter case we focus. Focusing on \( \frac{dw_k}{ds} \), for the product to vanish one of the Majorana points must become antipodal to \( w_k \), i.e. there exists at time \( s \) a \( w_{k'}(s) \) such that

\[
w_{k'}(s) = -\frac{1}{\bar{w}_k(s)}. \tag{2.54}
\]

At that instant, \( \frac{dw_k}{ds} = 0 \), but observe that this also holds true under \( k \to k' \), and \( \frac{dw_{k'}}{ds} = 0 \) as well. Consequently, both \( w_k \) and \( w_{k'} \) remain static for all \( s \). As such, we conclude that antipodal Majorana points are always fixed.

We can understand this by noting that antipodal Majorana points are actually Majorana points that are common to both \( |\Phi(t)\rangle \) and \( |\Theta \Phi(t)\rangle \). Suppose the Majorana points of \( |\Phi(0)\rangle \) are given by,

\[
a_1, -1/\bar{a}_1, a_2, -2/\bar{a}_2, \ldots, a_r, -1/\bar{a}_r, \xi_1, \ldots, \xi_p, \quad (2r + p = 2j), \tag{2.55}
\]

where the \( a'_i \)'s come in antipodal pairs. Since \( \Theta \) takes the Majorana points to their antipodes, the \( a'_i \)'s are
preserved; in other words, the Majorana points of $|\Theta\Phi(0)\rangle$ are

$$a_1, -1/\bar{a}_1, a_2, -2/\bar{a}_2, \ldots, a_r, -1/\bar{a}_r, -1/\bar{\xi}_1, \ldots, -1/\bar{\xi}_p.$$  \hspace{1cm} (2.56)

Now, because $|\Phi(t)\rangle$ is a linear combination of the $|\Phi(0)\rangle$ and $|\Theta\Phi(0)\rangle$, then when $|\Phi(0)\rangle$ and $|\Theta\Phi(0)\rangle$ have any Majorana points in common, so too will $|\Phi(t)\rangle$ share these Majorana points. To summarize, if a pair of Majorana points start out being antipodal, then they remain fixed at all times. In the future, we will factor out these fixed points and refer to the non-fixed Majorana points as “free” or “dynamical”.

Since the fixed Majorana points do not participate in the dynamics, the requirement of non-degenerate Majorana points can be relaxed to only requiring that none of the free Majorana points be degenerate. This includes states whose fixed antipodal points occur in pairs more than once.

Upon identification of the fixed Majorana points, the adiabatic equations (eq. 2.50) above can be simplified to describe that of the remaining $p$ free points,

$$\frac{d\xi_k}{ds} = -B(\xi_1, \ldots, \xi_p, a_1, \ldots, a_r)(1 + \xi_k\bar{\xi}_k)\eta \prod_{1 \leq i \leq p, k \neq i} \frac{1 + \xi_i \bar{\xi}_k}{\xi_k - \xi_i},$$  \hspace{1cm} (2.57)

where, $\eta \equiv \prod_{i=1}^{r} (-\bar{a}_i / a_i)$ is an $a$-dependent overall phase.

### 2.4 Adiabatic Dynamics and the Semiclassical Path Integral

The previously developed equations of motion describes the adiabatic rotation of any initial state and its time-reversed partner. In practical considerations however, only states of the lowest energy levels are of interest. Recall that for molecular magnets these are states which are localized in the classical minima. For the static case, the tunneling dynamics can be accurately described by the semiclassical action along instantons. Motivated by this, we seek a similar semiclassical interpretation for the adiabatic case.

Returning to the adiabatic body-frame propagator $U^b_{ad}$, the form of (eq. 2.13) suggests that we could arrive at a path-integral interpretation if we replace, in the time-slicing procedure, the full resolution of the identity, by the projection $P(0)$. Intuitively, this replacement restricts the classical phase space, so that instead of being able to access the entirety of $S^2$, now the trajectory can only access points near the contours of constant energy $E(0)$.

Unfortunately, directly approaching this procedure in analogy with the semiclassical path integral is
difficult, since doing so would require knowledge of the $P$-symbol of $\mathcal{P}$, i.e. an expression of the form

$$\mathcal{P}(0) = \frac{2j + 1}{4\pi} \int_S dA(z, \bar{z}) p(z, \bar{z}) |z| \langle z |.$$

(2.58)

For the full over-completeness relation 1 we know that $p(z, \bar{z}) = 1$, but in general the expression $p$ for an arbitrary operator is tedious [23]. An alternative but equivalent approach would be to start from the full body-frame propagator $U^b$ and then take the limit of $\epsilon \to 0$, while also dropping the dynamical phase. The latter is advantageous because in the body frame, the full Schrödinger’s equation reads,

$$i \frac{d}{dt} U^b(t) = \{ H_0 - i\epsilon K(t) \} U^b(t) \equiv \{ H_0 + \epsilon \sum_a Y_a(\epsilon t) J_a \} U^b(t)$$

(2.59)

i.e. that of a spin in $H_0$ perturbed by a small, slowly moving external field. This problem is readily amenable to perturbation methods in path integrals, and the various phase terms can be easily identified.

Let us consider the propagator from time $t_0$ to time $t_0 + \delta s/\epsilon$, where $\delta s$ is a short duration on the slow timescale. The semiclassical transition probability is then,

$$\langle z_f | U^b(t_0 + \frac{\delta s}{\epsilon}; t_0) | \bar{z}_i \rangle = N_{ij}^{-1} \int \mathcal{D}(z, \bar{z}) \exp \{ iS_0 + i\epsilon S_1 \},$$

(2.60)

where $iS_0$ is the usual spin action for the static Hamiltonian $H_0$, and the perturbation $S_1$ is

$$i\epsilon S_1 \equiv -ij\epsilon \sum_a \int_{t_0}^{t_0 + \delta s/\epsilon} dt Y_a(\epsilon t) s_a(z(t), \bar{z}(t)).$$

(2.61)

Since $\epsilon$ is a small parameter appearing both in the strength, at lowest order we are able to work with the classical trajectories of the static Hamiltonian $h_0$; and since $\epsilon$ appears also in the timescale of the perturbation, we are afforded the method of averaging, whereby the contribution from the fast-moving classical trajectory is averaged over. Explicitly, writing $Z_0$ and $\bar{Z}_0$ as the zeroth-order classical solution with constant energy $E_0$ and period $T_p(E_0)$, we have

$$\langle z_f | U^b(t_0 + \frac{\delta s}{\epsilon}; t_0) | \bar{z}_i \rangle \approx N_{ij}^{-1} \int \mathcal{D}(z, \bar{z}) \exp \{ iS_0[Z_0, \bar{Z}_0] \}$$

$$\times \{ 1 - ij\delta s \sum_a Y_a(s) \times \frac{1}{T_p} \int_{t_0}^{t_0 + T_p} dt s_a(Z_0(t), \bar{Z}_0(t)) \}. $$

(2.62)
To get from (eq. 2.62) to the adiabatic propagator, we observe that the action $i\mathcal{S}_0$ contains three terms,

$$i\mathcal{S}_0[Z_0, \bar{Z}_0] = j \log(1 + \bar{z}_i Z_0(t_0)) + j \log(1 + z_f \bar{Z}_0(t_0 + \delta s/\epsilon))$$

$$+ i \int_{t_0}^{t_0 + \delta s/\epsilon} \frac{dt}{i} \frac{j \bar{Z}_0 Z_0 - Z_0 \bar{Z}_0}{1 + Z_0 \bar{Z}_0} - i \int_{t_0}^{t_0 + \delta s/\epsilon} dt h_0(Z_0, \bar{Z}_0).$$

(2.63)

By our paradigm, the dynamical phase will be discarded; in addition, the boundary term will need to be modified, due to the projection operator $\mathcal{P}(0)$. However, we can still easily read off the adiabatic correction, i.e. the $\delta s$ term, independent of these modifications.

To illustrate these ideas let us consider the familiar example of a spin processing in a slowly varying magnetic field of constant unit strength,

$$\mathcal{H}(t) \equiv -\sin \theta \cos \phi J_1 - \sin \theta \sin \phi J_2 - \cos \theta J_3,$$

(2.64)

and for the eigenspace of energy $E = -m$, the projection operator is simply $\mathcal{P}(0) = |j, m\rangle \langle j, m|$, and the infinitesimal propagator from Kato’s equation reads,

$$\langle z_f | \mathcal{U}^\mu_{ad}(s_0 + \delta s; s_0) | \bar{z}_i \rangle = \langle z_f | j, m \rangle \langle j, m | \bar{z}_i \rangle \{1 - i\delta s \sum_a Y_a(s) \langle j, m | J_a | j, m \rangle \},$$

$$= N_{ij}^{-1} (2j)! (2\bar{z}_i)^{j+m} (j + m)! (j - m)! \{1 - im \delta s Y_3(s) \}.$$ (2.65)

Next we look at the path integral approach. The zeroth order semiclassical solution is given by

$$Z_0(t) = e^{a_I} e^{-it - ia_R}, \quad \bar{Z}_0(t) = e^{-b_I} e^{+it + ib_R},$$

(2.66)

where $a_R$, $a_I$, and $b_R$, $b_I$ are real numbers. By demanding that $h_0(Z_0, \bar{Z}_0)$ be a constant real number $\mu_3$ between $-j$ and $+j$, we have that $a_R = b_R$, and the additional requirements that

$$j \frac{e^{a_I - b_I} - 1}{e^{a_I - b_I} + 1} = \mu_3, \quad \bar{z}_i = e^{-b_I + ia_R}, \quad z_f = e^{a_I - ia_R - iT},$$

(2.67)

the latter two equalities coming from the boundary conditions. Inserting this solution into (eq. 2.62), and using the fact that the integrals of $s_1(Z_0, \bar{Z}_0)$ and $s_2(Z_0, \bar{Z}_0)$ over a period $T_p (= 2\pi$ in this case) vanish, we
arrive at,
\[
\langle z_f | \mathcal{U}^b(t_0 + \frac{\delta s}{\gamma}, t_0) | \bar{z}_i \rangle = e^{i\mu_3 T N^{-1}_j \sum_m (2j)! (j + m)!} e^{-i(j + \mu_3)T} \{1 - i\mu_3 \delta s Y_3(s)\}.
\] (2.68)

Comparing now the two results (eq. 2.65) and (eq. 2.68), we see that the two results agree if,

1. $\mu_3/j \to m/j$. This is natural in the semiclassical limit of $j \to \infty$.
2. The dynamical phase $e^{i\mu_3 T}$ in result (eq. 2.68) is discarded.
3. The summation over all $m$ in (eq. 2.68) is restricted only the term $m = \mu_3$. This is the aforementioned modification of the boundary term, due to the effect of the enveloping $\mathcal{P}(0)$ terms in (eq. 2.13).

Both results show that the adiabatic correction is a term $(1 - i\mu \delta s Y_3(s))$, which when iterated over all $s$, for a closed circuit $C$ of the parameters $\theta$, $\phi$ and $\psi$, furnishes the well known Berry’s phase for spin,

\[
e^{i\gamma_{geo}} = \exp \{i m \oint_C \cos \theta d\phi\}.
\] (2.69)

As stated before, since the eigenspace is one-dimensional the geometric contribution is simple a phase. In the next section we shall see how to apply these ideas to the doubly-degenerate quadrupole Hamiltonian.

### 2.4.1 Non-Abelian Holonomy and the Quadrupole Hamiltonian

We turn our attention next to the instantons of the quadrupole Hamiltonian (eq. 1.28), reproduced here for reference,

\[
s_1(\tau | \tau_c, p) = +p \cosh(\varphi_\alpha) \text{sech}(\tau - \tau_c),
\]

\[
s_2(\tau | \tau_c, p) = -i p \sinh(\varphi_\alpha) \text{sech}(\tau - \tau_c),
\]

\[
s_3(\tau | \tau_c) = + \tanh(\tau - \tau_c),
\] (2.70)

where $p = \pm 1$ denotes the winding and $\tau_c$ indicates the tunneling epoch. We will work in the basis of eigenstates localized to the classical minima, and in the semiclassical limit at zero field these are given precisely by the coherent states $|\bar{z}_+\rangle$ and $|\bar{z}_-\rangle$ pointing at the north and south poles, respectively. The quantities of interest then are the diagonal and off-diagonal elements of the infinitesimal holonomy, i.e. the transition amplitudes $|\bar{z}_-\rangle \to |\bar{z}_-\rangle$ and $|\bar{z}_-\rangle \to |\bar{z}_+\rangle$ in a short duration $\delta s$.

Let us first look at the diagonal term. Here the semiclassical trajectory is approximately that of a point which remains stationary at the classical minima, i.e. $s_3(\tau) = \pm 1$, $s_1(\tau) = s_2(\tau) = 0$. For concreteness we
consider the north-pole minima. Then in (eq. 2.62) the terms in the curly braces reduce to \(1 - ij\delta sY_3(s)\). The action, meanwhile, is zero along this stationary trajectory. As a result, we have,

\[
\langle z_+ | \mathcal{U}^b(t_0 + \delta s/\epsilon) | \bar{z}_+ \rangle = 1 - ijY_3(s)\delta s.
\] (2.71)

Next we look at the off-diagonal term. Here we will find, in Euclidean time, that

\[
\langle z_+ | \mathcal{U}^b(t_0 + \delta s/\epsilon) | \bar{z}_- \rangle = \delta s \epsilon N^{-1} \sum_p F e^{-S^E_0[p]} \left\{ 1 + \epsilon j \sum_a Y_a(s) \int_{\delta s/2\epsilon}^{\delta s/2\epsilon} d\tau s_a(t[p]) \right\},
\] (2.72)

where the additional prefactor of \(\frac{\delta s}{\epsilon}\) comes from summing over all epochs of the instanton. In writing the above we have swept over a subtlety: strictly speaking, the “period” of an instanton is undefined, since the instanton is an open trajectory that takes infinite time to complete. The correct limiting procedure, however, is to replace the \(T_p\) in (eq. 2.62) by \(\frac{\delta s}{\epsilon}\). Continuing, for half-integer \(j\) the \(O(1)\) term will vanish, as explained in (sec. 1.4.1),

\[
N^{-1} \sum_p F e^{-S^E_0[p]} = 0, \quad \text{half-integer } j,
\] (2.73)

and for the \(O(\epsilon)\) term the \(Y_3\) component will vanish for the same reason. The integral over the remaining hyperbolic secant term yields \(\pi\), so in total this gives us, after rotating back to real time,

\[
\langle z_+ | \mathcal{U}^b(t_0 + \delta s/\epsilon) | \bar{z}_- \rangle = j\pi \delta s N^{-1} \sum_p F e^{-S^E_0[p]} [Y_1(s) \cosh(\varphi_\alpha) - iY_2(s) \sinh(\varphi_\alpha)].
\] (2.74)

Since we can also solve for the infinitesimal adiabatic holonomy via propagation of Kato’s equation (eq. 2.9), this suggests we can identify,

\[
\langle z_+ | \mathcal{J}_1 | \bar{z}_- \rangle = j\pi N^{-1} \sum_p F e^{-S^E_0[p]} \cosh(\varphi_\alpha), \quad \langle z_+ | \mathcal{J}_2 | \bar{z}_- \rangle = j\pi N^{-1} \sum_p F e^{-S^E_0[p]} \sinh(\varphi_\alpha),
\] (2.75)

and we confirm this equality numerically in (tab. 2.1).

2.4.2 Method of Multiple Timescales and Hannay’s Angle

We conclude this section by comparing the quantum geometric phase with its classical counterpart, the Hannay Angle. In light of the semiclassical path integral, it is natural to expect that the two should be related in some way. To this end, define the new time coordinates \(u = t\) and \(s = \epsilon t\) and separate the total
Table 2.1: Comparison of the off-diagonal Berry’s phase at several values of half-integer spins, for both the semiclassical calculation (eq. 2.75), and for the result from numerical diagonalization, using the Mn4O3 value of $\alpha = 0.041$. The $J_3$ are negligibly small in the numerical case, and in the semiclassical case it is exactly zero.

<table>
<thead>
<tr>
<th>$j/2$</th>
<th>Semiclassical</th>
<th>Numerical</th>
<th>Semiclassical</th>
<th>Numerical</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/2</td>
<td>$-9.94 \times 10^{-5}$</td>
<td>$-9.59 \times 10^{-5}$</td>
<td>$10.4 \times 10^{-5} i$</td>
<td>$9.99 \times 10^{-5} i$</td>
</tr>
<tr>
<td>9/2</td>
<td>$-2.98 \times 10^{-6}$</td>
<td>$-2.90 \times 10^{-6}$</td>
<td>$3.11 \times 10^{-6} i$</td>
<td>$3.02 \times 10^{-6} i$</td>
</tr>
<tr>
<td>11/2</td>
<td>$-8.31 \times 10^{-8}$</td>
<td>$-8.12 \times 10^{-8}$</td>
<td>$8.66 \times 10^{-8} i$</td>
<td>$8.46 \times 10^{-8} i$</td>
</tr>
<tr>
<td>13/2</td>
<td>$-2.20 \times 10^{-9}$</td>
<td>$-2.16 \times 10^{-9}$</td>
<td>$2.29 \times 10^{-9} i$</td>
<td>$2.25 \times 10^{-9} i$</td>
</tr>
</tbody>
</table>

In particular, we focus on the $O(\epsilon^0)$ and $O(\epsilon^1)$ terms. The $O(\epsilon^0)$ equation reads,

$$\frac{\partial Z_0}{\partial u} = \frac{i}{2j} (1 + Z_0 \bar{Z}_0)^2 \frac{\partial}{\partial z} h(Z_0, \bar{Z}_0; s),$$

$$\frac{\partial \bar{Z}_0}{\partial u} = -\frac{i}{2j} (1 + Z_0 \bar{Z}_0)^2 \frac{\partial}{\partial z} h(Z_0, \bar{Z}_0; s),$$

which we recognize is just the equation of motion for a static hamiltonian frozen at the instant $s$, whose solution will furnish a family of trajectories $Z_0(u, s)$, $\bar{Z}_0(u, s)$ parametrized by $s$. Continuing, the $O(\epsilon^1)$
solution reads,
\[
\begin{align*}
\frac{\partial Z_1}{\partial u} - iF_z(Z_0, \bar{Z}_0; s)Z_1 - i\bar{F}_z(Z_0, \bar{Z}_0; s)\bar{Z}_1 &= -\frac{\partial Z_0}{\partial s}, \\
\frac{\partial \bar{Z}_1}{\partial u} + i\bar{F}_z(Z_0, \bar{Z}_0; s)Z_1 + iF_z(Z_0, \bar{Z}_0; s)\bar{Z}_1 &= -\frac{\partial \bar{Z}_0}{\partial s},
\end{align*}
\]
(2.81)
which is a forced linear equation in \(Z_1\) and \(\bar{Z}_1\). In fact it is (eq. 2.81) which governs the \(s\)-dependence of \(Z_0\) and \(Z_0\), and this is due to our demand that \(\sum_k \epsilon^k Z_k\) be a uniformly convergent expansion over all \(u\), which requires that the correction \(Z_1\) be uniformly bounded. This requirement then places restrictions on the forcing terms \(\frac{\partial Z_0}{\partial u}\) and \(\frac{\partial \bar{Z}_0}{\partial u}\), primarily that they cannot give rise to *secular terms* in the solution of \(Z_1\) of \(\bar{Z}_1\). We will see how this is manifest in the subsequent examples.

Focusing now on the case of adiabatic rotations, we know that in the body frame the effective Hamiltonian can be written as \(h(z, \bar{z}; \epsilon t) = h_0(z, \bar{z}) + \epsilon j \sum_a \gamma_a \epsilon \gamma_a(z, \bar{z})\), and so in this case we can further split \(F(z, \bar{z}; s)\) into \(F_0(z, \bar{z}) + \epsilon F_1(z, \bar{z}; s)\), where
\[
F_0(z, \bar{z}) = \frac{1}{2j}(1 + z\bar{z})^2 \frac{\partial h_0}{\partial z}, \quad F_1(z, \bar{z}; s) = \frac{1}{2}Y_1(s)(1 - z^2) + i\frac{1}{2}Y_2(s)(1 + z^2) + Y_3(s)z, \quad (2.82)
\]
and the \(O(\epsilon^0)\) and \(O(\epsilon^1)\) equations of motion read,
\[
\begin{align*}
\frac{\partial Z_0}{\partial u} &= +iF_0(Z_0, \bar{Z}_0), \quad \frac{\partial Z_1}{\partial u} - iF_0(z, \bar{Z}_0)Z_1 - i\bar{F}_0(z, \bar{Z}_0)\bar{Z}_1 &= +iF_1(Z_0, \bar{Z}_0; s) - \frac{\partial Z_0}{\partial s}, \\
\frac{\partial \bar{Z}_0}{\partial u} &= -i\bar{F}_0(Z_0, \bar{Z}_0), \quad \frac{\partial \bar{Z}_1}{\partial u} + i\bar{F}_0(z, \bar{Z}_0)Z_1 + iF_0(z, \bar{Z}_0)\bar{Z}_1 &= -iF_1(Z_0, \bar{Z}_0; s) - \frac{\partial \bar{Z}_0}{\partial s}.
\end{align*}
\]
(2.83)
As an example, we illustrate once again with the well studied case \(\mathcal{H}_0 = -J_3\). This gives \(h_0(z, \bar{z}) = -j s_3(z, \bar{z})\) and \(F_0(z, \bar{z}) = -z, \quad F_0(\bar{z}, \bar{z}) = -\bar{z}\), from which we easily obtain the zeroth order solution,
\[
Z_0(u, s) = e^{-iu - ia(s)}, \quad \bar{Z}_0(u, s) = e^{iu + ib(s)}, \quad (2.84)
\]
where \(a\) and \(b\) are as yet undetermined functions of \(s\). In general there need not be any relationship between \(a\) and \(b\), but if we demand that the trajectory traces out a constant contour of real energy, then we must have that,
\[
a_R = b_R, \quad \frac{da_R}{ds} = \frac{db_R}{ds}, \quad (2.85)
\]
where \(a_R \equiv \Re\{a\}, \quad a_I \equiv \Im\{a\}\), etc. Continuing, the first order solution reads,
\[
\begin{align*}
\frac{\partial Z_1}{\partial u} + iZ_1 &= +\frac{1}{2}Y_1(s)(1 - Z_0^2) - \frac{1}{2}Y_2(s)(1 + Z_0^2) + iY_3(s)Z_0 + iZ_0\frac{da_R}{ds} + i\frac{da_I}{ds}, \\
\frac{\partial \bar{Z}_1}{\partial u} + i\bar{Z}_1 &= -\frac{1}{2}Y_1(s)(1 - \bar{Z}_0^2) - \frac{1}{2}Y_2(s)(1 + \bar{Z}_0^2) - iY_3(s)\bar{Z}_0 - i\bar{Z}_0\frac{da_R}{ds} + i\frac{da_I}{ds}.
\end{align*}
\]
(2.86)
From this we see that secular terms could potentially arise, unless we eliminate from the RHS of (eq. 2.86) any forcing terms that are in resonance with the natural frequency of the LHS. In this case these are the terms proportional to $Z_0$ and $\bar{Z}_0$, and they are removed if we demand,

$$\frac{da_R}{ds} + i \frac{da_I}{ds} = -Y_3(s),$$

(2.87)

which gives us $a_I = \text{const}$, and,

$$\frac{da_R}{ds} = -Y_3(s) = \cos \theta \frac{d\phi}{ds} + \frac{d\psi}{ds}.$$  \tag{2.88}

Integrating $da_R/ds$ from the initial to the final time gives us the adiabatic phase. In particular if the parameters execute a closed circuit, then the resulting angle is,

$$\gamma_{\text{geo, hannay}} = \oint_C \cos \theta d\phi,$$  \tag{2.89}

which we recognize as solid angle traced out by the external field. Finally, substituting the adiabatic trajectory into the original path integral recovers the Berry’s phase (eq. 2.69). This is an example of the heuristic relationship that the Berry’s phase and the Hannay angle are related via [5]

$$\frac{\partial \gamma_{\text{geo, berry}}}{\partial m} = \gamma_{\text{geo, hannay}},$$  \tag{2.90}

where $m$ is the quantum number which corresponds classically to the adiabatic invariant.

Next, one wonders if it is possible to repeat the same derivations along the tunneling instantons of the Mn4 molecular magnet. In this case however we will find that the procedure is not so straightforward, and the above analysis ultimately fails. Firstly, it is not clear that when one analytically continues to the complex plane, that the concept of “uniformly bounded” still makes sense. This is not problematic however, since we can still be guided by our paradigm of avoiding secular terms, i.e. terms polynomial in time. Secondly, the instantons correspond to trajectories along the separatrix of the classical Hamiltonian. This problem, unfortunately, is more severe.

To illustrate this failure, let us continue with the naïve derivation for the tunneling case. Working instead in coordinates $s_3$ and $C \equiv \cosh(2\varphi)$ and Euclidean “fast” time $\tau$ and “slow” time $\lambda$, the zeroth order equations of motion read,

$$\frac{\partial S_{3,0}}{\partial \tau} = 1 - S_{3,0}^2, \quad \frac{\partial C_0}{\partial \tau} = 0,$$  \tag{2.91}

42
yielding the solution,

\[
S_{3,0}(\tau, \lambda) = \tanh(\tau + f(\lambda)), \quad C_0(\tau, \lambda) = -\coth \rho = -1/\alpha.
\]  

(2.92)

(note that by demanding the energy be constant, we must have \( C_0 \) be constant, i.e. \( \partial C_0/\partial \lambda = 0 \) as well).

Here, \( f(\lambda) \) plays the role of the Hannay angle. Along this trajectory, the first order equations become,

\[
\frac{\partial}{\partial \tau} \begin{bmatrix} S_{3,1} \\ C_1 \end{bmatrix} + Q(\tau) \begin{bmatrix} S_{3,1} \\ C_1 \end{bmatrix} = \begin{bmatrix} (1 - S_{3,0}^2)^{1/2} \cosh \rho \frac{p}{\sqrt{2}} A - \frac{\partial S_{3,0}}{\partial \lambda} \\ S_{3,0}(1 - S_{3,0}^2)^{-1/2} \cosh \rho \sqrt{2} \alpha A - 2Y_3 \cosh \rho \end{bmatrix},
\]  

(2.93)

where recall that \( p = \pm 1 \) is the winding of the instanton, and where we have additionally defined,

\[
Q(\tau) \equiv \begin{bmatrix} 2S_{3,0} & (1 - S_{3,0}^2) \cosh \rho \sinh \rho \\ 0 & -2S_{3,0} \end{bmatrix}, \quad A = (1 - \coth \rho)^{-\frac{1}{2}} Y_1 - i(1 - \coth \rho)^{-\frac{1}{2}} Y_2.
\]  

(2.94)

The solution to the system of equations \( \dot{y} + Qy = f \) is given by \( y(\tau) = G^{-1}(\tau) \int d\tau G(s)f(s) + y_0(\tau) \), where \( G \) solves \( \dot{G} = GQ \), and \( y_0 \) is the solution to the homogeneous equation. In this case \( G \) may be solved by

\[
G = \begin{bmatrix} 0 \\ b \cosh^2(\tau + f(\lambda)) & \frac{a}{2} \cosh \rho \sinh \rho \{\tanh(\tau + f(\lambda)) + (\tau + f(\lambda)) \sech^2(\tau + f(\lambda))\} \end{bmatrix},
\]  

(2.95)

for arbitrary non-zero constants \( a \) and \( b \). In integrating \( G \) against the forcing term, we’ll find that secular terms arise unless

\[
\frac{df}{d\lambda} = -\frac{p}{\sqrt{2}} A \cosh \rho \sec(\tau + f(\lambda)) - Y_3 \cosh \rho \tanh(\tau + f(\lambda)),
\]  

(2.96)

but this is an inconsistency, since we started out demanding that \( f \) be a function of \( \lambda \) only. By casual inspection, if one averages the right hand side of (eq. 2.96), then one can arrive at an answer with the correct ingredients as that in (eq. 2.74),

\[
\int d\tau \frac{df}{d\lambda} = -\frac{\pi p}{\sqrt{2}} A \cosh \rho, \quad \langle z_+ | \hat{U}_\alpha^0(t_0 + \delta s/\epsilon) | z_- \rangle = -\frac{j i \delta s}{\cosh \rho} \lambda^{-1} \sum_p F e^{-S_\alpha^p} \int d\tau \frac{df}{d\lambda}.
\]  

(2.97)

While potentially promising, it is clear that a more careful interpretation and methodical approach is needed.
2.5 Illustrations and Results

Let us now give several illustrations of the preceding derivations, with particular emphasis on the Mn4 example.

First, we look at the configurations of the Majorana points for the eigenstates of $\mathcal{H}_0$, for which there are a total of five doubly degenerate levels when $j = 9/2$. Due to the relatively large value of the axial anisotropy $D$ compared to $E$, the Hamiltonian is close to that of $\mathcal{J}_0^2$, and as a result the Majorana points will tend to cluster about the poles (fig. 2.3). But unlike the Majorana points of $|j,m\rangle$ which simply condense at the poles, the small $\mathcal{J}_1^2$ and $\mathcal{J}_2^2$ terms will cause some repulsion between them.

Due to the double degeneracy however, there is freedom in the choice for the basis of the eigenspace. One particularly illuminating choice is that of states polarized along the hard-axis direction $\hat{s}_1$ (which can be constructed by applying a small external field $X_1$ and letting the field strength gradually go to zero). In (fig. 2.4) we see that for the ground states, the Majorana points tend to distribute themselves along flow lines $\nabla h(z, \bar{z})$ in regions of maximal energy; while for the first excite states a pair of points from each state have relocated themselves close to the minima; for the second excited state an additional pair, etc. In addition, for the first, second and third excited states we find that the points about the poles of one state very closely overlap with that of its Kramers pair. We remark however that for this choice of states the magnetization $\langle J \rangle$ becomes significantly reduced, and may consequently be very difficult to measure.

Next we consider adiabatic holonomy arising from rotations about a fixed axis $\hat{n} = \sin \eta \cos \chi \hat{e}_1 + \sin \eta \sin \chi \hat{e}_2 + \cos \eta \hat{e}_3$. For such rotations we are guaranteed to have the state return to itself (in the body frame) after some time $s_f$, which need not coincide in general with the period of rotation $2\pi$.

The motion of the Majorana points can be quite complicated. The greatest intricacy occurs for the eigenstates of higher energy levels, for which the Kramers pairs communicate more strongly. As an example we plot in (fig. 2.5) for one full cycle, for various rigid axis orientations. Observe that the trajectories can depend sensitively on the axis orientation; in particular, closed cycles of individual points can combine into larger cycles in which the zeros permute locations. Furthermore, we can see that in some cases it is possible for most of the dynamics to be carried by a single Majorana point.

In conclusion, we have shown that the motion of Majorana points can provide visual insight into the evolution of the quantum spin state undergoing non-Abelian Berry transport. We have derived the equations of motion for these points, focusing primarily on the case when the degenerate subspace consists of a Kramers pair of eigenstates for a time-reversal invariant, half-integer spin system. Focusing on the minimal case of quadrupole Hamiltonians, even the simple case of rigid axis rotations can lead to intricate motion. We have also shown that for the practical case where only the lowest energy levels are considered, the elements of
Figure 2.3: The Majorana points of the eigenstates of $H$, for which the expectation $\langle J \rangle$ is the largest about the $z$-axis. The blue and red points denote the Majorana points of the eigenstate and its Kramers pair. In order from left to right and top to bottom, we have (a) ground state, (b) first excited state, (c) second excited state, (d) third excited state, and (e) highest state. In the background we have plotted the energy contours of the corresponding semiclassical Hamiltonian $\langle z | H | z \rangle$. 

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Figure 2.4: The Majorana points of the eigenstates of $\mathcal{H}$, for which the expectation $\langle \mathcal{J} \rangle$ is the largest about the $x$-axis. The blue and red points denote the Majorana points of the eigenstate and its Kramers pair. In order from left to right and top to bottom, we have (a) ground state, (b) first excited state, (c) second excited state, (d) third excited state, and (e) highest state. In the background we have plotted the energy contours of the corresponding semiclassical Hamiltonian $\langle z | \mathcal{H} | \bar{z} \rangle$. Note that in subfigures (b), (c), and (d), the points around the poles actually very closely overlap — for example, the dot in the north pole for the first excited state (b) is actually a pair (blue and red) of points.
Figure 2.5: Adiabatic evolution, in the body frame, of the Majorana points for rigid axis rotation about the direction $\hat{n} = (\sin \eta \cos \chi, \sin \eta \sin \chi, \cos \eta)$, for (a) $\eta = 88^\circ$, $\chi = 90^\circ$, (b) $\eta = 92^\circ$, $\chi = 90^\circ$, (c) $\eta = 45^\circ$, $\chi = 85^\circ$, and (d) $\eta = 45^\circ$, $\chi = 86^\circ$. The points correspond to that of the highest level state, for which there is the most overlap between its points and that of its time-reversed partner. The gradient in color corresponds to the direction of time, with red indicating initial time and black indicating final time. Note that a slight perturbation in the rotation axis can also dramatically change the topology of the trajectories.
the Berry connection can be obtained semiclassically via the method of instantons. Finally, we have made connection between the quantum and classical geometric phases for the Abelian case, and we have provided a suggestion for exploration of the non-Abelian case.
Chapter 3

Phonoemissive Decay of Spin Magnetization at Low Temperatures

Tunneling between the two lowest energy levels of single molecule magnets with Ising type anisotropy, accompanied by the emission or absorption of phonons, is considered. Quantitatively accurate calculations for the Golden-rule transition probability of such tunneling are performed for a model Hamiltonian especially relevant to the best studied example, Fe8. A semiclassical approach based on spin coherent state path integrals is used, furnishing a closed-form approximation. This result is found to be in good agreement with numerical high-order perturbation theory, and is consistent with previous approaches to the problem.

3.1 Introduction

For a single molecular magnet that is truly isolated, measurements of its magnetic moment should show coherent, oscillatory behavior that flip-flops at a frequency given by the tunnel splitting. In nature this is essentially never the case, and several experiments [35, 40] show that spin relaxation is slow, with non-exponential behavior in time. The current theoretical understanding of this slow relaxation [33, 42] is that interactions of the molecular spins with the nuclear spins render the quantum tunneling of the former incoherent; but because the nuclear spins that couple to a given molecular spin can exchange only a rather limited amount of energy, the requirement of near-degeneracy of the Zeeman levels of the molecular spins is weakened only moderately, and the two levels must lie within a narrow window of each other in order for transitions to occur. Further relaxation can only take place due to the intermolecular dipole field, which can be quite inhomogeneous. If this field happens to be such at a given molecular spin site as to bring that spin into near degeneracy, it will be able to flip. This flip will change the field at other sites, potentially allowing those spins to relax. Monte Carlo and kinetic equation studies based on this model have been done by several authors [22, 34], all of whom obtain slow relaxation, and in some cases, an initial square-root time dependence, as seen experimentally.

A central feature of the above model is that the transition rate between the $m = \pm j$ levels is insensitive
to which one is lower in energy. It thus allows the magnetization of a bulk sample to relax without relaxation of the energy, and the relaxation is always toward the state of zero magnetization. As a result, this model cannot explain magnetization experiments, in which a magnetic field is applied to an initially demagnetized sample. In this case, it is essential to understand the relaxation of energy as that is what drives the change in the magnetization from zero to a nonzero value.

The obvious environment to which energy can be transferred is the phonons. The immediate puzzle is that the spin-phonon interaction typically involves processes with $\Delta m = 1$ or $\Delta m = 2$, while in the cases of Fe8 and Mn12 we require $\Delta m = 20$. Thus the relaxation must take place via a combination of spin tunneling and phonon emission. If we accept this hypothesis, the program of understanding the magnetization experiments in molecular magnetic solids divides into two parts. The first part is to understand the relaxation mechanism in a single molecule and calculate the relevant rate. The second part is to insert this rate into whatever theory (for example, the kinetic equations) governs the dynamics of the dipole-coupled molecules, and thus understand the behavior of the bulk solid. These two parts are logically separate and entail rather different ideas.

In this chapter we address the first part. A calculation of phonoemissive tunneling was in fact done in 1995 [32], and again more recently by [11]. Further, the first one is done for a tetragonal spin anisotropy in the plane perpendicular to the primary (Ising) anisotropy axis, while the second one is done for biaxial anisotropy. Our goal is to improve upon these calculations, and we will do so by constructing the influence functional arising from the bath variables (sec. 3.2), and working to second order in the tunnel splitting $\Delta$ of the spin system (sec. 3.3), a.k.a. the so called “Golden-Rule” limit [21]. While it is known that for phonons in 3D the transition rate remains coherent (i.e. the tunnel splitting will not be renormalized to zero so we always get some coherent flip-flop), it suffices to work in the golden rule limit since typically the spin couples not only to phonons, but also other environments such as nuclear spins, which render the tunneling incoherent. In sec. 3.3.2 we present an alternative calculation for the one-phonon limit using high-order perturbation and show that the two methods yield consistent results. In sec. 3.4 we outline the generalization to higher phonon order in the presence of low external bias. Finally in sec. 3.5 we compare our formulation to previous work, and discuss the implications for Fe8.

### 3.1.1 Minimal Theoretical Model

We shall take the spin Hamiltonian to be that given by (eq. 1.2), and restrict $\mathbf{H}$ to lie in the $xz$ plane. In the presence of phonons, there will be a local strain tensor $\epsilon_{ab}$, with respect to which the interaction may expanded (there is also a local rotation tensor $\omega_{ab}$, but for due to simplifications made later, we will not
need to consider it). To linear order then, the spin-phonon interaction can be very generically written as

$$H_{sp} = \sum_{\mu} \sum_{a,b} F_{ab}^\mu (\mathcal{J}) \epsilon_{ab},$$  \hspace{1cm} (3.1)$$

where $a_\mu^\dagger$ and $a_\mu$ are phonon creation and annihilation operators for the mode $\mu$, and $F_{ab}^\mu (\mathcal{J})$ are functions of $\mathcal{J}$. Next, time-reversal invariance at zero field imposes that at lowest order the function $F$ must be \textit{quadratic} in the $\mathcal{J}$’s. Therefore the simplest interaction of a single spin at the origin with the environmental phonons can be written as,

$$H_{sp} = \frac{1}{2} \sum_{a,b,c,d} \Lambda_{abcd} (\partial_a u_b(0) + \partial_b u_a(0)) \{\mathcal{J}_c, \mathcal{J}_d\},$$  \hspace{1cm} (3.2)$$

where we’ve only needed to keep the anti-commutator terms, since the commutator can be reduced to terms linear in $\mathcal{J}$. Here, $\Lambda_{abcd}$ is the magnetoelastic tensor, and $u(x)$ is the material displacement field of the solid at position $x$,

$$u(x) = \sum_{\mu} \sqrt{\frac{\hbar}{2m\Omega_\mu N}} \epsilon_\mu (a_\mu e^{ik_\mu \cdot x} + a_\mu^\dagger e^{-ik_\mu \cdot x}),$$  \hspace{1cm} (3.3)$$

where $m$ is the mass per unit cell of the lattice, $N$ is the number of units cells in the solid, $a_\mu^\dagger$ and $a_\mu$ are the creation and annihilation operators for phonons of mode $\mu$, and $k_\mu$, $e_\mu$, and $\Omega_\mu$ are the wavevector, polarization, and frequency of that mode. Since the bias energies of interest are on the order of 1K, which is low compared to the Debye temperature of the material ($\approx 33$K) [16], we need only consider the low energy acoustic modes.

In general the numerous tensor components of $\Lambda$ are difficult to pin down experimentally, but the strength of the tensor components are known to be comparable to $D$ [11]. Therefore, an easy and reasonable simplification is to replace the 81 tensor components by an overall constant $\Lambda$, and contract the spin indicies with the strain indices. This also explains why we discard the local rotation: since the spin indices are symmetric and $\omega_{ab}$ is antisymmetric, then even if we included the local rotation the contraction will yield zero anyway.

Next, we must exclude from the interaction terms of the form $\mathcal{J}_3^2$. Mathematically, the $\mathcal{J}_3^2$ terms do not induce transitions between the different levels, but rather shift the $D$ term of original spin Hamiltonian, and so this artificial renormalization must be subtracted off by hand. Furthermore, the $m = \pm j$ states of the molecule are long-lived, and may be regarded as leading to quasi-equilibrium states of the solid as a whole. In particular, the solid should have no strain in these states. This requirement, along with the linearity of $V$ in the strain, implies that $\langle j, +j | V | j, +j \rangle$ and $\langle j, -j | V | j, -j \rangle$ should vanish, and the omission of $\mathcal{J}_3^2$ ensures this.
\[ c, \alpha = E/D, \]
\[ \Omega_0 = \frac{2j-1}{\hbar} \sqrt{D^2 - E^2}, \]
\[ X = g\mu_B H (2j - 1) D \sqrt{1 - \alpha^2}^{-1}, \]
\[ \varepsilon = -2jX_3, \]
\[ \gamma = \frac{C}{D} \frac{(2j-1)(2j-2)(2j-3)}{j(2j-1)(2j-3)}, \]
\[ \lambda = \frac{\lambda^2}{\sqrt{2\pi N \Omega_0}}, \]
\[ q^\mu = k^\mu c/\Omega_0, \]
\[ u = \Omega_0 t, \]
\[ \beta = \frac{\hbar \Omega_0/k_B \Theta}{\lambda^2 j^2 (j - \frac{1}{2})^2 \frac{1}{15\pi^2} V N (\Omega_0 c)^3}, \]
\[ \eta = \frac{\lambda^2}{\sqrt{2\pi N \Omega_0}}, \]
\[ \omega_\mu = \Omega_\mu / \Omega_0, \]
\[ q^\mu = k^\mu c/\Omega_0, \]
\[ u = \Omega_0 t, \]
\[ \beta = \frac{\hbar \Omega_0/k_B \Theta}{\lambda^2 j^2 (j - \frac{1}{2})^2 \frac{1}{15\pi^2} V N (\Omega_0 c)^3}, \]
\[ \eta = \lambda^2 j^2 (j - \frac{1}{2})^2 \frac{1}{15\pi^2} V N (\Omega_0 c)^3, \]

Table 3.1: Table of definitions for rescaled dimensionless variables.

With all of the above simplifications, we get,
\[ H^{sp} = i\Lambda \sum_\mu k \sqrt{\frac{\hbar}{2m \Omega_\mu N}} (a_\mu - a_\mu^\dagger) \sum_{a,b} \{(k_\mu^a e_\mu^b + k_\mu^b e_\mu^a) \times \frac{1}{2} \{J_a, J_b\}. \]

where \( \hat{k}_\mu \equiv k_\mu / k \), and where the prime on the summation reminds us that we discard the \((a,b) = (3,3)\) contribution. Throughout the rest of this chapter we will work in dimensionless variables (tab. 3.1), in addition to the \( j \)-rescaled spins defined in chapter 1. The Hamiltonian is then written as,
\[ H = H_s - jX_3 S_3 + H_{ph} + i \sum_\mu (a_\mu - a_\mu^\dagger) \Psi_\mu, \]
\[ H_{ph} = \sum_\mu \omega_\mu a_\mu^\dagger a_\mu, \]
\[ H_s = -\frac{j}{2} \cosh \rho S_3^2 + \frac{j}{2} \sinh \rho (S_1^2 - S_2^2) - jX_1 S_3 + j\gamma (S_4^1 + S_4^1), \]
\[ \Psi_\mu = j(j - \frac{1}{2}) \lambda_\mu \sum_{a,b} \{(q_\mu^a e_\mu^b + q_\mu^b e_\mu^a) S_{ab}\}, \]

and its corresponding semiclassical symbol \( h \) can be attained by the cosmetic replacement \( a_\mu^\dagger \to \zeta, a_\mu \to \zeta \), and,
\[ \Psi_\mu \to \psi_\mu(z, \bar{z}) \equiv j(j - \frac{1}{2}) \lambda_\mu \sum_{a,b} \{(q_\mu^a e_\mu^b + q_\mu^b e_\mu^a) s_a(z, \bar{z}) s_b(z, \bar{z}), \]

along with the semiclassical symbols of the \( S \) operators discussed previously. As written however, the action of the semiclassical Hamiltonian diverges, and just as in the case for [4] one must correct for these divergences with the addition of counterterms. The justification for these counterterms is given in section (D), and the
full semiclassical Hamiltonian is given explicitly by,

\[
h = -\frac{j}{2} \cosh \rho s_3^2 + \frac{j}{2} \sinh \rho (s_1^2 + s_2^2) - jX_1 s_1 + j\gamma \frac{z^4 + \bar{z}^4}{(1 + z\bar{z})^4} - jX_3 s_3
\]

\[
+ \sum_{\mu} \omega_{\mu} \bar{\zeta}_{\mu} \zeta_{\mu} + i \sum_{\mu} (\zeta_{\mu} - \bar{\zeta}_{\mu}) \psi_{\mu} + \sum_{\mu} \frac{1}{\omega_{\mu}} \psi_{\mu} (z, \bar{z})^2,
\]

(3.7)

where the latter can be most simply understood as “completing the square” in the oscillator variables, i.e. \(a_{\mu} \rightarrow a_{\mu} - i \Psi_{\mu}/\omega_{\mu}\). At this point the usual procedure is to arrive at an effective action by integrating over the bath variables, solve the equations of motion for \(z, \bar{z}\), and expand the action to Gaussian order. The resulting solution for \(z\) and \(\bar{z}\) will undoubtedly be complicated, but if the coupling is small, then to lowest order it is enough to consider the solution to the unperturbed system.\(^1\)

### 3.2 Phonon Bath in 3D and the Debye Model

#### 3.2.1 Coherent State Path Integrals

By working in the coherent state path integral formulation, we are able to explicitly integrate out the phonon degrees of freedom, leaving us with a path integral only in the spin variables. Recall that the harmonic oscillator and spin coherent states are given, respectively, by,

\[
|\bar{\zeta}\rangle = e^{-\zeta \overline{\zeta}/2} \exp(\zeta a^{\dagger}) |0\rangle, \quad |\bar{z}\rangle = (1 + z \bar{z})^{-j} \exp(z J_+) |j, -j\rangle,
\]

(3.8)

where \(\zeta\) is a coordinate in the complex plane, and \(z\) is a coordinate on the Riemann sphere.

Now let \(|\{\bar{\zeta}_{\mu,0}, \bar{z}_0\}\rangle\) be an initial bath/spin coherent state, and \(|\{\bar{\zeta}_{\mu,f}, \bar{z}_f\}\rangle\) be a final state. The transition amplitude for this process to take place starting at time \(u = -T/2\) and ending at \(u = T/2\) is given by,

\[
\langle \{\zeta_{\mu,f}, z_f\} | \exp(-i\mathcal{H}T) | \{\zeta_{\mu,0}, \bar{z}_0\} \rangle
\]

\[
= \mathcal{N}_{0,f}^{-1} \int_{z(-T/2) = z_0}^{z(T/2) = z_f} D(z, \bar{z}) \exp(i S_\mu [z, \bar{z}]) \times \prod_{\mu} \mathcal{K}_{\mu} (\zeta_{\mu,0}, \bar{\zeta}_{\mu,0}; \zeta_{\mu,f}, \bar{\zeta}_{\mu,f} | z, \bar{z})
\]

(3.9)

where \(S_\mu [z, \bar{z}]\) is the spin action in absence of the phonon bath, and where \(\mathcal{K}_{\mu}\) represents the path integral over the oscillator degrees of freedom, subject to the initial and final spin configurations. Since the Hamiltonian

\(^{1}\)If \(\eta\) is a small parameter, then \(S_0[z_0 + \eta z_1, \bar{z}_0 + \eta \bar{z}_1] + \eta S_1[z_0 + \eta z_1, \bar{z}_0 + \eta \bar{z}_1] \approx S_0[z_0, \bar{z}_0] + \eta S_1[z_0, \bar{z}_0],\) since \(\delta S_0[z_0, \bar{z}_0] = 0\), thus killing the \(\eta\) expansion in \(S_0\).
is quadratic in $a_\mu$ and $a_\mu^\dagger$, the path integral can be evaluated directly. Defining for convenience,

$$\psi_\mu(z, \bar{z}) = j(j - \frac{1}{2})\lambda q_\mu (2\omega_\mu N)^{1/2} \sum_{k,l}' (q^\mu_k \phi^l_k + q^l_k \phi^\mu_k) \sigma_{kl}(z, \bar{z}),$$

(3.10)

$$\sigma_{kl}(z, \bar{z}) = s_k(z, \bar{z})s_l(z, \bar{z}) + \frac{1}{2\gamma - 1} \delta_{kl},$$

the oscillator path integrals evaluate to,

$$\mathcal{K}_\mu(\zeta_\mu, 0; \zeta_\mu, f; \bar{\zeta}_\mu, f | z, \bar{z})$$

$$= \exp\{-\frac{1}{2} \zeta_\mu, 0 \bar{\zeta}_\mu, 0 - \frac{1}{2} \zeta_\mu, f \bar{\zeta}_\mu, f + \bar{\zeta}_\mu, 0 \zeta_\mu, f e^{-i\omega_\mu T}\}$$

$$\times \exp\{\zeta_\mu, 0 \int du e^{-i\omega_\mu(u+T/2)} \psi_\mu(u) - \zeta_\mu, f \int du e^{-i\omega_\mu(T/2-u)} \psi^*_\mu(u)\}$$

(3.11)

$$\times \exp\{-\frac{1}{2} \int du du' e^{-i\omega_\mu |u-u'|} \psi_\mu(u) \psi^*_\mu(u')\}.$$  

It remains to perform the sum over all configurations of the initial and final phonon states, which we do in the appendix. At this stage, the influence functional may be grouped into the following products,

$$\exp \Phi \equiv \exp \{Q^{ab}[z_+; z_-] + Q^{em}[z_+; z_-]\} \exp \{R[z_+]\} \exp \{R[z_-]^*\},$$

(3.12)

where we have separated out the terms that involve interactions between the forward and the backward paths,

$$R[z_+] = -\sum_\mu \frac{1}{2} \int du du' \left\{ \frac{\cosh(\omega_\mu |u-u'| - \beta\omega_\mu/2)}{\sinh(\beta\omega_\mu/2)} + \frac{2i}{\omega_\mu} \delta(u - u') \right\} \psi_\mu^+(u) \psi_\mu^+(u'),$$

(3.13)

$$R[z_-]^* = -\sum_\mu \frac{1}{2} \int du du' \left\{ \frac{\cosh(\omega_\mu |u-u'| + \beta\omega_\mu/2)}{\sinh(\beta\omega_\mu/2)} - \frac{2i}{\omega_\mu} \delta(u - u') \right\} \psi_\mu^-(u) \psi_\mu^-(u'),$$

as well as the interacting cross terms,

$$Q^{em}[z_+; z_-] = \sum_\mu \frac{1}{1 - e^{-\beta\omega_\mu}} \int du du' e^{+i\omega_\mu(u-u')} \psi_\mu^+(u) \psi_\mu^-(u'),$$

$$Q^{ab}[z_+; z_-] = \sum_\mu \frac{e^{-\beta\omega_\mu}}{1 - e^{-\beta\omega_\mu}} \int du du' e^{-i\omega_\mu(u-u')} \psi_\mu^+(u) \psi_\mu^-(u').$$

(3.14)

The superscripts “ab” and “em” indicate phono-absorptive and phono-emissive terms. Note that the ratio of coefficients is precisely the Boltzmann factor $e^{-\beta\omega_\mu}$, which is a statement of detailed balance. Note also that exchanging $\psi_\mu^+ \leftrightarrow (\psi_\mu^-)^*$ has the effect of taking $\exp \{\Phi\} \rightarrow \exp \{\Phi^*\}$, while taking $\psi_\mu^+ \equiv (\psi_\mu^-)^*$ leads to $\Phi = 0$, in accordance with Feynman and Hibbs rules I and II [9].
Finally, in the limit of zero temperature, the $\beta$-dependent factors in equations (3.13) and (3.14) tend to,

$$\frac{\cosh(\omega_\mu |u - u'| \mp \beta \omega_\mu / 2)}{\sinh(\beta \omega_\mu / 2)} \to e^{\mp i \omega_\mu (u - u')}, \quad \frac{1}{1 - e^{-\beta \omega_\mu}} \to 1, \quad \frac{e^{-\beta \omega_\mu}}{1 - e^{-\beta \omega_\mu}} \to 0.$$  \hspace{1cm} (3.15)

In particular, the phono-absorptive term is completely suppressed, consistent with the fact that there are no phonons present in the environment from which energy may be absorbed.

### 3.2.2 Debye Model and Super-Ohmic Spectral Density

Let us next perform the summation over all phonon modes. For each mode, the label $\mu$ explicitly denotes a wavevector $\mathbf{q}$, and a polarization $s$, where $s$ may either be the longitudinal or one of the two transverse polarizations. To begin, we introduce the spectral density tensor as,

$$J_{ijkl}(\omega) \equiv \frac{\pi}{2N} \sum_\mu \frac{q^2_\mu}{\omega_\mu} (\hat{q}^\mu_i e^\mu_j + \hat{q}^\mu_j e^\mu_i)(\hat{q}^\mu_k e^\mu_l + \hat{q}^\mu_l e^\mu_k) \delta(\omega - \omega_\mu),$$  \hspace{1cm} (3.16)

and, assuming the oscillator frequencies are dense enough to be approximated as a continuum, we may pass from a summation to an integral in the usual way,

$$\sum_\mu \to V \frac{\Omega_0}{8\pi^3} \sum_s \int_0^\infty dq q^2 \int_{S^2} d^2 \hat{q},$$  \hspace{1cm} (3.17)

so that the terms in the influence functional may be expressed via an integral of the spectral density. For example, $Q_{em}[z_+; z_-]$ reads,

$$Q_{em}[z_+; z_-] = j^2 (j - \frac{1}{2})^2 \lambda^2 \sum_{i,j,k,l} \int_0^\infty J_{ijkl}(\omega) \frac{\omega^3 \, d\omega}{1 - e^{-\beta \omega}} \int dudu' e^{i \omega (u - u')} \sigma^+_{ij}(u) \sigma^-_{kl}(u'),$$  \hspace{1cm} (3.18)

and likewise for the others in (3.13) and (3.14). In order to make further progress, we assume that only the low frequency acoustic modes are of any relevance to us, and so the dispersion relation may be modeled as,

$$\omega_L = \frac{c}{c_L} q, \quad \omega_T = \frac{c}{c_T} q,$$  \hspace{1cm} (3.19)

with $c_L$ and $c_T$ being the speeds of sound for the longitudinal and transverse modes. Since the linear dispersion only holds for low frequencies, we must be mindful that our subsequent calculations never invoke the high-frequency behavior of the phonons. Fortunately, we will find in our calculations that there is always a high frequency cutoff, either set explicitly by the external bias $\varepsilon$, or entering inherently via the instanton.
width.

Continuing, we work out the tensors arising from the integral over the wavevector directions. Relegating details to the appendix, we’ll find that,

\[ J_{ijkl}(\omega) = \frac{1}{15\pi} \frac{V}{N} \left( \frac{\Omega_0}{c} \right)^3 (g^L_{ijkl} + g^T_{ijkl}) \omega^3, \quad (3.20) \]

where we’ve defined,

\[ g^L_{ijkl} = \left( \frac{c}{c_L} \right)^5 (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \]
\[ g^T_{ijkl} = \left( \frac{c}{c_T} \right)^5 (-\delta_{ij}\delta_{kl} + \frac{3}{2} \delta_{ik}\delta_{jl} + \frac{3}{2} \delta_{il}\delta_{jk}). \quad (3.21) \]

It remains to contract the indices into those of the \( \sigma \)'s, and once we have done that it helps to group each result into two sets: those containing spin components \( s_1s_3, s_2s_3 \); and those containing \( s_1s_1, s_2s_2 \), and \( s_1s_2 \). The motivation for doing so is that, if we write out the corresponding quantum matrix elements, e.g. \( s_1s_3 \sim \frac{1}{2} J_1 J_3 + \frac{1}{2} J_3 J_1 \), then those from the first set involve transitions that differ in quantum number \( \Delta m = \pm 1 \), while those from the second set involve \( \Delta m = \pm 2 \).

The resulting expressions are of the form,

\[ R[z_+] = -\frac{\eta}{2} \int_0^\infty d\omega \omega^3 \int dud' \frac{\cosh(\omega|u-u'| - \beta\omega/2)}{\sinh(\beta\omega/2)} + \frac{2i}{\omega} \delta(u-u') \{ M_1(u,u'|z_+) + M_2(u,u'|z_+) \}, \]

\[ Q^{em}[z_+; z_-] = \eta \int_0^\infty d\omega \frac{\omega^3}{1 - e^{-\beta\omega}} \int dud' e^{+i\omega(u-u')} \{ N_1(u,u'|z_+, z_-) + N_2(u,u'|z_+, z_-) \}, \]

\[ Q^{ab}[z_+; z_-] = \eta \int_0^\infty d\omega \frac{\omega^3 e^{-\beta\omega}}{1 - e^{-\beta\omega}} \int dud' e^{-i\omega(u-u')} \{ N_1(u,u'|z_+, z_-) + N_2(u,u'|z_+, z_-) \}, \quad (3.23) \]

where we have defined,

\[ \eta \equiv \lambda^2 j^2 (j - \frac{1}{2})^2 \frac{1}{15\pi^2} \frac{V}{N} \left( \frac{\Omega_0}{c} \right)^3, \quad (3.24) \]

as a proxy for the perturbative coupling, and where the lengthy expansions for \( M \) and \( N \) in terms of the \( \sigma \)'s will be given below. It is worth mentioning that the cumbersome \( O(\frac{1}{2}) \) constant factors in \( \sigma_{kl} = s_k s_l + \frac{1}{2j-1} \delta_{kl} \) are actually irrelevant and can be dropped. To see this, consider that for any function of just one variable, \( f(u) \), such that \( \int du f(u) \) and \( \int du f'(u) \) are finite, we have that,

\[ \int \int dud'e^{+i\omega(u-u')} f(u) = 2\pi \delta(\omega) \int du f(u) e^{+i\omega u}, \quad (3.25) \]
\[
\int \int du' \left\{ \frac{\cosh(u|u-u'| - \beta \omega/2)}{\sinh(\beta \omega/2)} \right\} + \frac{2i}{\omega} \delta(u - u') f(u) = 2\pi \delta(\omega) \coth(\frac{\beta \omega}{2}) \int du f(u). \tag{3.26}
\]

Therefore, as long as the spectral density goes to 0 as \( \omega^2 \) or faster, these \( O(1/j) \) terms vanish, and it suffices to replace \( \sigma_{kl} \) by just \( s_k s_l \). Employing the shorthand that \( s_k^L \) stands for \( s_k s_l \) evaluated along \( z \pm \), and that the absence of presence of a prime ‘ indicates whether the term is a function of \( u \) or \( u' \), then the lengthy expressions for \( M_1 \) and \( M_2 \) read,

\[
M_1(u, u'|z_+) = (4(\frac{e}{\tau})^5 + 6(\frac{e}{\tau})^5)\{s_{13}^+ s_{13}^+ + s_{23}^+ s_{23}^+ \},
\]

\[
M_2(u, u'|z_-) = (\frac{e}{\tau})^5 \{3 s_{11}^+ s_{11}^+ + s_{22}^+ s_{22}^+ + s_{11}^+ s_{11}^+ + 4 s_{12}^+ s_{12}^+ \}
\]

\[
\quad + (\frac{e}{\tau})^5 \{2 s_{11}^+ s_{11}^+ + 2 s_{22}^+ s_{22}^+ - s_{11}^+ s_{11}^+ + 4 s_{12}^+ s_{12}^+ \}, \tag{3.27}
\]

and \( N_1, N_2 \) read,

\[
N_1(u, u'|z_+, z_-) = (4(\frac{e}{\tau})^5 + 6(\frac{e}{\tau})^5)\{s_{13}^- s_{13}^- + s_{23}^- s_{23}^- \},
\]

\[
N_2(u, u'|z_+, z_-) = (\frac{e}{\tau})^5 \{3 s_{11}^- s_{11}^- + s_{22}^- s_{22}^- + s_{11}^- s_{11}^- + 4 s_{12}^- s_{12}^- \},
\]

\[
\quad + (\frac{e}{\tau})^5 \{2 s_{11}^- s_{11}^- + 2 s_{22}^- s_{22}^- - s_{11}^- s_{11}^- + 4 s_{12}^- s_{12}^- \}. \tag{3.28}
\]

### 3.3 The Golden Rule and the One-Instanton Approximation

Here we outline the calculation of the transition rate to lowest order in \( \Delta \), a.k.a. the ”Golden Rule” result. Since each instanton contributes one order of \( \Delta \), this is essentially the one-instanton approximation. Precisely, let \( z_+(u) \equiv z(u|u_+, p_+) \) and \( z_-(u) \equiv z(u|u_-, p_-) \) be the “+” and the “−” trajectories, where \( u_+ \), \( p_+ \) are the tunneling epoch and the winding of the “+” trajectory, respectively; and similarly for the “−” trajectory. The golden rule result is then given by,

\[
P(T, \beta) = N_0^{-2} \sum_{p_+} \sum_{p_-} F_{p_+} F_{p_-} \int_{-T/2}^{T/2} du_+ \int_{-T/2}^{T/2} du_- e^{i S_0[p_+] - i S_0[p_-]} B[u_+] B[u_-]^* \times \exp \{ R[p_+] \} \exp \{ R[p_-]^* \} \exp \{ Q^{ss}[u_+, p_+; u_-, p_-] + Q^{ee}[u_+, p_+; u_-, p_-] \}, \tag{3.29}
\]

where \( S_0[p_+] \) denotes the semiclassical action evaluated along \( z(u|u_+, p_+) \), and \( F_{p_+} \) denotes the corresponding fluctuation determinant. Note that \( S_0[p_+] \) is typically translationally invariant under time, and so is independent of the tunneling epoch \( u_+ \). In addition, the bias factors and the fluctuation determinant
typically do not depend on the winding $p$. The bias factors become,

$$
\begin{align*}
\mathcal{B}[u_+] &= \exp \left\{ -\frac{i\varepsilon}{2} \int du \, s_3(u|u_+,p_+) \right\}, \\
\mathcal{B}[u_-] &= \exp \left\{ +\frac{i\varepsilon}{2} \int du \, s_3(u|u_-,p_-) \right\}.
\end{align*}
$$

(3.30)

Roughly speaking, the semiclassical action and the fluctuation determinant summed over all trajectories (in this case differentiated by the two windings) combine to give the tunneling element $\Delta_{p+}$ between the two resonant levels, i.e.,

$$
\mathcal{N}_0^{-1} \sum_{p+} \mathcal{F} \exp^{iS_0[p_+]} \rightarrow \frac{1}{2} \Delta,
$$

(3.31)

while the bias factors furnish a term that is approximately the exponential of the time difference between the two instanton tunneling epochs,

$$
\mathcal{B}[u_+][\mathcal{B}[u_-]] = e^{i\varepsilon(u_+-u_-)},
$$

(3.32)

which, when integrated over $u_+$ and $u_-$ will, in the limit of long $T$, tend toward a delta-function that acts to enforce energy conservation.

As an illustration, suppose that we suppress all coupling to the environment, so that $R = Q^{ab} = Q^{em} = 0$. The golden-rule transition rate (eq. 3.29) then reads,

$$
\mathcal{P} = \frac{\Delta^2}{4} \int_{-T/2}^{T/2} du_+ \int_{-T/2}^{T/2} du_- e^{i\varepsilon(u_+-u_-)} = \frac{\Delta^2 \sin^2(\varepsilon T/2)}{4(\varepsilon/2)^2},
$$

(3.33)

where the sinc-squared terms approach a delta function in the limit of $\varepsilon T \gg 1$,

$$
2\pi T D_2(x;T) \equiv \frac{\sin^2(xT/2)}{(x/2)^2} \sim 2\pi T \delta(x),
$$

(3.34)

so the transition is forbidden unless $\varepsilon \rightarrow 0$, in which case it limits to $\mathcal{P} = \Delta^2 T^2/4$. It is helpful to compare result (eq. 3.33) to the exact result for the two-level system,

$$
|\langle \downarrow | e^{-iT\left(\frac{1}{2} \Delta \sigma_+ + \frac{1}{2} \varepsilon \sigma_+\right)} |\downarrow \rangle|^2 = \frac{\Delta^2 \sin^2(\varepsilon T/2)}{\Delta^2 + \varepsilon^2} \approx \frac{\Delta^2 \sin^2(\varepsilon T/2)}{4(\varepsilon/2)^2},
$$

(3.35)

where the last approximation holds in the limit $\Delta \ll \varepsilon$.

Continuing, we look at the roles played by the environmental terms in (eq. 3.29). At one instanton, the terms $R[p_+]$ and $R[p_-]$ (which, like $S_0$, are also independent of the tunneling epoch) combine with the
original action to renormalize the tunneling element,

$$\Delta_p \rightarrow \tilde{\Delta}_p \equiv \Delta_p \exp(R[p]),$$

(3.36)

though this effect is typically small.

Finally, the effects of dissipation are encoded in the cross terms $Q^{ab}$ and $Q^{em}$, which are explicitly dependent on both the windings $p_+, p_-$, as well as the difference in time $u_+ - u_-$ between the two tunneling epochs.

It should be noted that the expressions in (3.29) are given in real time, and since strictly speaking the instanton solutions only exist in the continuation to Euclidean time, we must be careful to interpret the integrals in the transition rate appropriately. Assuming such a continuation is possible\(^2\), we may replace the integral along the real time axis with one along the imaginary axis. Cosmetically, this means replacing $i u \rightarrow \tau, i T \rightarrow \zeta$, etc. Once we have performed the integral in $\tau, \tau'$ space, we rotate back to arrive at a result in real time.\(^3\)

Following the above procedure, we’ll find that,

$$Q^{em}_E = \eta \int_0^\infty d\omega \omega^3 \int d\tau d\tau' e^{\omega(\tau-\tau')} \left( N_1(\tau - \tau_+, \tau' - \tau_- | p_+; p_-) + N_2(\tau - \tau_+, \tau' - \tau_- | p_+; p_-) \right),$$

(3.37)

and also (using that the continuation of $\delta(u)$ is $i\delta(\tau)$),

$$R_E[p] = -\frac{\eta}{2} \int_0^\infty d\omega \omega^3 \int d\tau d\tau' \left( \frac{\cosh(\omega|\tau-\tau'| - \beta\omega/2)}{\sinh(\beta\omega/2)} - \frac{2}{\omega} \delta(\tau - \tau') \right) \left( M_1(\tau, \tau'|p) + M_2(\tau, \tau'|p) \right).$$

(3.38)

### 3.3.1 The Semiclassical One-Phonon Perturbative Result

Recall that the coefficient $\eta$ is defined as $\eta \equiv \lambda^2 j^2 (j - \frac{1}{2})^2 \frac{1}{16\pi^2} \frac{V}{N} (\frac{\Omega}{e})^3$, where $\lambda$ characterizes the phonon coupling. For the transition probability therefore, the one-phonon result corresponds to the $O(\lambda^2)$ result,
a.k.a. the $O(\eta)$ term, which can be read off from (eq. 3.29),
\[
P^{\text{em}} = -\eta N_0^{-2} \sum_{p_+} \sum_{p_-} e^{2 \mathcal{E}_0 [p_+] S_0 [p_-]} \int \int_{-c/2}^{c/2} d\tau_+ d\tau_- \ exp \left\{ -\frac{\epsilon}{2} \int d\tau'' (s_3 (\tau'')_+ - s_3 (\tau'')_-) \right\}
\times \int_0^\infty \frac{d\omega \omega^j}{1 - e^{-\beta \omega}} \int \int d\tau d\tau' e^{+\omega (\tau - \tau')} \left\{ N_1 (\tau - \tau_+, \tau' - \tau_- | p_+, p_-) + N_2 (\tau - \tau_+, \tau' - \tau_- | p_+, p_-) \right\}.
\] (3.39)

(The $\eta$ contributions from the $R_E$ term will not contribute, since the rest of the integral will fail energy conservation for non-zero $\epsilon$). Equation 3.39 is for the phono-emissive contribution. The phono-absorptive contribution $P^{ab}$ is modified by taking $\omega^3 \to \omega^3 e^{-\beta \omega}$ in the numerator of the $\omega$ integral, and taking $e^{+\omega (\tau - \tau')} \to e^{-\omega (\tau - \tau')}$. The full contribution is $P = P^{\text{em}} + P^{ab}$.

**Results for $\gamma = 0$, $X_1 = 0$**

It remains to evaluate $N_1$, $N_2$ and $s_3$ along the instantons, whose exact form depends on the parameters of the Hamiltonian. Let us first look at the results from (eq. 1.28) for the Hamiltonian in absence of fourth-order anisotropies and hard-axis external fields. Reading off the solution (eq. 1.28), we have,
\[
N_1 = p_+ p_- B_1 \text{sech} (\tau - \tau_+) \text{tanh} (\tau - \tau_-) \text{sech} (\tau' - \tau_-),
N_2 = B_2 \text{sech}^2 (\tau - \tau_+) \text{sech}^2 (\tau' - \tau_-),
\] (4.0)

where we have temporarily defined the cumbersome material-dependent prefactors,
\[
B_1 = \left\{ 4 \left( \frac{\epsilon}{c T} \right)^5 + 6 \left( \frac{\epsilon}{c T} \right)^5 \right\} \cosh (4 \varphi_a),
B_2 = \left\{ \left( \frac{\epsilon}{c T} \right)^5 (2 + \cosh (4 \varphi_a)) \right\} + \left( \frac{\epsilon}{c T} \right)^5 \left[ \frac{1}{2} + \frac{3}{2} \cosh (4 \varphi_a) \right].
\] (4.41)

The integrals over sech$^2(\tau)$ and sech$(\tau) \text{tanh}(\tau)$ are elementary, and after shifting the variables $\tau \to \tau + \tau_+$, etc, we arrive at,
\[
\int \int d\tau d\tau' e^{+\omega (\tau - \tau')} N_1 = -p_+ p_- B_1 e^{+\omega (\tau_+ - \tau_-)} \pi \omega^2 \sec^2 (\pi \omega / 2), \quad \text{for} \quad -1 < \Re \{ \omega \} < +1,
\int \int d\tau d\tau' e^{+\omega (\tau - \tau')} N_2 = B_2 e^{+\omega (\tau_+ - \tau_-)} \pi \omega^2 \csc^2 (\pi \omega / 2), \quad \text{for} \quad -2 < \Re \{ \omega \} < +2.
\] (4.34)

(If $\omega$ is not within the ranges specified, the integral becomes divergent; we will comment on the physical interpretation of this shortly). Continuing, the bias factor in this case evaluates exactly to $e^{\sigma (\tau_+ - \tau_-)}$, which, combined with the $e^{+\omega (\tau_+ - \tau_-)}$ terms in (eq. 3.42) and integrated over $\tau_+$ and $\tau_-$ furnish the expected energy conservation factor $2 \pi \kappa D_2 (\omega + \epsilon; -i \kappa)$ (eq. 3.34). As a check, recall that $\epsilon = -2j X_3$, where $X_3$ is the field
along the easy axis in the direction of $+\hat{e}_3$. For positive $X_3$, the $m = -j$ well is metastable and the $m = +j$
well is stable; and so in order to tunnel from $s_3 = -1$ to $s_3 = +1$ whilst emitting a phonon, the energy $\omega$ of
the phonon must equal $2jX_3$. For negative $X_3$, the $m = -j$ becomes the stable well, and the phono-emissive
tunneling from $s_3 = -1$ to $s_3 = +1$ is suppressed (as expected) since the range of integration of $\omega$ does not
permit the negative energies.

Now, utilizing the delta function to replace $\omega \rightarrow -\varepsilon$ and collecting our results thus far, we have,

$$P_{em} = -2\pi^3 i\eta \frac{(-\varepsilon)^5 \sec^2(\pi\varepsilon/2)}{1 - e^{+\beta\varepsilon}} B_1 \Theta(-\varepsilon) e^{+\frac{\varepsilon B_1}{\Delta}} \left( \sum_{p+} \sum_{p-}(p+p_+\varepsilon)e^{S_b^R[p+]}e^{S_b^R[p-]} \right).$$

(3.43)

It remains to perform the sum over the windings. The summation for the $B_2$ term will again yield the tunnel
splitting $\Delta$, while the summation for the $B_1$ term will yield zero for integer $j$. (For half-integer $j$ the splitting
vanishes, and so the spin fails to tunnel in the first place. See section 1.4.1 for details). After rotating back
to real time, the one-phonon one-instanton phonoemissive tunneling probability reads,

$$P_{em} = 2\pi^3 T\eta B_2 \frac{\Delta^2}{4} \frac{(-\varepsilon)^5 \csc^2(\pi\varepsilon/2)}{1 - e^{+\beta\varepsilon}} \Theta(-\varepsilon),$$

(3.44)

where $\Theta(x)$ is the Heaviside function.

Now let us return to the point made earlier about the divergence of the integrals, which is also reflected in
(eq. 3.44) at $\varepsilon = \pm 2, \pm 4, \pm 6$, etc. Recall that the energy spacing between the ground state doublet and the
first excited doublet is on the order of $\varepsilon \sim \Delta m \sim 1$ (working in units of $\hbar\Omega_0$). However, since the csc term
involved only integrals of spin components of $\Delta m = 2$, this first resonance is not reachable, and hence the
divergence occurs at the second excited doublet, with $\varepsilon \sim 2$. By contrast, the sec term arises from integrals
of $\Delta m = 1$ spin components, and in that case the first excited doublet is reachable, and the divergence at
$\varepsilon = 1$ is seen. In other words, the divergence of the integrals is precisely reflecting the fact that, at large
enough bias $\varepsilon$, we are no longer working within the ground-state doublet; instead we are hitting resonance
with higher excited states, for which the instanton description breaks down.

The above derivations have been carried out for the phono-emissive process. The calculation for the
phono-absorptive rate is similar and is easily reproduced. In summary, we find that the transition probabil-
ities are given by,

$$P = 2\pi T\eta \times \left\{ B_2 \frac{\Delta^2}{4} \frac{(-\varepsilon)^5 \pi^2 \csc^2(\pi\varepsilon/2)}{1 - \exp\{+\beta\varepsilon\}} \Theta(-\varepsilon) + B_2 \frac{\Delta^2}{4} \frac{\varepsilon^5 \pi^2 \csc^2(\pi\varepsilon/2)e^{-\beta\varepsilon}}{1 - \exp\{-\beta\varepsilon\}} \Theta(\varepsilon) \right\}.$$ 

(3.45)
Equation (3.45) is an extension of the result obtained in [11] (eq. 27), in which transitions only between the lowest levels \( m = j \), \( m = -j \), \( m = j - 1 \), and \( m = j + 1 \) are considered. In particular, only the \( \mathcal{P} \sim \varepsilon^3 \) dependence is captured. By contrast, the semiclassical result considers transition between all possible \( m \) levels, and in doing so illustrates the additional behavior beyond \( \varepsilon^3 \).

**Results for \( \gamma \neq 0, X_1 = 0 \)**

At this point, we can see that the general form of the phonoemissive one-phonon Golden rule transition probability is given by

\[
\mathcal{P}_{\text{em}} \sim \frac{2\pi T \eta (-\varepsilon)^3}{1 - e^{\frac{-\beta \varepsilon}{2}}} \Theta(-\varepsilon) \sum_{p_+} \sum_{p_-} F^2 e^{S_{\theta}^p[p_+] e^{S_{\theta}^p[p_-]}} \times \int \int d\tau d\tau' e^{-\varepsilon(\tau - \tau')} \{ N_1(\tau, \tau'|p_+, p_-) + N_2(\tau, \tau'|p_+, p_-) \}.
\]

where we note that in this case, although \( s_3 \) is not given exactly by \( \tanh(\tau) \), it is still reasonable to approximate the bias term as \( \exp \{ -(\varepsilon/2) \int d\tau'' (s_3(\tau''|\tau_+) - s_3(\tau''|\tau_-)) \} \approx \exp \{ \varepsilon(\tau_+ - \tau_-) \} \) (see fig. 1.8).

From the form of \( N_1 \) and \( N_2 \) (eq. 3.28) we see that the integral is separable, and it suffices to compute an expression of the form,

\[
I_{ab}(\varepsilon) \equiv \int_{-\infty}^{\infty} d\tau e^{\pm \varepsilon \tau} s_a(\tau)s_b(\tau).
\]

The exact answer is difficult to obtain in this case, since the trajectory \( s_a \) can only be calculated numerically; however, one can still deduce certain properties of these integrals by exploring the symmetries of the trajectories.

For \( \gamma \neq 0 \) (but still working under the assumption that \( X_1 = 0 \)), we can immediately see that the \( \Delta m = 2 \) terms \( (I_{11}, I_{12}, I_{22}) \) will be insensitive to the winding \( p \), since it always appears as \( p^2 \). Furthermore, since \( s_1 \) and \( s_2 \) are both even functions of \( s_3 \) (which is itself an odd function of \( \tau \)), we can replace the exponential factor with its symmetrized version — thus showing that the integral itself is symmetric under \( \varepsilon \leftrightarrow -\varepsilon \). By the same arguments, the \( \Delta m = 1 \) terms \( (I_{13}, I_{23}) \) are antisymmetric in \( \tau \) and will hence be an odd function in \( \varepsilon \). Thus we have,

\[
I_{ab}(\varepsilon) = \begin{cases} 
\int_{-\infty}^{\infty} d\tau \cosh(\varepsilon \tau)s_a(\tau)s_b(\tau), & \text{if } (a,b) = (1,1), (1,2), (2,2), \\
\int_{-\infty}^{\infty} d\tau \sinh(\varepsilon \tau)s_a(\tau)s_b(\tau), & \text{if } (a,b) = (1,3), (2,3). 
\end{cases}
\]

Just as in the \( \gamma = 0 \) case however, since the \( \Delta m = 1 \) terms are sensitive to the winding, then for integer spin and \( X_1 = 0 \) they will not contribute. To obtain the final result, one needs to sum together the \( I_{ab} \) terms in
Results for $\gamma = 0$, $X_1 \neq 0$

We conclude our semiclassical analysis by looking at the case where $\gamma = 0$ and $X_1 \neq 0$, for which the instantons are again exactly solvable. But unlike in the previous sections, now $s_3$ is no longer a pure real variable, and consequently the $\Delta m = 1$ contributions cannot be discarded (this makes sense since the only $\Delta m = 1$ term in the spin hamiltonian comes from the transverse field).

Furthermore, there is an additional subtlety that now the $s_1$ component acquires a nonzero equilibrium point, i.e. $s_1 \rightarrow X_1 \sqrt{(1 - \alpha)/(1 + \alpha)}$ as $\tau \rightarrow \pm \infty$. As such, the integrals of $N_1$ and $N_2$ will diverge unless we subtract off this equilibrium, i.e. we must shift $s_1 \rightarrow \tilde{s}_1 \equiv s_1 - X_1 \sqrt{(1 - \alpha)/(1 + \alpha)}$.

Lastly, even though $s_3$ now contains a winding dependent imaginary component, the integral of the imaginary part of $s_3(\tau) - s_3(\tau')$ remain zero. The real part, on the other hand, no longer saturates at $\pm 1$, but rather at $\pm \sqrt{1 - X_1^2(1 - \alpha)/(1 + \alpha)}$, and the effect of this is to rescale the bias value of $\varepsilon$ in the resulting delta function; however, for small values of $X_1$ this effect is negligible.

3.3.2 The Numerical One-Phonon Perturbative Result

As a benchmark of our semiclassical results, we present an alternative numerical calculation of the transition rate from $|j,-j\rangle$ to $|j,+j\rangle$ via high-order perturbation theory. The same approach was carried out by [30] to calculate the tunnel splitting and locate the diabolical points for an isolated molecular magnet. The main idea is that for small values of $\alpha$, $\gamma$, $X_1$, and $\lambda$, the corresponding terms may be regarded as perturbations. In particular the $X_1$ value should be small, i.e. below the first non-trivial diabolical point. Recall that at larger $X_1$ it is no longer valid to consider $|j, \pm j\rangle$ as states localized at the classical minima of the Hamiltonian, since the latter will cant toward the equator, and as such the perturbative calculation is no longer meaningful.

To proceed, we work in the eigenbasis $|j, m\rangle$ for spin and $|\{n\}\rangle$ for the phonons. The reference Hamiltonian then reads,

$$
H_{\text{ref}} = -j \left\{ \frac{1}{2} \cosh \rho S_3^2 + X_3 S_3 \right\} + \sum_{\mu} \omega_\mu a_\mu^\dagger a_\mu,
$$

and the perturbations read

$$
H_{\text{pt}} = H_1 + H_2 + H_4 + V,
$$

where we have defined,

$$
H_1 = -j X_1 S_1, \quad H_2 = \frac{j}{2} \sinh \rho (S_1^2 - S_2^2), \quad H_4 = j \gamma (S_+^4 + S_-^4).
$$
(We do not need to worry about counterterms in the above, since they already occur at a higher order than that of our expansion). The usual time-dependent perturbation then gives,

$$\exp \{-i\mathcal{H}T\} = 1 + (-i) \int_0^T du_1 \tilde{\mathcal{H}}_{\text{pt}}(u_1) + (-i)^2 \int_0^T du_1 \int_0^{u_1} du_2 \tilde{\mathcal{H}}_{\text{pt}}(u_1)\tilde{\mathcal{H}}_{\text{pt}}(u_2) + \ldots,$$

(3.52)

with $\tilde{\mathcal{H}}_{\text{pt}}(u)$ being the perturbation in the interaction picture. We must take the matrix element of this operator between the initial and final states, where the final state differs from the initial one by $\Delta m = 2j$, (for Fe8, $\Delta m$ is 20). To get such a large change in $m$ one must go to an order such that there are sufficiently many interaction terms $\tilde{\mathcal{H}}_{\text{pt}}(u)$ (hence the name “high-order-perturbation”), and there are many ways to achieve this. For example, at the sixth order, we could select the following sequence of terms to yield a total change of $\Delta m = 20$:

$$\tilde{\mathcal{H}}_2(u_6), \tilde{\mathcal{H}}_4(u_5), \tilde{\mathcal{H}}_4(u_4), \tilde{\mathcal{H}}_4(u_3), \tilde{\mathcal{V}}(u_2), \tilde{\mathcal{H}}_2(u_1),$$

(3.53)

and at the seventh order we could select

$$\tilde{\mathcal{H}}_2(u_7), \tilde{\mathcal{V}}(u_6), \tilde{\mathcal{H}}_4(u_5), \tilde{\mathcal{H}}_4(u_4), \tilde{\mathcal{H}}_4(u_3), \tilde{\mathcal{H}}_4(u_2), \tilde{\mathcal{H}}_1(u_1).$$

(3.54)

It is evident that each sequence can be considered to correspond to a discrete path in the space of Zeeman states. There is a countably infinite number of such paths, and the exact answer must include contributions from all of them. To keep the calculation tractable, therefore, we make the following additional simplifications.

First, we divide the path into different types of classes, characterized by how many times each of the $\mathcal{H}_1$, $\mathcal{H}_2$, $\mathcal{H}_4$, and $\mathcal{V}$ appears. We demand that all classes be subject to the constraint that the quantum number $m$ be strictly increasing along the path (assuming we are making the $j \rightarrow -j$ transition; otherwise we demand it be strictly decreasing). Thus, in the $\Delta m = 20$ example, the sequence,

$$\tilde{\mathcal{H}}_2(u_8), \tilde{\mathcal{H}}_2(u_7), \tilde{\mathcal{V}}(u_6), \tilde{\mathcal{H}}_4(u_5), \tilde{\mathcal{H}}_4(u_4), \tilde{\mathcal{H}}_4(u_3), \tilde{\mathcal{H}}_4(u_2), \tilde{\mathcal{H}}_1(u_1).$$

(3.55)

will be ignored since, when we compare it to 3.54, it is seen to require a step in which $m$ decreases.

Second, we demand that in each path, $\mathcal{V}$ appear once and only once. If it does not appear at all, we cannot allow for energy conservation if there is a non-zero bias, and so the path in question cannot contribute to the incoherent transition rate (it is instead part of the contribution to $\Delta$, the coherent flip-flop tunnel splitting). And if it appears more than once, then it corresponds to a multi-phonon process which, for weak bath coupling, may be neglected.
In the transition matrix element, therefore, we need only display the phonon occupation number of the mode that is affected, and the transition probability simplifies to,

\[
P = \sum_\mu \sum_{n_\mu} e^{-\beta \omega_\mu n_\mu} \frac{1}{2^{\text{ph}_\mu}} |\langle n_\mu + 1, j | \exp \{- iT\mathcal{H} \} | n_\mu, -j \rangle|^2 + \sum_\mu \sum_{n_\mu} e^{-\beta \omega_\mu n_\mu} \frac{1}{2^{\text{ph}_\mu}} |\langle n_\mu - 1, j | \exp \{- iT\mathcal{H} \} | n_\mu, -j \rangle|^2
\]

(3.56)

where we have explicitly separated the phono-emissive and phono-absorptive processes, and it is understood that we employ the perturbation expansion (eq. 3.52) with the simplifications already mentioned.

Next we note that since \(\mathcal{V}\) is to appear only once in the expansion of \(\exp \{- i\mathcal{H}T\}\), the phonon part of the transition matrix is always,

\[
\langle n_\mu + 1 | a_\mu^\dagger n_\mu \rangle = \sqrt{n_\mu + 1}, \quad \langle n_\mu - 1 | a_\mu | n_\mu \rangle = \sqrt{n_\mu},
\]

(3.57)

for emission and absorption respectively. Summing over the Boltzmann weight then gives precisely the Bose thermal occupation numbers

\[
\langle n_\mu + 1 \rangle = \frac{1}{1 - e^{-\beta \omega_\mu}}, \quad \langle n_\mu \rangle = \frac{e^{\beta \omega_\mu} - 1}{e^{\beta \omega_\mu} - 1}.
\]

(3.58)

The remaining \(\mathcal{H}_\text{pt}(u_i)\) in any path give rise to a number of factors of the form \(e^{-i(\epsilon_k - \epsilon_l)u_i}\), where \(\epsilon_k\) and \(\epsilon_l\) are the energies of intermediate states along the path. When we integrate over all of the \(u_i\), all but one of these integrations will generate energy denominators of the form \((\epsilon_k - \epsilon_l)\), and the remaining one will generate an overall sinc function which, upon squaring, can be replaced by \(T:\delta(\epsilon_f - \epsilon_i)\) by standard arguments. The upshot is that,

\[
P = 2\pi T \sum_\mu \delta(\epsilon + \omega_\mu) |\mathcal{F}_\mu,em|^2 + 2\pi T \sum_\mu \delta(\epsilon - \omega_\mu) |\mathcal{F}_\mu,ab|^2.
\]

(3.59)

Here, the quantity \(\mathcal{F}\) is a transition matrix element with the following structure,

\[
\mathcal{F} = \sum_{\{s\}} \frac{\langle f | \mathcal{H}_\text{pt} | s_{n-1} \rangle \langle s_{n-1} | \mathcal{H}_\text{pt} | s_{n-2} \rangle \cdots \langle s_1 | \mathcal{H}_\text{pt} | i \rangle}{(\epsilon_i - \epsilon_{n-1})(\epsilon_i - \epsilon_{n-2}) \cdots (\epsilon_i - \epsilon_1)},
\]

(3.60)

where the \(s_k\)'s denote intermediate states (here, \(s\) labels the spin state \(m\) and the \(\mu\)-th mode occupation number \(n_\mu\)), with energies \(\epsilon_k\) (which include that of the phonon), the \(\mathcal{H}_\text{pt}\) are the interactions in the usual Schrödinger picture, and the sum is over all paths from \(s = (-j, n_\mu)\) to \((j, n_\mu, \pm 1)\) with the restrictions
aforementioned. If the term is for an emissive process, then along the way the phonon number must decrease by one; and if it’s absorptive then it must increase by one.

We can make some final simplifications by anticipating the structure of the sum over phonon modes. Recall that

\[ S_{ab} \equiv \{ J_a, J_b \} \]

\[ \frac{2j(j-\frac{1}{2})}{2} \]  

(3.61)

There are a total of six such terms but, as explained previously we omit the \( S_{33} \) term (even if such a term were present, it would lead to a \( \Delta m = 0 \) process which is discarded in accord with our path requirements).

Now, just as in the semiclassical calculation we can group the remaining five operators into those with \( \Delta m = 1 \) and those with \( \Delta m = 2 \), where the operators exhibit the symmetry that,

\[ \langle m + 2 | S_{11} | m \rangle = i \langle m + 2 | S_{12} | m \rangle = - \langle m + 2 | S_{22} | m \rangle , \]

\[ \langle m + 1 | S_{13} | m \rangle = i \langle m + 1 | S_{23} | m \rangle , \]

(3.62)

and likewise for their complex conjugates. Under our lowest-order approximation it is precisely these matrix elements which enter the summation. Since the terms in (eq. 3.60) must contain one and only one of the five \( S_{ab} \)'s, we can likewise divide up the \( F \)'s into two groups by \( \Delta m \). And since each of these five terms will bring along with it a factor of \( i j(j-\frac{1}{2})\lambda(\hat{q}_a \hat{e}_b + \hat{q}_b \hat{e}_a) \), we can carry out the phonon mode summation exactly as in the previous section. The end result is that,

\[ P_{em} = 2\pi T \eta \int_0^\infty \frac{\omega^3 d\omega}{1 - \exp \{-\beta \omega\}} \delta(\epsilon + \omega) \left\{ (8(\frac{\epsilon}{\epsilon_\alpha})^5 + 12(\frac{\epsilon}{\epsilon_\tau})^5)|F_{em}^1|^2 + (8(\frac{\epsilon}{\epsilon_\alpha})^5 + 12(\frac{\epsilon}{\epsilon_\tau})^5)|F_{em}^2|^2 \right\} , \]

\[ = \frac{2\pi T \eta (-\epsilon)^3}{1 - \exp \{+\beta \epsilon\}} \left\{ (8(\frac{\epsilon}{\epsilon_\alpha})^5 + 12(\frac{\epsilon}{\epsilon_\tau})^5)|F_{em}^1(-\epsilon, X_1)|^2 + (8(\frac{\epsilon}{\epsilon_\alpha})^5 + 12(\frac{\epsilon}{\epsilon_\tau})^5)|F_{em}^2(-\epsilon, X_1)|^2 \right\} , \]

(3.63)

where \( F_{em}^1 \) is an expression of the form (eq. 3.60) with the \( H_{pt} \) standing for either \( H_1, H_2, H_4 \) (eq. 3.51), or one instance of \( S_{13} \); and likewise for \( F_{em}^2 \) but with \( S_{11} \) replacing \( S_{13} \). As before, \( P_{ab} \) is obtained similarly, and the total transition probability (at one phonon) is the sum of both terms.

At this stage, the \( F_1 \) and \( F_2 \) are functions of the transverse external field \( X_1 \) and the bias \( \epsilon \) (as a proxy for \( X_3 \)). Algorithmically therefore, one needs to set \( X_1 \) and \( \epsilon \), and perform the sum (eq. 3.60). The enumeration of all such paths, subject to our restrictions, is easily automated to a computer algebra system.

Though we have only computed the case for tunneling from \( m = -j \to m = +j \) for the phonoemissive process, the other processes can be easily obtained from the present result. First we have that,

\[ |F_{em}^1(\epsilon, X_1)|_{\pm j \to \mp j}^2 + |F_{em}^2(\epsilon, X_1)|_{\pm j \to \mp j}^2 = |F_{1}^{ab}(\epsilon, X_1)|_{\pm j \to \mp j}^2 + |F_{2}^{ab}(\epsilon, X_1)|_{\pm j \to \mp j}^2 , \]

(3.64)
where we have put in the tunneling direction explicitly. To understand this, observe that for every path \(s_0, s_1, \ldots, s_f \) occurring in the sum for the LHS of (eq. 3.64), a corresponding reversed path \(s_f, \ldots, s_1, s_0 \) occurs on the RHS. The numerators of these paths are complex conjugates of each other, while the energy denominators end up being the same, as a consequence of energy conservation. Equation (3.64) is essentially the statement of detailed balance.

Next, we also have that,

\[
|F_{\text{em}}/\text{abs}^1(\varepsilon, X_1)|^2 - j \rightarrow +j + |F_{\text{em}}/\text{abs}^2(\varepsilon, X_1)|^2 + j \rightarrow -j = |F_{\text{em}}/\text{abs}^1(-\varepsilon, X_1)|^2 + j \rightarrow -j + |F_{\text{em}}/\text{abs}^2(-\varepsilon, X_1)|^2 + j \rightarrow +j, \tag{3.65}
\]

from which time-reversal symmetry follows. This is due to the invariance of the system under \( m \rightarrow -m \) and \( X_3 \rightarrow -X_3 \), since under this combined transformation the denominators remain unchanged; while for the numerators, those paths containing a coupling-term with \( \Delta m = \pm 1 \) will change sign, and those with \( \Delta m = \pm 2 \) are unchanged. In other words,

\[
F_1(\varepsilon) = -F_1(-\varepsilon), \quad F_2(\varepsilon) = F_2(-\varepsilon). \tag{3.66}
\]

After taking the squared absolute values, the two answers are again the same. Furthermore, from (eq. 3.66) we see that, due to the antisymmetry of \( F_1 \) in \( \varepsilon \), its contribution must vanish at \( \varepsilon = 0 \).

Finally we look at \( F_1 \) and \( F_2 \) as a function of \( X_1 \). When \( j \) is an integer, the transition from \(-j \rightarrow +j\) (and vice versa) must take an even number of steps in \( m \). Since \( \mathcal{H}_2 \) and \( \mathcal{H}_4 \) have even \( \Delta m \), the remaining combination of \( \mathcal{H}_1 \) (through which the external field \( X_1 \) appears) and \( \mathcal{S}_{\text{ab}} \) must also result in an even \( \Delta m \). Therefore, the \( F_1 \) term is an odd function of \( X_1 \), while the \( F_2 \) term is an even function. Consequently, the \( F_1 \) contribution also vanishes at \( X_1 = 0 \), in accordance with the semiclassical result.

### 3.3.3 Comparison between Numerical and Semiclassical Results

In this section we compare the semiclassical and numerical results for the one-phonon Golden-rule transition rate, and discuss our findings.

First we look at the results for the \( \gamma = 0, X_1 = 0 \) case. From equations (3.45) and (3.63), it suffices to compare the numerically calculated factor \((8(c/c_L)^5 + 12(c/c_T)^5)|F_{\text{em}}^2(-\varepsilon, 0)|^2\), with the semiclassical factor \((\Delta^2/4)B_2\varepsilon^2\pi^2\csc^2(\pi \varepsilon/2)\), where we recall that \( B_2 = (c/c_L)^5(2 + \cosh(4\varphi_\alpha)) + (c/c_T)^5((1/2) + (3/2)\cosh(4\varphi_\alpha)) \). Note that when \( \alpha \) is small, the \( \cosh(4\varphi) \) factor dominates, so it is possible to approximate \( B_2 \) as

\[
B_2 \approx \frac{1}{8} \cosh(4\varphi_\alpha)(8(c/c_L)^5 + 12(c/c_T)^5), \tag{3.67}
\]
the advantage of which is that we can further out factor out the bath-dependent constants $c_L$ and $c_T$ from each of the above results. We plot the results in (fig. 3.1) and (fig. 3.2).

![Figure 3.1: Comparison of the numerical result $|\mathcal{F}_2^{nm}|^2$ (in black dotted) and the semiclassical result $|f(\varepsilon)|^2 \equiv \frac{1}{8}(\frac{\Delta}{2})^2 \cosh(4\phi_{\alpha})\varepsilon^2 \pi^2 \csc^2(\pi \varepsilon/2)$ (in red), as well as a rescaled fit $|f(\varepsilon/\varepsilon_{res,1})|^2$ (in grey).](image)

At low biases, we see that the semiclassical (shown in red) and the numerical results (shown in black dots) agree, but there is considerable departure at higher biases, particularly beyond the first resonance ($\varepsilon \approx 1$). For reasons discussed earlier, we don’t expect the result to hold past point anyway; however, it is interesting to see that if we rescale the $\varepsilon$ dependence of the semiclassical result, then we again recover considerable agreement to well past the first resonance. The reason for this is simple: numerically, the first resonance does not occur exactly at $\varepsilon = 1$, but rather at

$$
\varepsilon_{res,1} = \frac{\sinh(\rho)}{1 - 1/(2j)}.
$$

(3.68)

Rescaling the semiclassical result by this factor gives produces a much better fit, and shows that the numerical result can be described rather well by a function of the form $\pi^2 \varepsilon^2 \csc^2(\pi \varepsilon/2)$.

It will also be enlightening to explore the validity of the result beyond the first resonance, and this is plotted in (fig. 3.2). There, we see that the semiclassical and numerical results still agree qualitatively, though as expected there will be greater departure at larger biases. As we remarked earlier, in the $X_1 = 0$ case we don’t see the expected divergence at $\varepsilon \approx \varepsilon_{res,1}$, $3\varepsilon_{res,1}$, ... because for the $\Delta m = 2$ transitions these
odd-numbered resonances are skipped over.

Figure 3.2: Same as that in (fig. 3.1), but computed for biases beyond several resonances.

Next, we run the same routine but for the experimentally more relevant case of non-zero $\gamma$. Here we took $\gamma = -0.0615$, the parameter relevant for Fe8. The value of $\alpha$ is left unchanged. Once again we see that we have good agreement for low values of the external bias (fig. 3.3), particularly if we rescale the semiclassical $\varepsilon$ dependence by the resonance value $\varepsilon_{\text{res},1}$. It is worth noting that a non-zero value of $\gamma$ increases the tunneling probability by almost 3 orders of magnitude.

Despite the fact that both methods agree, now we have a result that is purely numerical. Motivated by the previous $\gamma = 0$, $X_1 = 0$ closed form solution, one might ask if an approximation of the same form can be found for the present case. By fitting our result to a function of the form,

$$|f(\varepsilon)|^2 \equiv \frac{A\pi^2}{4} (\varepsilon/\varepsilon_0)^2 \csc\left(\frac{\pi}{2}(\varepsilon/\varepsilon_0)\right)^2, \quad (3.69)$$

we find that $A = |\mathcal{F}_2^m(0)|^2$, and,

$$\varepsilon_0 = 1.14, \quad (3.70)$$

for our values of Fe8 (fig. 3.4). A similar functional form is obtained for other randomly generated parameters of $\alpha$ and $\gamma$ as well. Such an approximation can be motivated from the discussion in (sec. 1.4) where it was shown that the $\gamma \neq 0$, $X_1 = 0$ instanton can be approximated by $s_3(\tau) \approx \tanh(\Omega(0)\tau)$; but we cannot
directly import the $\gamma = 0, X_1 = 0$ result, since in the present case it will not be true that $\cosh(2\varphi)$ is constant.

![Figure 3.3: Comparison of the numerical result for $|F^m_2|^2$ (in black dotted) and the corresponding semiclassical result (in red), as well as a rescaled fit (in grey), of the case with non-zero $\gamma$.](image)

Finally, we look at the case for $\gamma = 0$ and $X_1 \neq 0$ (fig. 3.5). Again for small values of $X_1$ we see that the results agree. In particular, we recover the resonance at $\varepsilon \approx 1$ due to the $\Delta m = 1$ contributions. The values of $X_1$ used here is relatively small compared to the critical value of $2\alpha/\sqrt{1-\alpha^2} = 0.319$ for the Fe8 value of $\alpha = 0.157$; but for larger values of $X_1$, we must keep in mind that the numerical FGR procedure and the semiclassical calculation become essentially different, as explained in (sec. 3.3.2).

It is interesting to note that as we increase $X_1$, the values at low bias decrease. This is again a reflection of the fact that for integer spin the zero-field tunneling splitting is at its maximal value, and as we increase $X_1$ the tunnel splitting will start decreasing, until we reach the first diabolical point.

### 3.4 Zero-Temperature, Low-Bias Influence Functional

For practical purposes it is enough to look at just the one-phonon, $\beta \to \infty$ result; but for low bias, it is worthwhile to extend the integral to all phonons. We should note that here, “all-phonons” is still in the context of assuming that the interaction is linear in the strain; it is not the same as a multi-phonon process that could arise from including, say, terms quadratic in the strain. From the above considerations in section
3.3.1, we see that we can always write the dissipative term in the influence functional as,

\[ Q_{\text{em}} = \eta \int_0^\infty d\omega \omega^3 e^{i\omega(u_+ - u_-)} F_{\text{em}}(\omega, \eta | p_+, p_-), \quad (3.71) \]

where we have,

\[ F_{\text{em}} = \int \int d\tau d\tau' e^{i\omega(\tau - \tau')} \left\{ N_1(\tau, \tau', \eta | p_+, p_-) + N_2(\tau, \tau', \eta | p_+, p_-) \right\}, \quad (3.72) \]

since the tunneling epoch \( \tau_+ \) and \( \tau_- \) can be shifted outside of the integral by a translation of variables. Here we have included the dependence of \( \eta \) explicitly, since once we are beyond the \( O(\eta) \) approximation the semiclassical trajectory itself must be modified to take into account the fact that in general the equations of motion depend on \( \eta \). The golden-rule result can be given, after defining \( u \equiv u_+ - u_- \) and taking the limit of \( T \to \infty \), that,

\[ P \sim TN_0^{-2} \sum_{p_+} \sum_{p_-} F^2 e^{i\delta_0 + R(\eta | p_+) + i\delta_0 + R(\eta | p_-)} \int_{-\infty}^\infty du e^{i\epsilon u} \exp \{ Q_{\text{em}}[u, \eta | p_+, p_-] \}. \quad (3.73) \]

Let us comment briefly on the meaning of this integral. If we were to try to evaluate \( Q_{\text{em}}[u, \eta | p_+, p_-] \) first, we would arrive at an ill-defined, possibly divergent integral. But just as in the one-phonon case where
the bias provides an external cutoff, in the multiphonon case it suffices to carry out each integral only up to a cutoff that is on the order of \( \varepsilon \), so that for small enough \( \varepsilon \) we never reach the divergence. Explicitly, if we expand out the exponential in powers of \( \eta \) we will find the integral to be of the form,

\[
\mathcal{P} \sim \int_{-\infty}^{\infty} du e^{i\varepsilon u} \sum_{n=0}^{\infty} \frac{\eta^n}{n!} \left\{ \prod_{k=1}^{n} \int_{0}^{\infty} d\omega_k \omega_k^3 F_{\text{em}}(\omega_k, \eta) \right\} \times e^{i\sum_{k=1}^{n} \omega_k},
\]

\[
= \sum_{n=0}^{\infty} \frac{\eta^n}{n!} \left\{ \prod_{k=1}^{n} \int_{0}^{\infty} d\omega_k \omega_k^3 F_{\text{em}}(\omega_k, \eta) \right\} \times \int_{-\infty}^{\infty} du e^{i\varepsilon u + \sum_{k=1}^{n} \omega_k}, \tag{3.74}
\]

so that by energy conservation, none of the \( \omega_k \)'s in each integral may exceed \( -\varepsilon \). As such, it is permissible to replace the \( \omega \) region of integration by any interval \([0, \Lambda]\) such that \( -\varepsilon < \Lambda \), and it is in this sense that the integral exists. In practice, one could introduce an artificial cutoff function to make the integral converge, and then slowly relax the cutoff.

The closed form of the integrals are difficult to obtain in general, but in the limit of low bias, one could
more usefully obtain an expansion in terms of \( \varepsilon \). To illustrate, we start with,

\[
I_{\text{em}}(c) \equiv \int_{-\infty}^{\infty} du e^{i\varepsilon u} \exp \left\{ \eta \int_{0}^{\infty} d\omega \omega^3 F_{\text{em}}(\omega, \eta) e^{i\omega u e^{-c\omega}} \right\}, \tag{3.75}
\]

where \( c > 0 \) to assist with convergence, and will eventually be taken to \( 0^+ \). Continuing, we make the change of variables \( x \equiv \varepsilon u \) and \( \nu \equiv \omega/\varepsilon \), leading us to,

\[
I_{\text{em}}(c) = \frac{1}{\varepsilon} \int_{-\infty}^{\infty} dx e^{ix} \exp \left\{ \eta \varepsilon^4 \int_{0}^{\infty/\varepsilon} d\nu \nu^3 F_{\text{em}}(\varepsilon \nu, \eta) e^{i(x-\varepsilon\nu)} \right\}. \tag{3.76}
\]

(The “\( \sim \)” in the second line of (eq. 3.76) indicates equivalence in the asymptotic sense only, which arises from bringing the summation of the Taylor expansion outside of the integral). The lowest non-vanishing order of the exponential is \( \varepsilon^4 \), and after restoring the original variables we find,

\[
\exp \{ Q_{\text{em}} \} \sim \exp \left\{ \frac{6\eta F_{\text{em}}(0, \eta)}{(u + i0^+)^4} \right\}. \tag{3.77}
\]

This gives the influence functional in the low-bias limit. As a check we show that we recover the one-phonon result for the \( \gamma = 0, X_1 = 0 \) instanton. In that case we have \( F_{\text{em}}(0) = 4B_2 \). Expanding \( \exp \{ Q_{\text{em}} \} \) to first order in \( \eta \), the transition probability reads

\[
\mathcal{P} \sim \frac{\Delta^2}{4} T \times 24\eta B_2 \int_{-\infty}^{\infty} du e^{i\varepsilon u} \left( u + i0^+ \right)^4. \tag{3.78}
\]

Utilizing Jordan’s lemma, for \( \varepsilon < 0 \) we can close the contour in the lower complex half-plane, enclosing the pole at \( u = -i0^+ \). Taking the residue of the fourth-order gives us \( \mathcal{P} = \frac{\Delta^2}{4} T \times 8\pi\eta B_2(-\varepsilon)^3 \). For \( \varepsilon > 0 \), we close the contour in the upper-half plane, thus avoiding the pole and yielding the expected result of 0.

The advantage of an expression like (eq. 3.77) is that it may be incorporate into models with other environmental baths, such as that of nuclear spins [42]. In general, the total influence function is the product of the influence functions from each individual environment. Returning to the case of only phonons, we have the result for small \( \eta \), low \( \varepsilon \), and zero temperature, that the one-instanton golden-rule transition probability goes like

\[
\mathcal{P} \approx \frac{2\pi T \Delta^2}{4} \Theta(-\varepsilon) \times \sum_{n=1} \frac{(6\eta F_{\text{em}}(0, \eta))^n}{n!(4n-1)!} (-\varepsilon)^{4n-1}, \tag{3.79}
\]

where \( \Delta \) is the renormalized tunnel splitting, which we discuss in the next section. That the above series
converges can be verified by the ratio test.

### 3.4.1 Renormalized Tunnel Splitting

Recall that the phonon bath will act to renormalize the tunnel splitting via the $R$ factors defined in (eq. 3.22). This is completely analogous to the “Adiabatic Renormalization” discussed in the literature [4,6,17,21], addressing the idea that the high-frequencies oscillators will track the spin almost instantaneously, and thus giving it an effective mass. A crude but enlightening calculation [21] shows that the renormalization factor is approximated by,

$$
\tilde{\Delta} \sim \Delta \times \exp \left\{ -A \int_{\omega_c}^{\omega_i} d\omega \frac{J(\omega)}{\omega^2} \right\}, \tag{3.80}
$$

where the term in the exponential is often called the Franck-Condon factor. Here, $\omega_c$ is a lower frequency cutoff (the phonons below this frequency are no longer considered "fast"), and $\omega_i$ is an upper frequency cutoff given by the instanton width. For ohmic ($J(\omega) \sim \omega$) and subohmic ($J(\omega) \sim \omega^s, s < 1$) baths the lower cutoff $\omega_c$ is crucial to understanding the infrared divergence (and is important in showing why, generically, the infrared divergent subohmic baths yield incoherent transitions — the tunneling element having been renormalized to zero — while the logarithmically divergent ohmic bath teeters on the borderline of incoherent and coherent, depending on the coupling strength). Fortunately for us, $J(\omega) \sim \omega^3$ (superohmic) so the divergence comes in not at the lower limit, but rather at the upper (as we’ve already encountered in previous calculations). In that case the upper cutoff is generically provided by the characteristic instanton frequency $\omega_i, (\sim 1$ in our units), and we show how this is borne out in the following calculations. As before we restrict our attention to the zero-temperature case.

As an illustration we consider again the $\gamma = 0, X_1 = 0$ instanton solutions, (i.e. working with the $O(\eta^1)$ approximation) in order to make some headway analytically. The integrals of interest here are $\int_0^\infty d\omega \omega^3 B_1(\omega)$ and $\int_0^\infty d\omega \omega^3 B_2(\omega)$, where

$$
B_1(\omega) \equiv \int d\tau d\tau' \left\{ e^{-\omega|\tau-\tau'|} - \frac{2}{\omega} \delta(\tau - \tau') + \frac{2}{\omega^3} \frac{\partial}{\partial \tau} \frac{\partial}{\partial \tau'} \delta(\tau - \tau') \right\} \text{sech}(\tau) \tanh(\tau) \text{sech}(\tau') \tanh(\tau'),
$$

$$
= -2\omega^2 \psi^{(1)}((\omega + 1)/2) + 4\omega - \frac{4}{3\omega} + \frac{28}{15\omega^3}, \tag{3.81}
$$

and,

$$
B_2(\omega) \equiv \int d\tau d\tau' \left\{ e^{-\omega|\tau-\tau'|} - \frac{2}{\omega} \delta(\tau - \tau') + \frac{2}{\omega^3} \frac{\partial}{\partial \tau} \frac{\partial}{\partial \tau'} \delta(\tau - \tau') \right\} \text{sech}^2(\tau) \text{sech}^2(\tau'),
$$

$$
= 2\omega^2 \psi^{(1)}(\omega/2) - 4\omega - 4 - \frac{8}{3\omega} + \frac{32}{15\omega^3}. \tag{3.82}
$$
Note that the $O(\omega^{-1})$ and $O(\omega^{-3})$ terms in the above equations are precisely the contributions from the delta function and its derivatives, the latter which we needed to add as an “additional counterterm” (see. D). Here, $\psi^{(1)}$ is the order-1 Polygamma function, $\psi^{(1)}(x) = \frac{d^2}{dx^2} \Gamma(x)$. These integrals converge to a finite number, and so the $\Delta$ does not get renormalized down to zero.

3.5 Discussion and Application

Let us see how well our calculations compare with previous results. In [32] the authors are concerned entirely with the case $E = 0$ (which is more relevant to Mn12 systems). Furthermore they work with $X_1 = 0$, and they also assume that the material is isotropic, so that there is no distinction between $c_L$ and $c_T$. Lastly, they assume that the spin-phonon interaction is of the form,

$$V = \sum_{\mu} \lambda_\mu (i F_\mu (\mathcal{J}) a_\mu - i F_\mu (\mathcal{J})^\dagger a_\mu^\dagger)$$

(3.83)

where due to their assumption of $E = 0$, at low bias any $\Delta m = 1, 2, 3$ terms of $F$ will not contribute, so they take the coupling to be

$$F_\mu = g_{1,\mu} J_4^4 + g_{2,\mu} J_2^4$$

(3.84)

In their calculations, the authors do not employ the spin states $|j, m\rangle$, but rather the states $|j, m^*\rangle$, which are linear combinations of the exact eigenstates of the pure spin Hamiltonian such that the state is localized in one well or the other. The cases of interest are $|j, \pm j^*\rangle$, formed from the the two lowest lying eigenstates, and since the overlap with $|j, \pm j^*\rangle$ and the coherent states $|\tilde{z}_\pm\rangle$ is very large, we expect our semiclassical result to work very well.

Without re-deriving the entire framework, the comparison essentially distills to the computation of the element

$$\langle j, +j^* | J_4^4 | j, -j^* \rangle \equiv (2j)(2j-1)(2j-2)(2j-3) \langle j, +j^* | S_+^4 | j, -j^* \rangle,$$

(3.85)

For our high-order numerical perturbation, this entails summing over all transition paths involving only the $\mathcal{H}_4$ and one $\mathcal{S}_+$, while for the semiclassical result we need to find the corresponding instanton and calculate the integral of $(s_1 + is_2)^4$ along the instanton, weighted by the splitting. Finally, it is not difficult to exactly diagonalize (numerically) the Hamiltonian and compute the state $|j, \pm j^*\rangle$, and provides an additional benchmark.

We tabulate our results for $\langle j, +j^* | J_4^4 | j, -j^* \rangle$ in (tab. 3.2), at zero bias, for increasing values of $j$. We find good agreement between all results. In particular, the Politi’s numbers were calculated using equation
Table 3.2: Results for \( \langle j, +j^* \mid J^4 \mid j, -j^* \rangle \), computed using \( C/D = -9.93 \times 10^{-5} \) and \( \varepsilon = 0 \). Politi’s numbers were calculated using equation 19 of [32]. An even closer agreement can be had if the result is multiplied by a prefactor of \( 256/\pi \varepsilon^4 \).

In [11] on the other hand, the transition rate was obtained by doing a second order Fermi golden rule calculation taking only the \( m = \pm (j - 1) \) states are intermediates, and using experimental data to obtain the tunneling amplitudes \( \Delta_{j-j+1} \) and \( \Delta_{-j+1} \rightarrow -j \). This is like the high-order perturbative calculation of the present paper, except that \( \mathcal{V} \) is restricted to act at either the first or last step of the available paths. At low \( \varepsilon \) these results are consistent with our present calculation, but again it fails to capture the behavior in \( \varepsilon \) past \( \varepsilon^3 \).

We now apply our calculations specifically to Fe8. Recall that the experimentally deduced parameters are \( j = 10 \), \( D = 0.292 \text{K} \), \( E/D = 0.157 \), and \( C/D = -9.93 \times 10^{-5} \). This gives us \( \Omega_0 = 7.17 \times 10^{11} \text{s}^{-1} \). For the spin-phonon interaction, we take \( \Lambda = 0.25 \text{K} \) as an estimate for the coupling, and [16, 47] \( \rho = 1.92 \text{g/cm}^3 \) which, along with a unit cell volume of 1956 \( \text{Å}^3 \) and Debye temperature of \( \Theta_D = 33 \text{K} \) implies an average sound speed of \( c = 1.4 \times 10^5 \text{cm/s} \). The speed of sound of similar materials is on the order of \( 10^6 \text{cm/s} \), and typically \( c_L \) is at least twice as large as \( c_T \). Since the speeds of sound occurs to the inverse fifth power, the \( c_T \) contribution dominates the \( c_L \) contribution (unfortunately it also contributes the largest source of error to the calculation). Using \( c_T = 10^5 \text{cm/s} \) and \( c_L = 2 \times 10^5 \text{cm/s} \) as representative measurements, we have,

\[
\eta' \left( \frac{c_L}{c_T} \right)^5 = 5.8 \times 10^{-8}, \quad \eta' \left( \frac{c_T}{c_L} \right)^5 = 1.8 \times 10^{-6}. \tag{3.86}
\]

In the magnetization and demagnetization experiments of interest [35, 45] the Fe8 system is held at zero transverse field, so the relevant situation is the one calculated in 3.3.1. At low bias the scale is set by the value of \( |\mathcal{F}_2^{\text{em}}|^2 \) at \( \varepsilon = 0 \), and this number is

\[
|\mathcal{F}_2^{\text{em}}(0)|^2 = 1.30 \times 10^{-16}, \tag{3.87}
\]

The low bias tunneling rate for \( m = -j \rightarrow m = +j \) is therefore given by \( \Gamma(\varepsilon) \approx \Gamma_0 \times (-\varepsilon)^3/(1 - e^{+\beta \varepsilon}) \),

<table>
<thead>
<tr>
<th>( j )</th>
<th>Semiclassical</th>
<th>High-Order Perturbation</th>
<th>Politi (eq. 19)</th>
<th>Exact Diagonalization</th>
</tr>
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<tbody>
<tr>
<td>6</td>
<td>( 1.914 \times 10^{-4} )</td>
<td>( 1.914 \times 10^{-4} )</td>
<td>( 1.413 \times 10^{-4} )</td>
<td>( 1.915 \times 10^{-4} )</td>
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<tr>
<td>8</td>
<td>( 3.088 \times 10^{-7} )</td>
<td>( 3.088 \times 10^{-7} )</td>
<td>( 2.225 \times 10^{-7} )</td>
<td>( 3.089 \times 10^{-7} )</td>
</tr>
<tr>
<td>10</td>
<td>( 9.817 \times 10^{-10} )</td>
<td>( 9.817 \times 10^{-10} )</td>
<td>( 6.972 \times 10^{-10} )</td>
<td>( 9.825 \times 10^{-10} )</td>
</tr>
<tr>
<td>12</td>
<td>( 5.66 \times 10^{-12} )</td>
<td>( 5.66 \times 10^{-12} )</td>
<td>( 3.98 \times 10^{-12} )</td>
<td>( 5.67 \times 10^{-12} )</td>
</tr>
</tbody>
</table>
where
\[
\Gamma_0 \equiv 2\pi \Omega_0 |\mathcal{F}_2^m(0)|^2 (8\eta(\frac{c}{c_x})^5 + 12\eta(\frac{c}{c_T})^5),
\]
\[= 1.32 \times 10^{-8}s^{-1}, \] (3.88)

which is woefully small compared to the timescale of the magnetization experiments (on the order of $10^3$s).
Therefore based on current estimates it seems an unlikely candidate for energy relaxation, despite being the simplest conceivable mechanism. To get comparable numbers, the speed of sound would need to be smaller by several orders of magnitude.

On the other hand, we have demonstrated the success of the semiclassical calculation, which is more physically intuitive and less computationally intensive than the higher-order perturbative methods, and was able capture the $\varepsilon$ dependence past the $\varepsilon^3$ behavior typically quoted from simple dimensional analysis. In particular, we were able to arrive at a closed-form solution for the $\gamma = 0$, $X_1 = 0$ case, and an approximate closed-form solution for the $\gamma \neq 0$, $X_1 = 0$ case. Thus we are optimistic about the success of instanton methods.
Chapter 4

Kinetic Equation of Magnetization

At low temperatures the molecular magnet can be modeled as system of classical Ising-like spins, interacting via dipolar coupling and placed in a constant external field. The magnetization dynamics will be analyzed both for simple-cubic and triclinic lattice geometries, and to do so, a set of kinetic equations for the spin distribution will be developed and solved numerically. It is found that the power law behavior for magnetization is not universal; rather, the exponent depends both on lattice geometry and external field strength. It is also found that phonoemissive transitions are not likely to be a contribution factor to the initial power-law behavior.

4.1 Introduction

Magnetic solids comprised of single molecular magnets, such as Fe8, can exhibit complicated magnetization behavior at low temperature, where the quantum mechanical nature of the molecular magnet spin is manifest. Of considerable interest is the initial time-dependence of the magnetization, and experiments [38,45] reveal that in Fe8, the magnetization behaves as,

\[ m(t) - m(0) \propto t^{1/2}, \quad (4.1) \]

for some short time interval, after which it switches to asymptotic behavior, limiting onto its equilibrium value \( m(\infty) \). The origin of the non-exponential behavior is attributed to the so-called “window-mechanism”, where the dynamics of a given spin is frozen unless the local bias experienced by the spin falls within a narrow region, \( \varepsilon \in [-W,W] \), called the reversible region. In demagnetization experiments, where the sample is allowed to relax at low temperatures from an initially saturated state, the 1/2 power was was explained by [34] through heuristic arguments. Later, [43] arrives at the same result by solving a set of rate equations for total spin population within the reversible region.

In both the above arguments, however, it was necessary to assume that the initial magnetization is close to saturation. Therefore it cannot explain the same power behavior that arises in magnetization
experiments, where an initially demagnetized sample is placed in an external field. Furthermore, it is a topic of controversy whether or not the $1/2$ exponent is truly universal, or if it is dependent on other factors such as lattice geometry and initial conditions [8].

The previous sections dealt with systems comprised of a single spin $J$ and environmental baths. This was necessary to understand the dynamics of an individual spin. Now we turn our attention to the magnetization of a solid block of such material, and so it is necessary to address the dynamics of many interacting spins. In the following it will be sufficient to model the crystal as a lattice of classical up/down spins, in what is known as a “long-ranged Glauber model”, where a spin $S$ at a given site has a flipping probability per unit time that is a function of net local bias $E$ experienced at the site, i.e.,

$$P(S(t + \delta t) = -s, E(t + \delta t) = \varepsilon | S(t) = s, E(t) = \varepsilon) \approx \Gamma_{ss}(\varepsilon)\delta t. \quad (4.2)$$

Note that despite the model being a classical treatment of the system, this transition rate incorporates the previously calculated quantum effects, such as tunneling in the presence of an environmental factors. Next, the Hamiltonian $\mathcal{H}$ and the local bias $E_a$ at site $a$ are given by,

$$\mathcal{H} = \sum_a E_a S_a, \quad E_a = \sum_{b \neq a} K_{ab} S_b + \varepsilon_{ext}, \quad (4.3)$$

where $K_{ab}$ is the dipole-dipole coupling between spin $S_a$ located at $r_a = (x_a, y_a, z_a)$, and spin $S_b$ located at $r_b = (x_b, y_b, z_b)$,

$$K_{ab} \equiv \frac{j^2 \mu_0 (g \mu_B)^2}{4\pi} \frac{1}{r_{ab}^3} (1 - 3(\hat{z} \cdot \hat{r}_{ab})^2) \equiv 2E_{dm} \frac{v}{r_{ab}^3} (1 - 3(\hat{z} \cdot \hat{r}_{ab})^2), \quad (4.4)$$

with $r_{ab} \equiv r_a - r_b$ and $r = |r|$. Note that the lattice structure of Fe8 is triclinic [47] (see fig. 4.1 for crystal parameters). Another commonly employed simplification is to treat the lattice as simple-cubic, and in this chapter we will treat both cases.

In (eq. 4.4), $E_{dm} \equiv (j^2 \mu_0 g^2 \mu_B^2)/(8\pi v)$ defines a characteristic dipolar coupling energy, and $v$ is the volume of the unit cell, which is also used to define a characteristic length $l = v^{1/3}$. In $E_{dm}$, recall that for Fe8 the Landé g-factor is $g \approx 2$, and $j = 10$. Finally, $\varepsilon_{ext}$ is the external bias due to the applied field,

$$\varepsilon_{ext} = -2jg\mu_B H_{z,ext}, \quad (4.5)$$

which is assumed uniform.
4.2 Transition Rate for Combined Environments

From [42], a suitable description for the combined nuclear and molecular spin environments can be given by the golden-rule influence functional,

\[
\exp \{ Q_{\text{nuc}}(u_1, u_2) \} \exp \{ Q_{\text{mm}}(u_1, u_2) \} = e^{i\varepsilon(u_1 - u_2)} e^{-\gamma_m |u_1 - u_2|} e^{-\frac{1}{2} W^2(u_1 - u_2)^2},
\]

(4.6)

from which the transition rate, in the limit of \( W \gg \Delta \), yields,

\[
\Gamma_{+-}(\varepsilon) = \Gamma_{-+}(\varepsilon) = \sqrt{\frac{2\pi}{4}} \frac{\Delta^2}{W} e^{-\frac{1}{2} (\varepsilon^2 / W^2)}.
\]

(4.7)

A critical characteristic of (eq. 4.7) is that it does not take into account the asymmetry in bias, i.e. that the transition rate from the metastable to the stable well is precisely the same as that from the stable to the metastable. Thus this can only be regarded as a “high-temperature” result, where the temperature of the experiment is high compared to the characteristic temperature of the bath. The magnetization and demagnetization experiments carried out are typically in the \( \sim 40\text{mK} \) range [45], while the bath energy scale
W is around 1 – 10 mK, so result (eq. 4.7) is a good approximation.

By comparison, the phonon bath energies are excited at the scale of the local bias, which is typically around 0.1 – 1 K and therefore much greater than the experimental temperature. In other words, when incorporating the phonons we must use a “low-temperature” approximation, and in that limit there will be a dramatic asymmetry between Γ₊₋ and Γ₋₊, differing in ratio by a Boltzmann factor. Including the phonon influence functional calculated previously (ch. 3), the total transition rate reads,

\[ \Gamma_{\pm\pm}(\varepsilon) = \frac{\Delta^2}{4T} \int_{-T/2}^{T/2} \int_{-T/2}^{T/2} du_1 du_2 e^{i(u_1-u_2)} e^{-\gamma_\mu \Delta |u_1-u_2|} e^{-\frac{1}{2} W^2(u_1-u_2)^2} e^Q_{\text{em}}(u_1,u_2)Q^{\text{ab}}(u_1,u_2), \]

where in the second line of (eq. 4.8) we have expanded w.r.t. to η, i.e. taken the one-phonon limit. We have also assumed, for simplicity, that the transverse field \( X_1 = 0 \), so the summation w.r.t. the winding \( p \) can be suppressed. In this case the \( Q \) functions read,

\[ Q_{\text{em}}(u_1,u_2) = \eta \int_0^\infty \frac{d\omega \omega^3}{1-e^{-\beta\omega}} e^{i\omega(u_1-u_2)} \int d\omega' e^{+i\omega(u-u')} N_2(u,u'), \]
\[ Q^{\text{ab}}(u_1,u_2) = \int_0^\infty \frac{d\omega \omega^3}{1-e^{-\beta\omega}} e^{-i\omega(u_1-u_2)} \int d\omega' e^{-i\omega(u-u')} N_2(u,u'). \]

Again for \( \Delta \ll W \), the integral over \( u_1 \) and \( u_2 \) can be carried out explicitly, and in the limit of \( T \to \infty \) we arrive at the following expression for the phonoemissive transition rate,

\[ \Gamma^{\text{ph,em}}_{\pm\pm}(\varepsilon) = \frac{\eta \Delta^2}{4} \int_0^\infty \frac{d\omega \omega^3}{1-e^{-\beta\omega}} \frac{\sqrt{2\pi} W}{\varepsilon} e^{-\frac{1}{2}(\varepsilon+\omega)^2/W^2} \int d\omega' e^{i\omega(u-u')} N_2(u,u'), \]

and similarly for the phono-absorptive rate. Now in the limit that \( W \ll \varepsilon \), one can expand the above integral in powers of \( W \), and to lowest order this gives,

\[ \Gamma^{\text{ph,em}}_{\pm\pm}(\varepsilon) = 2\pi \eta \frac{\Delta^2}{4} \frac{(-\varepsilon)^3 \Theta(-\varepsilon)}{1-e^{+\varepsilon\beta}} \int d\omega' e^{-i\varepsilon(u-u')} N_2(u,u') + \eta \times O(W), \]

which is precisely just the phonoemissive tunneling rate. Therefore, to obtain the total transition rate we simply need to sum the \( \Gamma \)'s of each environment.

To summarize, we write the transition rates explicitly. Note that for a single molecular magnet in isolation the relevant energy scale is given by \( \hbar \Omega_0 \), but for a lattice of such spins interacting via dipole-dipole coupling,
a more convenient scale is given by $E_{dm}$. In these units we have,

$$
\Gamma_{\text{nuc+mm}}(\varepsilon) = \frac{\Gamma_{0}^{\text{nuc+mm}}}{\sqrt{2\pi w^2}} \exp \{-\frac{1}{2}(\varepsilon/w)^2\}, \quad \Gamma_{\text{mm}}^{0} = \frac{2\pi}{\hbar E_{dm}} \frac{(\Delta / E_{dm})^2}{4},
$$

(4.12)

where $w \equiv W/E_{dm}$. For the phonon-mediated rates, we have,

$$
\Gamma_{+}^{\text{ph,em}}(\varepsilon) = \Gamma_{0}^{\text{ph}} \frac{(-\varepsilon)^3 H(-\varepsilon)}{1 - \exp \{\varepsilon/\theta\}} \phi(\varepsilon), \quad \Gamma_{-}^{\text{ph}}(\varepsilon) = \Gamma_{+}^{\text{ph,em}}(\varepsilon) + \Gamma_{+}^{\text{ph,ab}}(\varepsilon),
$$

(4.13)

where $H(x)$ is the Heaviside function, $\theta \equiv k_B \Theta / E_{dm}$ is the scaled temperature, $\tilde{\varepsilon}_0 \equiv \varepsilon \hbar \Omega_0 / E_{dm}$ is the scaling factor, and,

$$
\phi(\varepsilon) = \frac{\pi}{4} (\varepsilon / \tilde{\varepsilon}_0)^2 \csc^2\left(\frac{\pi}{2} (\varepsilon / \tilde{\varepsilon}_0)\right),
\Gamma_{0}^{\text{ph}} = \frac{2\pi \eta \Omega_0}{\hbar^2} |\mathcal{F}_2^{\text{em}}(0)|^2 \left(8\left(\frac{\varepsilon}{\eta T}\right)^5 + 12\left(\frac{\varepsilon}{\eta T}\right)^5 \left(\frac{E_{dm}}{\hbar \Omega_0}\right)^3\right).
$$

(4.14)

### 4.3 Kinetic Equation of Magnetization

Regardless of whatever the transition rate $\Gamma_{\sigma \bar{\sigma}}$ our theory furnishes, this rate can be plugged into the kinetic equations, a set of equations describing the evolution of the bias distributions, to yield the magnetization at later times. The development of the kinetic equation follows closely the ideas outlined in [22], and an alternative derivation starting from the Liouville equation is provided in the appendix (sec. G). Defining $f(s, \varepsilon; t)$ as the probability density of a spin with orientation $s$ experiencing a total local bias $\varepsilon$, the equations governing the distribution evolution is,

$$
\frac{\partial}{\partial t} f(s, \varepsilon) = -\Gamma_{ss}(\varepsilon)f(s, \varepsilon) + \Gamma_{s^{'}}(\varepsilon)f(s^{'}, \varepsilon) + \frac{d\varepsilon}{dt} \frac{\partial}{\partial \varepsilon} f(s, \varepsilon)
$$

$$
= \sum_{s^{'}} \int d\varepsilon' \mathcal{G}_{s^{'}}(\varepsilon')f(s^{'}, \varepsilon') \int d\varepsilon'' \sum_{k \neq i} \frac{1}{2} \{\delta(\frac{1}{2}(\varepsilon'' - \varepsilon)s' - K_{ik}) - \delta(\frac{1}{2}(\varepsilon - \varepsilon''))\}f(s, \varepsilon''),
$$

(4.15)

where $i$ labels some “central” spin of interest. For sufficiently large sample size the location of this central spin is irrelevant, so the label $i$ does not matter. Note that in deriving (eq. 4.15) we have made the closure assumption that the two-point distribution factorize simply into the product of one-point distributions.

Continuing, let us define the density of coupling $g(K)$ and the regularized density $g_R$,

$$
g(K) \equiv \sum_{j \neq 0} \delta(K - K_{0j}), \quad g_R(K) \equiv \sum_{j \neq 0} \{\delta(K - K_{0j}) - \delta(K)\}.
$$

(4.16)

Intuitively, $g(K)\delta K$ counts how many sites in the lattice have a coupling strength (relative to the central
site \( i = 0 \) between \( K \) and \( K + \delta K \). The regularized coupling \( g_R \) subtracts off the small \( K \) divergence in \( g(K) \), which typically goes as \( 1/K^2 \) [42]. We can think of this divergence as arising from sites located very far away from the central site. In simulations, one constructs a lattice of finite spatial extent, i.e. some ball of a given radius. The sum over \( \delta(K) \) then simply counts the number of sites within the ball, less the central site. The advantage of working with \( g_R \) is that, by making the radius of the ball larger one essentially only corrects for the values of \( g(\varepsilon) \) at \( \varepsilon = 0 \); but this same correction is subtracted out by the \( \delta \)-function in \( g_R \). Therefore, for a sufficiently large radius (about 30 sites or so) the computed \( g_R \) is essentially the same as that for an infinite system. Thus all information about the coupling is encapsulated within the density function \( g_R \), and the kinetic equation reads,

\[
\frac{\partial}{\partial t} f(s, \varepsilon) - \Gamma_{s\bar{s}}(\varepsilon) f(s, \varepsilon) + \Gamma_{\bar{s}s}(\varepsilon) f(s, \varepsilon) + \frac{d\varepsilon}{dt} \frac{\partial}{\partial \varepsilon} f(s, \varepsilon) = \sum_{s'} \int d\varepsilon' \Gamma_{s's'}(\varepsilon') f(s', \varepsilon') \int d\varepsilon'' \frac{1}{2} g_R(\frac{1}{2}(\varepsilon'' - \varepsilon)s') f(s, \varepsilon'').
\]

The terms on the LHS of (eq. 4.17) can be likened to the diffusion and force terms of the Boltzmann equation for a classical gas, and the RHS is analogous to the collision term.

The procedure for the numerical solution of these equations is described in the appendix (sec. H). In general the solution of the kinetic equation is significantly faster than a Monte-Carlo simulation of comparable system size, though this simplification comes at the cost of losing information about spin-spin correlations, i.e. approximating \( f(s_1, \varepsilon_1, s_2, \varepsilon_2) = f(s_1, \varepsilon_1) f(s_2, \varepsilon_2) \). Fortunately, spin-spin correlations are most significant between the closest neighbors, for which the potential change in bias on a target spin due to a neighboring spin’s flipping is large. In contrast, the spin-flip mechanism \( \Gamma_{s\bar{s}}(\varepsilon) \) dominates at low values of the bias \( \varepsilon \), the effect of which can only be due to those spins far away. Therefore, in neglecting the spin-spin correlations, we will eventually lose accuracy at large values of \( \varepsilon \) as we propagate the kinetic equations to longer times. Since we are only interested in the initial behavior of the magnetization, however, we are justified in truncating the kinetic equations at one-spin order.

### 4.4 Magnetization and Demagnetization Results

In this section we utilize the kinetic equations to solve for the magnetization and demagnetization dynamics of the Fe8 crystal. Throughout the section the following table of energy scales will be useful,

\[
E_{dm} = 6.37 \times 10^{-2} \text{K}, \quad \hbar\Omega_0 = 5.48 \text{K},
\]

\[
\Delta = 4.44 \times 10^{-8} \text{K}, \quad W \approx 10^{-2} \text{K},
\]

\[(4.18)\]
Figure 4.2: Histogram of the distribution of couplings, along with the function $g(K) = \frac{16\pi}{9\sqrt{3}}K^{-2}$, for a spherical cubic lattice (left) and Fe8 triclinic lattice (right). Small values of couplings correspond to far-away sites, for which the $1/K^2$ form applies well. At larger couplings the discrete nature of lattice comes into effect, and the histogram looks like delta-functions peaked at specific values. There the $1/K^2$ form becomes a poor description.

so that working in units of $E_{dm}$ we have $\hbar\Omega_0/E_{dm} = 85.87$ and $W/E_{dm} = 0.157$. We also have the following transition rates; working in the timescale,

$$\tau \equiv \frac{E_{dm}\hbar}{\pi\Delta^2} = 78.46\text{s},$$

(4.19)

the characteristic rate for the combined nuclear and dipolar environments is,

$$\Gamma_{0}^{dm} = \frac{1}{2}\tau^{-1} = 6.37 \times 10^{-3}\text{s}^{-1}.$$  

(4.20)

For the phonon-assisted transitions, due to the uncertainty in values of $c_L^5$ and $c_T^5$, we will let $\Gamma_0^{ph}$ range from $10^{-12}$ to $10^{-4}$ in units of $\tau^{-1}$. This corresponds approximately to letting the $c$’s vary by two orders of magnitude, starting from $c \approx 10^5\text{cm/s}$.

For both the simple-cubic and the Fe8 triclinic systems, we first create an extended lattice of $N \times N \times N$ sites along the crystal axes, within which we sculpt a sphere of radius $R$ (such that the sphere is completely enclosed within our extended lattice). Using this sphere we then calculate the density of couplings (see fig. 4.2). In this sense the system is analogous to Monte-Carlo simulations with open boundary conditions, whereas previous treatments [8] used periodic boundary conditions.
4.4.1 Demagnetization

First we look at demagnetization, for which a sample initially prepared to have a fully saturated magnetization, is allowed to relax at low temperature and zero field. In (fig. 4.3) we plot the evolution of the spin-up and spin-down bias distributions, for a spherical sample with simple cubic lattice configuration.

Initially all of the spins in the sample are pointed up; and since (it is known) that for such a geometry the dipole-dipole interactions yield a net sum of zero local field, the spin-up bias distribution is initially peaked at $\varepsilon = 0$ (assuming zero external field).

As we propagate our solutions we observe two primary effects. First we see the development of localized features at $\varepsilon = 0$, $\varepsilon = -4E_{\text{dm}}$, and $\varepsilon = 8E_{\text{dm}}$, especially at short times. The latter two values correspond to the change in bias from a spin flip due to a neighbor located along the $xy$ plane, and along the $z$ axis, respectively.

Additionally, we see that near $\varepsilon = 0$ the value of the up and down distributions tend toward each other, causing a drastic dip in the former and a peak in the latter. The width of these is on the order of $W$, reflecting the Gaussian in $\Gamma^{\text{nucl+mm}}(\varepsilon)$ (eqn. 4.7). The interval $\varepsilon \in [-W, W]$ is called the “reversible region” because, in absence of phonoemissive effects, a spin can only flip if its local bias is within this window. That they should approach each other can be seen if we define $\mu(\varepsilon) \equiv f_+(\varepsilon) - f_-(\varepsilon)$, the relative difference in population. Assuming that phonon effects are completely suppressed, the kinetic equation implies that

$$\frac{\partial}{\partial t} \mu(\varepsilon) = -2\Gamma(\varepsilon)\mu(\varepsilon) + O(f^2), \quad (4.21)$$

i.e. that differences in relative population get driven toward zero. The localized feature at $\varepsilon = 0$ is related to the phenomenon known as “hole-burning” which is observed in experiments, and is believed to the primary mechanism behind the square-root $t$ dependence.

Next, we look at the effect of phonons at low temperature, for a variety of strengths. The results are shown in (fig. 4.4). We see that short times (on the order of $1\tau$) the demagnetization curves behave as $\sqrt{t}$. At longer times, the effect of phonons causes the curves to diverge.

4.4.2 Magnetization

We turn our attention now to the magnetization experiments. To begin, let us describe the cooling protocol used to prepare the initial state of the sample. First the magnet is held at zero external field, and at a temperature $T = 2\text{K}$ that is high compared to the quantum-classical crossover temperature ($\approx 0.5\text{K}$ for Fe8), so that the system relaxes by thermal equilibration. After sufficiently long time, the system is rapidly
Figure 4.3: Evolution of the spin up (red) and spin down (blue) bias distributions for a spherical cubic lattice with initially saturated magnetization, using $\Gamma_0^{\text{mm}} = 0.5 \tau^{-1}$, $\Gamma_0^{\text{ph}} = 1.0 \times 10^{-4} \tau^{-1}$, and $W = 0.157 E_{\text{dm}}$, at $\beta E_{\text{dm}} = 1.592 (T = 40\text{mK})$. 
quenched to low temperature ($\approx 40\text{mK}$) so that the initial high-temperature spin configuration is effectively “frozen in”. Finally, an external longitudinal field is applied, and the dynamics of the magnetization is measured.

To prepare our initial state we first let our lattice evolve toward equilibrium via the metropolis algorithm, from an initial state of infinite temperature (i.e. each site is randomly spin up or down with probability $1/2$). In both cases we find that spin up and the spin down distribution are symmetric mirrors of each other about $\varepsilon = 0$. In particular, the difference in population between the spin up and spin down near the reversible region $\varepsilon \in [-W,W]$ is zero. Next, by applying an external bias both the spin up and the spin down distributions are translated by $\varepsilon_{\text{ext}}$, so that now there is a difference in population in the reversible region. Finally, because of this relative difference, the same mechanism responsible for the $\sqrt{t}$ behavior in the demagnetization case now produces a short-time power-law behavior in magnetization. See (fig. 4.5) for a demonstration of this scheme.

In (fig. 4.6) we look at a simple-cubic lattice, both for small phono-assisted transition rate $\Gamma_{0}^{\text{ph}} = 1.0 \times 10^{-12}\tau^{-1}$ and large phono-assisted rate $\Gamma_{0}^{\text{ph}} = 1.0 \times 10^{-4}\tau^{-1}$. When the phonon effects are small, we reproduce the $\sqrt{t}$ behavior in agreement with [8, 45]. By increasing the phonon effects, we see that 1) the initial exponent of the power law is modified, and 2) the final value of the magnetization is increased.

In (fig. 4.7) we rerun the kinetic equations for the Fe8 triclinic lattice. For large $\Gamma_{0}^{\text{ph}}$ we once again observe larger values of the final magnetization. At small $\Gamma_{0}^{\text{ph}}$, however we notice two additional curiosities:
Figure 4.5: Schematic of the cooling protocol. (a) The initial distribution at the infinite temperature limit (i.e. each spin is up or down with probability 1/2), so the distributions overlap. (b) Cooling down to equilibrium at 40mK. (c) External field is applied, causing a net shift in the distribution. Clock is started. (d) \( t = 0.15\tau \). Population in the reversible region start to converge. (e) Distribution at \( t = 1.05\tau \). (f) Distribution at \( t = 15\tau \). All simulations were run with \( \Gamma_0^{ph} = 1.0 \times 10^{-12}\tau^{-1} \) and \( \varepsilon_{ext} = 12.0E_{dm} \).
1) the initial exponent is no longer close to 0.5, but rather closer to 1.0; and 2) the timescale of magnetization is drastically increased. The latter may be explained as follows: rate of magnetization is related to the initial difference in population, $\delta f \equiv f(+,\varepsilon) - f(-,\varepsilon)$, in the reversible region (that is, $\varepsilon \in [W,-W]$). For the cubic lattice, $\delta f$ is about 2 orders of magnitude larger than that for the Fe8 triclinic lattice. To address both this small $\delta f$ as well as the former issue 1), we increase the values of the external bias so that the reversible region is far away the symmetric central Gaussian of the initial distribution (fig. 4.8). Now, at low $\Gamma_0^{\text{ph}}$ the initial power law behavior is more pronounced, and in particular we see that the exponent is strongly dependent on the value of the external bias. In particular, when then bias is large enough such that the population difference $\delta f$ is large, we once again recover the $\sqrt{t}$ exponent. The behavior for large $\Gamma_0^{\text{ph}}$ is qualitatively unchanged.

### 4.5 Discussion and Conclusion

It is found that the kinetic equation successfully reproduces known demagnetization behavior, consistent with previous results [22] as well as experiment. The novel application of the kinetic equations to magnetization, for the theoretical case of a simple cubic lattice, also reproduces the $\sqrt{t}$ power-law, consistent with previous work [8, 41]. In contrast to [41], however, we do not find the same power-law in all situations; rather, our result is more consistent with the findings of [8], who arrived at their conclusions via dynamic Monte-Carlo simulations. Ultimately the exponent of the power law is most sensitive to the initial population difference between the up and down spins within the reversible regime; and this is dependent both on the lattice geometry and the applied external bias.

Unfortunately, we were unable to pin down an exact exponent in the triclinic case. One reason could be that, unlike the demagnetization results where the initial distribution is sharply localized, here the initial magnetization is already very widely spread out, so it is possible that the incorporation of the two-site joint distribution is needed to obtain more precise results. One emphasis which must be made is that this imprecision is not due to finite-size effects. As explained in (sec. 4.3), all lattice information is contained in $g_R$, and going to larger system sizes only affects the values near $\varepsilon = 0$, which in $g_R$ remains unchanged.

Finally, it may be seen that, while changing the strength of the phonon effects (via tuning $\Gamma_0^{\text{ph}}$) does change the qualitative behavior of the initial power law, it does not do so in the expected way; that is, when $\Gamma_0^{\text{ph}}$ is large it fails to produce the power 0.5 for the simple-cubic case. This suggests that the role of phonons is not essential to the power law behavior of magnetization.
Figure 4.6: Magnetization $M/M_s$ vs time $t$ at $\beta E_{dm} = 1.592$ ($T = 40\text{mK}$) for various values of external bias, and for (top) $\Gamma_0^{ph} = 10^{-12}\tau^{-1}$ and (bottom) $\Gamma_0^{ph} = 10^{-4}$. Solid lines denote numerical kinetic equation solution, and dashed lines indicate the best fit to a power law.
Figure 4.7: Magnetization $M/M_s$ vs time $t$ at $\beta E_{dm} = 1.592$ ($T = 40\text{mK}$) for various values of external bias, and for (top) $\Gamma_0^{ph} = 10^{-12} \tau^{-1}$ and (bottom) $\Gamma_0^{ph} = 10^{-4} \tau^{-1}$. Solid lines denote numerical kinetic equation solution, and dashed lines indicate the best fit to a power law.
Fe8 Triclinic (using $\Gamma_0^{\text{ph}} = 1.0 \times 10^{-12} \tau^{-1}$)

Figure 4.8: Magnetization $M/M_s$ vs time $t$ at $\beta E_{\text{dm}} = 1.592$ ($T = 40$ mK) for various values of external bias, and for (top) $\Gamma_0^{\text{ph}} = 10^{-12} \tau^{-1}$ and (bottom) $\Gamma_0^{\text{ph}} = 10^{-4} \tau^{-1}$. Solid lines denote numerical kinetic equation solution, and dashed lines indicate the best fit to a power law.
Appendix A

Semiclassical Path Integral

In this section we briefly review the construction of the spin-coherent-state path integral, and outline how to obtain the equations of motion and ultimately the tunneling probability [12, 37].

The linchpin of the path integral is the over-completeness relation, which provides a starting point to semiclassics by furnishing a resolution of the identity in terms of an integral over phase space, in this case $S^2$ for spin,

$$1 = \frac{2j + 1}{4\pi} \int_{S^2} dA(z, \bar{z}) |\bar{z}\rangle \langle z|,$$  \hspace{1cm} (A.1)

where $j$ denotes that we are working in the spin-$j$ irreducible representation,

$$dA = \frac{2d\bar{z}dz}{i(1 + \bar{z}z)^2}$$  \hspace{1cm} (A.2)

is the area two-form on a sphere written in stereographic coordinates. The reason (eq. A.1) is called an over-completeness relation is that many of the points $z$ give overlapping contributions. (That this must be the case can be seen by comparing (eq. A.1) to the discrete version, $1 = \sum_{j=m=-j}^{j} |j, m\rangle \langle j, m|$.)

Using (eq. A.1), the next step is to perform the usual time-slicing procedure. Starting from a (possibly time-dependent) Hamiltonian $\mathcal{H}$, the propagator $U(t)$ is the solution to Schrödinger’s equation,

$$\frac{d}{dt} U(t) = -i\mathcal{H}(t) U(t), \hspace{1cm} U(0) \equiv 1.$$  \hspace{1cm} (A.3)

This solution may be written formally as the discretized limit of infinitesimal products,

$$U(t) = \lim_{N \to \infty} (1 - i\epsilon\mathcal{H}(t_N))(1 - i\epsilon\mathcal{H}(t_{N-1})) \cdots (1 - i\epsilon\mathcal{H}(t_1))(1 - i\epsilon\mathcal{H}(t_0)),$$  \hspace{1cm} (A.4)

where $\epsilon \equiv t/N$ and $t_k \equiv k\epsilon$. Between every such term $(1 - i\epsilon\mathcal{H}(t_k+1))$ and $(1 - i\epsilon\mathcal{H}(t_k))$, we can insert an over-completeness relation, integrated over the dummy variable $z_{k+1} \equiv z(t_{k+1})$. If we now define the
(unnormalized) propagator from $|\bar{z}_i\rangle$ to $|z_f\rangle$ as,

$$K(z_f, \bar{z}_i; T) \equiv (z_f|U(T)|\bar{z}_i), \quad (A.5)$$

then after performing the time-slicing we arrive at,

$$K(z_f, \bar{z}_i; T) = \lim_{N \to \infty} \prod_{l=1}^{N-1} \int_{S^2} \frac{2j+1}{4\pi} dA(z_l, \bar{z}_l) \times (1 + z(0)\bar{z}_i)^j(1 + \bar{z}(T)z_f)^j \prod_{k=0}^{N-1} (1 + iL_k), \quad (A.6)$$

where in the $N \to \infty$ limit we obtain,

$$1 + iL_k \equiv \langle z_{k+1} | (1 - i\mathcal{H}(t_k)) | \bar{z}_k \rangle \to \exp (iL_k), \quad (A.7)$$

and where,

$$iS[z, \bar{z}] \equiv \log \left\{ (1 + z(0)\bar{z}_i)^j(1 + \bar{z}(T)z_f)^j \prod_{k=0}^{N-1} (1 + iL_k) \right\}, \quad (A.8)$$

where,

$$\to j \log(1 + z(0)\bar{z}_i) + j \log(1 + \bar{z}(T)z_f) + \int_0^T dt \left\{ \frac{\bar{z}\dot{z} - \dot{\bar{z}}z}{1 + \bar{z}z} - ih(z, \bar{z}, t) \right\}. \quad (A.9)$$

Here, $h \equiv \langle z | \mathcal{H} | \bar{z} \rangle$ is the semiclassical Hamiltonian (or more technically the “Q-symbol” of $\mathcal{H}$).

The expression (eq. A.6) is still only formal, and in general it is difficult to find a closed-form solution. The advantage of recasting Schrödinger’s equation as a path integral, however, is that it becomes amenable to stationary phase approximations, especially in the large $j$ classical limit, which often still capture the essential behavior of the system. In the stationary phase approximation, one recognizes that the dominant contribution to the integral will be from critical trajectories $z_c(t)$, $\bar{z}_c(t)$ for which the action is stationary — in other words, satisfying,

$$\delta S[z_c(t), \bar{z}_c(t)] = 0. \quad (A.9)$$

Therefore, it is necessary only to include contributions about the critical trajectories $z_c$ up to Gaussian; that is, about each $z_c$ we expand

$$S = S[z_c, \bar{z}_c] + \frac{1}{2} \delta^2 S[z_c, \bar{z}_c], \quad (A.10)$$
and the approximate final amplitude as

\[ K \approx \sum_c \exp(iS[z_c, \bar{z}_c]) \int D(z, \bar{z}) \exp \left( \frac{i}{2} \delta^2 S[z_c, \bar{z}_c] \right), \tag{A.11} \]

where the subscript \( c \) labels the sum over semiclassical trajectories.

Taking the first variation of the action gives us,

\[ i \delta S = \int_0^T dt \delta z(t) \left\{ -2(1 + z \bar{z})^{-2} \frac{d \bar{z}}{dt} - i \frac{\partial h}{\partial \bar{z}} \right\} + \int_0^T dt \delta \bar{z}(t) \left\{ 2(1 + z \bar{z})^{-2} \frac{d z}{dt} - i \frac{\partial h}{\partial z} \right\} + \frac{2z(0)}{1 + \bar{z}(0)z(0)} \delta \bar{z}(0) + \frac{2\bar{z}(T)}{1 + \bar{z}(T)z(T)} \delta z(T), \tag{A.12} \]

from which we get the boundary conditions \( \delta \bar{z}(0) = 0, \delta z(T) = 0 \), and the equations of motion (eq. 1.18).

The brunt of the calculation is often borne by the second term,

\[ F_c = \int D(z, \bar{z}) \exp \left( \frac{i}{2} \delta^2 S[z_c, \bar{z}_c] \right), \tag{A.13} \]

called the Fluctuation Determinant, whose name comes from the fact that if we write out the second variation, we will find that,

\[ \frac{i}{2} \delta^2 S = -ij \int_0^T dt (1 + z_c(t)\bar{z}_c(t))^{-2} \left( \delta z(t) \quad \delta \bar{z}(t) \right) \begin{pmatrix} A - i \frac{d}{dt} & B \\ B & A + i \frac{d}{dt} \end{pmatrix} \begin{pmatrix} \delta z(t) \\ \delta \bar{z}(t) \end{pmatrix} \tag{A.14} \]

where we have defined,

\[ A = \frac{1}{2} \frac{\partial}{\partial z} \left( \frac{(1 + z \bar{z})^2}{2j} \frac{\partial h}{\partial \bar{z}} \right) + \frac{1}{2} \frac{\partial}{\partial \bar{z}} \left( \frac{(1 + z \bar{z})^2}{2j} \frac{\partial h}{\partial z} \right), \]

\[ B = \frac{\partial}{\partial z} \left( \frac{(1 + z \bar{z})^2}{2j} \frac{\partial h}{\partial \bar{z}} \right), \quad \bar{B} = \frac{\partial}{\partial \bar{z}} \left( \frac{(1 + z \bar{z})^2}{2j} \frac{\partial h}{\partial z} \right), \tag{A.15} \]

so that \( F_c \) takes the expression for the functional determinant of a linear operator. We omit the more subtle details of the calculation, which in particular addresses how to handle the zero mode that arises when dealing with the translational invariance of instantons [12], as well as the non-trivial appearance of an additional term called the Solari-Kochetov phase [37] that would not have been found by taking the naive continuum limit for the discretized path integral. Fortunately we need only make use of these results without concerning ourselves with these subtleties. It suffices to conclude this section by summarizing the
semiclassical approximation, that

\[ \mathcal{K}(z_f, \bar{z}_i; T) \approx \mathcal{N}_{0f}^{-1} \sum_c F_c e^{iS[z_c, \bar{z}_c]}, \quad (A.16) \]

where \( c \) labels all classical trajectories.
Appendix B

Coherent States and the Group Action

In this section we tabulate some useful results regarding the action of operators on the spin coherent states. Recall the definition that,

\[ |\bar{z}\rangle \equiv \exp(\bar{z}J_+), \quad |z\rangle \equiv \exp(zJ_-). \tag{B.1} \]

By direct verification, we can see that the action of \( J_3 \) and \( J_\pm \) are given by,

\[ (|z\rangle |J_\pm) = (z \frac{\partial}{\partial z} \pm \frac{j}{2}) (|z\rangle), \quad (|z\rangle |J_3) = (-z^2 \frac{\partial}{\partial z} + 2jz) (|z\rangle). \tag{B.2} \]

Since the majorana polynomial \( P_\Psi(z) \equiv (z|\Psi\rangle \rangle \), it is in this sense that quantum operators act on the space of polynomials via differential operators.

Next, it is useful to see how exponentials of the \( J_3 \) and \( J_\pm \) act. We find that,

\[ (|z\rangle \exp(\alpha J_-) = (z + \alpha), \quad (|z\rangle \exp(2\lambda J_3) = e^{2j\lambda} e^{2\lambda z}, \quad (|z\rangle \exp(\beta J_+) = (\beta z + 1)^2 \left( \frac{z}{\beta z + 1} \right), \tag{B.3} \]

so that the flow generated by the \( J \)'s correspond to Möbius transforms. The utility of (eq. B.3) is that we can always parametrize (up to coordinate singularities) any element of \( g \in \text{SL}(2, \mathbb{C}) \) as

\[ g = \exp\{\alpha J_+\} \exp\{2\lambda J_3\} \exp\{\beta J_-\}, \tag{B.4} \]

and since SU(2) is a subgroup of SL(2, \( \mathbb{C} \)), we are able to arrive at the group action of SU(2) on the coherent state polynomials. Explicitly, we find that for,

\[ g = \begin{pmatrix} u & -\bar{v} \\ v & \bar{u} \end{pmatrix}, \tag{B.5} \]

we have that,

\[ (|z\rangle g = (-\bar{v}z + \bar{u})^{2j} \left( \frac{uz + v}{-\bar{v}z + \bar{u}} \right), \quad \langle z| g = \left( \frac{\bar{v}z - \bar{u}}{\bar{v}z - u} \right)^j \left( \frac{uz + v}{-\bar{v}z + \bar{u}} \right). \tag{B.6} \]
Finally we look at the time-reversal operator \( \Theta \equiv \exp\{-i \pi J_2\} \), whose action on a spin coherent state is,

\[
\Theta |z\rangle = z^{2j} |1/z\rangle, \quad \Theta \langle \bar{z} | = (z/\bar{z})^j |1/z\rangle,
\]

(B.7)

and the action on the Majorana polynomial is,

\[
\Theta : P_\Psi(z) \mapsto (-z)^{2j} (P_\Psi(-1/\bar{z}))^*.
\]

(B.8)
Appendix C

Derivation of the Majorana Decomposition

Let $V_j$ be the spin-$j$ irreducible representation of SU(2), and let $|j, m\rangle$ be the basis for $V_j$. Let $|\uparrow\rangle$ and $|\downarrow\rangle$ be the spin-1/2 up and down states of $V_{1/2}$. First we show that,

$$|j, m\rangle = \sqrt{\frac{(2j)!}{(j+m)!(j-m)!}} |\uparrow\rangle^j |\downarrow\rangle^{j-m}, \tag{C.1}$$

where $|\phi\rangle^n \equiv |\phi\rangle \odot |\phi\rangle \odot \cdots \odot |\phi\rangle$ $n$ times. Recall that the symmetrization $\odot$ is defined as

$$|\chi_1\rangle \odot \cdots \odot |\chi_{2j}\rangle \equiv \frac{1}{(2j)!} \sum_{\pi \in S_{2j}} |\chi_{\pi(1)}\rangle \otimes |\chi_{\pi(2)}\rangle \cdots \otimes |\chi_{\pi(2j)}\rangle. \tag{C.2}$$

To establish that the left and the right hand sides of (eq. C.1) must at least be proportional, we first observe that

$$J_3 |j, m\rangle = m |j, m\rangle,$$

where we recall that

$$J_3 = J_3^{(1/2)} \otimes 1^{(1/2)} \otimes \cdots \otimes 1^{(1/2)} + 1^{(1/2)} \otimes J_3^{(1/2)} \otimes \cdots \otimes 1^{(1/2)}$$

$$\cdots + 1^{(1/2)} \otimes 1^{(1/2)} \otimes \cdots \otimes J_3^{(1/2)}, \tag{C.3}$$

and so $J_3 |\uparrow\rangle^j |\downarrow\rangle^{j-m} = m |\uparrow\rangle^j |\downarrow\rangle^{j-m}$, thus establishing that they belong to the same one-dimensional eigenspace. To establish the proportionality constant, we observe that

$$(|\uparrow\rangle^j |\downarrow\rangle^{j-m} , |\uparrow\rangle^{j+n} |\downarrow\rangle^{j-n}) = \delta_{mn} \frac{(j+m)!(j-m)!}{(2j)!}, \tag{C.4}$$

from which we are able to read off the normalization. The Kronecker delta arises because otherwise, for a mismatch in the number of $|\uparrow\rangle$’s and $|\downarrow\rangle$’s the inner product will always be zero (and alternatively reflects that they belong in different eigenspaces of $J_3$; and the combinatorial factor comes about from the following.
Consider,
\[
(|\chi_1\rangle \otimes \cdots \otimes |\chi_{2j}\rangle, |\xi_1\rangle \otimes \cdots \otimes |\xi_{2j}\rangle)
\]
\[
= \frac{1}{((2j)!)^2} \sum_{\sigma \in S_{2j}} \sum_{\pi \in S_{2j}} \langle \chi_\sigma(1)|\xi_{\pi(1)}\rangle \langle \chi_\sigma(2)|\xi_{\pi(2)}\rangle \cdots \langle \chi_\sigma(2j)|\xi_{\pi(2j)}\rangle.
\]
(C.5)
\[
= \frac{1}{(2j)!} \sum_{\pi \in S_{2j}} \langle \chi_1|\xi_{\pi(1)}\rangle \langle \chi_2|\xi_{\pi(2)}\rangle \cdots \langle \chi_2j|\xi_{\pi(2j)}\rangle.
\]

For \(\chi_1 = \xi_1 = \cdots = \xi_{j+m} = \xi_{j+m} = \uparrow\) and \(\chi_{j+m+1} = \xi_{j+m+1} = \cdots = \xi_{2j} = \xi_{2j} = \downarrow\), the last line of (eq. C.5) essentially counts the number of permutations which leave invariant the \(j + m\) spin ups in the front and the \(j - m\) spin downs in the back, and this is precisely \((j + m)!/(j - m)!\).

As an aside, by replacing each of the \(|\chi_i\rangle\) by \(|\bar{w}_i\rangle_{1/2}\), and using that the spin-1/2 inner product of two coherent states is \(|\bar{w}_1\rangle_{1/2}, |\bar{w}_j\rangle_{1/2}\rangle = (1 + w_i\bar{w}_j)\), we yield the normalization,
\[
N^2 = \left\| |\bar{w}_1\rangle_{1/2} \otimes \cdots \otimes |\bar{w}_{2j}\rangle_{1/2}\right\|^2 = \frac{1}{(2j)!} \sum_{\pi \in S_{2j}} \prod_{l=1}^{2j} (1 + w_l\bar{w}_{\pi(l)}).
\]
(C.6)

Having established the expression of the basis vectors \(|j, m\rangle\) in the Majorana parametrization, it remains to establish the result claimed in (eq. 2.28), and the connection is made through the (elementary) symmetric polynomials, \(e_n\), defined over \(N\) variables \(X_1, \ldots, X_N\) via the expansion,
\[
\prod_{n=1}^{N} (1 + \lambda X_n) = \sum_{k=0}^{N} \lambda^k e_k(X_1, X_2, \ldots, X_N).
\]
(C.7)

Now recall that \(|\bar{w}\rangle_{1/2} = |\downarrow\rangle + \bar{w} |\uparrow\rangle\) (a.k.a. the Bloch-sphere spinor representation, or the spin-1/2 coherent state representation), and consider that,
\[
|\bar{w}_1\rangle_{1/2} \otimes \cdots \otimes |\bar{w}_{2j}\rangle_{1/2} = \sum_{m=-j}^{m=j} e_{j+m}(\bar{w}_1, \ldots, \bar{w}_{2j}) |\uparrow\rangle^j |\downarrow\rangle^{j-m}.
\]
(C.8)

(the same algebraic manipulations which lead to eq. C.7 also lead to the equation above, with the cosmetic replacement of 1 by \(|\downarrow\rangle\) and \(\lambda\) with \(|\uparrow\rangle\)). Then using result (eq. C.1) to relate \(|j, m\rangle\) to the \(|\uparrow\rangle^{j+m} |\downarrow\rangle^{j-m}\), and then taking the inner product of \(|j, m\rangle\) with the spin-\(j\) coherent state \(|\tilde{z}\rangle\) (noting that combinatorial prefactor cancels precisely) yields,
\[
\left\langle |\tilde{z}\rangle, |\bar{w}_1\rangle_{1/2} \otimes \cdots \otimes |\bar{w}_{2j}\rangle_{1/2}\right\rangle = \sum_{m=-j}^{m=j} e_{j+m}(\bar{w}_1, \ldots, \bar{w}_{2j}) z^{j+m} = \prod_{k=1}^{2j} (1 + z\bar{w}_k),
\]
(C.9)
which gives (eq. 2.28). Alternatively, using (eq. C.8) and taking the inner product with $|j, m\rangle$ shows that,

$$e_{j+m}(\bar{w}_1, \ldots, \bar{w}_{2j}) = \sqrt{\frac{(2j)!}{(j+m)!(j-m)!}} \left( |j, m\rangle , |\bar{w}_1\rangle 1/2 \odot \cdots \odot |\bar{w}_{2j}\rangle 1/2 \right),$$

which gives an alternative interpretation of the elementary symmetric polynomials.

The upshot is that, for a state $|\Psi\rangle \propto |\bar{w}_1\rangle 1/2 \odot \cdots \odot |\bar{w}_{2j}\rangle 1/2$, (eq. 2.28) shows that the zeros of $P_\Psi(z) \equiv (z|\Psi\rangle$ are located at $\zeta = -1/\bar{w}_k$ (the overall proportionality constant does not affect the locations of the zeros). Conversely, since there is a one to one correspondence between a spin state and its Majorana polynomial, and since any degree $2j$ polynomial is determined up to normalization by its zeros, (eq. 2.28) shows that by taking the $w$’s to be antipodes of the zeros, i.e. $w_k = 1/\bar{\zeta}_k$, we can always construct a Majorana decomposition of the spin state. This establishes the decomposition.

It remains to reconcile what can potentially go wrong when one or more of the $w$’s tend to infinity. Looking at the corresponding spinor $|\bar{w}\rangle 1/2 = |\downarrow\rangle + \bar{w}|\uparrow\rangle$, it means that the spinor is wanting to tend toward being completely spin-up. This singularity is a failure of our particular coordinate system and, as before in the discussion of the zeros of the Majorana polynomial, is reconciled by recognizing that these points actually exist on the Riemann sphere.
Appendix D

Counterterms

The necessity of the counter-term $H_{ct}$ appearing in the total Hamiltonian can be motivated both physically and mathematically. Physically, the coupling to the bath oscillators will cause a shift in the equilibrium of the system variable, and the counter-terms are needed to correct for this shift. (For example, if the frequency of small oscillations about the minima of the uncoupled system is $\Omega$, then without the counterterms, the phonon coupling would cause a shift of this frequency). Mathematically, it can be thought as a remedy to the high-frequency divergence that may occur in integrating over all phonon energies. Without it, much of the subsequent calculations fall apart.

We adopt the latter viewpoint, and begin by understanding how to obtain an asymptotic expansion of the integral,

$$A(\omega) = \int \int_{\tau' < \tau} d\tau d\tau' f(\tau)g(\tau')e^{-\omega(\tau - \tau')}, \quad (D.1)$$

where $\omega > 0$. By writing

$$e^{\omega \tau'} = \frac{1}{\omega} \frac{\partial}{\partial \tau'} e^{\omega \tau'}, \quad (D.2)$$

and moving the partial derivative onto the rest of the integral, we have,

$$\int_{-\infty}^{\tau} d\tau' g(\tau')e^{\omega \tau'} = \frac{1}{\omega} g(\tau)e^{\omega \tau} - \frac{1}{\omega} \int_{-\infty}^{\tau} d\tau' g^{(1)}(\tau')e^{\omega \tau'}. \quad (D.3)$$

By iterating the same procedure, we arrive at an expansion in powers of $1/\omega$ as

$$A(\omega) = \frac{1}{\omega} \int_{-\infty}^{\infty} d\tau f(\tau)g(\tau) - \frac{1}{\omega^2} \int_{-\infty}^{\infty} d\tau f(\tau)g^{(1)}(\tau) + \frac{1}{\omega^3} \int_{-\infty}^{\infty} d\tau f(\tau)g^{(2)}(\tau) - \ldots. \quad (D.4)$$

Hence, if $\int d\tau f g$ converges to a non-zero value, then $A(\omega) \sim \omega^{-1}$. Otherwise, if $\int d\tau f g = 0$ then we go to the next order, etc.
To see how this applies to the counter-terms, consider next the integral given by

\[ B(\omega) = \int \int d\tau d\tau' f(\tau) f(\tau') e^{-\omega |\tau - \tau'|}, \]

\[ = \frac{2}{\omega} \int_{-\infty}^{\infty} d\tau f(\tau)^2 - \frac{2}{\omega^2} \int_{-\infty}^{\infty} d\tau f(\tau) f^{(1)}(\tau) + \frac{2}{\omega^3} \int_{-\infty}^{\infty} d\tau f(\tau) f^{(2)}(\tau) - \ldots \]  

(D.5)

and if \( \lim_{\tau \to \infty} f(\tau) = \pm \lim_{\tau \to -\infty} f(\tau) = \text{const} \), then

\[ \int_{-\infty}^{\infty} d\tau f(\tau) f^{(1)}(\tau) = 0, \quad \int_{-\infty}^{\infty} d\tau f(\tau) f^{(2)}(\tau) = -\int_{-\infty}^{\infty} (f^{(1)}(\tau))^2, \]

(D.6)

dec, and so provided that \( \int d\tau f^2 \) converges to a non-zero number, we have,

\[ \int \int d\tau d\tau' f(\tau) f(\tau') \left\{ e^{-\omega |\tau - \tau'|} - \frac{2}{\omega} \delta(\tau - \tau') \right\} \sim O(\omega^{-3}), \]

\[ \int \int d\tau d\tau' f(\tau) f(\tau') \left\{ e^{-\omega |\tau - \tau'|} - \frac{2}{\omega} \delta(\tau - \tau') + \frac{2}{\omega^3} \frac{\partial}{\partial \tau} \frac{\partial}{\partial \tau'} \delta(\tau - \tau') \right\} \sim O(\omega^{-5}), \]

etc. The combined effect of the bath oscillators is then given by an integral of the form,

\[ \int_{0}^{\infty} d\omega J(\omega) B(\omega), \]

(D.8)

where \( J(\omega) \) is the spectral density, typically modeled as a power law with positive exponent. Depending on the degree of \( J(\omega) \), the Dirac Deltas (and derivatives) subtract off infinities that would otherwise arise at the upper bound of the integral.

For the ohmic case \( J(\omega) \sim \omega \) considered in [4,6,17], it is necessary only to expand out to \( O(\omega^{-3}) \), which leads to the quadratic expansion of the last term in the effective Lagrangian,

\[ L_{\text{eff}}(Q, \dot{Q}, \tau) = L_0(Q, \dot{Q}) + \frac{1}{2} \int_{-\infty}^{\infty} d\tau' \times \frac{1}{2\pi} \int_{0}^{\infty} d\omega J(\omega) e^{-\omega |\tau - \tau'|}(Q(\tau) - Q(\tau'))^2, \]

(D.9)

for the system variable \( Q \).
Appendix E

The Influence Functional

Derivation of $\mathcal{K}_\mu$

The bath factor $\mathcal{K}_\mu$ is given formally by the SHO coherent-state path integral,

$$\mathcal{K}_\mu = e^{-\frac{1}{2} \xi_{\mu,f} \xi_{\mu,f}} e^{-\frac{1}{2} \xi_{\mu,0} \xi_{\mu,0}} \int_{\xi_{\mu}(u_0) = \xi_{\mu,0}} \mathcal{D}(\xi_{\mu}, \bar{\xi}_{\mu}) \exp \left\{ \frac{1}{2} \xi_{\mu}(u_0) \bar{\xi}_{\mu,0} + \frac{1}{2} \xi_{\mu,f} \bar{\xi}_{\mu,f} + iS_{\mu}[\zeta, \bar{\zeta}, z, \bar{z}] \right\}, \quad (E.1)$$

where $S_{\mu}$ is the harmonic oscillator action, given by,

$$S_{\mu}[\zeta, \bar{\zeta}, z, \bar{z}] = \int_{u_0}^{u_f} du \left\{ \frac{1}{2} \bar{\zeta}_{\mu} \dot{\zeta}_{\mu} - \frac{1}{2} \zeta_{\mu} \dot{\bar{\zeta}}_{\mu} - \omega_{\mu} \zeta_{\mu} \bar{\zeta}_{\mu} - i\psi_{\mu}(z, \bar{z})(\bar{\zeta}_{\mu} - \zeta_{\mu}) \right\}. \quad (E.2)$$

Since the path integral was constructed from a Hamiltonian that is linear in the generators of the algebra, the integral is exactly equivalent to its semiclassical contribution [36]. In other words, it suffices to solve for the classical equations of motion and insert the solution back into the action. By extremizing the action with respect to $\zeta_{\mu}$ and $\bar{\zeta}_{\mu}$, we arrive at the equations,

$$\begin{align*}
\frac{d}{du} \bar{\zeta}_{\mu} + i\omega_{\mu} \zeta_{\mu} &= -\dot{\psi}_{\mu}, \\
\bar{\zeta}_{\mu}(u_0) &= \bar{\zeta}_{\mu,0}, \\
\frac{d}{du} \zeta_{\mu} - i\omega_{\mu} \bar{\zeta}_{\mu} &= -\dot{\psi}_{\mu}, \\
\zeta_{\mu}(u_f) &= \zeta_{\mu,f},
\end{align*} \quad (E.3)$$

and the respective solutions,

$$\begin{align*}
\bar{\zeta}_{\mu}(u) &= \bar{\zeta}_{\mu,0} e^{-i\omega_{\mu}(u-u_0)} - \int_{u_0}^{u} du' e^{-i\omega_{\mu}(u-u')} \dot{\psi}_{\mu}, \\
\zeta_{\mu}(u) &= \zeta_{\mu,f} e^{-i\omega_{\mu}(u_f-u)} + \int_{u}^{u_f} du' e^{-i\omega_{\mu}(u'-u)} \dot{\psi}_{\mu}.
\end{align*} \quad (E.4)$$
Finally, putting everything back into the original action gives us an expression of the form,

\[ \mathcal{K}_\mu = \exp \left\{ -\frac{1}{2} \zeta_{\mu,0} \zeta_{\mu,0} + \zeta_{\mu,0} \zeta_{\mu,f} e^{-i\omega_\mu (u_f - u_0)} \right\} \]

\[ \times \exp \left\{ \zeta_{\mu,0} \int_{u_0}^{u_f} du e^{-i\omega_\mu (u - u_0)} \psi_\mu(u) - \zeta_{\mu,f} \int_{u_0}^{u_f} du e^{-i\omega_\mu (u_f - u)} \psi_\mu(u) \right\} \]

\[ \times \exp \left\{ -\frac{1}{2} \int_{u_0}^{u_f} d\mu e^{-i\omega_\mu |u_f - u|} \psi_\mu(u) \psi_\mu(u') \right\}. \]  

(E.5)

Now, using that,

\[ \langle \zeta | n \rangle = e^{-\frac{1}{2} \zeta \zeta^*} \frac{\zeta^n}{\sqrt{n!}} \]

we are able to express \( \mathcal{K}_\mu \) in the occupation basis as,

\[ \mathcal{K}_\mu[n_{\mu,0}, n_{\mu,f}] = \int \frac{d\zeta_{\mu,0} d\zeta_{\mu,f}}{2\pi i} \int d\zeta_{\mu,0} d\zeta_{\mu,f} \frac{(\zeta_{\mu,0})^{n_{\mu,0}} (\zeta_{\mu,f})^{n_{\mu,f}}}{\sqrt{n_{\mu,0}}! \sqrt{n_{\mu,f}}!} e^{-\frac{1}{2} \zeta_{\mu,0} \zeta_{\mu,0} e^{-\frac{1}{2} \zeta_{\mu,0} \zeta_{\mu,f}} K}. \]  

(E.7)

Though it is possible to explicitly integrate the above, we’ll leave it in its current form in anticipation of algebraic manipulations to follow in the following section.

**Derivation of the Influence Functional**

In this section we calculate the contribution of mode \( \mu \) to the influence functional; that is, we calculate

\[ \mathcal{F}_\mu = Z_{\mu}^{-1} \sum_{n_{\mu,0} = 0}^{\infty} \sum_{n_{\mu,f} = 0}^{\infty} e^{-\beta \omega_\mu n_{\mu,0} K} [n_{\mu,0}, n_{\mu,f}] [K [n_{\mu,0}, n_{\mu,f}]]^*. \]  

(E.8)

In the subsequent derivations we will find it economical to define,

\[ A_\mu^+ = \int_{u_0}^{u_f} d\mu e^{-i\omega_\mu (u - u')} \psi_\mu^+(u) \psi_\mu^+(u'), \quad (A_\mu^+)^* = \int_{u_0}^{u_f} d\mu e^{-i\omega_\mu (u - u')} (\psi_\mu^-(u))^* (\psi_\mu^-(u'))^*, \]

\[ B_\mu^+ = \int_{u_0}^{u_f} d\mu e^{-i\omega_\mu (u - u_0)} \psi_\mu^+(u), \quad (B_\mu^-)^* = \int_{u_0}^{u_f} d\mu e^{+i\omega_\mu (u - u_0)} (\psi_\mu^-)^*(u), \]

\[ C_\mu^+ = \int_{u_0}^{u_f} d\mu e^{-i\omega_\mu (u_f - u)} \psi_\mu^+(u), \quad (C_\mu^-)^* = \int_{u_0}^{u_f} d\mu e^{+i\omega_\mu (u_f - u)} (\psi_\mu^-)^*(u). \]  

(E.9)

Taking the product of \( K_\mu^+ [n_{\mu,0}, n_{\mu,f}] (K_\mu^- [n_{\mu,0}, n_{\mu,f}])^* \) (eqn. E.7) and summing over \( n_{\mu,0} \) and \( n_{\mu,f} \), the polynomial factors from the coherent state wavefunctions combine into exponentials, and the full expression for \( \mathcal{F}_\mu \) reads,

\[ \mathcal{F}_\mu = Z_{\mu}^{-1} (2\pi i)^{-4} \exp \left\{ -\frac{1}{2} A_\mu^+ - \frac{1}{2} (A_\mu^-)^* \right\} \]

\[ \times \int d\zeta_{\mu,0} d\zeta_{\mu,0} \int d\zeta_{\mu,f} d\zeta_{\mu,f} \int d\zeta_{\mu,0} d\zeta_{\mu,0} \int d\zeta_{\mu,f} d\zeta_{\mu,f} \exp P_{\mu}, \]

(E.10)
where \( P_\mu \) is the lengthy equation,

\[
P_\mu = \zeta_{\mu,0} \tilde{\zeta}_{\mu,0} e^{-\beta \omega_\mu} + \zeta_{\mu,f} \tilde{\zeta}_{\mu,f} + \zeta_{\mu,0} B_\mu^+ - \zeta_{\mu,f} C_\mu^+ + \zeta_{\mu,0}(B_{\mu}^*) - \tilde{\zeta}_{\mu,f}(C_{\mu}^*)
- \zeta_{\mu,0} \tilde{\zeta}_{\mu,0} - \zeta_{\mu,f} \tilde{\zeta}_{\mu,f} + \zeta_{\mu,0} \tilde{\zeta}_{\mu,0} e^{-i\omega_\mu(u_f - u_0)} - \tilde{\zeta}_{\mu,f} \tilde{\zeta}_{\mu,f} - \zeta_{\mu,0} \tilde{\zeta}_{\mu,f} + \zeta_{\mu,0} \tilde{\zeta}_{\mu,f} e^{i\omega_\mu(u_f - u_0)}.
\]

(E.11)

Next we repeatedly use, to great profit, the following result,

\[
\int_C \frac{d\bar{x} d\chi}{2\pi i} \exp \{-a\bar{x}\chi - b\chi - c\bar{\chi}\} = \frac{1}{a} \exp \left\{\frac{b c}{a}\right\},
\]

(E.12)

to successively integrate over all of the \( \zeta \) variables in \( P_\mu \). After this tedious but straightforward computation, we reduce \( \mathcal{F}_\mu \) to,

\[
\mathcal{F}_\mu = \exp \left\{ \frac{e^{-\beta \omega_\mu}}{1 - e^{-\beta \omega_\mu}} \left( (B_\mu^*) - C_\mu^+ e^{+i\omega_\mu(u_f - u_0)} \right) \left( B_\mu^+ - (C_\mu)^* e^{-i\omega_\mu(u_f - u_0)} \right) \right\}
\times \exp \left\{ -\frac{1}{2} A_\mu^+ - \frac{1}{2}(A_{\mu}^-)^* + C_\mu^+(C_\mu)^* \right\},
\]

(E.13)

By minding the symmetric/anti-symmetric parts of the integral with respect to \( u \leftrightarrow u' \), and possibly relabeling variables, we have,

\[
\left\{(B_\mu^*) - C_\mu^+ e^{+i\omega_\mu(u_f - u_0)} \right\} \left\{ B_\mu^+ - (C_\mu)^* e^{-i\omega_\mu(u_f - u_0)} \right\}
= -2 \int_{u' < u} dudu' \cos \omega_\mu(u - u') \left\{ \psi_\mu^+(u) - (\psi_\mu^-(u))^* \right\} \left\{ \psi_\mu^+(u') - (\psi_\mu^-(u'))^* \right\},
\]

(E.14)

and,

\[
-\frac{1}{2} A_\mu^+ - \frac{1}{2}(A_{\mu}^-)^* + C_\mu^+(C_\mu)^*
= - \int \int_{u' < u} dudu' \cos \omega_\mu(u - u') \left\{ \psi_\mu^+(u) - (\psi_\mu^-(u))^* \right\} \left\{ \psi_\mu^+(u') - (\psi_\mu^-(u'))^* \right\}
+ i \int \int_{u' < u} dudu' \sin \omega_\mu(u - u') \left\{ \psi_\mu^+(u) - (\psi_\mu^-(u))^* \right\} \left\{ \psi_\mu^+(u') + (\psi_\mu^-(u'))^* \right\}.
\]

(E.15)

Breaking apart the trigonometric factors into their constituent exponentials, and utilizing the identity that

\[
\frac{e^{-\beta \omega_\mu}}{1 - e^{-\beta \omega_\mu}} e^{-i(u-u')} + \frac{1}{2} e^{-i|u-u'|} = \frac{1 - \cosh(i\omega_\mu|u-u'| - \beta \omega_\mu/2)}{2 \sinh(\beta \omega_\mu/2)},
\]

(E.16)

we arrive at the desired result after incorporating the counterterm contributions.

Finally we verify Feynman and Hibbs rules I and II. Rule I is manifest, and for rule II, we note that we
can write the influence functional alternatively as,

\[ \exp \{ \Phi \} = \exp \left\{ -\sum_{\mu} \coth(\beta \omega_{\mu}/2) \int_{u' < u} du' \cos \omega_{\mu}(u - u') \{ \psi_{\mu}^+(u) - \psi_{\mu}^-(u)^* \} \{ \psi_{\mu}^+(u') - \psi_{\mu}^-(u')^* \} \right\} \]

\[ \times \exp \left\{ -\sum_{\mu} \int_{u' < u} du' (-i) \sin \omega_{\mu}(u - u') \{ \psi_{\mu}^+(u) - \psi_{\mu}^-(u)^* \} \{ \psi_{\mu}^+(u') + \psi_{\mu}^-(u')^* \} \right\} \]

\[ \times \exp \left\{ -\frac{1}{2} \sum_{\mu} \int du \left[ \frac{2i}{\omega_{\mu}} \{ (\psi_{\mu}^+(u))^2 - (\psi_{\mu}^-(u))^2 \} + \frac{2i}{\omega_{\mu}^3} \left( \frac{\partial \psi_{\mu}^+(u)}{\partial u} \right)^2 - \left( \frac{\partial \psi_{\mu}^-(u)}{\partial u} \right)^2 \right] \right\}. \]

(E.17)
Appendix F

Debye Model and Spectral Density Tensor

In this section we show how to sum over phonon polarization and directions. We remind ourselves that for our phonon coupling to the mode $\mu$ labeled by wavevector $q (= q\hat{q})$ and polarization $\hat{\epsilon}$, the term $\psi_\mu$ stands for,

$$\psi_\mu = j(j - \frac{1}{2})\lambda_\mu \sum_{k,l} (\hat{q}_k^\mu \hat{\epsilon}_l^\mu(\hat{q}) + \hat{q}_l^\mu \hat{\epsilon}_k^\mu(\hat{q}))\sigma_{kl}, \quad (F.1)$$

where the prime over the summation is to remind ourselves that we omit the $k = 3, l = 3$ term, and where $\sigma_{kl}$ and $\lambda_\mu$ are defined as,

$$\sigma_{kl} = s_k s_l + \frac{1}{2j - 1} \delta_{kl}, \quad \lambda_\mu = \lambda q_\mu (2N)^{-\frac{1}{2}} \omega_\mu^{-\frac{1}{2}}. \quad (F.2)$$

The fundamental fact that permits us to simplify the expression for the rate is that, for any $q$ the polarization vectors form a complete set, i.e.

$$\sum_s \hat{\epsilon}^a_s(q)\hat{\epsilon}^b_s(q) = \delta_{ab}. \quad (F.3)$$

Furthermore, it is clear that for the longitudinal mode ($s = L$), we have that $\hat{\epsilon}^L = \hat{k}$. It follows that, by subtracting off the contribution of the longitudinal modes from the completeness relation (eq. F.3), that,

$$\hat{\epsilon}_a^L \hat{\epsilon}_b^L = \hat{q}_a \hat{q}_b, \quad \sum_{s \neq L} \hat{\epsilon}_a^s \hat{\epsilon}_b^s = \delta_{ab} - \hat{q}_a \hat{q}_b. \quad (F.4)$$

First we look at the longitudinal modes. Consider the tensor

$$I_{ijkl} \equiv \int_{S^2} d^2\hat{q} \hat{q}_i \hat{q}_j \hat{q}_k \hat{q}_l. \quad (F.5)$$

Since this tensor is invariant under O(3) and is completely symmetric under all permutations of $i, j, k, l$, then it must take the form

$$I_{ijkl} = A(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \quad (F.6)$$
The normalization $A$ can then be found by contracting $i, j$ and $k, l$. The left hand side of the equation then becomes the surface area $4\pi$ of a sphere, and right hand side becomes $9 + 3 + 3 = 15$, yielding $A = 4\pi/15$.

For similar reasons, over two indices we must have

$$I_{ij} \equiv \int_{S^2} d^2 \hat{q} \hat{q} = \frac{4\pi}{3} \delta_{ij}. \quad (F.7)$$

Equations (F.6) and (F.7) are the building blocks from which the more complicated expressions in (eq. 3.21) are constructed.

In summary, for symmetric matrices $A$ and $B$, the longitudinal modes result in,

$$\int d^2 \hat{q} \sum_{i,j}^{'} \sum_{k,l}^{'} (\hat{q}_i \hat{e}^{L}_j + \hat{q}_j \hat{e}^{L}_i)(\hat{q}_k \hat{e}^{L}_l + \hat{q}_l \hat{e}^{L}_k)A_{ij}B_{kl} = \frac{16\pi}{15} (3A_{11}B_{11} + 3A_{22}B_{22} + A_{11}B_{22} + A_{22}B_{11} + 4A_{12}B_{12} + 4A_{13}B_{13} + 4A_{23}B_{23}), \quad (F.8)$$

and the transverse components result in,

$$\sum_{s=T} \int d^2 \hat{q} \sum_{i,j}^{'} \sum_{k,l}^{'} (\hat{q}_i \hat{e}^{s}_j + \hat{q}_j \hat{e}^{s}_i)(\hat{q}_k \hat{e}^{s}_l + \hat{q}_l \hat{e}^{s}_k)A_{ij}B_{kl} = \frac{16\pi}{15} (2A_{11}B_{11} + 2A_{22}B_{22} - A_{11}B_{22} - A_{22}B_{11} + 6A_{12}B_{12} + 6A_{13}B_{13} + 6A_{23}B_{23}). \quad (F.9)$$
Appendix G

The Kinetic Equations

Derivation from Liouville Equations

Consider a collection of $N$ Ising spins, whose local spin orientation is the random variable $S_i$, and whose local bias is $E_i$. The $N$-particle joint probability distribution is defined as,

$$\rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N, t)d^N\varepsilon \equiv \mathbb{P}(S_1(t) = s_1, \ldots, S_N(t) = s_N, E_1(t) = \varepsilon_1, \ldots, E_N(t) = \varepsilon_N). \quad (G.1)$$

Assuming that the process is Markov, the time evolution of $\rho$ due to changes in the spin configuration is given by,

$$\mathbb{P}({\{S(t + \delta t) = s\}}, {\{E(t + \delta t) = \varepsilon\}}) = \int d\varepsilon_1' \cdots \int d\varepsilon_N' \sum_{s_1} \cdots \sum_{s_N} T({\{s\}}, {\{\varepsilon\}}|{\{s'\}}, {\{\varepsilon'\}}) \mathbb{P}({\{S(t) = s'\}}, {\{E(t) = \varepsilon'\}}), \quad (G.2)$$

where the dynamics of the distribution depends on the details of the transition matrix $T$. In our case we assume that the flipping is a Poisson process, meaning that at most one spin can flip in time $\delta t$, and that two- or higher numbers of spin flips are ignored since these processes correspond to $O(\delta t^2)$.

The remaining processes can be grouped into the “one-flip” and the “no-flip” terms. Let us first address the one-flip process. Consider what happens if the $k$-th spin flips. The bias at site $i$ (for $i \neq k$) changes via $E_i \rightarrow E_i'$, where $E_i' - E_i = -2K_{ik}s_k$. Explicitly, we have,

$$\{s_1, \ldots, \bar{s}_k, \ldots, s_N, \varepsilon_1 - 2K_{1k}s_k, \ldots, \varepsilon_k, \ldots, \varepsilon_N - 2K_{Nk}s_k\} \rightarrow \{s_1, \ldots, s_k, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_k, \ldots, \varepsilon_N\}, \quad (G.3)$$

(where $\bar{s} \equiv -s$ for notational simplicity), and this process occurs with probability $\Gamma_{s_k, \bar{s}_k}(\varepsilon_k)\delta t$. Therefore,
the one-flip processes contribute,

\[
\{\text{one-flip}\} = \sum_k \delta t \Gamma_{s_k \bar{s}_k} (\varepsilon_k) \rho(s_1, \ldots, \bar{s}_k, \ldots, s_N, \varepsilon_1 - 2K_{1k}s_k, \ldots, \varepsilon_k, \ldots, \varepsilon_N - 2K_{Nk}s_k, t). \tag{G.4}
\]

Likewise, the no-flip process occurs with probability of one less the probability of a single flip, i.e.,

\[
\{\text{no-flip}\} = \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N) - \sum_k \delta t \Gamma_{\bar{s}_k s_k} (\varepsilon_k) \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N, t). \tag{G.5}
\]

Finally, if the local bias is explicitly time dependent (e.g., coming from an external field), then the corresponding change in probability is simply

\[
\{\text{bias}\} = -\sum_k \delta t \frac{d\varepsilon_k}{dt} \frac{\partial}{\partial \varepsilon_k} \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N, t). \tag{G.6}
\]

In total, the Liouville equation for the joint probability density reads,

\[
\frac{\partial}{\partial t} \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N, t) = \sum_k \Gamma_{s_k \bar{s}_k} (\varepsilon_k) \rho(s_1, \ldots, \bar{s}_k, \ldots, s_N, \varepsilon_1 - 2K_{1k}s_k, \ldots, \varepsilon_k, \ldots, \varepsilon_N - 2K_{Nk}s_k, t) \\
- \sum_k \Gamma_{\bar{s}_k s_k} (\varepsilon_k) \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N, t) - \sum_k \frac{d\varepsilon_k}{dt} \frac{\partial}{\partial \varepsilon_k} \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N, t). \tag{G.7}
\]

Next let us use this to express the one-point distribution function in terms of the two-point distribution, analogous to the BBGKY hierarchy of equations. Recall that the one-point function \(f^{(1)}\) and the two-point function \(f^{(2)}\) is defined by,

\[
f^{(1)}_i(s, \varepsilon, t) = \int d\varepsilon_1 \cdots d\varepsilon_N \sum_{s_1, \ldots, s_N} \delta(\varepsilon - \varepsilon_i) \delta_{ss_i} \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N, t),
\]

\[
f^{(2)}_{ij}(s, \varepsilon, s', \varepsilon') = \int d\varepsilon_1 \cdots d\varepsilon_N \sum_{s_1, \ldots, s_N} \delta(\varepsilon - \varepsilon_i) \delta_{ss_i} \delta(\varepsilon' - \varepsilon_j) \delta_{s's_j} \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N, t). \tag{G.8}
\]
Taking the partial derivative of \( f^{(1)} \) with respect to time and using the Liouville equation (eq. G.7) yields,
\[
\frac{\partial}{\partial t} f^{(1)}_i(s, \varepsilon) = \int d\varepsilon_1 \cdots d\varepsilon_N \sum_{s_1, \ldots, s_N} \delta(\varepsilon - \varepsilon_i) \delta_{ss_i} \sum_k \Gamma_{s_k s_k}(\varepsilon_k) \times \rho(s_1, \ldots, s_N, \varepsilon_1 - 2K_{1k} s_k, \ldots, \varepsilon_N - 2K_{Nk} s_k) - \int d\varepsilon_1 \cdots d\varepsilon_N \sum_{s_1, \ldots, s_N} \delta(\varepsilon - \varepsilon_i) \delta_{ss_i} \sum_k \Gamma_{s_k s_k}(\varepsilon_k) \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N) - \int d\varepsilon_1 \cdots d\varepsilon_N \sum_{s_1, \ldots, s_N} \delta(\varepsilon - \varepsilon_i) \delta_{ss_i} \sum_k \varepsilon_k \frac{\partial}{\partial \varepsilon_k} \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N),
\]
where now we can separate each of the sums over \( k \) into those with \( k = i \) and \( k \neq i \). The sums with \( k = i \) are evaluated as \( \Gamma_{ss}(\varepsilon)f^{(1)}_i(s, \varepsilon) \), \( -\Gamma_{ss}f^{(1)}_i(s, \varepsilon) \), and \( -\frac{\varepsilon_i}{\varepsilon} \frac{\partial f^{(1)}_i(s, \varepsilon)}{\varepsilon} \) respectively (doing so may require dummy variable relabeling tricks such as \( \bar{s}_i \leftrightarrow s_i \) and \( \varepsilon \rightarrow \varepsilon + 2K_{si} \)). For the \( k \neq i \) terms, we have,
\[
\int d\varepsilon_1 \cdots d\varepsilon_N \sum_{s_1, \ldots, s_N} \delta(\varepsilon - \varepsilon_i) \delta_{ss_i} \sum_k \Gamma_{s_k s_k}(\varepsilon_k) \times \rho(s_1, \ldots, s_N, \varepsilon_1 - 2K_{1k} s_k, \ldots, \varepsilon_N - 2K_{Nk} s_k) \]
\[
= \int d\varepsilon' \int d\varepsilon'' \sum_{s'} \sum_{k} \Gamma_{s's'}(\varepsilon') \delta((\varepsilon - \varepsilon'') + 2K_{ik}) \]
\[
\rho(s_1, \ldots, s_N, \varepsilon_1 - 2K_{1k} s_k, \ldots, \varepsilon_N - 2K_{Nk} s_k) - \int d\varepsilon_1 \cdots d\varepsilon_N \sum_{s_1, \ldots, s_N} \delta(\varepsilon'' - \varepsilon_i) \delta(\varepsilon' - \varepsilon_k) \delta_{ss_i} \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N),
\]
\[
= \frac{1}{2} \int d\varepsilon' \int d\varepsilon'' \sum_{s'} \sum_{k} \Gamma_{s's'}(\varepsilon') \delta(\frac{1}{2}(\varepsilon'' - \varepsilon) s' - K_{ik}) f^{(2)}_{ik}(s, \varepsilon'', s', \varepsilon'),
\]
for the first term, while for the other two we have,
\[
\int d\varepsilon_1 \cdots d\varepsilon_N \sum_{s_1, \ldots, s_N} \delta(\varepsilon - \varepsilon_i) \delta_{ss_i} \sum_k \Gamma_{s_k s_k}(\varepsilon_k) \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N) \]
\[
= \int d\varepsilon' \int d\varepsilon'' \sum_{s'} \sum_{k} \Gamma_{s's'}(\varepsilon') \delta(\varepsilon'' - \varepsilon) f^{(2)}_{ik}(s, \varepsilon'', s', \varepsilon'),
\]
and finally,
\[
\int d\varepsilon_1 \cdots d\varepsilon_N \sum_{s_1, \ldots, s_N} \delta(\varepsilon - \varepsilon_i) \delta_{ss_i} \sum_{k} \frac{\partial}{\partial \varepsilon_k} \rho(s_1, \ldots, s_N, \varepsilon_1, \ldots, \varepsilon_N) = 0,
\]
due to assumptions on the boundary conditions that \( \rho \rightarrow 0 \) as \( \varepsilon_a \rightarrow \pm \infty \) for any \( a \).
Putting it together, we find,

\[
\frac{\partial}{\partial t} f_1^{(1)}(s, \varepsilon) - \Gamma_{ss}(\varepsilon) f_1^{(1)}(\bar{s}, \varepsilon) + \Gamma_{s\bar{s}}(\varepsilon) f_1^{(1)}(s, \varepsilon) + \frac{d\varepsilon}{dt} \frac{\partial}{\partial \varepsilon} f_1^{(1)}(s, \varepsilon) = \frac{1}{2} \sum_{s'} \int d\varepsilon' \Gamma_{s's'}(\varepsilon') \int d\varepsilon'' \sum_{k \neq i} \{ \delta(1/2(\varepsilon'' - \varepsilon)s' - K_{ik}) - \delta(1/2(\varepsilon - \varepsilon'')) \} f_k^{(2)}(s, \varepsilon'', s', \varepsilon').
\]  

(G.13)

If we make the closure assumptions that,

1. \( f_{ij}^{(2)}(s, \varepsilon, s', \varepsilon') = f_i^{(1)}(s, \varepsilon)f_j^{(1)}(s', \varepsilon') \), for all \( i, j \),

2. \( f_i^{(1)}(s, \varepsilon) = f_j^{(1)}(s, \varepsilon) \equiv f(s, \varepsilon) \) for all \( i, j \),

then we may reduce the above equations to

\[
\frac{\partial}{\partial t} f(s, \varepsilon) - \Gamma_{s\bar{s}}(\varepsilon) f(\bar{s}, \varepsilon) + \Gamma_{s\bar{s}}(\varepsilon) f(s, \varepsilon) + \frac{d\varepsilon}{dt} \frac{\partial}{\partial \varepsilon} f(s, \varepsilon) = \frac{1}{2} \sum_{s'} \int d\varepsilon' \Gamma_{s's'}(\varepsilon') f(s', \varepsilon') \int d\varepsilon'' \sum_{k \neq i} \{ \delta(1/2(\varepsilon'' - \varepsilon)s' - K_{ik}) - \delta(1/2(\varepsilon - \varepsilon'')) \} f_k^{(2)}(s, \varepsilon'', s', \varepsilon').
\]  

(G.14)

**Theoretical Considerations**

First we show that probability is conserved under the evolution of the kinetic equations. By integrating \( \frac{\partial f}{\partial t} \) over all \( \varepsilon \) and summing over \( s \), the diffusion terms vanish by relabeling \( s \),

\[
- \int d\varepsilon \sum_s \Gamma_{s\bar{s}}(\varepsilon) f(\bar{s}, \varepsilon) + \int d\varepsilon \sum_s \Gamma_{s\bar{s}}(\varepsilon) f(s, \varepsilon) = 0,
\]

(G.15)

while the force term vanishes assuming that \( f(s, \varepsilon) \) vanishes as \( \varepsilon \to \pm \infty \). Finally, the collision term vanishes since the integral of \( g_R \) is zero, by virtue of the regularization,

\[
\int d\varepsilon \frac{1}{2} g_R(\varepsilon, \bar{e}) s = 0,
\]

(G.16)

so altogether this gives

\[
\frac{\partial}{\partial t} \int d\varepsilon \sum_s f(s, \varepsilon) = 0.
\]

(G.17)

Next we consider the equilibrium distributions (assuming \( \dot{\varepsilon} = 0 \), in the sense that \( \frac{\partial f^0}{\partial t} = 0 \). As such the integral of the equilibrium distribution \( \int d\varepsilon f^0_s(\varepsilon) \) is also static. Once again the collision terms vanish, and we are left with,

\[
\int d\varepsilon \Gamma_{+}(\varepsilon) f^0_+(\varepsilon) = \int d\varepsilon \Gamma_{-}(\varepsilon) f^0_-(\varepsilon),
\]

(G.18)
This expresses detailed balance between the + and the – states, i.e. the total rate of + → − must equal that of − → +. As such we define $T^0 \equiv \int d\varepsilon \Gamma_{+\leftarrow}(\varepsilon)f^0_-(\varepsilon) \equiv \int d\varepsilon \Gamma_{\leftarrow+}(\varepsilon)f^0_+(\varepsilon)$. We also define,

$$f \equiv f(+,\varepsilon) + f(-,\varepsilon), \quad \mu \equiv f(+,\varepsilon) - f(-,\varepsilon),$$

then, stationarity demands that,

$$\frac{\partial f^0}{\partial t} = 0 = T^0 \int d\varepsilon'' \{ \frac{1}{2}g_R(\varepsilon'' - \varepsilon) + \frac{1}{2}g_R(\varepsilon - \varepsilon'') \} f^0(\varepsilon''),$$

$$\frac{\partial \mu^0}{\partial t} = 0 = 2\Gamma_{+\leftarrow}(\varepsilon)f^0_-(\varepsilon) - 2\Gamma_{\leftarrow+}(\varepsilon)f^0_+(\varepsilon)$$

$$+ T^0 \int d\varepsilon'' \{ \frac{1}{2}g_R(\varepsilon'' - \varepsilon) + \frac{1}{2}g_R(\varepsilon - \varepsilon'') \} \mu^0(\varepsilon'').$$

One solution of interest is the $m^0 = \int d\varepsilon \mu^0(\varepsilon) = 0$ solution, given by $f^0_0(-,\varepsilon) = f^0_0(+,-\varepsilon)$. In that case $\mu^0(\varepsilon)$ is an antisymmetric function of $\varepsilon$, in which case the equilibrium solution must then satisfy $\Gamma_{+\leftarrow}(\varepsilon)f^0_0(-,\varepsilon) = \Gamma_{\leftarrow+}(\varepsilon)f^0_0(+,\varepsilon)$. 

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Appendix H

Numerical Propagation of Kinetic Equations

In this section we outline the numerical scheme employed. First we discretize the bias axis. The spacing \( \delta \varepsilon \) is chosen such that \( \Gamma(\varepsilon) \) can be appropriately resolved. In our case the smallest scale comes in from the sharply-peaked transition rate \( \Gamma^{\text{nuc}+\text{mm}} \), whose width is \( w \). Hence \( \delta \varepsilon \) should be chosen at the scale of \( w \) or smaller.

Once we have chosen \( \delta \varepsilon \), the bin widths \( \delta K \) for the coupling strength can be taken as \( \delta K = \delta \varepsilon \), since we probe the density of coupling strengths as \( g_R(\varepsilon/2) \). Therefore we discretize \( \varepsilon \) as \( \varepsilon_i \), and \( K \) as \( K_i \), such that \( \varepsilon_i - \varepsilon_j = (i - j)\delta \varepsilon \) and \( K_i - K_j = (i - j)\delta K \). We also center the discretization so that \( \varepsilon = 0 \) (and \( K = 0 \)) is amongst the points. Finally, we choose our maximum value of the bias range to be \( \varepsilon_{\text{max}} = 50 \) (in units of \( E_{\text{dm}} \)), which is typically large enough that the probability distributions decay well before reaching this limit. We must also keep in mind that the phonoemissive rate is invalid past the first resonance anyway, which in this case is reached at \( \varepsilon \approx 85 \) (in units of \( E_{\text{dm}} \)).

The value assigned to \( g_R(K_i) \) (for \( K_i \neq 0 \)) is the number of sites, within a ball of \( B_R \) of large radius \( R \), that have coupling strengths between \( [K_i - \frac{\delta K}{2}, K_i + \frac{\delta K}{2}] \). As discussed in (sec. 4.3), larger \( R \) means including far-away spins, which only contribute to the count near \( K \approx 0 \); for the regularized \( g_R \) this value is subtracted out. The numerical value assigned to \( g_R(0) \), therefore, is the value such that the sum of \( g_R(K_i)\delta K \) over all \( K_i \) yields 0.

Next we describe the numerical propagation of the kinetic equations. Define,

\[
p_{+,i} = f(+, \varepsilon_i), \quad p_{-,i} = f(-, \varepsilon_i),
\]

and also,

\[
G_{ij} = \frac{1}{2} g_R(\frac{1}{2}(\varepsilon_j - \varepsilon_i))\delta \varepsilon,
\]
the kinetic equations become,
\[
\frac{\partial}{\partial t} s_{i}(t) = \Gamma_{\bar{s} s}(\varepsilon_{i})p_{s,i}(t) - \Gamma_{\bar{s} s}(\varepsilon_{i})p_{s,i}(t)
+ \sum_{j} \Gamma_{-}(\varepsilon_{j})p_{+,j}(t) \sum_{i} G_{i,j}p_{s,i}(t) + \sum_{j} \Gamma_{+}(\varepsilon_{j})p_{-,j}(t) \sum_{i} (G_{i,j}p_{s,i})(t).
\] (H.3)

In practice $G$ will be a sparse matrix with a majority of the off-diagonal entries being zero, so the matrix multiplication in (eq. H.3) can be optimized to take advantage of this.

To propagate from $t$ to $t+\delta t$ we employ a Runge-Kutta 4-th order scheme. Recall that, for a vector-valued first-order autonomous ODE,
\[
\frac{\partial y}{\partial t} = f(y),
\] (H.4)
the standard RK4 solution is recursively given by
\[
\begin{align*}
k_{1}(t) &= f(y(t)), \\
k_{2}(t) &= f(y(t) + \frac{\delta t}{2} k_{1}(t)), \\
k_{3}(t) &= f(y(t) + \frac{\delta t}{2} k_{2}(t)), \\
k_{4}(t) &= f(y(t) + \delta t k_{3}(t)), \\
y(t + \delta t) &= y(t) + \frac{\delta t}{6} (k_{1}(t) + 2k_{2}(t) + 2k_{3}(t) + k_{4}(t)).
\end{align*}
\] (H.5)

By writing $p_{+,i}$ and $p_{-,i}$ as the entries of a single column vector $y = (p_{+,i}, p_{-,i})$ (likewise for $f$) the above procedure can be used to evolve the kinetic equations.
References


