Towards Landau-Zener-Stückelberg Interferometry on Single-molecule Magnets

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Abstract

Landau-Zener-Stückelberg (LZS) interferometry has been widely used in studying the coherence and the energy-level structure of two-level quantum systems such as superconducting qubits. Being an effective two-level system, single-molecule magnets (SMMs) have been suggested as one such system where the LZS interferometry can be applied. In this thesis, we try to perform the LZS interferometry on Mn$_3$ SMM ($S = 6$) using a loop-gap resonator to produce the large driving field that the interferometry requires. It is shown that we have to improve the $Q$ of the current resonator by two orders of magnitude to see the first few interference patterns in Mn$_3$. We present the results of using the loop-gap resonator in performing parallel-mode electron spin resonance spectroscopy on a Ni$_4$ SMM ($S = 4$). We report the observation of forbidden transitions and a possible observation of an excited spin state manifold with $S = 3$. 
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만저 에머스트에서의 사년간 글심양면으로 지원해주신 부모님에 감사합니다. 그리고 에니 파워요오 vs 플로이드 메이맥 경기들을 몹 수 있게 SBS 회원가입 까지 혼내희 해준 누나에게도 감사의 말 전합니다. 아직까지 발병 안 부리고 잘 보고 있는 다연아 너무 고맙다.

비록 멀리 떨어져있었지만 에 코미마다 응원해준 이민영상에게도 고맙다는 말을 하고 싶습니다. 더불어 지난 삼년간 같이 고생한 이지훈군과 이 weir 패러에게도 감사와 응원의 메시지를 보냅니다.

끝으로 가끔에 쏟나듯 응원해준 해준, 진년이, 현, 이민리, 타파영, 준에서도 호소마한 감사의 인사를 전합니다.

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Chapter 1

Introduction

1.1 Motivation

Over the last three decades, there has been much interest and effort in realizing a quantum computer. A quantum computer has a basic information processing unit called a qubit and is expected to outperform a classical computer in many specific problems such simulating quantum physics and factoring large numbers [1].

The working of a quantum computer relies on the quantum phenomena of superposition and entanglement of qubits. The qubits are realized from two-level quantum systems with two distinct quantum states such as the spin-projection states of an electron and the polarization states of a photon. To be realizable as qubits, these systems are required to retain their quantum behavior for long enough time for certain quantum operations to be performed. However, any two-level system in the real world interacts with the environ-
ment and loses its quantum behavior through decoherence over a certain time
interval \[T_2\]. This time interval is characterized by coherence time \(T_2\) of the
system, and it has become one of the most important criteria in evaluating a
two-level quantum system as a possible qubit [1].

In this context, devising a convenient probe to measure the coherence time
of a two-level system has become an important experimental task. Among
others, the Landau-Zener-Stückelberg (LZS) interferometry was suggested
by Shytov in 2003 as one such method with an advantage of using a low
frequency and a non-resonant method [3]. The basic idea behind the interfer-
ometry is that we can induce LZS interference, which is a coherent quantum
phenomenon, at a timescale much smaller than the coherence time of a two-
level system. The shape of this interference pattern then reflects how the
system interacts with the outside world and thus can be used to estimate \(T_2\).

In addition to measuring the coherence time of a two-level system, the
LZS interferometry can be used to probe the energy-level structure of the
system [4]. Again, the idea is to induce LZS interference and obtain spectro-
scopic information from the emerging interference pattern. Because it uses
the interference effect in inducing transitions rather than directly providing
the required energy, the LZS interferometry has several advantages over tra-
ditional frequency spectroscopy such as electron spin resonance (ESR) [4, 5].
These advantages will be further discussed later in this chapter.

In this thesis, I attempt to apply the LZS interferometry on single-molecule
magnets (SMMs). A SMM is a molecule with a high spin that behaves like
a paramagnet at low temperature [6]. Although the development and the
application of the LZS interferometry have largely been limited to superconducting qubits, which are a two-level system realized from a superconducting ring disconnected by a thin dielectric region called Josephson junction [7], a SMM has been suggested as another system where the application of the LZS interferometry is possible [4, 5]. Further details on the requirements and the necessary work to realize the LZS interferometry on SMMs will be provided shortly.

The significance of applying the LZS interferometry on SMMs is largely twofold; it will allow one to study the coherence in the spin dynamics of SMMs, and it will be a complementary method to probe the energy structure of SMMs. So far, I laid out the basic ideas that motivated the implementation of the thesis. For the rest of the introduction, I will explore these ideas in more details providing necessary background, and I will present the experimental scheme to realize the LZS interferometry on SMMs. Towards the end of the chapter, we will also see that the original plan to apply the LZS interferometry on SMMs took a slightly different turn and led to some interesting experimental results. Before moving on, however, I must introduce what the LZS interferometry really is.

1.2 The LZS interferometry in a nutshell

For a rough sketch of the LZS interferometry, let’s consider an arbitrary two-level system with two quantum states $|1\rangle$ and $|2\rangle$, where the Hamiltonian of
the system is given by

\[ \hat{H} = \frac{1}{2} (\epsilon \sigma_z + \Delta \sigma_x) \]  

(1.1)

where \( \sigma_z \) and \( \sigma_x \) are Pauli matrices and \( \epsilon \) and \( \Delta \) are parameters of the system in units of energy. States \( |1\rangle \) and \( |2\rangle \) are the eigenstates of \( \sigma_z \) and serve as basis states for the matrix representation of the Hamiltonian. We assume that \( \epsilon \) is an external parameter that we can control and that \( \Delta \) is a fixed parameter that belongs to the system. This quantity \( \Delta \) is called the tunnel splitting and plays an important role in the LZS interferometry as we will see shortly.

The general approach in laying out the theory of the LZS interferometry will be to present the resulting equations and then to interpret their physical meanings rather than to provide rigorous derivations for the equations. Although I will describe general procedures in qualitative terms, those who are interested in full derivations of the equations are directed to the cited work.

1.2.1 Avoided Crossing

In starting the discussion on the LZS interferometry, it is important to note that basis states \( |1\rangle \) and \( |2\rangle \) are not the energy eigenstates in general. We can see this more clearly in Equation 1.1 where \( \sigma_z \) and \( \hat{H} \) do not commute and thus do not share common eigenstates. However, in the limit where \(|\epsilon| \gg \Delta\), the \( \sigma_x \) term can be ignored in Equation 1.1, and the two basis states are the energy eigenstates with the Hamiltonian

\[ \hat{H} \approx \frac{1}{2} \epsilon \sigma_z. \]  

(1.2)
In this asymptotic regime, the energy of the system linearly depends on $\epsilon$. More explicitly, we can diagonalize the Hamiltonian in Equation 1.1 to obtain

$$E_{\pm} = \pm \frac{1}{2} \sqrt{\epsilon^2 + \Delta^2}$$  \hspace{1cm} (1.3)

where $E_{\pm}$ are the energy eigenvalues of the system. In the asymptotic regime where $|\epsilon| \gg \Delta$, the energy eigenvalues in Equation 1.3 becomes

$$E_{\pm} \approx \pm \frac{1}{2} \epsilon$$  \hspace{1cm} (1.4)

where they show linear dependence on $\epsilon$ as expected.

More importantly, in Equation 1.3, we see that the two energy eigenvalues are separated by amount $\Delta$ at $\epsilon = 0$ (Figure 1.1). As a result, the energy eigenvalues, which linearly depend on $\epsilon$ far away from $\epsilon = 0$, start to lose their linear dependence on $\epsilon$ as $\epsilon$ approaches 0, and the states repel each other with energy splitting $\Delta$ at $\epsilon = 0$. This behavior of the energy levels repelling each other is called an avoided crossing and constitutes one of the two requirements of the LZS interferometry. Although I only briefly introduce an avoided crossing in this chapter, we will see how it plays an integral role in the LZS interferometry in greater detail in the next chapter.

### 1.2.2 Single Crossing

So far, I introduced the system where the LZS interferometry can be performed, and the requirement was that the system must exhibit an avoided crossing. In the LZS interferometry, we induce an interference effect by driv-
ing a system across its avoided crossing multiple times. Before directly diving into the case of multiple crossings, I will first consider a simpler case where the system is driven across the avoided crossing once in a single, linear sweep.

So, let’s start with preparing our system far away from its avoided crossing by setting $\epsilon = \epsilon_0$ where $|\epsilon_0| \gg \Delta$. In this regime, basis states $|1\rangle$ and $|2\rangle$ are the energy eigenstates of the system. For convenience, I will pick state $|1\rangle$ to be the initial state of the system (Figure 1.2). Next, we drive the system across the avoided crossing by linearly sweeping $\epsilon$ such that $\epsilon$ in Equation 1.1 is replaced by

$$\epsilon(t) = \epsilon_0 + vt$$  \hspace{1cm} (1.5)$$

where $\epsilon_0$ is the initial detuning with $|\epsilon_0| \gg \Delta$ and $v$ is the speed of the sweep ($\dot{\epsilon} = v$) (Figure 1.3). The sweep continues until we reach the other asymptotic region across the avoided crossing. Although our initial state $|1\rangle$ is a stationary state in the two asymptotic regions where it is an energy eigenstate of the
system, it becomes subject to certain time evolution in the vicinity of the avoided crossing where the approximation in Equation 1.2 breaks down. This results in the possibility that the state of the system may not remain in state $|1\rangle$ at the end of the sweep. As a consequence, the state of the system at the end of the sweep is described by a superposition of basis states $|1\rangle$ and $|2\rangle$.

The probability of remaining in state $|1\rangle$ is precisely what Landau [8], Zener [9], Stueckelberg [10], and Majorana [11] calculated in the context of atomic collisions in 1932. It is called the Landau-Zener (LZ) probability and is given by

$$P_{LZ} = e^{-2\pi \Delta^2 / \hbar \nu}$$

(1.6)

where $P_{LZ}$ is the LZ probability that, in the context of LZ dynamics, the system undergoes a LZ transition [8–11]. A LZ transition is the case when a system undergoes a non-adiabatic transition from the ground state to the

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**Figure 1.2:** Initial setting for the system soon to be driven across the avoided crossing in a single, linear sweep of $\epsilon$. The red circle denotes the state of the system.
excited state when it is driven across the avoided crossing. For example, in our case, a LZ transition corresponds to the case where the system gets excited from its ground state, which is basis state $|1\rangle$ before the crossing, to its excited state, which is again $|1\rangle$ after the crossing. Note that both the ground state and the excited state are basis state $|1\rangle$ and that a LZ transition corresponds to the case where the system remains in its initial basis state after it is driven across the avoided crossing. The other case is when the system undergoes an adiabatic transition where the state remains in its ground state, which is initially basis state $|1\rangle$ before the crossing but becomes the other basis state $|2\rangle$ after the crossing. In this case, note that “remaining” in the ground state involves tunneling from its initial basis state $|1\rangle$ to the other $|2\rangle$ at the end of the crossing.

We can also interpret the result in Equation 1.6 in qualitative terms. Equation 1.6 shows that the LZ probability depends on two parameters $\Delta$ and $v$. 

Figure 1.3: Result of the single sweep across the avoided crossing. The state of the system becomes a superposed state of $|1\rangle$ and $|2\rangle$ after the sweep.
Parameter $\Delta$ represents the tunnel splitting between the two energy levels and can be viewed as the amount of energy the system has to “jump” over to go from its ground state to its excited state [12]. Therefore, a larger $\Delta$ corresponds a greater energy barrier to overcome and leads to a smaller $P_{LZ}$. Also, we can understand the effect of sweep speed $v$ on the LZ probability in terms of the adiabatic theorem. According to the theorem, the state of the system remains in its ground state if the change in its Hamiltonian is adiabatic [13]. Therefore, a smaller $v$ corresponds to a slower change in the Hamiltonian and leads to a larger value for $1 - P_{LZ}$, which in turn corresponds to a smaller $P_{LZ}$.

1.2.3 Multiple Crossings

In the previous section, we saw how the LZ probability depends on two parameters $\Delta$ and $v$ in the case of a single crossing. Now, we proceed to the case of multiple crossings where the system is repeatedly driven across the avoided crossing. In this case, each crossing can be treated as a single crossing, and we will see that an interference effect in the transition probability occurs over the subsequent sweeps. Again, we set the initial state to be in $|1\rangle$ at $\epsilon = \epsilon_0$ far away from the avoided crossing ($|\epsilon_0| \gg \Delta$). Next, we drive the system by harmonically sweeping $\epsilon$ with driving amplitude $A$ and angular frequency $\omega$ such that $\epsilon$ in Equation 1.1 is replaced by

$$\epsilon (t) = \epsilon_0 + A \sin(\omega t) \quad (1.7)$$
where $\epsilon_0$ is the initial detuning and $A \sin(\omega t)$ is the driving term. For the driving term to really drive the system across the avoided crossing with initial detuning $\epsilon_0$, we require the driving amplitude to be larger than the magnitude of the detuning ($A > |\epsilon_0|$). This constraint on $A$ is, in fact, the second requirement for the LZS interferometry. If the driving amplitude doesn’t meet this requirement, a system cannot be driven across its avoided crossing and LZS interference cannot occur.

During one sweep period $T = 2\pi/\omega$, the system is driven across the avoided crossing twice (Figure 1.4). For the first quarter of the sweep, the system is driven across the avoided crossing for the first time and put into a coherent superposition of $|1\rangle$ and $|2\rangle$ with the probability amplitudes determined by the LZ probability given in Equation 1.6 (Figure 1.4a). Right after the system is driven across the avoided crossing, the system acquires dynamic phase due to the energy difference between the two energy levels. For the second quarter of the sweep period, the system first accumulates dynamic phase until it reaches the avoided crossing for the second crossing in the reversed direction (Figure 1.4b). This puts the system into a new superposed state, and the system continues to accumulate yet more dynamic phase for the rest of the sweep period (Figures 1.4c and 1.4d)

In the strongly driven regime ($A, \hbar \omega \gg \Delta$), the relative phase the system acquires over one sweep period $T$ is entirely due to dynamic phase [14]:

$$\Delta \theta = \frac{1}{\hbar} \int_0^T \epsilon(t) \, dt$$

(1.8)
Figure 1.4: Schematic diagrams that sketch how the state of the system changes over one sweep period $T$. The red circles denote the state of the system at the given time, and the green arrow shows the direction of the sweep. The system is driven across the avoided crossing twice for the first half of the period, and acquires more dynamic phase for the remaining half.

where $\Delta \theta$ is the relative phase of the system after one sweep period $T$ [13]. Over the successive sweeps, an interference effect occurs in the transition probability with constructive interferences occurring whenever the relative phase is

$$\Delta \theta = 2n\pi$$

(1.9)

where $n$ is an integer [14]. We can modify the above equation using Equations 1.7 and 1.8 to obtain

$$\epsilon_0 = n\hbar\omega.$$  

(1.10)
Around these values of $\epsilon_0$, the transition probability between $|1\rangle$ and $|2\rangle$ forms a sharp resonant peak, forming an interference pattern [14]. Equation 1.10 also shows that the interference pattern can be interpreted as the result of multi-photon transitions with $n$ indicating the number of photons involved in each transition [14].

We can also see this more explicitly by analytically calculating the transition probability. In general, this can be done in two ways. In one scheme, we construct a transfer matrix $T$ that accounts for a single crossing by discretizing the problem into three stages [15]. In the first stage, the system acquires dynamic phase until it reaches the avoided crossing. In the second stage, the system is driven across the avoided crossing with a linear sweep and is put into a superposed state, which acquires further dynamic phase in the third stage. Each step is represented by a matrix operator, and the product of these matrices yields the final transfer matrix $T$ for a single sweep. Its conjugate $T^*$ then represents a sweep in the reversed direction, and traversing back and forth the avoided crossing is represented by the product $T^*T$. This final unitary matrix is then applied to an initial state to obtain the final state after the system is driven across its avoided crossing back and forth [15]. The transition probability after $2m$ crossings is then calculated by applying $(T^*T)^m$ on the initial state of the system.

The other simpler scheme involves transforming the Hamiltonian of the system given in Equation 1.1 with Equation 1.7 to a non-uniformly rotating frame and isolating the transitions with different $n$’s by using the Jacob-Anger expansion [12, 14]. This method treats each $n$-th transition separately, and
the total transition probability is calculated by summing up the individual probabilities. As a result, we obtain

\[ P = \sum_{n=-\infty}^{\infty} \frac{|\Delta_n|^2}{(\epsilon_0 - n\hbar \omega)^2 + |\Delta_n|^2} \sin^2 \left( \frac{\omega'_n t}{2} \right) \]  
(1.11)

where \( P \) is the full transition probability, \( \Delta_n \) is defined as

\[ \Delta_n = \Delta J_n \left( \frac{A}{\omega} \right) \]  
(1.12)

where \( \Delta \) is the tunnel splitting, \( J_n \) is a Bessel function of the first kind, \( A \) is the driving amplitude, and \( \omega'_n \) is given by

\[ \omega'_n = \sqrt{(\epsilon_0 - n\hbar \omega)^2 + |\Delta_n|^2} \]  
(1.13)

as shown in [14].

Ignoring the time dependence in Equation 1.11, we can see that a Lorentzian peak emerges around the values of \( \epsilon_0 \) that satisfy Equation 1.10, which results in an interference pattern as a function of \( \epsilon_0 \). Also, the full transition probability in Equation 1.11 oscillates with angular frequency \( \omega'_n/2 \), which in turn depend on driving amplitude \( A \) through Equations 1.12 and 1.13. At the constructive interferences (at \( \epsilon_0 = n\hbar \omega \)), the coefficient in Equation 1.11 becomes 1, and the angular frequency reduces to \( \Delta J_n (A/\omega)/2 \) with a fixed value of \( \omega \). As a whole, these two patterns - the resonance-like interference pattern along \( \epsilon \) and the oscillatory pattern along \( A \) - form the LZS interference in the transition probability.
At the $n$th transition, the area under the curve of the transition probability as a function of the driving amplitude $A$ is related to the coherence time of a system:

$$A_n = \frac{T_1 \Delta_n^2}{4\sqrt{T_1 T_2 \Delta_n^2 + 1}}$$ (1.14)

where $A_n$ is the area, $T_1$ is the relaxation time, and $T_2$ is the coherence time [14]. Through this relation, the LZS interference shows how a system interacts with the environment, and we can estimate the coherence time by measuring the area.

### 1.3 Amplitude Spectroscopy

In the previous section, we saw how LZS interference is formed when a system is repeatedly driven across its avoided crossing and how the coherence time of the system is related to the formed interference pattern. Another useful feature of the LZS interference is its relation to the tunnel splitting of a system as we can see in Equations 1.6 and 1.14. Through this relation, the LZS interferometry can also be used to measure the tunnel splitting and to probe the energy structure of a system.

It is worthwhile to mention that the basic idea of using the LZS interferometry as a spectroscopic tool is closely related to what Berns introduced as amplitude spectroscopy in 2008 [4]. In amplitude spectroscopy, one studies the energy-level structure of a multi-state quantum system by driving the system across more than one avoided crossing. As in the LZS interferometry, the state of the system is manipulated through an external parameter, and,
at a fixed value of this parameter, the driving amplitude is swept over a wide range such that the system is driven across several avoided crossings in one sweep. The measurement is then repeated over different values of the external parameter, and, as a result, a diamond-shaped interference pattern is acquired as a function of the external parameter and the driving amplitude [4]. This interference pattern contains the spectroscopic information of the system such as the location of the avoided crossings and can be used to characterize the energy-level structure of the system.

In his paper, Berns suggests amplitude spectroscopy as a spectroscopic tool complementary to frequency spectroscopy. Traditional frequency spectroscopy such as ESR acquires the spectroscopic data by tuning the frequency of the harmonic driving field to the energy gap between the two states of the system under study. Although widely successful, frequency spectroscopy has two major limitations [4]. First of all, frequency spectroscopy has been limited in studying the energy gaps in terahertz range due to the difficulty in building a stable frequency source in that range. Secondly, the use of various frequencies over a wide range is limited by the use of the waveguides the physical dimensions of which depend on the frequency in use. These limitations can be overcome by using the amplitude, rather than the frequency, of the driving field at a single, fixed frequency [4].

In the context of amplitude spectroscopy, the LZS interferometry is its scaled-down version. Unlike amplitude spectroscopy where a system is driven across several avoided crossings, the LZS interferometry drives a system across only one avoided crossing between the two energy levels of the system. Other
than that, both amplitude spectroscopy and the LZS interferometry are identical in their use of the driving amplitude to induce the LZS interference to probe the energy-level structure of a system. This then brings us back to the two requirements of the LZS interferometry. First of all, the system where the LZS interferometry or amplitude spectroscopy is applied must exhibit an avoided crossing in its energy-level structure. Also, the energy levels of the system must be well manipulated through an external parameter and it must produce a driving amplitude larger than initial detuning values.

1.4 Towards LZS interferometry on SMMs

A SMM is one such system where the two requirements of the LZS interferometry can be satisfied. Although a SMM is a multi-state system with multiple spin-projection states, a pair of the spin-projection states can be treated as an effective two-level system that exhibits an avoided crossing. Also, the energy levels of the system are easily manipulated by applying an external magnetic field, and providing a large driving field is possible with the use of a resonator.

Indeed, SMMs have already been suggested as a system where the use of the LZS interferometry is possible [4, 5]. Also, the existence of an avoided crossing in SMMs manifests itself in the quantum tunneling of magnetization [16], where the state of a SMM tunnels from one spin-projection state to the other through an energy barrier. Although a single crossing across an avoided crossing in SMMs has been studied in various contexts such as measuring the tunnel splitting [17], studying the decoherence [18], and controlling the magne-
tization [19], the experimental study on multiple crossings and the observation of resulting LZS interference have not been reported so far.

The experimental design for the LZS interferometry on SMMs largely follows that for typical ESR spectroscopy but with a notable difference. In ESR spectroscopy, a static field is applied to a sample to split the energy levels in the unpaired electrons of the sample, and a harmonic driving field is applied perpendicularly to the static field to drive the transitions between the electronic spin-projection states. In the LZS interferometry, a static field is also applied to a sample of SMMs to set the initial detuning value $\epsilon_0$. Then, unlike in usual ESR spectroscopy, a harmonic driving field is applied parallel with the static field to drive the system across its avoided crossing multiple times. This then indirectly induces transitions between the spin-projection states through an interference effect emerging from the coherent time evolution of the spin-projection states.

The most important experimental task in realizing the LZS interferometry is then to produce a large driving amplitude to drive a system across its avoided crossing back and forth. We try to achieve this by using a loop-gap resonator, which has been known to produce uniform, large driving field [20]. Because designing, fabricating, and characterizing a loop-gap resonator comprises a crucial portion of the experimental work in realizing the LZS interferometry, a large portion of the thesis will be devoted to providing details on these processes.

The rest of the thesis portrays an effort to use the fabricated resonator for the LZS interferometry. Unfortunately, however, we will see that our loop-
gap resonator produced a driving amplitude more than an order of magnitude smaller than the required value, thus failing to satisfy the second requirement of the LZS interferometry. When the driving amplitude is small \((A \ll \epsilon_0)\), a system is never driven across its avoided crossing, and the driving term is treated as a small perturbation to the system. In this regime, the experimental setup for the LZS interferometry is really a setup for parallel-mode ESR spectroscopy, where a small driving field parallel with the static field induces transitions by directly providing the required energy rather than by causing an interference effect. With this result, we performed parallel-mode ESR spectroscopy on the \(\text{Ni}_4\) SMM.

Performing parallel-mode ESR using a loop-gap resonator was fascinating in its own right. For one thing, our measurement showed the remarkable sensitivity of a loop-gap resonator where a frequency shift of one part per million of its operating frequency could be detected. This remarkable sensitivity led to a possible observation of chromium impurities in our setup. Also, in \(\text{Ni}_4\), we observed forbidden transitions between spin-projection states with \(\Delta m_s > 1\), which violates the quantum selection rules. We also observed transitions that might be related to the crossings between the \(S = 4\) manifold and the \(S = 3\) manifold in \(\text{Ni}_4\).

The real significance of the thesis is still twofold. First of all, it will portray the experimental scheme to realize the LZS interferometry on SMMs with detailed accounts on how to perform the interferometry using a loop-gap resonator. I hope that this account will serve as a starting point for future attempts to realize the LZS interferometry on SMMs. Secondly, the thesis will
present the results of using a loop-gap resonator in performing parallel-mode ESR spectroscopy on Ni$_4$. As already mentioned, this revealed many interesting features in Ni$_4$, and I hope the results will generate interests and insights in further studying the observed features.

1.5 Forthcoming Chapters

The structure for the rest of the thesis is straightforward. In Chapter 2, I revisit the avoided crossing and show its significance in LZS interferometry. Also, I give more detailed introduction to SMMs and discuss on how to visualize the LZS interferometry in terms of the double-well potential diagram. For the rest of the chapter, I compare ESR spectroscopy and LZS interferometry to further probe the significance of an avoided crossing in LZS interferometry and present parallel-mode ESR spectroscopy as an interesting limiting case of the LZS interferometry. In Chapter 3, I introduce the experimental scheme to realize the LZS interferometry on SMMs focusing on the use of a loop-gap resonator. Presented in the context of a general guideline to perform the LZS interferometry, the discussion also includes detailed accounts on how we followed this guideline. Also, I present the experimental procedure for the LZS interferometry on SMMs, which is the same as parallel-mode ESR performed for the thesis. In Chapter 4, I present the experimental results of performing parallel-mode ESR on Ni$_4$ using a loop-gap resonator. In Chapter 5, I provide an overall summary for the thesis and conclude the thesis with some thoughts on future directions.
Chapter 2

Theoretical Background

The important equations for the LZS interferometry have already been given in the previous chapter. In this chapter, I will further probe the significance of an avoided crossing in the LZS interferometry. First, by looking at how an avoided crossing affects the stationary states of a two-level system, we will see how it allows a superposition of two observable states. Then, a brief introduction on SMMs will follow presenting some useful tools in visualizing how the spin-projection states of an SMM are manipulated in the LZS interferometry. Returning to the main discussion, I will compare ESR spectroscopy with the LZS interferometry to see how an avoided crossing affects the dynamics of the spin-projection states in an SMM. We will see that simply changing the direction of the driving field in conventional ESR spectroscopy does not lead to the LZS interferometry and that an avoided crossing again plays an important role. Finally, I consider a limiting case of the LZS interferometry where the driving amplitude is smaller than the initial detuning and thus cannot drive
a system across its avoided crossing. We will see that, in this regime, the
LZS interferometry reduces to parallel-mode ESR spectroscopy and this will
be more relevant for the discussion of our experimental results.

2.1 Avoided Crossing

As I introduced in the beginning, an avoided crossing refers to the behavior of
two energy levels repelling each other. Although a mathematical treatment of
the avoided crossing can be done more generally in the context of an arbitrary
two-level system, I’ll pick a more familiar system, namely, a spin-$\frac{1}{2}$ particle
in the presence of an external magnetic field applied along the $z$-axis in the
Cartesian coordinates. In this case, the two spin-projection states along the
$z$-axis are the only two possible states of the system. The energy of the system
is given by

$$ E = -\mu \cdot B $$

(2.1)

where $E$ is the energy of the system, $\mu$ is the magnetic moment of the particle,
and $B$ represents the external field given by

$$ B = B_0 \hat{k} $$

(2.2)

where $B_0$ is the magnitude of the field and $\hat{k}$ is the unit vector along the $z$-axis.

With zero orbital angular momentum, the magnetic moment of the particle is
entirely due to its spin angular momentum:

$$\mu = \gamma \hat{S}$$  \hspace{1cm} (2.3)

where $\hat{S}$ is spin operator and $\gamma$ is the gyromagnetic ratio.

Putting Equations 2.1 to 2.3 together, we obtain the Hamiltonian of the system:

$$\hat{H} = -\gamma B_0 \hat{S}_z.$$  \hspace{1cm} (2.4)

For notational convenience, I will write $\hat{S}_z$ in terms of a Pauli matrix $\hat{\sigma}_z$ using the two spin-projection states along the $z$-axis as a basis and introduce parameter $\epsilon = \gamma \hbar B_0$ to obtain

$$\hat{H} = -\frac{1}{2} \epsilon \hat{\sigma}_z.$$  \hspace{1cm} (2.5)

Equation 2.5 shows that the Hamiltonian of the system commutes with $\hat{\sigma}_z$, and hence with $\hat{S}_z$. Therefore, the two spin-projection states along the $z$-axis, which are the eigenstates of $\hat{S}_z$, are also the energy eigenstates of the system. As a consequence, the two spin-projection states are stationary states; if the system is initially prepared in one of the spin-projection state, it will stay in that state forever. Also, the energy eigenvalues are

$$E_{\pm} = \pm \frac{1}{2} \epsilon$$  \hspace{1cm} (2.6)

where we see that the energy linearly depends on $\epsilon$ (Figure 2.1). Increasing the magnitude of the field linearly increases the energy difference between the
two states. Notice that in the absence of the magnetic field ($\epsilon = 0$), the two spin-projection states become degenerate with the energy eigenvalue equal to zero.

![Energy-level diagram for a spin-\(\frac{1}{2}\) particle in the presence of an external magnetic field](image)

Figure 2.1: Energy-level diagram for a spin-\(\frac{1}{2}\) particle in the presence of an external magnetic field. Each line shows the linear dependence of the energy of each spin-projection state on $\epsilon$.

To introduce an avoided crossing, let’s consider applying another magnetic field along the $x$-axis with a constant magnitude $B_1$. Although we’re applying an external field to introduce the avoided crossing for this specific example, I remind the reader that an avoided crossing is usually treated as inherent to the system. In the light of Equation 2.1, the Hamiltonian of the system becomes

$$
\hat{H} = -\gamma \left( B_0 \hat{S}_z + B_1 \hat{S}_x \right).
$$

Again, using the spin-projection states along the $z$-axis as our basis and in-
Introducing another parameter $\Delta = \gamma \hbar B_1$, we obtain

$$\hat{H} = -\frac{1}{2} (\epsilon \hat{\sigma}_z + \Delta \hat{\sigma}_x)$$  \hspace{1cm} (2.8)$$

which, without the minus sign, is identical to the Hamiltonian for the arbitrary two-level system with an avoided crossing introduced in the previous chapter.

Before we introduced the tunnel splitting $\Delta$, we saw that the two spin-projection states along the $z$-axis are the energy eigenstates and thus the stationary states of the system. Now we will see how the introduction of $\Delta$ changes the stationary states by solving the Schrödinger equation with the Hamiltonian given in Equation 2.8. Before actually solving the equation, we can already see in Equation 2.8 that the Hamiltonian no longer commutes with $\hat{\sigma}_z$ indicating that the spin-projections states along the $z$-axis are no longer stationary states and thus subject to certain time evolution. More explicitly, we can diagonalize the Hamiltonian to obtain the energy eigenvalues:

$$E_{\pm} = \pm \frac{1}{2} \sqrt{\epsilon^2 + \Delta^2}. \hspace{1cm} (2.9)$$

To find the energy eigenstates, which I denote as $|\psi_+\rangle$ and $|\psi_-\rangle$, we solve the time-independent Schrödinger equation:

$$\hat{H}|\psi_{\pm}\rangle = E_{\pm}|\psi_{\pm}\rangle. \hspace{1cm} (2.10)$$
First, I will solve the equation for $|\psi_+\rangle$, setting

$$
|\psi_+\rangle = \begin{pmatrix} a \\ b \end{pmatrix}
$$

where $|a|^2 + |b|^2 = 1$. Using the matrix representation given in Equation 2.8 and introducing $\Omega = \sqrt{\epsilon^2 + \Delta^2}$, we have

$$
- \begin{pmatrix} \epsilon & \Delta \\ \Delta & -\epsilon \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \Omega \begin{pmatrix} a \\ b \end{pmatrix},
$$

which yields

$$
- \epsilon a - \Delta b = \Omega a.
$$

Dividing both sides by $\Omega$ and introducing

$$
\cos 2\theta = \frac{\epsilon}{\Omega} \quad \text{and} \quad \sin 2\theta = -\frac{\Delta}{\Omega}
$$

as done in [21], we obtain

$$
- a \cos 2\theta + b \sin 2\theta = a.
$$

We can solve the above equation for $a$ and $b$ using the relevant trigonometric identities and the relation $|a|^2 + |b|^2 = 1$ to obtain one of the energy eigenstates:

$$
|\psi_+\rangle = \sin \theta |1\rangle + \cos \theta |2\rangle.
$$
Following the similar procedure for $|\psi_{-}\rangle$, we obtain

$$
|\psi_{-}\rangle = \cos \theta |1\rangle - \sin \theta |2\rangle.
$$

Equations 2.16 and 2.17 show that the two spin-projection states are no longer the stationary states of the system after we introduced $\Delta$. Also, returning to the energy eigenvalues in Equation 2.9, we see that the energy levels no longer cross but repel each other by $\Delta$ at $\epsilon = 0$ (Figure 2.2). An important consequence is that the system initially prepared in one of its spin-projection state can develop an amplitude in the other spin-projection state, allowing the system to be in a coherent superposition of the two states.

Figure 2.2: Diagram for a two-level system exhibiting an avoided crossing.
2.2 Single-molecule Magnet

As introduced in the previous chapter, SMM refers to a class of molecules that behave like a paramagnet at sufficiently low temperatures. An SMM is a few nanometers in size, and roughly $10^{15}$ SMMs form a crystalline sample [6]. Although a sample of SMMs is a macroscopic object with a typical size of a few hundreds of microns, it still shows many fascinating quantum phenomena such as the quantum tunneling of magnetization [16] and the Berry phase interference [17] [22]. In addition to these unique physical properties, an SMM is one of the smallest bistable magnets that have numerous practical applications ranging from data storage to quantum computing [6].

A typical SMM has a magnetic core comprised of transition ions and a ligand structure that surrounds the core. The transition ions at the core are strongly coupled with one another to yield a net rigid, high spin for the molecule [6]. On the other hand, the ligand structure serves as a buffer between neighboring molecules and prevent the intermolecular magnetic interactions. As a result, we treat a sample of SMMs as an ensemble of $\sim 10^{15}$ non-interacting, identical spins [6].

At low temperatures, the high spin of an SMM yields multiple spin-projection states along its preferred axis of magnetization, or the easy axis. The energy of each spin-projection state is given by the spin Hamiltonian characteristic of each SMM and can be modeled by a double-well potential diagram (Figure 2.4). Specifically, I will consider a Mn$_3$ SMM to discuss the spin Hamiltonian and the double-well potential.

Figure 2.3 shows an overhead view of a sample of Mn$_3$, chemically known
as \([\text{NE}_4]_3[\text{Mn}_3\text{Zn}_2(\text{salox})_3\text{O}(\text{N}_3)_6\text{Cl}_2]\). There are roughly \(10^{15}\) Mn\(_3\) molecules in the sample, and they crystallize into a tetragonal shape. The sample reflects the threefold (C\(_3\)) symmetry of the molecule. Each Mn\(_3\) contains three Mn\(^{III}\) ions, each of which has \(S = 2\), that contribute to a total spin \(S = 6\) of the molecule. The spin Hamiltonian of Mn\(_3\) is given by

\[
\hat{H} = -D \hat{S}_z^2 + B_4^0 \hat{O}_4^0 + B_4^3 \hat{O}_4^3 + B_6^6 \hat{O}_6^6 - \frac{\mu_B}{\hbar} \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} \tag{2.18}
\]

where the first four terms are anisotropic terms that reflect the symmetry of the molecule and the last term is the Zeeman term. The first and the second terms are the second-order and the fourth-order anisotropic terms, respectively, and give a rise to the energy barrier between the spin-projection states along the easy axis of the molecule at zero field (Figure 2.4). The third and the fourth terms are higher-order anisotropic terms that reflect the C\(_3\) symmetry of the molecule and can be decomposed to spin operators and ladder operators [23].
Lastly, the Zeeman term accounts for the interaction of the molecular spin with the external magnetic field. Through this term, we are able to manipulate the energy levels of the spin-projection states.

Figure 2.5 shows the energy level of each spin state projected along the easy axis of Mn$_3$. The two double-well potentials represent the energy of the spin-projection states at given magnetic fields. At zero field, the symmetric double-well potential reflects that the energy levels of all the spin-projection states are doubly degenerate except for state $|m_s = 0\rangle$ (the upper left panel in the figure). At a slightly higher field, the energy level of $|+6\rangle$ is at resonance with that of $|-5\rangle$, and this is reflected in the tilted double-well potential (the upper right panel in the figure). Note that the energy level diagram in the figure shows that the spin-projection states other than the pair of $|+6\rangle$ and $|-5\rangle$ are not exactly at resonance due to the anisotropic terms. Also, even
Figure 2.5: Energy-level diagram for Mn$_3$. The two double-well potentials at the top show the energy levels of the spin-projection states at given fields. The resonance between the states is marked by the blue double-head arrows.

between states $|+6\rangle$ and $|-5\rangle$, the energy levels are not completely degenerate at the resonance due to the avoided crossing shown in the lower left inset.

The energy-level diagram and the double-well potential are useful tools in visually understanding how the energy levels of the spin-projection states are manipulated in LZS interferometry. As we saw earlier, applying the magnetic field parallel with the easy axis of the molecule lowers the left well (Figure 2.4). Similarly, applying the field anti-parallel with the easy axis lowers the right well tilting the potential in the other direction. In the LZS interferometry, we
start by applying the static field to lower one well of the double-well potential populating the lowest energy state $|-6\rangle$ in the sample (the middle right in Figure 2.6). Then, we apply the field in the other direction to bring the energy levels of $|-6\rangle$ and $|+6\rangle$ just near the avoided crossing, as shown in the quasi-symmetrical double-well potential. Then, we apply the driving field parallel with the static field to drive the system across the avoided crossing multiple times. This results in rapidly tilting the two wells up and down in the double-well potential (the upper right panel in Figure 2.6) and in traversing the avoided crossing back and fourth in the energy diagram (the lower right panel in Figure 2.6).

Figure 2.6: Double-well potential representing the LZS interferometry.
2.3 Electron Spin Resonance

Before the introduction on SMMs, we saw how an avoided crossing changes the stationary states of a two-level system with the time-independent Hamiltonian. For the rest of the chapter, we will see how an avoided crossing affects the time evolution of the states when the Hamiltonian of the system changes with time. Specifically, I will first consider the case of no avoided crossing by looking at the system of an unpaired electron in ESR spectroscopy. Then, I will see how changing the direction of the driving field along the static field affects the time evolution of the states, which will address to the importance of an avoided crossing in the LZS interferometry scheme.

The basic theory of ESR can be presented in the system of an electron \( (S = 1/2) \) at rest in the presence of external magnetic fields. Because it is a spin-\( \frac{1}{2} \) particle, it has only two possible spin-projection states along an arbitrary axis in Cartesian coordinates. In this specific case, the electron has zero orbital angular momentum, and, as in Equation 2.3, the magnetic moment of the electron is entirely due to its spin angular momentum. For an electron, \( \gamma \) is given by

\[
\gamma = -\frac{g\mu_B}{\hbar}
\]  

(2.19)

where \( g \) is the electron \( g \)-factor, \( \mu_B \) is the Bohr magneton, and \( \hbar \) is the reduced Planck’s constant. Subsequently, the electron magnetic moment is given by

\[
\mu = -\frac{g\mu_B}{\hbar} \hat{S}.
\]  

(2.20)
Now imagine that we apply a magnetic field along the z-axis. In a classical picture, this results in the magnetic moment of the electron precessing about the z-axis with a fixed z-component. From the perspective of the z-component of the magnetic moment, this interaction can be viewed as the z-component aligning with the applied magnetic field to minimize the energy given by

\[ E = -\mu \cdot B \]  
(2.21)

where \( E \) is the energy of the system and \( B \) is the field. Using Equations 2.20 and 2.21, the Hamiltonian of the electron in the external magnetic fields is written as

\[ \hat{H} = \frac{g\mu_B}{\hbar} B \cdot \hat{S}. \]  
(2.22)

Equation 2.22 gives the general expression for the Hamiltonian of an electron in the presence of external magnetic fields. With this general expression, I will proceed to finding the Hamiltonian specific to ESR spectroscopy.

In ESR spectroscopy, a static field and a harmonic driving field is applied to a sample. First, for the static field, we have:

\[ B = B_0 \hat{k} \]  
(2.23)

where \( B_0 \) denotes the magnitude of the static field. Then, the Hamiltonian given in Equation 2.22 is rewritten as

\[ \hat{H} = \frac{g\mu_B B_0}{\hbar} \hat{S}_z. \]  
(2.24)
The two eigenstates of the above Hamiltonian are the eigenstates of spin operator $\hat{S}_z$ which corresponds to the two spin-projection states along the $z$-axis. Using these two eigenstates as a basis, we can obtain the matrix representation of the Hamiltonian as

$$\hat{H} = \frac{1}{2} g \mu_B B_0 \hat{\sigma}_z$$  \hspace{1cm} (2.25)$$

where I used the Pauli matrix $\hat{\sigma}_z$. As we can see in the above Hamiltonian, the consequence of applying the static field is the splitting of the energy levels for the two spin-projection states (Figure 2.7).

More explicitly, we can calculate the energy eigenvalues of the system:

$$E = m_s g \mu_B B_0$$  \hspace{1cm} (2.26)$$

where $m_s$ is the magnetic quantum number ($m_s = \pm 1/2$ for the electron). The energy difference between the two states is then given by

$$\Delta E = \Delta m_s g \mu_B B_0$$  \hspace{1cm} (2.27)$$

where $\Delta E$ is the energy difference and we have $\Delta m_s = 1$ for the electron. Equation 2.27 shows that the energy difference between the two states increases linearly with $B_0$ (Figure 2.7).

To drive a transition between the two spin-projection states, we apply a harmonic field perpendicular to the static field:

$$\mathbf{B} = B_0 \hat{k} + B_1 \cos(\omega t) \hat{i}$$  \hspace{1cm} (2.28)$$
where I added the harmonic term with magnitude $B_1$ and angular frequency $\omega$. The Hamiltonian of the system is modified accordingly:

$$\hat{H} = \frac{g \mu_B}{\hbar} \left( B_0 \hat{S}_z + B_1 \cos(\omega t) \hat{S}_x \right). \quad (2.29)$$

We can write this Hamiltonian more compactly by introducing $\omega_0 = g \mu_B B_0 / \hbar$ and $\omega_1 = g \mu_B B_1 / \hbar$:

$$\hat{H} = \omega_0 \hat{S}_z + \omega_1 \cos(\omega t) \hat{S}_x. \quad (2.30)$$

In ESR spectroscopy, the amplitude of the driving field is much smaller than the magnitude of the static field ($B_1 \ll B_0$). So, for $\omega_0$ and $\omega_1$, we have $\omega_0 \gg \omega_1$. For future reference, I will write the Hamiltonian in yet another
form using the eigenstates of \( \hat{S}_z \) as a basis and diving it into two parts where

\[
\hat{H}_0 = \frac{\hbar \omega_0}{2} \hat{\sigma}_z
\]  

(2.31)

is the time-independent part and

\[
\hat{H}' = \frac{\hbar \omega_1}{2} \cos(\omega t) \hat{\sigma}_x
\]  

(2.32)

is the time-dependent part.

The Hamiltonian given in Equations 2.31 and 2.32 characterizes ESR spectroscopy. Calculating the transition probability with the given Hamiltonian is in fact the famous Rabi problem, where the analytic solution for the probability can be found by solving the Schrödinger equation using the rotating wave approximation [24]. For the end result, we obtain

\[
P = \frac{\omega_1^2/4}{(\omega_0 - \omega)^2 + \omega_1^2/4} \sin^2 \left( \frac{\sqrt{(\omega_0 - \omega)^2 + \omega_1^2/4}}{2} t \right)
\]  

(2.33)

where \( P \) is the transition probability for the system initially in the up state to be in the down state [24]. The probability oscillates with time with frequency given by

\[
\Omega = \frac{\sqrt{(\omega_0 - \omega)^2 + \omega_1^2/4}}{2}
\]  

(2.34)

where \( \Omega \) is the Rabi frequency. Also the time-averaged probability forms a Lorentzian peak as a function of \( \omega \) and becomes maximum at \( \omega_0 = \omega \). Using the relation given in Equation 2.27 and rewriting \( \omega_0 \) as \( \omega_0 = g \mu_B B_0 / \hbar \), we
obtain the resonance condition for ESR spectroscopy:

\[ \Delta E = \hbar \omega, \quad (2.35) \]

where \( \Delta E \) is the energy gap between the two spin-projection states and \( \omega \) is the frequency of the driving field.

Equation 2.35 shows that, in ESR spectroscopy, we are inducing the transitions between the spin-projection states by tuning the frequency of the driving field to the energy gap between the states. When this resonance condition is met, the state of the unpaired electron oscillates between the two spin-projection states, absorbing and re-emitting the energy. Due to some dissipative mechanisms such as the spontaneous decay from the excited state to the ground state, the population difference between the two states occurs leading to more population for the lower energy state. As a result, there is a net absorption of energy by the sample from the driving field and this absorption is detected to study transitions in ESR spectroscopy.

Now consider a case where we apply the driving field parallel with the static field in ESR spectroscopy. This will change the time-dependent part of the Hamiltonian given in Equation 2.32 to \( \hat{H}' = \frac{\hbar \omega_1}{2} \cos (\omega_1 t) \hat{z} \), which yields the total Hamiltonian:

\[ \hat{H} = \hat{H}_0 + \hat{H}' = \frac{\hbar}{2} \left[ \omega_0 + \omega_1 \cos (\omega t) \right] \hat{z}. \quad (2.36) \]

We can immediately see that the total Hamiltonian commutes with \( \hat{z} \) in this case. This then makes the spin-projection states the energy eigenstates and
hence the stationary states of the system. As a consequence, if the system is initially put in one spin-projection state, it will forever stay in that state yielding the transition probability of zero. Therefore, simply changing the direction of the driving field in typical ESR spectroscopy does not lead to any interference effect, or, in fact, to any transition at all. (Note that it is a different case if the time-independent part of the Hamiltonian contains off-diagonal elements, and this is the case of parallel-mode ESR which will be discussed shortly.) This then brings us back to the role of an avoided crossing in the LZS interferometry; it is the presence of an avoided crossing that prevents the spin-projection states from being stationary states and permits transitions between the states.

The Hamiltonian in Equation 2.36 can be explicitly compared with the Hamiltonian for the LZS interferometry. Re-introducing the Hamiltonian for the LZS interferometry, we have

\[ \hat{H}_0 = \frac{1}{2} (\epsilon_0 \hat{\sigma}_z + \Delta \hat{\sigma}_x) \]  

for the time-independent part and

\[ \hat{H}' = \frac{1}{2} A \cos (\omega t) \hat{\sigma}_z \]  

for the time-dependent part. We see that, other than the amplitude of the driving term, the only difference is the tunnel splitting \( \Delta \) in the off-diagonal elements for the Hamiltonian of the LZS interferometry. Because the time-dependent Hamiltonian is not a small perturbation in this case, the transition
probability cannot be calculated using the Equation 2.33 and other mathematically more involved methods must be used as we saw in the introduction.

2.4 Parallel-mode ESR

There is an interesting limit where finding the transition probability for the Hamiltonian in Equations 2.37 and 2.38 is reduced to a simple Rabi problem. This is when we have $\epsilon_0 \gg A$ such that the time-dependent part of the Hamiltonian is a small perturbation compared to the time-independent part in Equations 2.37 and 2.38. In this regime, the rotating wave approximation holds, and transforming the Hamiltonian using the “right” basis states casts the problem into a Rabi problem where we can easily find the probability using the Rabi formula given in Equation 2.33.

In fact, we already found such basis states when we found the stationary states for a system with an avoided crossing where the Hamiltonian of the system had the same form as the time-independent part in Equation 2.37. Due to the absence of the minus sign in Equation 2.37, we have energy eigenvalues

$$E_{\pm} = \mp \frac{1}{2} \sqrt{\epsilon_0^2 + \Delta^2}$$

(2.39)

with the corresponding energy eigenstates $|\psi_{\pm}\rangle$ given by Equations 2.16 and 2.17. Using these states as the basis states, we obtain

$$\hat{H}_{0\pm} = \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix}$$

(2.40)
for the time-independent part and

\[ \hat{H}_\pm' = \begin{pmatrix} \langle \psi_+ | \hat{H}' | \psi_+ \rangle & \langle \psi_+ | \hat{H}' | \psi_- \rangle \\ \langle \psi_- | \hat{H}' | \psi_+ \rangle & \langle \psi_- | \hat{H}' | \psi_- \rangle \end{pmatrix} \]  \hspace{1cm} (2.41)
angular frequency given by

$$\Omega_{LZS} = \frac{\omega_1'}{2} = \frac{\Delta J_1(A/\omega)}{2\hbar^2}$$

where the last equality holds for $\epsilon_0 = \hbar \omega$ when $n = 1$. Since we have $A \gg \omega$, we have $J_1(A/\omega) \approx \frac{A}{2\omega}$ and hence

$$\Omega_{LZS} \approx \frac{\Delta A}{4\omega^2\hbar^2}$$

where we see that $\Omega \approx \Omega_{LZS}$ for $n = 1$ transition in the regime where the driving amplitude is small ($\epsilon_0 \gg A$). This shows that, although the observation of the LZS interference is not possible, transitions do occur in this parallel-mode ESR setting and the frequency of the oscillation in the transition probability can be found either by applying the Rabi dynamics or by using the theory of the LZS interferometry.

Indeed, there is a very subtle distinction between this parallel-mode ESR and applying the driving field parallel with the static field in usual ESR. For the former, transitions between the spin-projection states do occur because of the off-diagonal elements in its time-independent part of the Hamiltonian, and this originates from the avoided crossing inherent to the system under study. For the latter, transitions never occur because the spin-projection states are also the energy eigenstates of the system thus being the stationary states.
Chapter 3

Experimental Background

So far, we have discussed the theoretical aspects of the LZS interferometry focusing on the significance of an avoided crossing. In this chapter, I will provide the experimental scheme to realize the LZS interferometry on SMMs using a loop-gap resonator. Although fundamentally different, the LZS interferometry and ESR spectroscopy share a number of things in common in terms of the experimental design. In laying the experimental setup for the LZS interferometry, I will take advantage of this similarity and first introduce the setup for a typical ESR measurement.

The use of a resonator is especially important in the LZS interferometry as it produces the driving amplitude that drives a system across its avoided crossing. As briefly introduced in the beginning of the thesis, we used a resonator called a loop-gap resonator. Because designing, fabricating, and characterizing the resonator represents a crucial portion of the experimental work in realizing the LZS interferometry, I will provide more details on each process in this
Towards the end of the chapter, I provide the experimental procedure for the LZS interferometry, and this will be applied the same to parallel-mode ESR which we performed for the thesis.

### 3.1 Experimental Setup for ESR

![Diagram of ESR setup](image)

Figure 3.1: Schematic diagram for typical ESR spectroscopy.

Figure 3.1 shows an overview of the setup for a typical ESR measurement. Starting from the bottom of the diagram, we have Helmholtz coils that pro-
duce a uniform, static field at the midpoint along the rotational axis for the coils. At this region of uniform field, a resonator, which is a resonant cavity for this setup, is placed. This cavity is usually a metallic rectangular box or a metallic cylinder inside which microwaves form standing waves storing electromagnetic energy. A sample is placed inside the cavity at the region of the maximum radiative magnetic field. For a resonant cavity to work, there must be a frequency source that provides the microwaves that are coupled to the cavity. The frequency source generates the microwaves at frequencies near the resonant frequency of the cavity, and the waveguides or transmission lines (represented by black solid lines in the diagram) propagate the microwaves to the cavity. Once the propagated waves reach the cavity, they transfer their power to the cavity in a varying degree depending on their frequencies. At the resonant frequency, the maximum power transfer occurs between the waveguide and the cavity, and the power reflected from the cavity becomes minimum. As a consequence, a Lorentzian dip is formed in the reflected power as a function of the frequency (Figure 3.2). A directional coupler directs the reflected power toward a power diode, separating it from the incoming power. The diode then converts the reflected power to a voltage signal that a detecting instrument such as a lock-in amplifier can measure.

The use of a resonator is crucial in the measurement. Unlike optical spectroscopy where the larger population difference and the stronger transitions result in strong spectral lines, ESR has relatively weak signals. Therefore, a resonator is used to increase the sensitivity of the measurement by confining the microwave power to the region where the sample is placed. A typical cav-
A resonator is characterized by its resonant frequency and a quantity called $Q$ value or quality factor. The resonant frequency is the frequency at which the power reflected from the resonator is minimum and sets the frequency of the driving field in the context of ESR spectroscopy. Because the resonant frequency only depends on the geometry and the physical dimensions of a resonator, the working frequency can be varied by changing the physical dimensions of a resonator. In practice, however, this often involves fabricating a
new resonator, and is usually avoided by changing the static field to vary the required energy for the transition.

The $Q$ value is a dimensionless quantity that characterizes how efficiently a resonator stores the electromagnetic energy and is defined as

$$Q = \frac{2\pi \text{(energy stored)}}{\text{energy dissipated per cycle}}$$

where the energy dissipation comes in many forms such as heating and the skin effect [25]. The skin effect is a common source of dissipation; when electromagnetic waves are incident on the cavity wall, alternating current starts to flow on the surface of the wall, and this results in an effective resistance depending on the frequency of the electromagnetic waves [26].

In measuring the $Q$ of a resonator, we usually use another relation:

$$Q = \frac{f_0}{\text{FWHM}}$$

where $f_0$ is the resonant frequency, and FWHM is the full width at the half-maximum of the resonant peak (Figure 3.2) [25]. Equation 3.2 also suggests that the $Q$ is a measure of how sharp a resonant peak is. In general, a higher $Q$ corresponds to higher sensitivity of the measurement.

For a resonator to work, microwaves must be coupled into the resonator. The amount of coupling determines how efficiently the microwave power is transferred between waveguides and the resonator, and a resonator is called critically coupled when the maximum power transfer is achieved between the resonator and the waveguides. A critically coupled resonator has the maximum
sensitivity because a small change in the microwave power easily disrupts the critically coupled state. Because coupling a resonator is also an important procedure in the LZS interferometry, I will flesh out the coupling process in more detail using a cavity resonator as an example. Also, we will see how ESR signals are detected once the resonator is critically coupled. Although I pick a cavity resonator as an example, the basic ideas and the terminologies describing the process are the same for a loop-gap resonator.

In the case of a resonant cavity, coupling is usually achieved via a coupling iris (Figure 3.3) [27]. The size of the iris is controlled by lowering and raising the iris screw. At a certain position of the screw, the impedance of the cavity is perfectly matched with that of the waveguide, and the cavity becomes critically coupled. When this happens, all the microwave power is perfectly transferred from the waveguide to the cavity and no power gets reflected. At this state, a small absorption of the power by the sample easily disrupts the critically coupled state of the cavity. As a consequence, the $Q$ of the cavity decreases due to the additional loss of power to the sample. Also, because the cavity is no longer critically coupled, some power is reflected from the cavity and the resonant frequency shifts. Therefore, the decrease in the $Q$, the increase in the reflected power, and the shift in the resonant frequency are the ESR signals that detect the transitions in the sample, and can be most precisely detected when the cavity is critically coupled.

More technically, the coupling process can be understood in terms of the equivalent circuit of the resonator (Figure 3.4). In the regime where the wavelength of the electromagnetic waves is much longer than the dimensions of a
resonator, the resonator can be treated as an \( LRC \) circuit where an inductor, a resistor, and a capacitor are connected in series [27]. Inductance \( L \) and capacitance \( C \) determine the resonant frequency:

\[
\omega = \frac{1}{\sqrt{LC}}
\]  

(3.3)

where \( \omega \) is the resonant angular frequency. Resistance \( r \) represents the small dissipation of energy in general. The \( Q \) of the resonator itself is given by

\[
Q_u = \frac{\omega L}{r}
\]  

(3.4)

where \( Q_u \) is denoted as the unloaded \( Q \) [27].

The turn ratio \( n \) of the transformer in Figure 3.4 represents the size of
Figure 3.4: The equivalent circuit of a reflection cavity. The schematic was reproduced from [27].

the coupling iris. Hence, lowering and raising the screw can be thought of as increasing or decreasing the turn ratio. Another $Q$ value is defined to represent the power leaking out from the cavity:

$$Q_r = \frac{\omega L}{R_0 n^2}$$  \hspace{1cm} (3.5)

where $Q_r$ is called radiation $Q$ and $R_0$ is the combined impedance for the microwave source and the waveguides [27]. The $Q$ of the resonator when it is coupled to the microwave source is then given by

$$\frac{1}{Q_L} = \frac{1}{Q_u} + \frac{1}{Q_r}$$  \hspace{1cm} (3.6)
where $Q_L$ is called the loaded $Q$. The loaded $Q$ for the resonator is then

$$Q_L = \frac{\omega L}{R_0 n^2 + r}.$$  \hfill (3.7)

When the impedance of the cavity is perfectly matched to the external impedance, we have $R_0 n^2 = r$, and the loaded $Q$ becomes half of the unloaded $Q$.

For future reference, I also introduce several other parameters that indicate the coupling status of a resonator. First of all, we define a parameter called Voltage Standing Wave Ratio (VSWR) given by

$$\text{VSWR} = \frac{|V_{\text{max}}|}{|V_{\text{min}}|}$$  \hfill (3.8)

where $V_{\text{max}}$ and $V_{\text{min}}$ are the maximum and the minimum voltages in the waveguide respectively. When the resonator is critically coupled, the two values become equal, and we have $\text{VSWR} = 1$.

From VSWR, we define yet another parameter called reflection coefficient:

$$\Gamma = \frac{\text{VSWR} - 1}{\text{VSWR} + 1}$$  \hfill (3.9)

where $\Gamma$ is called the reflection coefficient. This quantity in fact measures how much power gets reflected from the cavity and becomes zero when the resonator is critically coupled.
3.2 Experimental Setup for LZS interferometry

Now that I have introduced the experimental setup for a typical ESR measurement and how a resonator is used to observe the ESR signals, I will proceed to presenting the experimental setup and the procedure for the LZS interferometry. In doing so, I will establish the context of the discussion as providing a guideline for performing the LZS interferometry on SMMs using a loop-gap resonator. At each stage of the discussion, I will include detailed accounts of how we followed this guideline for this thesis. Figure 3.5 shows an overview of the experimental setup, and we will discuss each part of the experimental apparatuses starting with the Physical Property Measurement System.

3.2.1 Physical Property Measurement System

One notable difference from the ESR setup is the use of a cryogenic device. Although it is not at all uncommon to use a cryogenic device in an ESR measurement, I previously excluded it for convenience in introducing the setup. In the LZS interferometry addressed in this thesis, however, a cryogenic device is essential since we are studying transitions in the spin states of SMMs, which are only observable at sufficiently low temperature. Without the cryostat, the effect of the thermal energy would be greater than the effect of the LZS interferometry on the spin dynamics of the molecules, and the spin states would be equally populated. Because the strength of the signals depend on the population difference between the states, this would result in very weak
Therefore, the interferometry is performed using a cryostat. The cryogenic system that we used is the Physical Property Measurement System (PPMS) manufactured by Quantum Design. The system consists of an external controller and a dewar inside which is a bath of liquid helium that surrounds the PPMS probe (Figures 3.6 and 3.7). The PPMS probe, which is shown in Figure 3.7, in turn, surrounds the space where a sample is placed. The PPMS offers temperature control between 400 K and 1.8 K, where it uses the cold helium vapor for cooling above 4.2 K. Below 4.2 K down to 1.8 K, the PPMS uses an external pump to lower the boiling point of the liquid helium inside the bath [29].
Figure 3.6: Schematic diagram for the PPMS dewar with copyrights by Quantum Design. The left is a bird-eye view on the top of the dewar, and the right shows the longitudinal cross-section of the dewar. The diagram was copied from the PPMS hardware manual with permission from Quantum Design [29].

The PPMS is also equipped with a built-in longitudinal superconducting magnet that produces the static field required for the LZS interferometry. It is shown at the bottom end of the PPMS probe in Figure 3.5. The magnet can generate the field up to 9T at a rate as low as 10.8 Oe/sec and as high as 199.9 Oe/sec.
3.2.2 Sample Probe

A sample probe must be used to place a sample inside a cryogenic device. Although specific designs vary depending on the experimental requirements, it must be equipped with waveguides or transmission lines to propagate the microwaves to couple a resonator. Figure 3.8 shows our home-built probe made by former student Spencer Adams and modified by another student Andrew Mowry, PhD student Yiming Chen, and former post-doc Mohammad Ashkezari. Its length is about 40 inches and designed to fit inside the sample space of the PPMS. The resonator sits inside a cylindrical shield and there are two rods made out of G10 epoxy that holds the shield at the bottom of the probe (Figure 3.8). The microwaves are fed through an SMA adaptor at the
probe head. A long semi-rigid SMA cable is used to propagate the microwaves from the head to the resonator. Spacers are used to hold the cables in place and prevent thermal convection to enhance the cooling efficiency.

Figure 3.8: Picture of sample probe. A schematic diagram for a shield that contains a resonator and a sample is drawn at the left of the picture.

### 3.2.3 Vector Network Analyzer

A vector network analyzer can be used as a source of the microwaves and measure the reflected power. Figure 3.5 shows how a vector analyzer is connected to the probe head. A vector network analyzer is an instrument that measures various network parameters such as the reflection coefficient and VSWR. It generates electromagnetic waves over a certain range of frequency and measures the magnitude and the phase of the reflected signal. Compared with the ESR setup, the vector analyzer does a combined work of the frequency source and the detecting instruments. For our setup, we use KEYSIGHT E5063A vector analyzer that can produce electromagnetic waves in the frequency range between 100 kHz and 18 GHz at powers ranging from −20 dBm to 0 dBm.
3.2.4 Loop-gap Resonator

In introducing the experimental setup for an ESR measurement, we discussed the importance of using a resonator to produce a driving field and to enhance the sensitivity of the measurement. For the same reason, the use of a resonator is also important in the LZS interferometry. Additionally, in the LZS interferometry, we require that the driving amplitude produced by a resonator must be large enough to drive a system across its avoided crossing.

A loop-gap resonator is one such resonator that has been known to produce a large, homogeneous field [20]. Figure 3.9 shows the loop-gap resonator fabricated for this thesis. It consists of a loop and a gap on a metallic disk, and it can be approximated as a lumped-element resonator where the loop works as an inductor and the gap works as a capacitor. Most of the radiative magnetic field is concentrated at the loop, producing highly uniform field, and most of the electric field is confined to the gap [20]. Because a resonator itself acts like a dipole radiator [20], a metallic shield is used to confine the electromagnetic waves and prevent the unwanted radiative loss. For this reason, the shield is treated as a part of a resonator.

Aside from the fact that it produces a large, uniform field, a loop-gap resonator also has a number of advantages over a cavity resonator. First of all, a loop-gap resonator has great design flexibility that allows the user to control its characteristic properties through a number of different design parameters [20]. For example, the user can increase the magnitude of the magnetic field at the loop without changing the resonant frequency by manipulating the loop size and the gap width accordingly. In addition to this design flexibility, a loop-
gap resonator has reasonable physical dimensions at low resonant frequencies compared with a cavity resonator [20]. For example, a loop-gap resonator operating at 4GHz is a few tenths of an inch in diameter, while a cavity resonator has dimensions of a few inches. The relatively small size of the loop-gap resonator is especially attractive in low temperature measurements where a resonator often has to be placed inside a cryogenic device [20].

![Figure 3.9: Picture of a loop-gap resonator.](image)

### 3.2.5 Loop-gap Resonator: Design

The design process for a loop-gap resonator is simple and straightforward. First, we estimate the necessary resonant frequency and the $Q$ based on the SMMs we study. In setting the resonant frequency, we take into account the tunnel splittings and the energy scales of the spin-projection states of a SMM. The resonant frequency of the resonator sets the frequency of the driving field
and hence determines the resonant values for the detuning:

\[ \epsilon_0 = n\hbar \omega = n\hbar f_0 \]  

(3.10)

where \( \epsilon_0 \) is the resonant detuning value where the constructive LZS interference occurs and \( f_0 \) is the resonant frequency of a resonator. In the LZS interferometry, we require the first resonant detuning value \((n = 1)\) to be far away from the avoided crossing of a system satisfying \( \hbar f_0 \gg \Delta \) where \( \Delta \) is the tunnel splitting of the system. Also, the associated photon energy must not be comparable to the energy gap between spin-projection states of the molecule to avoid inducing unwanted transitions between the states. For the thesis, we estimated the necessary resonant frequency based on a Mn\textsubscript{3} SMM. The relatively large energy scales \((\sim 100 \text{ GHz})\) between its spin-projection states allowed us to set the resonant frequency to be a few GHz.

Setting the \( Q \) of the resonator is important in two ways. For one, it is related to the sensitivity of the measurement with a higher \( Q \) corresponding to better sensitivity. For the other, the driving amplitude a loop-gap resonator can produce is proportional to the square-root of \( Q \). Because acquiring a large driving amplitude is our primary goal in using a loop-gap resonator, we aim for the highest \( Q \) we can achieve.

After estimating the necessary resonant frequency and \( Q \), we proceed to setting the design parameters of a loop-gap resonator shown in Figure 3.10. In setting the parameters, we need to consider several experimental constraints such as the available size of the resonator taking into account the use of a
shield and the available loop size. In our case, the resonator had to be placed inside the sample space of the PPMS, the diameter of which is about an inch. Considering the use of a shield, we roughly set the diameter of the resonator to be a few tenths of an inch. Also, the loop size had to be relatively large for a sample of SMMs to be placed inside.

![Diagram of a loop-gap resonator parameters](image)

**Figure 3.10:** Diagram that shows the design parameters of a loop-gap resonator (Z, resonator thickness; r, loop radius; W, gap width; t, gap separation).

We set the rest of the parameters based on the published design equations for a loop-gap resonator. First of all, the resonant frequency of the resonator is determined by the inductance and the capacitance of the resonator:

\[
f_0 = \frac{1}{2\pi \sqrt{LC}}
\]  

(3.11)
where $f_0$ is the resonant frequency. Inductance $L$ and capacitance $C$ can be estimated from various design parameters:

$$L = \frac{\mu_0 \pi r^2}{Z} \quad (3.12)$$

where $\mu_0$ is the permeability in free space, $r$ the radius of the loop, and $Z$ the thickness of the resonator [30], and

$$C = \frac{\epsilon W Z}{t} \quad (3.13)$$

where $\epsilon$ is the permittivity, $W$ the gap width, and $t$ the gap separation [30]. The critically coupled $Q$ can be estimated using

$$Q_L = \frac{\pi f_0 L}{R} \quad (3.14)$$

where $Q_L$ is the critically coupled loaded $Q$ [31]. Resistance $R$ is due to skin effect and can be estimated by

$$R = 2 \sqrt{\frac{\mu_0 \pi f_0}{\sigma}} \left( \frac{\pi r + \frac{W}{3}}{Z} \right) \quad (3.15)$$

where $\sigma$ is the conductivity of the resonator [31]. This resistance increases at higher frequency as the alternating current flows at the surface with a shallower depth, decreasing its effective cross-sectional area and thus increasing the resistance. Finally, the amplitude for the magnetic field at the loop is
approximately given by

\[ B_1 \sim \sqrt{\frac{Q P}{f_0 r^2 Z}} \]  \hspace{1cm} (3.16)

where \( B_1 \) denotes the magnitude of the field and \( P \) is the incident power \[30\].

In relation to the LZS interferometry, the driving amplitude produced by a loop-gap resonator is

\[ A \approx g \mu_B B_1 \]  \hspace{1cm} (3.17)

where \( A \) is the driving amplitude.

Because the driving amplitude is directly proportional to \( B_1 \) as in Equation 3.17, we try to increase the magnetic field by minimizing the thickness and the loop size of the resonator according to Equation 3.16. Because a decrease in the loop size leads to a decrease in the inductance and hence to an increase in the resonant frequency according to Equations 3.11 and 3.12, we tried to compensate for the effect by increasing the capacitance. To increase the capacitance, we increased the gap width and decreased the gap separation according to Equation 3.13. The numeric values we set for the design parameters are shown in Figure 3.11. Note that the two holes towards the edge in the figure are for a supporting mechanism that will be discussed later and are not related to the design parameters that affect the working of the resonator.

Choosing the material for the resonator is also important because higher conductivity of the resonator leads to a larger magnetic field according to Equations 3.14 and 3.16. For our resonator, we used oxygen-free high conductivity (OFHC) copper, which has high electrical conductivity of \( 5.91 \times 10^7 \) Siemens/m at room temperature \[32\]. Because the conductivity of the OFHC
copper increases by a few orders of magnitude at cryogenic temperatures [33], we also expected that the magnetic field would increase accordingly.

Designing a shield is also important since it is treated as a part of a resonator. Setting the geometry and the dimensions of a shield largely depends on the dimensions of a resonator and other experimental settings. Figure 3.12 shows the blueprint for the shield fabricated for this thesis. A cylindrical cavity was the most natural geometry to surround a disk-shaped resonator and also to be fitted inside the sample space of the PPMS. The inner diameter was set to be larger than the diameter of the resonator and the outer diameter was set to be fitted into the sample space. Setting the inner height is very important to prevent the resonant frequency of the shield itself from conflicting with that of the resonator, and we set the inner height for our shield accordingly.

In designing the shield, we also need to consider the supporting and coupling mechanism for the resonator. In our case, we designed the shield to be a two-piece object with a top cap and a body (Figure 3.12). To securely
hold the resonator inside the shield, two holes were drilled and tapped on the inner bottom surface of the shield body, and alumina (Al$_2$O$_3$) screws were used to fasten the resonator to the surface with alumina washers in-between to prevent shortening the two objects (Figure 3.13). The alumina screws and washers were used for their excellent insulating properties and high thermal conductivity [34].

For the coupling mechanism, we decided to couple the resonator capacitively. This involved using an antenna made of a semi-rigid SMA coax cable with the outer conductor peeled off at one end and the inner tip bent perpendicularly to the gap of the resonator such that the tip is parallel with the electric field lines in the gap (Figure 3.13). The tip of the coax then works as an antenna radiating microwaves that are coupled to the resonator. To realize this coupling scheme, we drilled hole A through the top cap (Figure 3.12) for the antenna to be inserted. To account for the bending of the inner tip, the hole was drilled slightly off center. Another small hole B was drilled through the top cap for the venting purpose. Venting the air out of the inside of the shield is important to prevent its condensation which might degrade the $Q$ value of the resonator. The diameter of this hole was set to be less than a tenth of the relevant wavelength to prevent radiation of the microwaves.

For the assembly of the two shield pieces, we drilled four holes through the edge of the top cap and drilled and tapped the matching holes on the top surface of the body wall, and brass screws were used to fasten the two pieces. Finally, holes C were tapped on the outer surface of the top cap for the G10 rods of the sample probe to hold the shield. Because the shield also has to
be highly conductive to confine the microwaves, we used OFHC copper as the material for the shield body. For the top cap, we used brass instead of OFHC copper due to machining difficulty in drilling the small venting hole on copper. Because the top cap is rather far away from the resonator and the conductivity of brass is in the same order of copper, the effect of the change in the material for the top cap should be very small on the $Q$ of the resonator.

Figure 3.12: Blueprint for the shield. The top figures show the top cap and the bottom ones show the shield body. All dimensions are in inches.

After setting the design parameters for the resonator, it is desirable to use simulation software to estimate the resonant frequency and the $Q$ of a resonator in further modifying the design parameters. Although the design equations show the general relations among the design parameters, they are
limited in accurately predicting the resonant frequency and the $Q$ due to some mathematical approximations and unaccounted effects such as the effect of the shield. For example, the resonant frequency estimated with the design equations was more than two orders of magnitude greater than the simulated value and the measured value.

I used software called the High Frequency Structural Simulator (HFSS). The software numerically solves the Maxwell’s equations with given boundary conditions using the finite element method and can calculate the S-matrix when there an excitation port is assigned. I used this function to run a virtual reflection measurement for the resonator. First of all, I used the provided
design parameters to draw a model for the resonator and assigned an excitation port (Figure 3.13). From doing a reflection measurement, I tried to estimate the resonant frequency and $Q$ the given design parameters produce. Also, I varied the gap between the resonator and the antenna to see how the coupling affects the $Q$ of the resonator.

Figure 3.14 shows the simulation result at three different states of coupling. The resonant frequency was estimated to be 3.9(1) GHz, and the $Q$ roughly ranged from 860 to 2440 depending on the amount of coupling. Note that the small shift in the resonant frequency is due to the varied position of the coupling antenna.

![HFSS Simulation](image)

Figure 3.14: HFSS simulation result for a loop-gap resonator.
3.2.6 Loop-gap Resonator: Fabrication, Assembly, and Characterization

The fabrication method for the designed loop-gap resonator may vary depending on the machining capability, but one thing to keep in mind throughout the process is to minimize the scratches on the resonator. Scratches on the resonator increase the surface loss and might result in degrading the $Q$ value. For our case, we used a CNC (Computer Numerical Control) milling machine to fabricate two resonators, A and B, with the same dimensions as well as the shield. In fabricating the coupling antenna, a lathe is recommended for peeling off the outer conductor for a clean cut. Otherwise, the antenna might not go through the cap. To minimize the scratches, the machined resonator was polished following the procedure given in Appendix A.

In the assembly process, a resonator is placed inside a shield and a coupling antenna is assembled to the shield. The process again varies depending on the design of the resonator and the coupling method, but it is important to keep in mind that some parts such as the coupling antenna might have to be readjusted after the initial assembly to optimize the coupling to the resonator. For this reason, it is desirable to have some flexibility in the assembly scheme where pieces like the coupling antenna can be disassembled and reassembled with relative ease.

In our case, we first fastened the resonator to the inner bottom surface of the shield body using the alumina screws and washers as discussed before. The coupling antenna was then inserted through hole A on the top cap (Figure 3.12). After adjusting the position for the antenna accordingly, I soldered it to
the cap following the method outlined in Appendix B. Because the bent tip of the coupling antenna might cause a problem in inserting the antenna through the hole, it is recommended to insert an unbent coax and to solder it first before bending the tip. Finally, the shield body and the top cap were assembled with the metal screws. To prevent possible leaks of microwave power, we applied conductive grease for the matching surfaces between the top cap and the shield body.

After the initial assembly, one should experimentally measure the resonant frequency and the $Q$ of the resonator through either a reflection measurement or a transmission measurement. In a reflection measurement, one sweeps the frequency of the electromagnetic waves at a given power and the power reflected from the resonator is measured as a function of frequency. Because the reflected power becomes minimum at the resonant frequency, a resonant peak forms a dip in the reflected power. In searching for the resonance, we have to make sure that the observed resonance is really from the resonator. We can do this by putting an absorbent foam to the loop of the resonator to see if this eliminates the previously observed resonance. Also, one can try to shift the resonant frequency of an observed peak by placing a dielectric material in the gap to see if this results in shifting the resonant frequency. Once the resonant frequency is found, we measure the $Q$ either by measuring the FWHM of the peak or fitting it to a Lorentzian function.

In addition to measuring the resonant frequency and the $Q$, one must try to optimize the coupling for the resonator. The critical coupling can be achieved by measuring the maximum $Q$ of the resonator and then adjusting
relevant coupling parameters to obtain a half of the maximum value. Also, one can try to obtain the VSWR of 1 or the reflection coefficient of zero as we previously discussed. Finally, it is important to note that the critical coupling at room temperature does not necessarily lead to the critical coupling at low temperature, so we must keep in mind the operating temperature for the measurement and try to achieve the critical coupling at that temperature.

In our case, we performed a reflection measurement on the two resonators A and B using a VNA at room temperature. Figure 3.15 shows the simple setup. The measurement was consistent with the simulation result. The resonant frequency was measured to be 4.000 GHz for Resonator A and 3.988 GHz for Resonator B with negligible uncertainties for the first four significant figures of the value. Subsequently, the FWHM was measured by fitting the resonant peak using a Lorentzian fit:

\[
P = \frac{(\text{FWHM}/2)^2}{(f - f_0)^2 + (\text{FWHM}/2)^2} + B
\]

where \(P\) is the reflected power, \(f\) is the frequency, \(A\) is the peak height, and \(B\) is the offset. Then the \(Q\) was measured using Equation 3.2. The measured \(Q\) was 870(10) for A and 800(20) for B at room temperature. We confirmed that the observed resonances are from the resonators by killing the resonances with an absorbent foam.

In achieving the critical coupling, we measured the VSWR using the VNA and adjusted various coupling parameters to achieve the VSWR of 1.12 at temperatures below 20 K. To do this, we first changed our experimental setting
to use the sample probe to hold the shield. Then, we tried to obtain the VSWR slightly greater than 1 at room temperature in the probe setting. When put inside the PPMS and lowered to temperature below 20 K, the thermal contraction resulted in further affecting the VSWR making the value closer to 1.

Specifically, the coupling was controlled by adjusting the distance between the resonator and the tip of the antenna as well as the orientation of the tip relative to the gap of the resonator (Figure 3.16). In changing the distance, we could either vary the number of the washers between the resonator and the shield or adjust the position of the coupling antenna. Because the washer had a nominal thickness of 0.025 in, a relatively small adjustment in the coupling distance could be easily made. For a bigger adjustment, I resoldered the coupling antenna to reset its position. Also, the orientation of the tip could be changed to vary the coupling. Aligning the tip parallel to the gap decreased the coupling while aligning it perpendicular to the gap increased the coupling.

After achieving the critical coupling for the resonator, we can have a rough
estimate of the driving amplitude of the resonator by measuring the $Q$ at the temperature at which the LZS interferometry will be performed. This requires doing a low-temperature reflection measurement using the sample probe, and it is recommended to keep tracking the resonance after each modification to the experimental setting. For example, one might want to confirm that the resonance is seen when the sample probe is inside the PPMS at room temperature. Once we reach the operating temperature, we repeat the measurement to measure the $Q$ value and roughly estimate the driving amplitude using Equations 3.16 and 3.17.

In our case, we measured the $Q$ of the resonator at 1.8 K. While we reached the low temperature, we carefully tracked the resonance (Figure 3.17). At low temperatures, the resonant frequency slightly increases as the dimensions of the resonator become smaller due to thermal contraction. Also, because the conductivity of copper increases at low temperatures, the $Q$ value consequently increased. The $Q$ was measured to be $\sim 2500$ (Resonator A). Using Equation
3.16 with $Q=2500$, $P=0.001$ W (the maximum power the VNA can produce), $f_0=4$ GHz, $r=0.03$ in, $Z=0.02$ in, we obtain $\sim 1.4$ G for the amplitude of the field. In terms of the driving amplitude divided by $h$ ($A/h = g\mu_B B_1/h$), we have $A/h \sim 25$ kHz, which is more than one order of magnitude smaller than the first detuning value divided by $h$ ($\epsilon_0/h = f_0 = 4$ GHz). To see the interference pattern, the driving amplitude must be larger than the second detuning value ($\epsilon_0/h = 2f_0 = 8$ GHz). In terms of the $Q$ of the resonator, this requires us to improve the $Q$ by more than two orders of magnitude on top of using the higher power (1 W). More detailed discussion on this direction will be provided in Chapter 5.

3.2.7 Experimental Procedure

After fabricating the resonator and evaluating its resonant frequency and the driving amplitude, we are ready to perform the LZS interferometry on SMMs. First of all, we need to determine how to mount a sample on the resonator. In our case, a piece of sapphire glass was cut into the size of the loop and affixed to the bottom surface of the resonator with vacuum grease. This allowed us to put a sample inside the loop where the magnetic field is most uniform. Devising a way to mount the sample before characterizing the resonator is important because the background signal associated with the method of mounting a sample can be included in the characterization process.

Before the actual measurement on a sample, it is important to well characterize the resonant frequency, the $Q$, and the reflected power at resonance of the resonator over a wide range of experimental parameters. The usual ex-
Figure 3.17: Temperature Dependence for Resonator A. As the temperature decreases, the resonant frequency slightly increases due to the thermal contraction of the resonator.

Experimental parameters include temperature, input microwave power, and the magnitude of the static field. As discussed earlier, the resonant frequency, the $Q$, and the reflected power at resonance are monitored to detect the signals from the sample, and characterized signals of the resonator alone serve as the background that we can compare our sample signals with. For this reason, estimating a range of experimental parameters for the actual measurement is important in characterizing the resonator.

Figures 3.18 and 3.19 show our characterization of the two resonators. The
figures show the temperature dependence of the three characterized signals measured at -5 dBm for Resonator A and 0 dBm for Resonator B. As we can see in the figures, there are some transitions observed in the absence of any sample. The resonant frequency plots in both figures show the remarkable sensitivity of the resonators where the frequency shifts on the order of 10 kHz (Resonator A) and on the order of 1 kHz (Resonator B) are detected. Rough simulation indicated that the detected transitions might be due to the chromium impurities (Cr$_{III}$) from the sapphire glass. Also, the metal polisher used in polishing the resonator is another possible source of chromium impurities.

After a thorough characterization of the resonator, we need to mount a sample of SMMs inside the loop. In mounting the sample, it is important to place it at the center of the loop for the sample to experience the most homogeneous field. Also, we have to orient the easy axis of the sample along the direction of the static field to perform the LZS interferometry. It is recommended to carefully mount the sample under a microscope wearing gloves to prevent any pollution on the resonator and the sample. A small amount of vacuum grease can be applied to hold the sample on the sapphire glass.

After the sample mounting, we use the sample probe to hold the resonator and start the measurement inside the PPMS. At this stage, it is important to carefully move the probe not to disturb the placement and the orientation of the sample. After the probe is inserted inside the PPMS, we record the shape of the resonant peak over different sets of experimental parameters. Then, we fit the peak to a Lorentzian to acquire the resonant frequency, the
$Q$, and the reflected power at the resonance. Usually, we set the power and the temperature first and record the resonances while sweeping the magnetic field over a certain range. This then shows how the three ESR signals change over the field and can reveal if any transitions are occurring inside the sample. As discussed earlier, the transitions in the sample are detected in the form of the decrease in the $Q$, the shift in the resonant frequency, and the increase in the reflected power at resonance. These three signals are then compared with one another along with the background signals to confirm the transitions in the sample.
Figure 3.18: Characterization for Resonator A.
Figure 3.19: Characterization for Resonator B.
Chapter 4

Experimental Results

In this chapter, I present the result of performing parallel-mode ESR on Ni$_4$ SMM using the fabricated loop-gap resonator. I will give brief background on the molecule and present the acquired reflection spectra for with the analysis of the observed transitions.

In identifying the transitions in the spectra, I used a MATLAB-based software called the EasySpin. The software simulates a number of different types of ESR measurement in the given experimental setup where the user sets the Hamiltonian of the system and other parameters such as the orientation of the sample and the temperature. In analyzing the spectra for Ni$_4$, I used the software to simulate the result of parallel-mode ESR setting the Hamiltonian for each molecule with the Hamiltonian parameters given in the published literature.

Setting the temperature for the simulation was straightforward, but I’d like to point out that all the measurements were taken between 1.8 K and
20 K. This is in the regime where the thermal energy (1 K ∼ 20.8 GHz in terms of frequency) is greater than the transition energy (∼ 4 GHz in terms of frequency), and hence the transitions we observe over the whole temperature range include transitions in the excited states as well as in the ground states.

The orientation of the sample in the EasySpin is determined by two parameters θ and φ. The angle θ measures the angle between the static field and the easy axis of the molecule, and the angle φ measures the angle between the direction of the static field and one of the hard axes of the molecule. Because accurate measurement of these angles was limited, especially for φ angle, I first used rough estimates to acquire simulation results and adjusted the angles to reproduce the measured spectra.

4.1 Ni₄ Single-molecule Magnet

Figure 4.1: Picture of a Ni₄ sample mounted on the resonator.

A Ni₄ SMM is chemically known as [Ni(hmp)(dmb)Cl]₄ where hmp is the
anion of 2-hydroxymethylpyridine and dmb is 3,3-dimethyl-1-butanol [35]. The molecule has four ferromagnetically coupled Ni\(\text{II}\) ions \((S = 1)\) at the core, and this yields a ground state of \(S = 4\) for the molecule at low temperature [36] [37]. The hydrocarbon compounds surround the core and minimizes the intermolecular interactions [38]. The molecule has fourfold rotational \((S_4)\) symmetry about its easy axis [38] and crystallizes into a tetragonal bipyramidal shape [37]. Figure 4.1 shows a Ni\(_4\) sample mounted on our loop-gap resonator. Because a Ni\(_4\) sample has no solvate molecules, each molecule in the sample experiences relatively uniform microenvironment, resulting in the ESR signals that are narrower and sharper than in many SMMs [37] [39].

The spin Hamiltonian of Ni\(_4\) is given by

\[
\hat{H} = -DS_z^2 - BS_z^4 + C(S_z^1 + S_z^4) - \frac{\mu_B}{h} \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}
\]

(4.1)

where \(D\) is the second-order zero-field-splitting (zfs) parameter, and \(B\) and \(C\) are the fourth-order zfs parameters [37]. de Loubens et al. obtained the Hamiltonian parameters by measuring the magnetization: \(D = 0.75K, B = 7 \times 10^{-3}K, C = 2.9 \times 10^{-4}K, g_x = g_y = 2.23\) and \(g_z = 2.3\) [37]. The first two terms in the Hamiltonian are the uniaxial anisotropic terms which make the molecule a bistable magnet at low temperature with an energy barrier \(DS_z^2 \approx 12K\) between the spin-projection states \((m_s = \pm 4)\) along the easy axis. The third term is another fourth-order anisotropic term which is responsible for the fast tunneling of magnetization at zero field [40].

Figure 4.1 shows a sample of Ni\(_4\) mounted on the resonator. The mea-
surement was conducted using the VNA at a fixed power of $-5$ dBm. The temperature range for the data is from 2 K to 20 K with an incremental step of 1 K. At each temperature, the static field was swept from 0 T to 8 T at a rate of 10.8 Oe/sec.

### 4.1.1 Experimental Result

Figure 4.2 shows the reflection spectra we acquired for Ni$_4$ as a function of the magnitude of the static field. Because the signals from the sample were strong enough to be observed in the reflected power spectra, I only present the reflected power spectra where the increased in the power reflects transitions of the sample. In the figure, I divided the observed features into five groups and I will try to address them one by one first starting with Peaks B and C.

**Peak B, Peak C:** These peaks correspond to transitions between $|+3\rangle$ and $|-3\rangle$ and between $|+4\rangle$ and $|-4\rangle$, respectively. Figure 4.6 shows one simulation result for Ni$_4$ with the sample oriented with $\phi = 40^\circ$ and $\theta = 90^\circ$ that reproduces these peaks at 2 K and 20 K. The temperature dependence of the peak values is analyzed in Figure 4.3 for Peak B and in Figure 4.4 for Peak C. In comparing the temperature dependence with the simulation result, I multiplied a normalizing factor to the simulated results and added an offset to account for the background offset in the measured spectra.

The figures show good agreement between the measured spectra and the simulation. For Peak B, the peak value increases up to 4 K where the transition rate becomes the greatest. Up to 4 K, the population difference between states $|+3\rangle$ and $|-3\rangle$ increases as the excited $|+3\rangle$ makes transitions to the higher
energy state $|−2\rangle$ with the help of the thermal energy while $|+4\rangle$ state cannot make transitions to $|−3\rangle$ due to its slightly higher energy barrier (Figure 4.6). Hence, in this temperature range, the population in $|+3\rangle$ decreases while the population in $|−3\rangle$ remains relatively the same, resulting in increased population difference. However, above 4 K, the thermal energy is big enough to induce the transitions between $|+4\rangle$ and $|−3\rangle$ so the population in $|−3\rangle$ grows along with $|+3\rangle$ resulting in a net decrease in the population difference which is reflected in the decrease in the peak values in Figure 4.3. As the temperature increases above 4 K, the two states $|+3\rangle$ and $|−3\rangle$ get more equally populated and the population difference deceases resulted in the decreased peak values.

Unlike in Peak B, however, the peak values in Peak C decreases exponentially as the temperature increases (Figure 4.4). This is because this is the transitions in the ground spin-projection states where the population of the two states becomes comparable with relatively less thermal energy. Conversely, the transition rate is the maximum at the lowest temperature, indicating that it is the transition between the ground states.

**Peak A**: This peak corresponds to the excited state transitions either between $|+2\rangle$ and $|−2\rangle$ or between $|+1\rangle$ and $|−1\rangle$. Although the simulation in Figure 4.6 doesn’t explicitly show this peak at the provided orientation of the sample, small changes in the orientation reproduced Peak A with the transitions between the indicated excited states. Because our transition energy ($\sim 4$ GHz in terms of frequency) is small compared to the energy scale of the Ni$_4$ molecule, a small change in the Hamiltonian parameters as well as in the angles for the orientation of the sample results in drastic changes in the
spectra. Figure 4.5 shows the temperature dependence of Peak A.

**Feature D**: This feature suggests an existence of an excited state manifold with $S = 3$ where the spin of one Ni$^{II}$ ion is flipped yielding the net molecular spin of $S = 3$ for a Ni$_4$ molecule. Because the transitions are at high fields with our transition frequency equal to 4 GHz, it is very unlikely that we are inducing transitions within $S = 4$ manifold. One possible interpretation is that the transitions are related to the crossings of the $S = 3$ manifold with the $S = 4$ manifold. Figure 4.7 shows a possible crossing between $S = 3$ and $S = 4$ manifolds. Although the simulation does not completely reproduce the feature, it conveys the basic idea for the possible transitions when there is such crossing. The bottom plot in the figure shows the magnetic field values at which the transition energy is equal to the energy gap between the states.
Figure 4.2: Reflection Spectra for Ni$_4$
Figure 4.3: Temperature dependence for peak B

Figure 4.4: Temperature dependence for peak C
Figure 4.5: Temperature Dependence of Peak A
Figure 4.6: EasySpin Simulation Result for Ni$_4$
Figure 4.7: Simulation work that shows a possible crossing between $S = 3$ manifold and $S = 4$ manifold. The top plot shows the energy diagram for the spin manifolds. The middle plot shows the measured reflection spectra at high fields. The bottom plot shows the field value where the transition energy is equal to the energy difference between the states.
Chapter 5

Conclusion

So far, this thesis portrayed an effort to realize the LZS interferometry on SMMs experimentally. Starting from the basic theory for the LZS interferometry in the introduction, we saw how an avoided crossing plays a crucial role in putting the state of a system into a superposition and how this leads to an interference pattern when the system is driven across the avoided crossing multiple times.

In Chapter 2, we further studied the significance of an avoided crossing in the LZS interferometry by comparing it with ESR spectroscopy. Importantly, we saw that simply changing the direction of the driving field does not lead to LZS interference without the presence of an avoided crossing in the system. We also saw an interesting limit of the LZS interferometry where the Bessel-function dependence of the LZS interference could be accurately calculated by using the simple Rabi formula. In fact, we saw that this is the case of parallel-mode ESR spectroscopy, which we performed on Ni₄.
In Chapter 3, we discussed the experimental scheme to realize the LZS interferometry on SMMs using a loop-gap resonator. The loop-gap resonator was integral in the realization of the LZS interferometry for its capability of producing a large magnetic field. However, in our case, the resonator produced the driving amplitude one order of magnitude smaller than the initial detuning value and thus more about two orders of magnitude smaller than the required value to observe the interference effect.

Then, we moved on to study Ni$_4$ with parallel-mode ESR using the loop-gap resonator. The result showed that we could induce normally forbidden transitions by manipulating the direction of the field to affect the matrix elements for the relevant transitions. We also observed a possible evidence for the crossing between $S = 3$ and $S = 4$ manifolds from the transitions observed at high fields.

5.1 On pursuing the goal

Although we could not realize the LZS interferometry in this thesis, we can still further pursue the goal first by trying to increase the $Q$ of the loop-gap resonator. Although we initially expected the $Q$ of the resonator to be much higher at low temperatures due to the substantial decrease in the resistivity of copper, the actual measurement and further study showed that the effect of the decreased resistivity is smaller than expected with only three orders of magnitude increase in the conductivity [33]. However, there is still a chance that we’re not achieving the maximum $Q$ due to the surface loss and other impuri-
ties. Also, the copper is easily oxidized with the water molecules, which results in the increase in effective resistance. Therefore, one direction to achieve the higher $Q$ would be to eliminate these sources of degradation by gold-plating the resonator.

Also, to increase the $Q$, we could still modify some design parameters such as the loop size and the thickness of the resonator. Considering a small sample size of typical SMMs (a few hundreds of microns for Mn$_3$), we can still reduce the current loop size (which is in 1.5 mm in diameter) by one order of magnitude. However, the effect of changing the loop size on the resonant frequency also has to be considered, and appropriate modifications on the gap width or the gap separation are necessary.

Lastly, we could use a higher input power to increase the driving amplitude. We expect that we can increase the power by three orders of magnitude from the current value of 0.001 mW to 1 W, and this will increase the driving amplitude approximately by one and a half order of magnitude. However, the use of high power must be carefully done considering the heating of the environment.

5.2 New Roads

5.2.1 Cr$^{III}$ impurities

One of the interesting result of using the loop-gap resonator was the detection of the frequency shift in the order of a few kHz. Compared with the resonant frequency of 4 GHz of the resonator, this is one part per million of the resonant
frequency and shows remarkable sensitivity of the resonator.

Rough simulation work and the fact that we observe the transitions using two different resonators indicate that the observed transitions are due to the chromium impurities. The two resonator shares the possible sources of these impurities such as the sapphire glass for the sample mounting and the use of the metal polisher that contained chromium.

On top of doing more rigorous simulation work, we can experimentally try to track down the source the transitions by eliminating each source one by one. The sapphire glass could be most easily eliminated from the setup, and cleaning the resonator could be done relatively easily.

5.2.2 Spin Manifolds in Ni$_4$

Another interesting observation was the transitions occurring at high fields (7 T – 8 T) which might indicate the crossing between $S = 3$ and $S = 4$ manifolds in the molecules. We can further study this crossing between manifolds by varying the orientation of the sample and doing measurements at even higher temperatures. This will reveal more information about the $S = 3$ manifold and give more concrete information about the energy gap between the two manifolds at zero field.
Appendix A

Polishing Procedure for a
Loop-gap Resonator

Polishing the fabricated loop-gap resonator is important in achieving the higher $Q$ of the resonator by removing the scratches on the surface of the resonator and thereby decreasing the surface loss. Although the specific procedures in the polishing methods vary, they all share the same idea of making finer scratches to remove coarser scratches. In my case, I followed the following procedures:

1. Prepare several diamond sandpapers over a range of different grits.

2. Grind each surface of the resonator against the prepared diamond paper starting from the roughest to the finest grits. In this process, it is important to apply the force uniformly over the surface of the resonator. Otherwise, one might end up removing only a portion of the scratches on the surface. If the scratches are noticeably deep, try using a regular sandpaper for a starter.
Griding for about 10 minutes for each surface is sufficient to remove small scratches.

3. Apply metal polisher such as Simichrome to rub out the dirt like the copper grains against a non-abrasive towel. Keep rubbing out until no dark stains are coming out of the resonator.

4. Finish with an industrial detergent to clean any chemicals on the surface of the resonator. Water should be used with care as it leads to oxidation that degrades the $Q$. So, it is important to dry out the water immediately after cleaning the resonator.
Appendix B

Soldering Tip for Coupling Antenna

In assembling the resonator pieces, it is important to acquire some skills to solder the coupling antenna to the top cap of the shield as one would frequently face situations where one has to modify the position of the antenna. Because the top cap has a relatively large size, it is almost impossible to solder the pieces using a regular soldering iron. So, a hot plate is recommended to first heat up the top cap to the temperature where the solder just starts to melt. Then, one can use the regular soldering iron to further increase the temperature in the region where one applies the solder. At the right temperature, the solder melts only when the soldering iron provides the excess heat and solidifies quickly after one puts away the soldering iron. In my case, I used the following steps:

1. Place the top cap on the hot plate for about 15 minutes at the heat level of 7. 2. Use a hollow cylindrical piece of aluminum to hold the top cap
on the plate. So, the aluminum piece is inserted between the top cap and the hot plate to provide space for the antenna and to transfer the heat. 3. Insert the antenna through the hole and lock its position using a soldering arm. Use the soldering iron to solder the pieces.
Bibliography


