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EXPLORING NON-EQUILIBRIUM THERMODYNAMICS AND QUANTUM FLUCTUATIONS: PERSPECTIVES FROM SPIN-1 SYSTEMS IN NMR.

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Abstract

This dissertation explores the non-equilibrium thermodynamics of quantum systems, specifically focusing on spin-1 nuclei and the dual influences of external perturbations and quadrupolar interactions. We first analyze the dynamic responses of these nuclei to external perturbations, utilizing principles from quantum and statistical mechanics. By manipulating a work parameter and treating work as a random variable, we collect data from finite-duration cyclic processes to compute the generated work distribution. We then extend our investigation to the contributions of quadrupolar interactions, comparing their effects with those of external perturbations. Through this comprehensive analysis, we derive key equilibrium quantities, such as the free energy difference between initial and final states, while deepening our understanding of work distribution properties. Overall, this research enhances our insights into the complex dynamics of non-equilibrium quantum thermodynamics and sets the stage for future explorations of quantum systems under varying conditions.

Dedication

To my Mom and Dad

Acknowledgment

In the name of Allah, the Most Beneficent, the Most Merciful. First of all I would like to thank the almighty God for his guidance and help throughout mylife. I am very thankful to Allah Almighty for giving me the skills, the ability, and the courage to complete this task. I would like to express my deepest gratitude to my advisor Dr. Mulugeta Bekela, for his continuous support, follow up, advise and friendly approach. I also want to thank my mother, Mrs. Marena Hamda, for her life-long assistance in my education and beyond of all for her moral support. I wish her long life and may Allah have mercy over her and reward her with Jannah. Finally, I wish to thank all my friends, relatives and statistical and computational physics group who were involved, directly or indirectly in this work.

Contents

List of Figures

List of Acronyms

NMR	Nuclear Magnetic Resonance
MR	Magnetic Resonance
MRI	Magnetic Resonance Imaging
RF	Radio Frequency

List of Publications

1. Non-equilibrium thermodynamics in NMR: understanding quadrupolar spin-1 systems. By Mohammed Mahmud, Yigermal Bassie and Mulugeta Bekele; Journal of Physics: Condensed Matter, Volume 37, Number 1; https://doi.org//10.1088/1361-648X/ad7ac2, (Published)
2. Thermal and Quantum Fluctuation Effects on Non-Spherical Nuclei: The Case of Spin-1 System. By Mohammed Mahmud1, Yigermal Bassie and Mulugeta Bekele1; Condens. Matter 2022, 7(4), 62; https://doi.org/10.3390/condmat7040062, (Published)
3. A computational investigation of cis-gene regulation in evolution. By Mohammed Mahmud, Mulugeta Bekele and Narayan Behera; Theory Biosci. 142, 151–165 (2023). https://doi.org/10.1007/s12064-023-00391-3., (Published)

Chapter 1

Introduction

1.1 Background

Quantum thermodynamics[1] is an emerging field that seeks to unify the principles of quantum mechanics with classical thermodynamics. Explores how macroscopic thermodynamic laws emerge from the quantum-mechanical description of microscopic systems. Unlike classical thermodynamics, which focuses primarily on macroscopic variables such as pressure, temperature, and volume, quantum thermodynamics emphasizes the role of quantum fluctuations and the influence of microscopic interactions on these macroscopic properties.

In classical thermodynamics [2, 3], systems are typically assumed to be in or near equilibrium, and the laws of thermodynamics describe the exchange of energy, work, and heat between systems. However, many quantum systems of interest, especially at the atomic and molecular levels, operate far from equilibrium. In such non-equilibrium situations, traditional thermodynamic approaches are insufficient for describing these systems. Instead, quantum thermodynamics seeks to extend these classical principles to systems that are far from equilibrium, small in size, and are influenced by quantum effects.

This field has become particularly relevant in recent years due to advances in experimental techniques that allow for the precise control and measurement of small quantum systems. Experiments on single molecules, atoms, and even quantum bits (qubits) have inspired new models and approaches to understanding thermodynamics at the quantum scale. The development of powerful numerical methods[4–8], novel theoretical tools [9–11] and a well-established experimental technique [12–21] used in quantum information science and thermodynamics has further accelerated research in this area.

1.2 Quantum Thermodynamics: Key Concepts

At the core of quantum thermodynamics is the idea that quantum systems, when driven out of equilibrium, exhibit behavior that is fundamentally different from classical systems. One of the key differences is how work and heat are treated. In quantum systems, work is a fluctuating quantity, and its distribution must be described statistically [22–25]. This is in contrast to classical systems, where work is typically a deterministic quantity.

Much of the research in quantum thermodynamics focuses on the study of small systems that exhibit significant quantum fluctuations [26, 27]. These fluctuations are often characterized by random variations in quantities such as energy, work, and heat, which in turn affect the system's overall thermodynamic properties. For example, the fluctuation theorems of Crooks [28] and Jarzynski [29] have provided significant insight into the thermodynamics of small systems. These theorems relate the properties of non-equilibrium processes to equilibrium quantities, allowing for the prediction of thermodynamic behavior even in systems far from equilibrium.

Another important aspect of quantum thermodynamics is the role of the environment. In real-world situations, it is impossible to completely isolate a quantum system from its surroundings. The interaction between a system and its environment often leads to decoherence — the loss of quantum information from the system to the environment which must be taken into account when modeling the system's evolution. This interaction introduces additional complexities, as it can affect the work and heat exchanged with the system.

1.3 Motivation and Objective of the Study

The primary motivation for this study is to explore the thermodynamic properties of small quantum systems, particularly when they are driven out of equilibrium. Specifically, we focus on the behavior of spin-1 systems in the context of Nuclear Magnetic Resonance (NMR). NMR systems offer a convenient platform for studying quantum thermodynamic phenomena due to their high degree of controllability and the ability to manipulate their quantum states using external magnetic fields.

The main objective of this work is to investigate the distribution of work performed on a spin-1 system during a nonequilibrium process. By treating work as a random variable, we aim to understand how quantum fluctuations influence the thermodynamic properties of small quantum systems. In particular, we are interested in studying the work distribution and its statistical properties, such as mean and variance, in a spin-1 system subjected to time-dependent external magnetic fields. Additionally, we examine the system's dynamical evolution, focusing on how it transitions between different quantum states when driven by a work protocol.

1.4 Scope of the Study

This study is primarily concerned with the theoretical modeling and analysis of spin-1 nuclei in a non-equilibrium thermodynamic process. We consider a quantum system initially in a strong static magnetic field, which is then perturbed by a small time-dependent radio frequency (RF) magnetic field. The system's response to this perturbation is analyzed, and the work performed on the system is computed using quantum-mechanical principles.

The study is divided into the following key areas:
Work Distribution: We calculate the distribution of work performed on the spin-1 system during the non-equilibrium process, treating work as a fluctuating quantity.
Quantum Fluctuations: We investigate how quantum fluctuations affect the thermodynamic properties of the system, particularly the distribution of work and the free energy differences between initial and final states.
Non-equilibrium Dynamics: We study the system's dynamical response to the time-dependent magnetic field, focusing on how the system evolves from one quantum state to another and how this evolution affects the system's thermodynamic properties.
Comparison with NMR Experiments: Although this is a theoretical study, our aim is to compare our findings with experimental results from NMR systems, which can serve as a testing ground for

these theoretical predictions.

1.5 Significance of the Study

The research presented in this thesis contributes to the growing field of quantum thermodynamics by providing new insights into the behavior of small quantum systems far from equilibrium. By focusing on spin-1 systems, we provide a concrete example of how quantum fluctuations influence the thermodynamic properties of a quantum system. The theoretical framework developed in this work can be applied to other quantum systems, making it a valuable contribution to the broader understanding of quantum thermodynamics.

Furthermore, the results of this study have potential applications in quantum information science, where understanding the thermodynamic properties of small quantum systems is crucial for the development of quantum technologies. For example, the ability to control and manipulate the work performed on a quantum system is essential for the development of efficient quantum engines and heat pumps.

1.6 Structure of the Thesis

The remainder of this thesis is organized as follows.
Chapter 2: Offers a review of the literature focused on spin physics and the principles of nuclear magnetic resonance (NMR), which form the basis for the model used in this study. It also outlines the theoretical framework of quantum thermodynamics, emphasizing work fluctuations and their measurement in small quantum systems. Additionally, this chapter includes a quantum thermodynamic description of the spin-1 system and the model used to analyze the system's behavior in a time-dependent magnetic field. **Chapter 3:** Discusses the models and methodologies utilized in this investigation. **Chapter 4:** Presents the results obtained and provides a discussion of these findings. **Chapter 5:** Summarizes the key findings of the study, offering conclusions and suggestions for future research. **Appendices:** Provide detailed mathematical derivations and supporting calculations for the results presented in the main chapters.

Chapter 2

LITERATURE REVIEW

The study of quantum systems, particularly those driven out of equilibrium, has gained significant interest in recent years. As thermodynamics extends into the quantum domain, it becomes crucial to investigate the unique behaviors and characteristics of quantum systems under non-equilibrium conditions. This chapter aims to provide a comprehensive review of the fundamental concepts of spin physics, Nuclear Magnetic Resonance (NMR), and quantum thermodynamics, with a particular focus on work fluctuations in spin-1 systems. By exploring the relevant literature, we build a solid theoretical framework for understanding the non-equilibrium thermodynamic properties of quantum systems, especially spin-1 systems in NMR.

2.1 Spin Physics and Nuclear Magnetic Resonance (NMR)

This section provides an overview of spin dynamics, focusing on nuclear spins in a magnetic field. It covers essential concepts such as atomic and nuclear structure, nuclear magnetism, spin precession, spin states, spin-spin interactions, and the fundamentals of Nuclear Magnetic Resonance (NMR). These principles form the conceptual basis for understanding nuclear spin interactions and NMR phenomena.

Atoms and Nuclei

Atoms, the basic units of matter, consist of electrons and nuclei. Both electrons and nuclei exhibit the property of spin. Electrons, which carry a negative charge, occupy orbitals surrounding the nucleus. The nucleus, located at the atom's center, consists of protons (positively charged) and neutrons (uncharged). Since the nucleus contains protons, it is inherently positively charged.

The atomic nucleus possesses four key physical properties: mass, electric charge, magnetism, and spin. While properties like mass and electric charge significantly influence atomic behavior—such as determining the heat capacity, viscosity, and chemical properties—the magnetic and spin properties play a more subtle but crucial role, especially in quantum mechanics and applications like quantum computing [30, 31].

The contributions from circulating electric currents and electron magnetic moments are typically much larger than those from nuclear magnetic moments. For example, the bulk magnetism of materials like iron is predominantly due to electron magnetic moments, not nuclear magnetism. Consequently, nuclear magnetism plays a minimal role in the atomic or molecular structure of matter, though it becomes essential in specialized contexts, such as nuclear magnetic resonance [32] and quantum information processing [33].

It is well known in electromagnetic theory that the magnetism of a matter may arise from three sources: **(1)** from the circulation of electric currents, **(2)** from the magnetic moments of the electrons, and **(3)** from the atomic nuclei magnetic moments. The electronic contributions **(1)** and **(2)** are almost always many orders of magnitude larger than the nuclear contribution **(3)**. This implies that the nuclear magnetism is very weak when compared to that of electrons. For example, the bulk magnetism of some materials, such as iron, is due to the electrons, not to the nuclei. As a consequence, the nuclear magnetism plays little role in atomic or molecular structure of matter.

Nuclear and Electron Magnetic Moments

While the magnetism from circulating currents is easily understood via elementary physics (e.g., a magnetic field generated by a current in a loop), the magnetism arising from the intrinsic magnetic moments of nuclei and electrons is more complex. Both nuclei and electrons possess intrinsic magnetic moments, not due to current circulation, but as a fundamental property of their spin.

The magnetic moments μ_I and μ_S for nuclei and electrons, respectively, are related to their spin via the following expressions:

$$\mu_I = g_I \frac{e\hbar}{2m_p}\sqrt{I(I+1)} \quad (2.1)$$

and

$$\mu_S = g_S \frac{e\hbar}{2m_e}\sqrt{S(S+1)} \quad (2.2)$$

where e is the elementary charge, $\hbar$ is Planck's constant, m_p and m_e are the proton and electron masses, and g_e, and g_I are the respective g-factors for the nucleus and electron.

Spin: Intrinsic Angular Momentum

The spin of a nucleus means that it behaves as though it is "spinning" like a tiny planet. However, this is a quantum mechanical property and does not imply actual rotation in the classical sense. Spin is an intrinsic form of angular momentum, fundamentally different from the classical angular momentum $\hat{\mathbf{L}}$, which is associated with the rotation of an object around a point.

The spin angular momentum and magnetic moment are proportional, given by the relations:

$$\hat{\mu} = \gamma \hat{S} \quad (2.3)$$

or

$$\hat{\mu} = \gamma \hat{I} \quad (2.4)$$

where γ is the gyromagnetic ratio, typically expressed in units of $rads^{-1}Tesla^{-1}$.

In classical mechanics [34], a rigid body can have two types of angular momentum: orbital angular momentum ($L = \mathbf{r} \times \mathbf{P}$), associated with motion around a center of mass, and spin angular momentum ($S = I\omega$), associated with rotation about an internal axis. In quantum mechanics [35], the total spin angular momentum for particles like electrons and nuclei is quantized, taking values of $[S(S+1)]^{1/2}$ for electron spin, $\hat{S}$ and $[I(I+1)]^{1/2}$ for nuclear spin $\hat{I}$.

An electron with spin $\hat{S}$ or a nucleus with spin $\hat{I}$ has $(2S+1)$ or $(2I+1)$ sub-levels, which are degenerate in the absence of external fields. However, when subjected to a magnetic or electric field, these sub-levels can experience energy shifts.

Magnetic Moments and Energy

The nuclear magnetic moment is proportional to the spin angular momentum, **I**, as:

$$\mu = \gamma \hat{\mathbf{I}} = \gamma(\hat{\mathbf{I}}_{\mathbf{x}} + \hat{\mathbf{I}}_{\mathbf{y}} + \hat{\mathbf{I}}_{\mathbf{z}}) \tag{2.5}$$

The corresponding nuclear magnetic energy for a spin **I** in a magnetic field **B** depends on the dot product of the magnetic moment and the magnetic field:

$$\hat{H} = -\mu \cdot \mathbf{B} = -\gamma(\mathbf{B}_{\mathbf{x}}\hat{\mathbf{I}}_{\mathbf{x}} + \mathbf{B}_{\mathbf{y}}\hat{\mathbf{I}}_{\mathbf{y}} + \mathbf{B}_{\mathbf{z}}\hat{\mathbf{I}}_{\mathbf{z}}) \tag{2.6}$$

This energy is minimized when the magnetic moment is aligned with the external magnetic field and maximized when aligned in the opposite direction [35].

In general, the intrinsic angular momentum (spin) and magnetic moment of nuclei play a pivotal role in nuclear spin interactions and NMR. While nuclear magnetism is much weaker than electron magnetism, it is this property that allows for the detailed study and manipulation of spin states in quantum systems, a key area of investigation in both quantum thermodynamics and NMR-based technologies [36].

2.2 Nuclear Magnetism

The study of magnetism focuses on the interactions between matter and magnetic fields, as well as the magnetic properties of matter itself. A magnetic field is a fundamental concept in this discipline, describing a property of space around magnetic objects or moving charges. It can be detected through the force it exerts on a probe, for example, a wire carrying an electric current.

In classical physics [37], the magnetic effect of a proton is attributed to its electric charge. A moving charge, akin to an electric current, generates a magnetic field. Similarly, a rotating charge generates a magnetic effect along the axis of rotation, producing what is known as a magnetic moment. Fundamental particles exhibit magnetic moments, just as they possess spin angular momentum.

Interestingly, despite being electrically neutral, neutrons also exhibit magnetic moments due to their intrinsic spin. This demonstrates that an electric charge is not a prerequisite for nuclear magnetism. In fact, modern quark theory [38] suggests a reverse relationship, proposing that magnetism might be the cause of electric charge.

As discussed earlier, one of the four key properties of atomic nuclei is their magnetism, which arises from the angular momentum of the nucleus. Since nuclei contain positively charged protons and uncharged neutrons, the nucleus as a whole is positively charged. When the nucleus rotates due to its spin, it generates a local magnetic field or magnetic moment. This magnetic moment, generated by nuclear spin rotation, is a crucial factor in magnetic resonance experiments and aligns parallel to the axis of rotation.

Although nuclear magnetism and nuclear spin have negligible effects on the macroscopic chemical and physical properties of materials, they provide invaluable tools for probing the microscopic structure of matter without causing disturbances [39, 40].

2.2.1 Nuclear Spin

As mentioned earlier, atomic nuclei possess spin as an intrinsic property. The spin of the nucleus causes it to rotate about an axis perpendicular to the direction of rotation. This rotation generates a local magnetic field or magnetic moment, indicating that any nucleus with spin is inherently magnetic.

The spin of atomic particles is quantized, meaning it takes on discrete values. These values depend on the number of protons (atomic number) and neutrons in the nucleus. Based on these numbers, atomic nuclei fall into three categories regarding their spin values: **1) Zero Spin (I = 0)** : Nuclei with an even number of protons and neutrons (such as ^{12}C, with 6 protons and 6 neutrons, and ^{12}O, with 8 protons and 8 neutrons) have zero net nuclear spin. These nuclei are magnetically neutral and cannot interact with external magnetic fields. **2) Half-Integral Spin (I = 1/2, 3/2, 5/2, ...):** Nuclei with an odd total number of protons and neutrons, or an odd atomic weight, have half-integral spin values. An example of such a nucleus is ^{13}C (with 6 protons and 7 neutrons). **3)Integral Spin (I = 1, 2, 3, ...):** Nuclei with an odd number of protons but an even atomic weight have integral spin values. Examples include ^{2}H and ^{6}Li (lithium). This can be summarized in Table 1.1 below as:

Spin Value I	Atomic Composition	Examples
I=0	Even protons + Even neutrons	^{12}C, ^{16}O
I=1/2, 3/2, . . .	Odd total protons + neutrons or odd atomic weight	^{13}C, ^{31}P
I=1, 2,3, . . .	Odd protons + Even atomic weight	^{2}H, ^{6}Li

The spin of the nucleus is a vital factor in determining its magnetic properties, and this quantization of spin values plays a central role in nuclear magnetic resonance (NMR) and other quantum mechanical phenomena.

The concept of Spin Precession

Just as the angular momentum of a rotating object is represented by a vector, the angular momentum of a particle with spin is also a vector. This vector indicates the axis of rotational motion, commonly referred to as the spin polarization axis [41]. For particles such as atomic nuclei, the spin polarization axis can point in various directions in space. For example, in the absence of an external magnetic field, the spin vectors of protons in hydrogen atoms are randomly oriented. This results in a continuous distribution of spin orientations, as illustrated in Figure 2.1. However, when the sample is placed in a

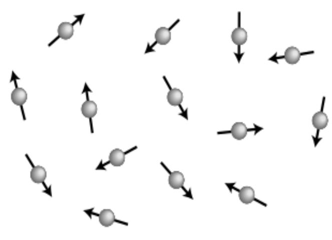


Figure 2.1: Randomly directed spin polarizations.

strong static magnetic field of magnitude $\mathbf{B_0}$, the individual protons begin to precess (rotate) around an axis perpendicular to the direction of the magnetic field. This precession is a direct result of the interaction between the nuclear spin and the external magnetic field. As a result, the spin vectors of the nuclei tilt slightly away from the axis of the magnetic field, with each precession axis remaining parallel to $\mathbf{B_0}$.

Assuming the magnetic field $\mathbf{B_0}$ is aligned along the z-axis, the motion of each nucleus can be described in coordinates perpendicular to the x- and y-axes and parallel to the z-axis. The transverse (perpendicular) components of the motion vary cyclically over time due to the precession, while the longitudinal (parallel) components remain constant. The spin polarization axis traces a cone-shaped path around the magnetic field, maintaining a constant angle between the spin axis and the direction of the magnetic field. This motion is referred to as spin precession.

The behavior of spins in this way is due to the fact that they possess both angular momentum and magnetic moments. The presence of angular momentum significantly alters the dynamic properties of the magnetic moment. The magnetic moment of a nucleus may either align with the spin polarization axis (for nuclei with $\gamma > 0$), or in the opposite direction (for nuclei with $\gamma < 0$).

In equilibrium and in the absence of a magnetic field, the distribution of magnetic moments is isotropic, meaning all possible directions are equally represented [32]. However, when an external magnetic field is applied, the spin polarization axis begins to precess around the field, maintaining a constant angle between the magnetic moment and the field. This motion, known as Larmor precession, occurs at a specific frequency called the Larmor frequency ω_0, which is proportional to the strength of the magnetic field $\mathbf{B}_0$. The Larmor frequency is given by:

$$\omega_0 = \gamma \mathbf{B_0} \tag{2.7}$$

where γ is the gyromagnetic ratio of the nucleus. The stronger the magnetic field, the faster the precession of the spin.

2.2.2 Nuclear Spin States

When a nucleus is placed in a strong static magnetic field $\mathbf{B}_0$, its angular momentum becomes quantized, adopting one of $2\hat{I}+1$ possible orientations with respect to the magnetic field. For nuclei with $\hat{I} = \frac{1}{2}$ (such as ^1H and ^{13}C, there are two possible orientations: one parallel to the external field (lower-energy state) and one anti-parallel (higher-energy state). The potential energy of a nucleus in a magnetic field is given by:

$$E = -\mu B_0 \cos\theta \tag{2.8}$$

where μ is the magnetic moment, $\mathbf{B}_0$ is the strength of the magnetic field, and θ is the angle between the nuclear spin axis and the magnetic field. In most cases, the nuclear spin axis is aligned with the direction of the external field (taken as the z-axis), and the potential energy simplifies to

$$E = -\mu B_0. \tag{2.9}$$

When electromagnetic radiation of the correct frequency is applied, it can induce transitions between adjacent energy levels. The relationship between the frequency v of this radiation and the magnetic field strength $\mathbf{B}_0$ is governed by the Larmor equation:

$$v = \frac{\gamma \mathbf{B_o}}{2\pi} \tag{2.10}$$

In general, nuclei with spin $\hat{I}$ may have $2\hat{I}+1$ different orientations, each with its characteristic energy. Nuclei with $\hat{I} = \frac{1}{2}$ have a symmetrical charge distribution around the nucleus, while nuclei with $\hat{I} > \frac{1}{2}$ have an asymmetrical charge distribution, leading to an electric quadrupole moment, $\hat{Q}$ [41].

2.2.3 Spin in a static magnetic field

A magnetic field of uniform field strength is called a homogeneous field, of which field lines are drawn as equidistant, straight lines running in parallel. If this magnetic field strength does not vary with time it is known as a static field. The main role of this static magnetic field is to split the orientation of nuclear spins, which were in random distribution in the absence of external magnetic field. For example, in the body tissue, the static magnetic field is used to generate a preferred orientations of the spins, parallel as well as anti-parallel to the field lines: $|\uparrow\rangle$ spin up and $|\downarrow\rangle$ spin down are the two preferred spin orientations [42]. More precisely, the two spin orientations, up and down, correspond to two different energy states. The up spin has a lower energy (E_-) than in the field-free space (E); the down spin has a higher energy (E_+). The lower energy state is the preferred in the magnetic field: more spins jump into the lower energy state (E_-) than into the higher one (E_+). If the ratio of up and down spins is the same, the spins could cancel for the most part. But, practically, there is a small majority of excess spins in the up direction which leaves the down spins in the minority.

Most of the measurable macroscopic effects are due to the excess in spin magnets. This excess in spin magnets (**m**) is known as the magnetization (**M**) of the ensemble. The source for the magnetization of the ensemble is the energy split of the spins in the magnetic field. After the ensemble is disturbed by application of external static magnetic field, it takes a certain time for the magnetization to reattain its initial value. But after its recovery of its initial magnetization, the ensemble will be in a state of energy equilibrium.

For a nuclear spin in an external static magnetic field of magnitude, $\mathbf{B}_0$, applied along the z-axis (which is the axis of rotation of the spin), the quantum mechanical Hamiltonian for the interaction of a nuclei spin of magnetic moment, $\mu_z = \gamma \hat{I}_z$, to the the static magnetic field is given by:

$$\begin{aligned} \hat{H}_0 &= -\mu \cdot \mathbf{B_0} \\ &= -\gamma B_0 \hat{I}_z \end{aligned} \tag{2.11}$$

This interaction energy, $\hat{H}_0$ is called the nuclear Zeeman interaction. The term γB_0 may be identified as the Larmor frequency of spin $\hat{\mathbf{I}}$. Thus we can rewrite it as $\omega_0 = \gamma B_0$, where, ω_0 is the Larmor frequency in megahertz (MHz), B_0 the magnetic field strength in tesla (T) that the nuclei experiences, and γ is a constant for each nucleus in MHz/T, known as the gyromagnetic ratio.

Then the Schrodinger equation corresponding to the Hamiltonian of Eq. (2.11) is given by:

$$\begin{aligned} i\hbar\frac{\partial|\psi(t)>}{\partial t} &= -\hat{\mu} \cdot \mathbf{B_0}|\psi(\mathbf{t})> \\ &= -\omega_0 \hat{I}_z|\psi(t)> \end{aligned} \tag{2.12}$$

2.2.4 Spin in a rotating magnetic field

In order to cause transitions between spin states, the second radio frequency field is applied perpendicular to the original static magnetic field. Let us consider the time varying (alternating) radio frequency pulse with in the x-y plane given as:

$$\vec{B}_1(t) = |B_1|(\cos\omega t\hat{x}, \sin\omega t\hat{y}, 0) \tag{2.13}$$

This transversal radio frequency field is the component of the vector that rotates about the external field in the x-y plane. This means that by applying magnetic field in perpendicular direction (a 90 degree pulse), magnetization flips in the transverse direction, that is, the x-y plane. For the nuclei of spin initially in static magnetic field, B_0 (along z-axis), the applied radio frequency field causes the spin nuclei to lose its original equilibrium.

As long as the r.f. pulse is present, two magnetic fields are in effect: (i) the static magnetic field, B_0, which is static and strong, and (ii) for a short time, a weak rotating r.f. magnetic field, $B_1(t)$.
The effective Hamiltonian is then given as:

$$
\begin{aligned}
\hat{H}_{\text{eff}} &= -\hat{\mu}\cdot\mathbf{B_{eff}} \\
&= -(\mu_x\hat{x}+\mu_y\hat{y}+\mu_z\hat{z})\cdot[B_0\hat{z}+|B_1|(\cos\omega t\hat{x}+\sin\omega t\hat{y})] \\
&= -\gamma(I_x\hat{x}+I_y\hat{y}+I_z\hat{z})\cdot[B_0\hat{z}+|B_1|(\cos\omega t\hat{x}+\sin\omega t\hat{y})] \\
\hat{H}_{\text{eff}} &= -\gamma B_0\hat{I}_z-\gamma B_1(\cos\omega t\hat{I}_x+\sin\omega t\hat{I}_y) \qquad (2.14)\\
\hat{H}_{\text{eff}} &= \hat{H}_0+\hat{H}_1(t) \qquad (2.15)
\end{aligned}
$$

The Hamiltonian in question is often referred to as the rotating frame Hamiltonian. It's important to note that for a spin-1 system, the matrix representation of the nuclear spin components is defined as follows:

$$
\hat{I}_z=\begin{pmatrix}1&0&0\\0&0&0\\0&0&-1\end{pmatrix}\;;\qquad \hat{I}_x=\begin{pmatrix}0&\frac{1}{\sqrt{2}}&0\\\frac{1}{\sqrt{2}}&0&\frac{1}{\sqrt{2}}\\0&\frac{1}{\sqrt{2}}&0\end{pmatrix};\qquad \hat{I}_y=\begin{pmatrix}0&\frac{-i}{\sqrt{2}}&0\\\frac{i}{\sqrt{2}}&0&\frac{-i}{\sqrt{2}}\\0&\frac{i}{\sqrt{2}}&0\end{pmatrix} \qquad (2.16)
$$

These matrices represent the components of the angular momentum for a nuclear spin-1 system, where $\hat{I}_x$, $\hat{I}_y$, and $\hat{I}_z$ correspond to the x, y, and z components of the spin operator, respectively.

In order to study the non-equilibrium properties of the system under study, we must know the initial thermal state and the time evolution operator, $\hat{U}(t)$, which is the solution of the Schrodinger equation of the following form:

$$
\begin{aligned}
i\hbar\frac{\partial|\psi(t)>}{\partial t} &= -\hat{\mu}\cdot\mathbf{B}_{eff}|\psi(t)> \\
i\hbar\partial_t\hat{U}(t) &= \hat{H}_{eff}\hat{U}(t) \qquad (2.17)
\end{aligned}
$$

2.3 Nuclear Magnetic Resonance

Magnetic resonance is a process by which a physical excitation (resonance) is set up via magnetism. It is based upon the interaction between a particle that possesses spin and charge (electrons and other subatomic particles), and an applied magnetic field. While any atomic particles having charge and spin, and producing spin angular momentum can be examined using magnetic resonance (MR) techniques [32], in our study we focus on the magnetic resonance produced due to the interaction of atomic nuclei and the external magnetic field, and the use of MR techniques for their study, formally known as Nuclear Magnetic Resonance (NMR).

On the other hand, nuclear magnetic resonance (NMR) is a physical phenomenon in which nuclei in a strong static magnetic field are perturbed by a weak oscillating magnetic field, in the near field. Then the nuclei respond to the perturbation by producing an electromagnetic signal, with a frequency characteristic of that of the magnetic field at the nucleus. This process occurs near resonance, when the oscillation frequency matches the intrinsic frequency of the nuclei. The phenomenon of magnetic resonance mainly depends on the strength of the static magnetic field, the chemical environment, and the magnetic properties of the isotope involved.

The nuclear magnetic resonance process have been used to develop magnetic resonance imaging and for nuclear magnetic resonance spectroscopy technology. The technology is also being used to develop nuclear magnetic resonance quantum computers. More generally, magnetic resonance (MR) is a measurement technique used to examine atoms and molecules. One illustrative case, is the case where the nuclear magnetic resonance (NMR) spectroscopy is used in the study of molecular structure through measurement of the interaction between an oscillating radio frequency electromagnetic field and a collection of nuclei immersed in a strong external magnetic field. These nuclei are components of atoms that, in turn, are assembled into molecules. Therefore, a nuclear magnetic resonance spectrum, can provide detailed information about molecular structure and dynamics, information that would be difficult, even may not be possible, to obtain by any other methods.

The phenomenon of nuclear magnetic resonance is based on the fact that the nuclei of certain elements, possessing a spin angular momentum and an associated magnetic moment, is allowed to interact magnetically with external magnetic field. At first, When such nuclei are placed in a strong static magnetic field, they can adopt one of a number of quantized orientations. Each of these orientations correspond to a particular energy level. The orientation with the lowest energy is the one in which the nuclear magnetic moment is most closely aligned with the external magnetic field while the orientation with the highest energy is the one in which the nuclear magnetic moment is least closely aligned with the field. Secondly, as relatively weak oscillating radio frequency magnetic field is applied to the nuclei, which is already in static magnetic field, the nuclei in the lower energy level absorb the RF energy and the nuclei in the upper energy level are stimulated to emit their energy [43]. As more energy is transmitted, the nuclei populations of the two levels (the lower energy level and the higher energy level) will gradually equalize. At this moment, no further net absorption of energy is possible, and this condition is known as saturation condition or equilibrium condition. But, there is a limited amount of energy that a collection of nuclei can absorb before they become saturated.

The principle of NMR usually involves three sequential steps: (1) the polarization (alignment) of the magnetic nuclear spins in an applied strong static magnetic field, B_0. (2) The perturbation of this alignment of the nuclear spins by a relatively weak oscillating magnetic field, usually referred to as a radio-frequency (RF) pulse, where the oscillation frequency required for significant perturbation is dependent upon the static magnetic field (B_0) and the nuclei of the sample. (3) The detection of the resonance signal during or after the RF pulse, due to the voltage induced in a detection coil by precession of the nuclear spins around B_0. After an RF pulse, the precession usually occurs with the nucleus's intrinsic Larmor frequency, ω_0, but the nuclei in itself does not involve transitions between spin states or energy levels [42].

One of the area where we apply the concepts of quantum-thermodynamics is a magnetic resonance experiment, where a typical setup consists of a sample of non-interacting spin particles (electrons, nucleons, etc.) placed under a strong static magnetic field $\mathbf{B}_0$ in the z direction, and is perturbed externally by a relatively very small magnetic field, $\vec{B}_1$. The role of this perturbation is to bring the sample system out of equilibrium condition [44]. The Hamiltonian of this interaction of the system to the externally imposed magnetic fields can be described as:

$$\hat{H} = -\mu \cdot \mathbf{B} \tag{2.18}$$

where $\vec{B} = \vec{B}_0 + \vec{B}_1$

In magnetic resonance experiments the measuring device called nuclear magnetic resonance spectrometer may be used to supply three kinds of magnetic fields: 1) The main super-conducting solenoid which provides a very strong, very homogeneous, static magnetic field $\mathbf{B}_0$, and 2) The radio frequency (RF) coil in the probe that generates an oscillating magnetic field, $\mathbf{B}_1(t)$. In normal circumstances this field is spatially homogeneous as possible. 3) The third one might be the gradient field.

In general, the nuclear magnetic resonance involves transitions between the energy levels (or changes in the orientation of the nuclei as it is exposed to the external magnetic field). The transitions among energy levels may be induced by the absorption of radio frequency radiation of the correct frequency, which is measurable on a recorder in the form of a NMR signal of the nucleus [45].

2.4 Quantum Thermodynamics: Work Fluctuations and Measurements

In this chapter we focus on the theoretical discussion of work distribution and its measurements in quantum thermodynamics. In the concept of quantum thermodynamics the work done on/by the system may arise from thermal fluctuations or quantum fluctuations or both. Due to the complexity of the dynamics taking place at atomic or molecular level, the work done as a result of quantum fluctuation is considered to be a random variable. Thus, in quantum thermodynamic description, work is taken as random variable. This quantum thermodynamics considers the case of exploring the dynamics of the quantum system as it is driven out of equilibrium by suddenly imposing the external driving parameter. In this chapter we will also discuss Jarzynski relations, which takes into account fluctuations in non-equilibrium dynamics, and connect it to equilibrium properties of thermodynamical relevance with explicit non-equilibrium features.

2.5 Thermodynamic description of work

An important aspect of thermodynamic processes are their energetic impact. For example, if any physical system is brought in contact to a heat reservoir then the energy of the system may flow between the system and the reservoir. Such energy exchanged is what is known as heat energy. This exchange of heat energy between the two may change the internal energy of the system. But the internal energy of any system may also change by means of an external agent which manually changes some parameters in the Hamiltonian of the system. This type of change in energy of the system is called work.

Any system of the world is either in its own progressive change or in continuous interaction with its environments. This implies that any system is the result of the change which modifies its states or which modify the system itself. Such changes of the system can be expressed in terms of the heat absorbed or released by the system and through the change in the Hamiltonian of the system. Generally speaking, heat and work are not properties of the system. Rather, they are the outcomes of processes which alter the state of the system. If during a certain interval of time an amount Q of heat entered the system and a work W was performed on the system, energy conservation implies that the total energy of the system must have changed by:

$$\Delta U = Q + W, \tag{2.19}$$

This is the familiar first law of thermodynamics. When $W > 0$ it is said that the external agent performed work on the system. On the other hand, when $W < 0$ it is said that the system performed work on the external agent.

Accordingly, the first law of thermodynamics states that the internal energy of a given system can change in two ways: 1) by adding heat or 2) by adding work. This further inserts that heat and work refers to two different process types rather than two different forms of energy. These two different processes are related to the typical means of control available in the thermodynamic setting. As the internal energy is the average energy of the system under consideration, for a given thermal state, there are two fundamental ways for change: Change the state of the system or change the system itself.

The change in the thermal state of a given system is related with heat while the change of the system is related to work. The change of the system requires to modify certain parameters that specify the system; in principle, such modifications might affect anything, from the particle mass to the particle-particle interactions. Some of these parameters include the volume of a container, an electric or magnetic field, or the stiffness of a harmonic trap. But a simple and well established parameter (because easily accessible) would be the volume of a gas. Indeed, to compress a gas, say, requires work. So to do work on a system or by the system means performing work on a system (or by a system) through change of some parameter λ in the Hamiltonian [46]. Since λ is used as an external agent that do work on the system, it can be called as the work parameter. When an external agent changes λ, it is performing work on the system.

In order to describe exactly how the work was performed we must specify the protocol to be used. This means specifying exactly under what conditions are the changes being made and with what time-dependence is λ changing. We usually assume that the process lasts between a time $t = 0$ and a time $t = \tau$, during which $\lambda(t)$ varies according to some predefined function $\lambda(t)$, from an initial value $\lambda_i = \lambda(0)$ to a final value $\lambda_f = \lambda(\tau)$.

Overall, describing an arbitrarily fast (non-equilibrium) process can be a very difficult task since it requires information about the dynamics taking place within the system and how the system is coupled to its environment. Instead, thermodynamics usually focuses on quasi-static processes, in which λ changes very slowly in order to ensure that throughout the process the system is always in thermodynamic equilibrium [47].

The advantage of a quasi-static process is that the system always remain in equilibrium throughout the process. For instance, consider the process of compressing a gas with a piston. If you compress it very quickly, different parts of the gas will have different temperatures and densities. So a quick compression pushes the system away from equilibrium. But if we compress it very slowly, at each instant the system has enough time to adjust itself to the changes and therefore always remain in equilibrium. Quasi-static processes are therefore a temporal. That is, one does not need to specify the function $\lambda(t)$, but merely the initial and final λ values.

One of the most important example of quasi-static process is the isothermal process, in which the temperature of the system is kept constant throughout the protocol. Because work usually changes the temperature of an isolated system, to ensure a constant temperature the system must remain coupled to a heat reservoir. Note that an isothermal process must necessarily be quasi-static, if not, the temperature the system will not remain constant or homogeneous. In fact, intensive quantities such as temperature and pressure are defined only in thermal equilibrium, so any process where these quantities are kept fixed must be quasi-static.

The work done on an isothermal process can not be fully converted into useful work for the reason that part of the energy is consumed as heat. The remaining part of the energy is called the free energy and is defined as:

$$\Delta F = F(T, \lambda_f) - F(T, \lambda_i). \tag{2.20}$$

Accordingly Eq. (2.19) can be rewritten as:

$$W = \Delta F = F(T, \lambda_f) - F(T, \lambda_i) = \Delta U - Q. \tag{2.21}$$

The energy is free because it is the part of ΔU that may be used to perform work.

On the other hand, if the undergoing isothermal process is not quasi-static (performed so too quickly), the initial state is still $F(T, \lambda_i)$ while the final state will not be the same to $F(T, \lambda_f)$, which is the one measured in quasi-static case. Instead, the final state will be something complicated which depends exactly on how the process was performed (see Fig. 2.2). This indicates that, if a system which is initially coupled to the heat reservoir is leaved alone (de-touched from the heat bath) after the protocol is over, it will eventually relax to the state $F(T, \lambda_f)$; which in turn shows that a certain amount of work W was performed to take the system from $F(T, \lambda_i)$ to $F(T, \lambda_f)$. But this work is not the same to the change in free energy, ΔF, given in Eq. (2.20), which holds only in the case of quasi-static processes.

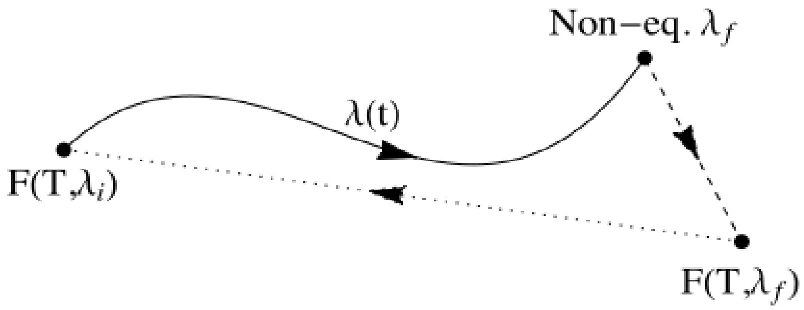


Figure 2.2: Diagram of a non-equilibrium process. Through the protocol $\lambda(t)$, the system is taken from an initial state $F(T, \lambda_i)$ to a final non-equilibrium state with parameter λ_f (solid line). After the process is done, the system will eventually relax from the non-equilibrium state to the equilibrium state $F(T, \lambda_f)$ (dashed line) [46]

In general, since work in non-equilibrium process can not be easily expressed in terms of the change in free energy of the system, a famous inequality which stems directly from the second law of thermodynamics, can be used to express it [48]. It states that the work done in the non-equilibrium process always be larger or equal to ΔF:

$$W \geq \Delta F \tag{2.22}$$

with the equality holding only for isothermal and quasi-static processes. From this inequality equation, one can understand that the minimum amount of work needed to change the free energy of a system is equal to ΔF, and will be accomplished in an isothermal (quasi-static) process. Any other protocol will require more work. The difference $W_{irr} = W - \Delta F \geq 0$, known as the irreversible work, therefore represents the extra work that had to be done due to the particular choice of the work parameter.

The inequality in Eq. (2.22) can be easily demonstrated to be a direct consequence of the second law of thermodynamics. In the Lord Kelvin postulation, the second law states that "A transformation whose only final result is to transform into work, heat extracted from a source which is at the same temperature throughout, is impossible [49]. The key part of this statement is the expression "only final result. It means that it is impossible to extract work from a bath at a fixed temperature, without changing anything else (such as the thermodynamic state of the system).

To clarify what is formulated in Eq. (2.22), consider the three trajectories shown in Fig. (2.2) where the whole process is divided into 3 steps. In the first step, a certain amount of work W is performed in a non-equilibrium process. In the second, without performing work, the system is allowed to relax from the non-equilibrium state to the final state of $F(T,\lambda_f)$. Finally, in the third process (represented by a dotted line), the system is allowed to go quasi-statically from $F(T,\lambda_f)$ back to $F(T,\lambda_i)$. The amount of work required for this return journey can be expressed as:
$W_{return} = -\Delta F$ for the reason that the reverse process is a quasi-static one. Now, we are back to the original state, having performed a total work of $W + W_{return} = W - \Delta F$. But, according to the second law thermodynamics, this total work cannot be negative for the reason that no work can be extracted from a reservoir at a fixed temperature, without any changes in the state of the system. This implies that because it is impossible to extract work from a reservoir at a fixed temperature, the total work done must be greater than zero (0), $W - \Delta F \geq 0$. This is what is formulated in Eq. (2.22).

2.6 Isothermal processes in equilibrium statistical mechanics

Consider the case where the system of interest, having Hamiltonian of $H(\lambda_i)$, was initially in thermal equilibrium with heat bath at inverse temperature $\beta = \frac{1}{K_B T}$. Then, the quantum counterpart of the canonical distribution for the system, with Hamiltonian $\hat{H}$ operator and kept in contact with heat reservoir of constant temperature,can be given in terms of the Gibb's density matrix of the form:

$$\rho_{th} = \frac{e^{-\beta \hat{H}}}{Z} \tag{2.23}$$

where Z-is the partition function and is given as $Z = tr(e^{-\beta \hat{H}})$, and $\beta = \frac{1}{T}$ (where we have used $k_B = 1$). If the system was initially in state $|n\rangle$ with an energy eigenvalues of E_n, the probability of finding the system in this state can be given as:

$$P_n = \langle n|\rho_{th}|n\rangle = \frac{e^{-\beta E_n}}{Z}, \tag{2.24}$$

where P_n is the probability of finding the system in the state $|n\rangle$. Then the average (internal) energy of the system becomes

$$U = \langle \hat{H} \rangle = tr(\hat{H}\rho_{th}) = \sum_n E_n P_n. \tag{2.25}$$

Let the system is undergoing an isothermal quasi-static process and parameterized by a quantity λ that expresses the path along the process. To analyze the process quantitatively, it is possible to decompose the path into a series of infinitesimal processes, where λ is changed slightly to $\lambda + d\lambda$. The full process is then simply the sum effect of these small steps. As the external parameter, λ, change from λ to $\lambda + d\lambda$, both E_n and P_n will change. Hence, U will change by:

$$dU = \sum_n d(E_n P_n) = \sum_n [d(E_n)P_n + E_n d(P_n)]. \tag{2.26}$$

The above equation, Eq. (2.26), has an interesting physical interpretation. Since the change in λ is infinitesimal and instantaneous, immediately after this change, the system has not yet responded to it. This corresponds to the first term: it is the average of the energy change dE_n over the old (unperturbed) probabilities P_n . In the second term, the energy is fixed and the probabilities change. We interpret this as the second step, where the system adjusts itself with the bath in order to return to equilibrium. So each infinitesimal process may be separated in two parts. The first part is the work performed and the second is the heat exchanged as the system relaxes to equilibrium. This help us to define:

$$\delta W = \sum_n d(E_n)P_n \tag{2.27}$$

and

$$\delta Q = \sum_n E_n d(P_n) \tag{2.28}$$

so that Eq. (2.26) may be written as:

$$dU = \delta Q + \delta W \tag{2.29}$$

Where we have used δ instead of d simply to emphasize that heat and work are not exact differentials.

To show that δW is related to the change in the free energy of the system, let we use the definition

$$F = -T \ln Z. \tag{2.30}$$

The differential form of this free energy (F) can be expressed as:

$$dF = \frac{-T}{Z}dZ = \frac{-T}{Z}d(\sum_n e^{\frac{-E_n}{T}}) = \frac{-T}{Z}\sum_n [\frac{-1}{T}(dE_n)e^{\frac{-E_n}{T}}] = \sum_n (dE_n)\frac{e^{\frac{-E_n}{T}}}{Z}. \tag{2.31}$$

where we have used $Z = \sum_n e^{\frac{-E_n}{T}}$ for T is a temperature which is constant.

Eq. (2.31) is precisely equal to Eq. (2.27), and so we conclude that for an infinitesimal isothermal process,

$$\delta W = dF \tag{2.32}$$

From this result, Eq. (2.20) is recovered by integrating over the several infinitesimal steps.

Similarly, to relate δQ in Eq. (2.28) to the Shanon entropy of the system, defined as

$$S = -\sum_n p_n \ln p_n \tag{2.33}$$

let we invert Eq. (2.24) and have $E_n = -T\ln(ZP_n)$. Next we substitute this in Eq. (2.28) and separate the two terms, one proportional to $\ln(Z)$ and the other to $\ln(P_n)$. The term with $\ln(Z)$ will be

$$-T\sum_n \ln(Z)d(P_n) = -T\ln(Z)d(\sum_n P_n) = 0, \tag{2.34}$$

since $\sum_n P_n = 1$ and $d(1) = 0$ Thus, we are left only with

$$\delta Q = -T\sum_n d(P_n)\ln P_n. \tag{2.35}$$

But now note that, by the chain rule,

$$d(\sum_n P_n \ln P_n) = \sum_n d(P_n)\ln P_n + \sum_n \frac{P_n}{P_n}d(P_n) \tag{2.36}$$

and the last term is also zero for the same reason as above. Hence, we conclude that

$$\begin{aligned} \delta Q &= -T(\sum_n dP_n \ln P_n) \\ &= Td(-\sum_n P_n \ln P_n) = TdS. \end{aligned} \tag{2.37}$$

Here it is important to note that this relation expressed in Eq. (2.37), holds only for infinitesimal processes. For finite and irreversible processes, there may be additional contributions to the change in entropy. We see that even though δQ is not a function of state, it is related to the variation of a quantity (entropy, S) which is a function of state.

All the above calculations show how to use the Gibb's theory, which is a microscopic description of thermal processes, to relate work and heat with thermodynamic quantities such as free energy and entropy and to enlighten the physical meaning of these quantities. Therefore, here it possible to concluded that it is possible to give microscopic definitions to thermodynamic quantities such as heat and work. Moreover, it is possible to relate them to functions of state which can be constructed from the initial density matrix ρ_{th} . While these thermodynamic quantities may be defined independently of statistical mechanics, it is believed that the microscopic description helps to clarify their physical interpretations of the dynamical process taking place at atomic or molecular level..

In general, it is necessary to catch up that in an isothermal quasi-static process, which assumes the system's temperature of the system to remains constant throughout the protocol, it is important to realize that the system cannot be isolated from its environments. This implies that, even though, the process is very slow in quasi static process there exist heat exchange between the system and the environment. This can be readily seen by considering the compression of a gas with a piston. When the gas is compressed, it warms up. To keep the system's temperature constant, some energy must be released to the environment, which further tells that in an isothermal process the system must always be remain in contact with a heat reservoir at a fixed temperature. It is also important to note that there is a slight ambiguity in the term isothermal process. One may choose it to mean that the temperature of the system is always constant, or for it to mean that the temperature of the bath is constant. Thus, it is possible to conclude that for the temperature of the system to remain constant, the process must be quasi-static. For, in a non-equilibrium process, the temperature will not remain constant or homogeneous. In fact, intensive quantities, such as temperature and pressure, are only defined in equilibrium.

2.7 Quantum thermodynamic description of Work

2.7.1 Work as a random variable

The great insight into the properties of non-equilibrium processes could be gained by treating work as a random variable [13, 24, 50]. This means that when dealing with microscopic system (small size systems), the fluctuations at quantum level may perturb our measurements of the work distribution. More precisely, each time we measure the work done we may obtain the slightly different measurements due to this quantum fluctuations, although the fluctuations at quantum levels in many cases are negligibly small. Hence, work may be treated as a random variable. But the idea that fluctuations at quantum level are negligibly small, does not stop us from interpreting W in this way; rather when dealing with microscopic systems, this interpretation becomes essential because fluctuations become more significant in the study of molecular or atomic theory. A famous example is the measurement of the work performed when folding RNA molecules [6]. Because the process is strongly affected by thermal fluctuations (Brownian motion), each time the experiment is performed, a different work W must be done to achieve the same outcome.

Accordingly, it can be said that in addition to thermal fluctuations, some microscopic systems also have a strong contribution from quantum fluctuations. These fluctuations[27] are related to the fact that in order to access the amount of work performed in a system, one must measure its energy and therefore collapse the wave-function. As is known from quantum mechanics, when this is done the system may tend to different states with different probabilities Eq. (2.24). So in addition to the thermal fluctuations, we may also have inherently quantum fluctuations.

The Jarzynski equality

Observation is a central theme not only in quantum mechanics but also in thermodynamics. Not being an observable does not mean that work or heat could not be measured at all. However, the strategy implemented in quantum mechanics is not the same to that of thermodynamics. This means that in quantum mechanical measurement, the work can be reduced to two separate energy measurements, one at the beginning and the other one at the end of the process. Of course, for this strategy to hold one has to make sure that no heat has been exchanged in parallel. Such quantum processes under observation have been studied in the context of the so-called quantum Jarzynski relation. The results are measurement-induced fluctuations [51]. These fluctuations are quantum mechanical in origin, but, nevertheless, fulfill the same relations as derived within a classical context.

Usually, our knowledge of non-equilibrium processes is restricted only to inequalities such as Eq. (2.22). But, Jarzynski [52] had formulated the equality equation by considering work, W, as a random variable. Accordingly, it inserts that one may obtain an equality equation, even for the process performed arbitrarily far from equilibrium.

Consider several realizations of a non-equilibrium process, such as that described by the solid line in Fig. 2.2. At each realization the system must always be prepared in the same initial state. Then by executing the protocol one can measure the total work W performed. After repeating this process many times, one may construct the probability distribution of the work, $P(W)$. From this probability any average may be computed. For instance the average work will be

$$\langle W \rangle = \int W P(W) dW \tag{2.38}$$

Or we may study the average of other quantities such as $\langle W^2 \rangle$ and so on. In each realization we computed the work W and use this data to construct the statistics of work, from which all sorts of averages may be computed.

The Jarzynski's main result was to show that the statistical average of $e^{-\beta W}$ should satisfy:

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F} \tag{2.39}$$

where $\Delta F = F(T, \lambda_f) - F(T, \lambda_i)$. Such a relation has substantial importance in quantum-thermodynamic description of the system, since it holds for the average value of the calculations done for the processes performed arbitrarily far from equilibrium. And it is an equality, which is a much stronger statement than the inequalities used in thermodynamics. The appearance of $F(T, \lambda_f)$ in $\Delta F = F(T, \lambda_f) - F(T, \lambda_i)$ of Eq. (2.39) does not necessarily represents the final state of the process (it would only be the final state in a quasi-static process). Instead, $F(T, \lambda_f)$ is the state that the system wants to go, but cannot do so because the process is too quick.

By using Jensen's inequality relation, now, it is possible to show that the inequality in Eq. (2.22) is contained within the Jarzynski's equality. The Jensen's inequality states that:

$$\langle e^{-\beta W} \rangle \geq e^{-\beta \langle W \rangle} \tag{2.40}$$

Then combining this $\Big($Eq. (2.40)$\Big)$ with Eq. (2.39) yields:

$$\langle W \rangle \geq \Delta F. \tag{2.41}$$

This relation inserts that, for non-equilibrium process, the average work is always greater than the change in the free energy, ΔF. So when work is treated as a random variable, the old results from thermodynamics can be recovered for the average work.

2.7.2 Non-equilibrium unitary dynamics

Consider a system described by a time-dependent Hamiltonian, $\hat{H}(t)$, whose time-dependence is realized via externally applied parameter, $\lambda(t)$, which we refer to the work parameter (or an externally driving work parameter). Moreover, let us assume that at time $t = 0$ the system is in thermal equilibrium with heat reservoir of constant temperature, given in terms of $\beta = \frac{1}{K_B T}$. Hence, the system can be described by the Gibb's density matrix as:

$$\rho_{th} = \frac{e^{-\beta H_0}}{Z_0} \tag{2.42}$$

where $H_0 = H(\lambda_0)$ and $Z_0 = Z(\lambda_0) = \sum e^{-\beta \hat{H}_0}$ is a canonical partition function corresponding to the initial state of the system.

Assume that the system was evolving with time before it was coupled to the reservoir. Then it is allowed to equilibrate with a heat reservoir at temperature T. By de-touching the system from the bath after it equilibrate with it, and then measure the energy of the system. Here, let we assume the system is initially in a quantum state $|n\rangle$ with energy eigenvalues E_n^0 and the corresponding energy eigenvectors of $\hat{H}_0 = \hat{H}(\lambda_0)$. Then the state $|n\rangle$ is obtained with probability

$$P_n = \langle n|\rho_{th}|n\rangle = \frac{e^{-\beta E_n^0}}{Z_0} \tag{2.43}$$

Immediately after this measurement is made, implement (set on) the protocol, $\lambda(t)$, that help to disturb the system that was in state $|n\rangle$ and to take the system out of equilibrium. The deriving parameter, $\lambda(t)$, is a chosen transformation that modifies itself in time by changing λ from $\lambda(0) = \lambda_i$ to $\lambda(\tau) = \lambda_f$. Then, by assuming a constant switching rate, $\frac{d\lambda}{dt}$, different realizations (work measurements) can be measured over a total switching time, $\tau = t_f$. If we assume that during the first instance of energy measurement, the system was not in contact with the bath (or the contact with the bath was very weak), then it is possible to approximate the process as unitary evolution. Accordingly, the state of the system at any given time t will be given by

$$|\psi(t)\rangle = U(t)|n\rangle \tag{2.44}$$

where $U(t)$ is the time-evolution operator, which satisfies Schrodinger's equation:

$$i\partial_t U = \hat{H}(t)U, \; U(0) = 1 \tag{2.45}$$

If at the end of the process the measured energy of the system is assumed to be E^τ, then the Hamiltonian of the system become $\hat{H}_f = \hat{H}(\lambda_\tau)$ and therefore may have completely different energy levels (eigenvalues) E_m^f in a new eigenvectors $|m\rangle$. Thus, the probability that we now measure an energy E_m^τ can be given as:

$$P_m = \langle m|\rho_{th}|m\rangle = \frac{e^{-\beta E_m^f}}{Z_f}, \tag{2.46}$$

which indicates that the change found in $|m\rangle$ after a time τ .

According to quantum theory [53, 54], given the spectral decompositions of the initial and final Hamiltonian:

$$\hat{H}(\lambda_0) = \hat{H}_0 = \sum E^0{}_n |E^0{}_n\rangle\langle E^0{}_n| \tag{2.47}$$

and

$$\hat{H}(\lambda_\tau) = \hat{H}_\tau = \sum E^\tau{}_m |E^\tau{}_m\rangle\langle E^\tau{}_m| \tag{2.48}$$

respectively, the energy difference between the two outcomes $E^\tau{}_m - E^0{}_n$ may be interpreted as the work performed by the external driving force in a single realization of the protocol.

Particularly, for the case where no heat may be exchanged with the environment immediately after the protocol is applied, any change in the energy must necessarily be attributed to the work performed by the external driving force. Hence, for the energy obtained in the first measurement, E_n^0 and the energy obtained in the second measurement, $E^\tau{}_m$, the work performed by the external agent can be given as:

$$W = E^\tau{}_m - E_n^0 \tag{2.49}$$

Both E_n^0 and E_m^τ are fluctuating quantities which change during each realization of the experiment. The first energy E_n^0 is random due to thermal fluctuations and the second energy, E_m^τ, is random due to quantum fluctuations. Consequently, W is considered as a random variable, encompassing both the fluctuations.

Eq.(2.49) shows that work is a quantity which requires two measurements to be accessed and hence cannot be associated with a quantum mechanical observable. In general, as understood from the above derivations, the work is not a property of the system, but rather the outcome of a process performed on the system.

The particular value of the work W in Eq. (2.49) occurs with probability $p^0{}_n\, p^\tau{}_{m|n}$ for a quantum system undergoing a transformation that changes its Hamiltonian as $\hat{H}_0 \to \hat{H}_\tau$ in a time τ. The corresponding probability distribution of work is given by:

$$P(W) = \sum p^0{}_n p^\tau{}_{m|n} \delta(W - (E^\tau{}_m - E_n^0)) \tag{2.50}$$

where $p^0{}_n = \frac{e^{-\beta E_n^0}}{Z(\lambda_0)}$, which keeps track of the initial thermal statistics, and $p^\tau{}_{m|n} = \frac{e^{-\beta E_m^\tau}}{Z(\lambda_\tau)}$, which embodies the transition probability arising from the change of basis.

Instead of dealing directly with Eq. (4.16), it is convenient to use the Fourier transform of the work distribution or work characteristic function:

$$G(r,\tau) = \int P(W) e^{irW} dW \tag{2.51}$$

which is referred to as the characteristic function of the work distribution and it can be formulated as:

$$G(r,\tau) = \sum_{n,m} p^0{}_n p^\tau{}_{m|n} e^{ir(E^\tau{}_m - E_n^0)} dW \tag{2.52}$$

$$= tr(U e^{-ir\hat{H}_0} \rho_{th} U^\dagger e^{ir\hat{H}_\tau}) \tag{2.53}$$

where ρ_{th} is the initial thermal state of the system, and r represent the time propagator generated by the forward protocol.

If it is concerned with a specific driving protocol, known as sudden quench, where $\lambda(t)$ is abruptly changed from its initial value to the final one; the unitary time evolution operator reads $\hat{U}_{\tau,0} = \hat{1}$

and any dependence on τ disappears. Thus we will refer to the work distribution and characteristic function simply as $P(W,\tau) = P(W)$ and $G(r,\tau) = G(r)$.

Thus, the work probability distribution (or equivalently its characteristic function) introduced above helps for the formulation of quantum versions of the fundamental fluctuation theorem. The usefulness of the work characteristic function becomes apparent when calculating the moments of the work probability distribution explicitly. Indeed, the k^{th} moment of $P(W)$ can be obtained from the characteristic function as:

$$\langle W^k \rangle = (-i\hbar)^k \frac{\partial^k}{\partial r^k} G(r)|_{r=0} \tag{2.54}$$

Chapter 3

Models and Methodology

This chapter utilizes a theoretical framework to explore the non-equilibrium thermodynamics of spin-1 quadrupolar systems through two models: one focusing on the interaction of spin-1 nuclei with external fields (both static and rotating magnetic fields) without considering quadrupolar interactions, and the other that incorporates these interactions. The spin-1 system is connected to a heat bath at temperature T, with the assumption of extremely weak coupling, ensuring that energy relaxation and decoherence rates remain minimal, allowing for unitary evolution. Initially, the system is allowed to equilibrate with the heat bath before undergoing a finite-time cyclic process, during which data is collected at each cycle.

By employing mathematical modeling and numerical simulations, the study addresses the Schrodinger equation to investigate the system's behavior. It provides insights into quantum thermodynamics and work distributions in the spin-1 system, which can occupy three quantum states denoted by the quantum numbers m (where $m = \pm 1$ and 0). The research emphasizes transitions between these states when a weak oscillating magnetic field acts as a quantum perturbation, promoting dynamics akin to magnetic resonance. The model describes performing work on the spin-1 nuclei through changes in a work parameter, $\lambda(t) = \mathbf{B}_1(t)$, in the Hamiltonian $\hat{H}(t)$, with a weak alternating magnetic field as the work parameter. The cyclic process involves switching on the magnetic field, measuring energy values at the start and end, and repeating this procedure multiple times to gather sufficient statistical data.

In order to describe exactly how the work is performed on a nuclei of spin-1, we must specify the protocol to be used. This means, specifying exactly under what condition is the change being made and with what time dependence is $\lambda = B(t)$ changing. We usually assume that the process lasts between a time $t = 0$ and a time $t = \tau$, during which λ varies according to some predefined function $\lambda(t)$, from an initial value $\lambda_i = \lambda(0)$ to a final value $\lambda_f = \lambda(\tau)$.

3.1 Model-1: Spin-1 System in Static and Rotating Fields (No Quadrupole Interaction)

The first model considers a collection of spin-1 quadrupolar nuclei subjected to a strong static magnetic field $\mathbf{B}_0$ aligned along the z-axis, and a weak rotating r.f. field $\mathbf{B}_1(t) = |B_1|(\sin\omega t, \cos\omega t, 0)$ in the xy-plane where , $|B_1|$ denotes the amplitude of the r.f. field, $\mathbf{B}_1(t)$ serves as the time-dependent externally controlled work parameter, $\lambda(t)$. In this model, quadrupolar interactions are neglected, and the system is described solely by its interaction with the external magnetic fields. The system

Hamiltonian as the system interacts with these external magnetic fields will be given as:

$$\begin{aligned}\hat{H}(t) &= -\mu\cdot\mathbf{B}\\ &= -\gamma B_0\hat{\mathbf{I}}_z - \gamma B_1\Big(\sin\omega t\hat{\mathbf{I}}_y + \cos\omega t\hat{\mathbf{I}}_x)\Big)\\ &= -\omega_0\hat{\mathbf{I}}_z - \omega_1(\hat{\mathbf{I}}_x\cos\omega_z t + \hat{\mathbf{I}}_y\sin\omega_z t) \qquad (3.1)\\ \hat{H}(t) &= \hat{H}_0 + \hat{H}_1(t) \qquad (3.2)\end{aligned}$$

where we have used $\omega_0 = \gamma B_0$ and $\omega_1 = \gamma B_1$.

3.1.1 Hamiltonian and Energy levels

In this study, the strong static magnetic field, $B_0\hat{z}$, is used to split the energy of the nuclei into three energy levels, the energy-level diagram for a spin-1 nucleus **I** (as shown in Figure 3.1), therefore, has three energy levels, spaced evenly by $\omega_0 = \gamma B_0$ in natural units, if the quadrupole interaction is ignored.

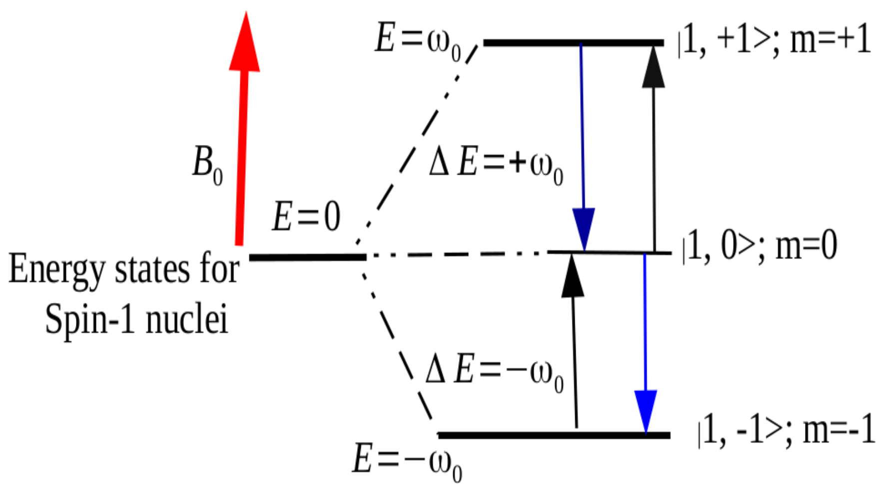


Figure 3.1: The representation of energy levels of spin-1 nuclei.

The Schrodinger equation for a nuclear spin in a strong static magnetic field oriented along the z-direction is:

$$i\frac{\partial|\psi\rangle}{\partial t} = \hat{H}_0|\psi\rangle = -\mu_z\cdot\mathbf{B}_0|\psi\rangle = -\omega_0\mathbf{I}_z|\psi\rangle. \qquad (3.3)$$

where we have assumed $\hbar = 1$. Since the Hamiltonian H_0 is proportional to the operator $\mathbf{I}_z$, $\mathbf{H}_0$ and $\mathbf{I}_z$ commute, and therefore, they share common eigenstates. This will become clearer when we express the Hamiltonian as a matrix in the Zeeman eigenbasis of $\hat{\mathbf{I}}_z$.

Because the static magnetic field is uniform, the orientation of the spin changes periodically. This implies that if the spin is initially aligned along the z-direction, it periodically returns to that orientation. Since Equation (3.3) is the time-independent Schrödinger equation, its solution will be:

$$|\psi(t)\rangle = e^{(i\omega_0\hat{I}_z t)}|\psi(0)\rangle. \qquad (3.4)$$

This implies that if the state of the spin system is known at one point in time, then it is possible to predict it at later times by applying the time-dependent Schrodinger equation to each individual spin. Accordingly, for the spin-1 nuclei coupled to the heat bath at inverse temperature, β, the state of the system can be expressed by the Gibbs density matrix as

$$\rho_{th} = \frac{e^{-\beta \hat{H}_0}}{Z_0}, \tag{3.5}$$

where Z_0 is the initial partition function which ensures the normalization condition of the state density matrix.

Let E_n^0 and $|n\rangle$ be the eigenvalues and eigenvectors of the Hamiltonian $H_o = H(\lambda_0)$. Then, the probability P_n of having the system in the state $|n\rangle$ with energy eigenvalue E_n^0 will be

$$P_n = \langle n|\rho_{th}|n\rangle = \frac{e^{-\beta E_n^0}}{Z_0}. \tag{3.6}$$

Since the Hamiltonian, $\hat{H}_0$, given in Equation (3.3) is already diagonal in the usual Zeeman basis which diagonalizes $\hat{\mathbf{I}}_z$, Equation (3.5) can be rewritten in matrix form as

$$\rho_{th} = \frac{1}{Z_0}\begin{pmatrix} e^{\frac{\omega_0}{T}} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{\frac{-\omega_0}{T}} \end{pmatrix}.$$

The partition function is the trace of this matrix,

$$Z_0 = tr(e^{\frac{-\hat{H}_0}{T}}) = 1 + e^{\frac{\omega_0}{T}} + e^{\frac{-\omega_0}{T}}. \tag{3.7}$$

Using the hyperbolic trigonometric relations of the form: $e^{\pm x} = \frac{1\pm\tanh(\frac{x}{2})}{1\mp\tanh(\frac{x}{2})}$, the thermal density matrix can be rewritten in a convenient way as

$$\rho_{th} = \frac{1}{3+f^2}\begin{pmatrix} 1+2f+f^2 & 0 & 0 \\ 0 & 1-f^2 & 0 \\ 0 & 0 & 1-2f+f^2 \end{pmatrix} \tag{3.8}$$

where we have used $f = \tanh(\frac{x}{2})$ and $x = \frac{\omega_0}{T}$

3.1.2 Evolution in a Static and Rotating Magnetic Fields

Immediately after the first energy measurement, we initiate the r.f. field

$$\mathbf{B}_1(t) = B_1(\cos\omega_z t\hat{x} + \sin\omega_z t\hat{y}). \tag{3.9}$$

where ω_z may be positive or negative. Although $B_1 \ll B_0$, it plays the role to tip the magnetization away from the z-axis into the xy-plane giving rise to the nuclear magnetic resonance (NMR) signal in the form of an induced voltage in an orthogonal plane.

Our system under the collective action of the strong static field, $\mathbf{B}_0$ and an alternating weak radio frequency field, $\mathbf{B}_1(t)$ can be described as

$$\mathbf{B}(t) = B_0\hat{z} + B_1(\cos\omega_z t\hat{x} + \sin\omega_z t\hat{y}). \tag{3.10}$$

The magnetic spin Hamiltonian (which describes the way the nuclear magnetic energy changes as the nuclei rotate) will be

$$\begin{aligned}\hat{H}(t) &= -\mu\cdot\mathbf{B}\\ &= -\omega_0\hat{\mathbf{I}}_z-\omega_1(\hat{\mathbf{I}}_x\cos\omega_z t+\hat{\mathbf{I}}_y\sin\omega_z t) \qquad (3.11)\\ \hat{H}(t) &= \hat{H}_0+\hat{H}_1(t) \qquad (3.12)\end{aligned}$$

where we have used $\omega_0=\gamma B_0$ and $\omega_1=\gamma B_1$. Thus, the total Hamiltonian of the sample has a time-independent z-component, $H_0=-\omega_0$, and a circularly polarized field representing a magnetic field rotating in the xy-plane, $H_1(t)=-\omega_1(\cos\omega_z t+\sin\omega_z t)$.

Now, by using the matrix form of nuclear spin components for the spin-1 system, $\hat{I}_z$, $\hat{I}_x$, and $\hat{I}_y$ the matrix representation of the above time-dependent Hamiltonian in Equation (3.25) will become

$$\hat{H}(t)=\begin{pmatrix}-\omega_0 & -\frac{\omega_1}{\sqrt{2}}(\cos\omega_z t-i\sin\omega_z t) & 0\\ -\frac{\omega_1}{\sqrt{2}}(\cos\omega_z t+\sin\omega_z t) & 0 & -\frac{\omega_1}{\sqrt{2}}(\cos\omega_z t-i\sin\omega_z t)\\ 0 & -\frac{\omega_1}{\sqrt{2}}(\cos\omega_z t+i\sin\omega_z t) & \omega_0\end{pmatrix}. \qquad (3.13)$$

We note here that as a result of this time-dependent field, the system evolves in time.

To study the non-equilibrium properties of the system, we must know the initial thermal state, ρ_{th}, given in Equation (3.3) and the time-evolution operator, $\hat{U}(t)$ given as

$$\psi(t)=\hat{U}(t)|n\rangle;\hat{U}(t=0)=\mathbb{1}. \qquad (3.14)$$

where $|n\rangle$ represents one of the three possible states of the spin-1 system $|1,1\rangle$ or $|1,0\rangle$ or $|1,-1\rangle$.

The Schrodinger equation corresponding to this Hamiltonian, $\hat{H}(t)$, can be given as

$$\begin{aligned}i\partial_t\hat{U}(t) &= \hat{H}(t)\hat{U}(t)\\ i\partial_t\hat{U}(t) &= \{-\omega_0\hat{\mathbf{I}}_z-\omega_1(\hat{\mathbf{I}}_x\cos\omega_z t+\hat{\mathbf{I}}_y\sin\omega_z t)\}\hat{U}(t) \qquad (3.15)\end{aligned}$$

where we have used $\partial_t=\frac{\partial}{\partial_t}$. Substituting the value of $\hat{H}(t)$ from Equation (3.13) into Equation (3.15) yields

$$i\frac{\partial\hat{U}(t)}{\partial t}=\begin{pmatrix}-\omega_0 & -\frac{\omega_1}{\sqrt{2}}e^{-i\omega_z t} & 0\\ -\frac{\omega_1}{\sqrt{2}}e^{i\omega_z t} & 0 & -\frac{\omega_1}{\sqrt{2}}e^{-i\omega_z t}\\ 0 & -\frac{\omega_1}{\sqrt{2}}e^{i\omega_z t} & \omega_0\end{pmatrix}U(t). \qquad (3.16)$$

where we have used the Euler formula: $e^{\pm i\omega_z t}=\cos\omega_z t\pm i\sin\omega_z t$.

For the spin-1 system, the unitary time evolution operator, $\hat{U}(t)$, can be expressed in matrix form (by using Zeeman basis) as

$$\hat{U}(t)|n\rangle = \begin{pmatrix}\hat{U}_+(t)\\ \hat{U}_0(t)\\ \hat{U}_-(t)\end{pmatrix}. \qquad (3.17)$$

Then, by substituting Equation (3.17) into Equation (3.16) and performing matrix multiplication it yields:

$$i\begin{pmatrix}\partial_t\hat{U}_+(t)\\ \partial_t\hat{U}_0(t)\\ \partial_t\hat{U}(t)\end{pmatrix}=\begin{pmatrix}-\omega_0\hat{U}_+(t)-\frac{\omega_1}{\sqrt{2}}\hat{U}_0(t)e^{-i\omega_z t}\\ -\frac{\omega_1}{\sqrt{2}}\hat{U}_+(t)e^{i\omega_z t}-\frac{\omega_1}{\sqrt{2}}\hat{U}_-(t)e^{-i\omega_z t}\\ -\frac{\omega_1}{\sqrt{2}}\hat{U}_0(t)e^{i\omega_z t}+\omega_0\hat{U}_-(t).\end{pmatrix}. \qquad (3.18)$$

This leads to the three coupled equations

$$\begin{aligned} (1) \qquad i\partial_t \hat{U}_+(t) &= -\omega_0 \hat{U}_+(t) - \frac{\omega_1}{\sqrt{2}} \hat{U}_0(t) e^{-i\omega_z t} \\ (2) \qquad i\partial_t \hat{U}_0(t) &= -\frac{\omega_1}{\sqrt{2}} (\hat{U}_+(t) e^{i\omega_z t} + \hat{U}_-(t) e^{-i\omega_z t}) \\ (3) \qquad i\partial_t \hat{U}_-(t) &= -\frac{\omega_1}{\sqrt{2}} \hat{U}_0(t) e^{i\omega_z t} + \omega_0 \hat{U}_-(t). \end{aligned} \tag{3.19}$$

3.1.3 Time Evolution and Rotating frame

The time-dependence in the coefficients of these three equations can be eliminated by defining a new time-varying operator by the transformation method. This transformation corresponds to going to a coordinate system that rotates with an angular frequency ω_z about the z-axis

$$\hat{U}'(t) = e^{i\omega_z t \hat{I}_z} \hat{U}(t) \Longrightarrow \hat{U}(t) = e^{-i\omega_z t \hat{I}_z} \hat{U}'(t). \tag{3.20}$$

Accordingly, the three coupled equations in Equation (3.19) can be rewritten as

$$(1) \qquad i\partial_t \hat{U}'_+(t) = -(\omega_0 + \omega_z) \hat{U}'_+(t) - \frac{\omega_1}{\sqrt{2}} \hat{U}'_0(t) \tag{3.21}$$

$$(2) \qquad i\partial_t \hat{U}'_0(t) = -\frac{\omega_1}{\sqrt{2}} \left\{ \hat{U}'_+(t) + \hat{U}'_-(t) \right\} \tag{3.22}$$

$$(3) \qquad i\partial_t \hat{U}'_-(t) = (\omega_0 + \omega_z) \hat{U}'_-(t) - \frac{\omega_1}{\sqrt{2}} \hat{U}'_0(t). \tag{3.23}$$

As a result, the modified Schrodinger equation (in terms of $\hat{I}_z$ and $\hat{I}_x$) will become

$$i\partial_t \hat{U}'(t) = \{-(\omega_0 + \omega_z)\hat{I}_z - \omega_1 \hat{I}_x\} \hat{U}'(t). \tag{3.24}$$

Hence, the modified quantum mechanical time-independent Hamiltonian (in angular frequency units) for the spin-1 nuclei placed in an external magnetic field consisting of a static field, B_0 along the z-axis and a weak radio frequency (r.f) field, of amplitude B_1 , polarized along the x-axis will be

$$\hat{H}' = \{-(\omega_0 - \omega)\hat{I}_z - \omega_1 \hat{I}_x\} \tag{3.25}$$

Note that we are considering the case where the oscillating r.f field is rotating along with the precessing spin (clockwise direction, $\omega_z = -\omega$) and will partake in resonance.

The solution to Equation (3.24) will be

$$\hat{U}'(t) = \hat{U}'(0) e^{-i\hat{H}' t} = e^{-i\hat{H}' t} \qquad \Longrightarrow \hat{U}(t) = e^{-i\omega_z t \hat{I}_z} e^{-i\hat{H}' t} \tag{3.26}$$

where for unitary operator $\hat{U}(t=0) = \hat{U}'(t=0) = \mathbb{1}$.

3.1.4 Effective Magnetic Field and Precession

Physically, Equation (3.25) states that in the rotating frame, the moment acts as though it effectively experienced a static magnetic field, H_{eff}. The moment therefore precesses in a cone of fixed angle θ about the direction of H_{eff} at an angular frequency γH_{eff}. The situation is illustrated in Figure 3.2 for a magnetic moment initially oriented along the z-direction.

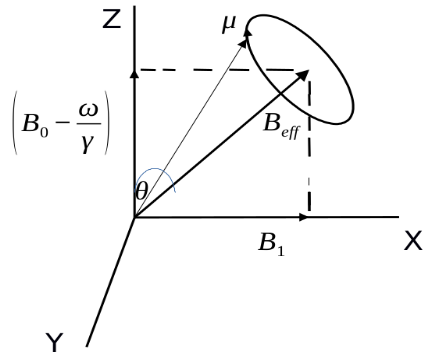


Figure 3.2: The precession of the nuclei spin under the effective field.

From Equation (3.24) we understood that the time-dependence of the externally applied radio frequency field, $\mathbf{B}_1(t)$, or its Hamiltonian, $\hat{H}_1(t)$, has been eliminated. In fact, we recognize it as representing the coupling of the nuclei spin with an effective field, $\mathbf{B}_{\text{eff}}$. So the nuclei spin acts as though it experiences effectively a magnetic field B_{eff} which can be defined mathematically as

$$B_{\text{eff}} = \Omega = \sqrt{B_1^2 + (B_0 - \frac{\omega}{\gamma})^2}. \tag{3.27}$$

The angle θ can be obtained from the components of the effective field as

$$\theta = \tan^{-1}(\frac{B_1}{(B_0 - \frac{\omega}{\gamma})}). \tag{3.28}$$

As a result, the corresponding effective energy operator, $\hat{H}'$, can be expressed in terms of θ as

$$\hat{H}' = -\gamma\Omega(\hat{I}_z \cos\theta + \hat{I}_x \sin\theta). \tag{3.29}$$

This is the polar form representation of the modified Hamiltonian, $\hat{H}'$; where θ is an angle between the effective field and the axis of rotation (z-axis).

Now, by substituting this form of $\hat{H}'$ in Equation (3.29) into Equation (3.26) one can obtain the full time evolution operator, $\hat{U}(t)$, in matrix form as

$$\hat{U}(t) = \begin{pmatrix} e^{i\omega_z t} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\omega_z t} \end{pmatrix} e^{i\alpha\hat{M}} \tag{3.30}$$

where we have used $\alpha = \gamma\Omega t$ and $\hat{M} = \hat{I}_z \cos\theta + \hat{I}_x \sin\theta$. The operator $\hat{M}$ satisfies the conditions: $\hat{M} = \hat{M}^{2n+1}$ and $\hat{M}^2 = \hat{M}^{2n}$. Whenever this is true, a direct Taylor series expansion of $e^{-i\hat{H}'} = e^{i\alpha\hat{M}}$ where α is a constant, gives

$$e^{i\alpha\hat{M}} = \hat{1} + i\hat{M}\sin\alpha - (1-\cos\alpha)\hat{M}^2. \tag{3.31}$$

Then, after solving for the matrix form of $\hat{M}$, and $\hat{M}^2$ and substituting their value in Equation (3.31) one can obtain the full time evolution operator, $\hat{U(t)}$, as

$$\hat{U}(t) = \begin{pmatrix} \nu(t) & -e^{-i\omega_z t}\upsilon^*(t) & -\chi^*(t) \\ -\upsilon^*(t) & 1-2e^{-i\omega_z t}\chi(t) & \upsilon(t) \\ -\chi(t) & e^{i\omega_z t}\upsilon(t) & \nu^*(t) \end{pmatrix}. \tag{3.32}$$

where we have defined

$$\nu(t) = e^{-i\omega_z t}\left\{\frac{\sin^2\theta}{2} + \left(1 - \frac{\sin^2\theta}{2}\right)\cos\alpha + i\cos\theta\sin\alpha\right\}; \tag{3.33a}$$

$$\upsilon(t) = \frac{\sin\theta}{\sqrt{2}}\Big(\cos\theta(1-\cos\alpha) + i\sin\alpha\Big); \tag{3.33b}$$

$$\chi(t) = e^{i\omega_z t}\Big(\frac{\sin^2\theta}{2}(1-\cos\alpha)\Big). \tag{3.33c}$$

3.1.5 Transition Probabilities

To obtain a better physical interpretation of Equation (3.32), let us consider the situation where the system initially starts in the pure state (eigenstate) $|1,1\rangle$ of $\hat{I}_z$. Then, the probability that after a time 't' the system will be found in state $|1,0\rangle$ will be

$$\begin{aligned} Prob._{|+1\rangle\rightarrow|0\rangle} &= \Big|\langle 1,0|U(t)|1,1\rangle\Big|^2 \\ &= \upsilon(t)\upsilon^*(t) = \Big|\upsilon(t)\Big|^2. \end{aligned} \tag{3.34}$$

Then, by substituting for $\upsilon(t)$ from Equation (3.33) we obtain

$$Prob._{|+1\rangle\rightarrow|0\rangle} = \sin^2\theta(1-cos\alpha) - \frac{\sin^4\theta}{2}(1-cos\alpha)^2. \tag{3.35}$$

Similarly, the probability that the system of spin-1 nuclei that was in state $|1,1\rangle$ will be found in state $\langle 1,-1|$ can be given as

$$Prob._{|+1\rangle\rightarrow|-1\rangle} = \Big|\chi(t)\Big|^2 = \frac{\sin^4\theta}{4}(1-\cos\alpha)^2. \tag{3.36}$$

Moreover, the unitary condition

$$U^\dagger(t)U(t) = \mathbb{1}. \tag{3.37}$$

implies that $|\nu(t)|^2 + |\upsilon(t)|^2 + |\chi(t)|^2 = 1$. This further gives $|\nu(t)|^2 = 1 - \{|\upsilon(t)|^2 + |\chi(t)|^2\}$, which represents the probability that no transition occurs. From Equation (3.33) we have seen that $\nu(t), \upsilon(t), \chi(t)$ are all the functions of $\sin\theta$. Therefore, this attributes a physical meaning to the angle θ, defined in Equation (3.28) as representing the transition probability.

In fact, at resonance, where $\omega_z = -\gamma B_0$ or $\omega = \gamma B_0$ we have: $\sin\theta = 1$ and $\cos\theta = 0$. Hence, at resonance Equation (3.33) can be rewritten as:

$$\nu(t) = \frac{e^{-i\omega_z t}}{2}[1+\cos\alpha] \Longrightarrow \nu^*(t) = \frac{e^{i\omega_z t}}{2}[1+\cos\alpha] \tag{3.38a}$$

$$\upsilon(t) = \frac{i}{\sqrt{2}}\sin\alpha \Longrightarrow \upsilon^*(t) = \frac{-i}{\sqrt{2}}\sin\alpha \tag{3.38b}$$

$$\chi(t) = \frac{e^{i\omega_z t}}{2}(1-\cos\alpha) \Longrightarrow \chi^*(t) = \frac{e^{-i\omega_z t}}{2}(1-\cos\alpha) \tag{3.38c}$$

For further discussion of the dynamics taking place as the nuclei of spin-1 interact with external magnetic field, having obtained the initial density matrix, ρ_{th}, and the full time-evolution operator, $\hat{U}(t)$, it is necessary to study spin polarization. The evolution of any observable A is given as

$$\langle A\rangle_{th} = tr\{\hat{U}^\dagger(t)A\hat{U}(t)\rho_{th}\}. \tag{3.39}$$

3.2 Model-2: Incorporating Quadrapolar Interactions

3.2.1 Spin-1 Quadrupolar System in Static Fields

Let's consider a collection of spin-1 quadrupole nuclei that interact weakly with each other and are placed within a strong static magnetic field, denoted as $\mathbf{B}_0$, aligned along the z-axis. In addition to this dominant external interaction caused by the strong static magnetic field, $\mathbf{B}_0$, there exists a static component of the quadrupole interaction resulting from the coupling of spin-1 with the nuclear quadrupole moment. This static component can induce a shift in the Zeeman levels and often acts to inhibit the exchange of spin between different transitions. Consequently, each nucleus in the system has three possible quantum state orientations: parallel, anti-parallel, or perpendicular to the external magnetic field ($\mathbf{B}_0$). The spin Hamiltonian describing the interaction of each individual spin-1 quadrupole nuclei with the static fields can be expressed as:

$$\hat{H}_i = \hat{H}_0 + \hat{H}_Q \quad = \quad -\mu \cdot \mathbf{B}_0 + \hat{H}_Q^{(1)} + \hat{H}_Q^{(2)} + \hat{H}_Q^{(3)} + ... \tag{3.40}$$

where $\hat{H}_0$ refers to the Hamiltonian corresponding to the dominant external magnetic field, $\mathbf{B}_0$, and $\hat{H}_Q^j$ is the j^{th} order quadrupolar Hamiltonian of the system under study.

Here, our specific focus is on deuterium atomic nuclei, where the magnitude of its quadrupolar coupling constant, symbolized as C_Q, is assumed to be smaller than the Larmor frequency. As a result, the quadrupolar interaction Hamiltonian given in $Eq.$(3.40) can be truncated to its first-order term and is given as

$$\begin{aligned} \hat{H}_Q^{(1)} &= \omega_Q^{(1)} \times \frac{1}{6}\left(3\hat{I}_z^2 - 2\hat{I}(\hat{I}+1)\right) \\ &= \omega_Q^{(1)} \times \frac{1}{6} 3\hat{I}_z^2 - 2\mathbb{1} \end{aligned} \tag{3.41}$$

where $\omega_Q^{(1)} = 3\pi C_Q$ refers to the first-order quadrupolar coupling.

This truncation of $\hat{H}_Q$ corresponds to applying static perturbation theory at the first order with respect to the dominant Hamiltonian, $\hat{H}_0$. The Hamiltonian in unperturbed state, which incorporates the first-order high field-truncated quadrupolar Hamiltonian, is given by

$$\begin{aligned} \hat{H}_i &= \hat{H}_0 + \hat{H}_Q^{(1)} \\ &= -\mu \cdot \mathbf{B}_0 + \omega_Q^{(1)} \times \frac{1}{6}\left(3\hat{I}_z^2 - 2\mathbb{1}\right) \\ &= -\omega_0 \hat{I}_z + \frac{1}{6}\omega_Q^{(1)} \hat{A}_Q \end{aligned} \tag{3.42}$$

where we have defined

$$\hat{A}_Q = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{3.43}$$

The energy-level diagram for this quadrapolar spin-1 nuclei, therefore, has three energy levels, spaced evenly by ω_0 (in natural units), if the quadrupolar interaction is ignored and spaced by $\omega_0 \pm \frac{1}{2}\omega_Q^{(1)}$ if the first order quadrupolar interaction is considered. Therefore, the appearance of the energy-level diagram may change as a result of quadrupolar interaction as shown in the Figure 3.3. As it can be

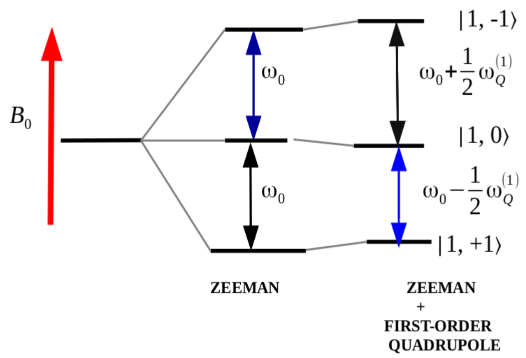


Figure 3.3: The representation of energy levels of quadrupole spin-1 nuclei.

understood from the figure a positive quadrupolar coupling $\omega_Q^{(1)}$ shifts the states $|1,\pm 1\rangle$ up in energy, whereas the central state $|1,0\rangle$ shifts down in energy by twice as much. All shifts are in the opposite direction if $\omega_Q^{(1)}$ is negative.

The dynamics of the spin quadrupolar system, accounting for minor quadrupole effects, in the dominant magnetic field aligned along the z-direction can be described using the Schrodinger equation as follows:

$$i\hbar\frac{\partial|\psi\rangle}{\partial t} = \Big(\hat{H}_0 + \hat{H}_Q\Big)|\psi\rangle = \Big(-\omega_0\hat{I}_z + \frac{1}{6}\omega_Q^{(1)}\hat{A}_Q\Big)|\psi\rangle. \tag{3.44}$$

$\hbar$ is set to unity.

The solution of Equation (3.44) will take the form of:

$$|\psi(t)\rangle = e^{\left(i\omega_0\hat{I}_z + \frac{1}{6}\omega_Q^{(1)}\hat{A}_Q\right)t}|\psi(0)\rangle. \tag{3.45}$$

This result states that if we know the initial state of the spin system at a specific time, we can predict the subsequent states of each individual spin.

For an ensemble of quadrupole spin-1 nuclei in a strong magnetic field ($B_0 \gg \omega_Q^{(1)}$) and coupled to a heat bath at inverse temperature β, the state of the system can be described by the thermal density matrix, ρ_{th}, as it given in equation (3.8).

3.2.2 Dynamics of the Spin-1 Quadrupolar System in a Time-Varying Field

We now consider the temporal evolution of the spin-1 quadrupolar system under the influence of both a strong static magnetic field $\mathbf{B}_0$ and a weak rotating radio frequency (r.f.) field $\mathbf{B}_1(t) = b(\cos\omega_z t\hat{x} + \sin\omega_z t\hat{y})$. The total magnetic field acting on the system is:

$$\mathbf{B}(t) = B_0\hat{z} + b(\cos\omega_z t\hat{x} + \sin\omega_z t\hat{y}). \tag{3.46}$$

Below we investigate the combined effects of these fields and analyze their time evolution.

The dynamics of the system, under the combined influence of the static and time varying fields, can be described in terms of spin Hamiltonian, which elucidates the alterations in nuclear magnetic energy due to the rotation of the nuclei, can be expressed as:

$$
\begin{aligned}
\hat{H}(t) &= -\mu \cdot \mathbf{B}(t) + \hat{H}_Q \\
&= -\omega_0 \hat{\mathbf{I}}_z - \omega_1 (\hat{\mathbf{I}}_x \cos\omega_z t + \hat{\mathbf{I}}_y \sin\omega_z t) + \frac{1}{6}\omega_Q^{(1)} \hat{A}_Q \\
\hat{H}(t) &= \hat{H}_0 + \hat{H}_1(t) + \hat{H}_Q^{(1)}
\end{aligned} \tag{3.47}
$$

In this context, the total Hamiltonian of the sample is split into two parts: a time-independent component $\left(\hat{H}_i = \hat{H}_0 + \hat{H}_Q^{(1)}\right)$ and a time-dependent component $\left(\hat{H}_1(t) = -\omega_1 (\hat{\mathbf{I}}_x \cos\omega_z t + \hat{\mathbf{I}}_y \sin\omega_z t)\right)$. The presence of the time-dependent field is crucial as it induces time evolution in the system.

By utilizing the matrix representation of nuclear spin-1 components, ($\hat{I}_z$, $\hat{I}_x$, $\hat{I}_y$) and the quadrapolar operator given in equation(3.43) the matrix representation of the time-dependent Hamiltonian in Equation (3.1) can be represented as follows:

$$
\hat{H}(t) = \begin{pmatrix} -\omega_0 + \frac{1}{6}\omega_Q^{(1)} & -\frac{\omega_1}{\sqrt{2}}(\cos\omega_z t - i\sin\omega_z t) & 0 \\ -\frac{\omega_1}{\sqrt{2}}(\cos\omega_z t + \sin\omega_z t) & -\frac{1}{3}\omega_Q^{(1)} & -\frac{\omega_1}{\sqrt{2}}(\cos\omega_z t - i\sin\omega_z t) \\ 0 & -\frac{\omega_1}{\sqrt{2}}(\cos\omega_z t + i\sin\omega_z t) & \omega_0 + \frac{1}{6}\omega_Q^{(1)} \end{pmatrix}. \tag{3.48}
$$

The time evolution process will be carried out by employing the time-dependent Schrodinger equation as follows:

$$
\begin{aligned}
i\partial_t \hat{U}(t) &= \hat{H}(t)\hat{U}(t) \\
&= \Big\{ -\omega_0 \hat{\mathbf{I}}_z - \omega_1 (\hat{\mathbf{I}}_x \cos\omega_z t + \hat{\mathbf{I}}_y \sin\omega_z t) + \frac{1}{6}\omega_Q^{(1)} \hat{A}_Q \Big\} \hat{U}(t)
\end{aligned} \tag{3.49}
$$

The matrix form of this equation will be:

$$
i\frac{\partial \hat{U}(t)}{\partial t} = \begin{pmatrix} -\omega_0 + \frac{1}{6}\omega_Q^{(1)} & -\frac{\omega_1}{\sqrt{2}}e^{-i\omega_z t} & 0 \\ -\frac{\omega_1}{\sqrt{2}}e^{i\omega_z t} & -\frac{1}{3}\omega_Q^{(1)} & -\frac{\omega_1}{\sqrt{2}}e^{-i\omega_z t} \\ 0 & -\frac{\omega_1}{\sqrt{2}}e^{i\omega_z t} & \omega_0 + \frac{1}{6}\omega_Q^{(1)} \end{pmatrix} U(t) \tag{3.50}
$$

where we have defined: $e^{\pm i\omega_z t} = \cos\omega_z t \pm i\sin\omega_z t$, which is the Euler formula.

For the three state system the operator, $\hat{U}(t)$, can be defined in matrix form, the Zeeman basis, as follows:

$$
\hat{U}(t)|n\rangle = \begin{pmatrix} \hat{U}_+(t) \\ \hat{U}_0(t) \\ \hat{U}_-(t) \end{pmatrix}. \tag{3.51}
$$

By substituting Equation (3.51) into Equation (3.50) and performing matrix multiplication, we obtain:

$$
i\begin{pmatrix} \partial_t \hat{U}_+(t) \\ \partial_t \hat{U}_0(t) \\ \partial_t \hat{U}(t) \end{pmatrix} = \begin{pmatrix} \Big(-\omega_0 + \frac{1}{6}\omega_Q^{(1)}\Big)\hat{U}_+(t) - \frac{\omega_1}{\sqrt{2}}\hat{U}_0(t)e^{-i\omega_z t} \\ -\frac{\omega_1}{\sqrt{2}}\hat{U}_+(t)e^{i\omega_z t} - \frac{\omega_1}{\sqrt{2}}\hat{U}_-(t)e^{-i\omega_z t} - \frac{1}{3}\omega_Q^{(1)}\hat{U}_0(t) \\ -\frac{\omega_1}{\sqrt{2}}\hat{U}_0(t)e^{i\omega_z t} + \Big(\omega_0 + \frac{1}{6}\omega_Q^{(1)}\Big)\hat{U}_-(t). \end{pmatrix}. \tag{3.52}
$$

This results in a set of three coupled equations:

$$
\begin{aligned}
i\partial_t \hat{U}_+(t) &= \Big\{-\omega_0 + \frac{1}{6}\omega_Q^{(1)}\Big\}\hat{U}_+(t) - \frac{\omega_1}{\sqrt{2}}\hat{U}_0(t)e^{-i\omega_z t} \\
i\partial_t \hat{U}_0(t) &= -\frac{\omega_1}{\sqrt{2}}\Big(\hat{U}_+(t)e^{i\omega_z t} + \hat{U}_-(t)e^{-i\omega_z t}\Big) - \frac{1}{3}\omega_Q^{(1)}\hat{U}_0(t) \\
i\partial_t \hat{U}_-(t) &= -\frac{\omega_1}{\sqrt{2}}\hat{U}_0(t)e^{i\omega_z t} + \Big\{\omega_0 + \frac{1}{6}\omega_Q^{(1)}\Big\}\hat{U}_-(t)
\end{aligned}
\tag{3.53}
$$

By using the rotating frame approximation method and introducing the new time-varying operator:

$$\hat{U}'(t) = e^{i\omega_z t\hat{I}_z}\hat{U}(t) \Longrightarrow \hat{U}(t) = e^{-i\omega_z t\hat{I}_z}\hat{U}'(t). \tag{3.54}$$

we can eliminate the time-dependent coefficients. This transformation allows us to work in a frame where the oscillating r.f. field is rotating in sync with the precessing spin in a clockwise direction ($\omega_z = -\omega$). This resonance condition is important for studying the behavior of the system under the influence of the r.f. field.

By substituting Equation (3.54) into Equation (3.53), we can obtain the following result:

$$i\partial_t \hat{U}'_+(t) = \Big\{-\Delta\omega + \frac{1}{6}\omega_Q^{(1)}\Big\}\hat{U}'_+(t) - \frac{\omega_1}{\sqrt{2}}\hat{U}'_0(t) \tag{3.55}$$

$$i\partial_t \hat{U}'_0(t) = -\frac{\omega_1}{\sqrt{2}}\{\hat{U}'_+(t) + \hat{U}'_-(t)\} - \frac{1}{3}\omega_Q^{(1)}\hat{U}'_0 \tag{3.56}$$

$$i\partial_t \hat{U}'_-(t) = \Big\{\Delta\omega + \frac{1}{6}\omega_Q^{(1)}\Big\}\hat{U}'_-(t) - \frac{\omega_1}{\sqrt{2}}\hat{U}'_0(t) \tag{3.57}$$

where we have defined $\Delta\omega = \omega_0 - \omega$.

Consequently, we can rewrite Equation (3.49) in a new form as:

$$i\partial_t \hat{U}'(t) = \{-\Delta\omega\hat{I}_z - \omega_1\hat{I}_x + \frac{1}{6}\omega_Q^{(1)}\hat{A}_Q\}\hat{U}'(t). \tag{3.58}$$

From this, we obtain the new time-independent Hamiltonian (in unit of angular velocity) of the form:

$$
\begin{aligned}
\hat{H}' &= -\Delta\omega\hat{I}_z - \omega_1\hat{I}_x + \frac{1}{6}\omega_Q^{(1)}\hat{A}_Q \\
&= \hat{H}'_{eff} + \hat{H}_Q^{(1)}
\end{aligned}
\tag{3.59}
$$

where we define $\hat{H}'_{eff} = \Delta\omega\hat{I}_z - \omega_1\hat{I}_x$ as the effective Hamiltonian due to the effective external magnetic field, $\hat{B}_{eff}$. In the rotating frame, the magnetic moment experiences this effective magnetic field and precesses in a cone of a fixed angle, θ, about the direction of $\hat{B}_{eff}$ at an angular frequency, $\gamma\hat{B}_{eff}$.

Indeed, the nuclei spin can be interpreted as being coupled to an effective field, $\mathbf{B}_{\text{eff}}$. As a result, the nuclei spin behaves as if it is subjected to an effective magnetic field. Mathematically, this effective magnetic field can be defined as:

$$B_{\text{eff}} = \Omega = \sqrt{b^2 + \Delta\omega^2}. \tag{3.60}$$

The value of the angle θ can be determined as follows:

$$\theta = \tan^{-1}(\frac{b}{\Delta\omega}). \tag{3.61}$$

The solution to Equation (3.58) can be obtained as follows:

$$\hat{U}'(t) = \hat{U}'(0)e^{-i\hat{H}'t} = e^{-i\hat{H}'t} \qquad \Longrightarrow \hat{U}(t) = e^{-i\omega_z t\hat{I}_z}e^{-i\hat{H}'t} \tag{3.62}$$

Here, it is specified that the unitary operator $\hat{U}'(t=0) = \mathbb{1}$ holds true.

By substituting Equation (3.59) into Equation (3.62), one can derive the complete time evolution operator, $\hat{U}(t)$, in matrix form as follows:

$$\begin{aligned}
\hat{U}(t) &= e^{i\omega_z t}e^{i\alpha\hat{M}}e^{\frac{1}{6}\omega_Q^{(1)}t} \\
&= \begin{pmatrix} e^{i\omega_z t} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\omega_z t} \end{pmatrix} e^{i\alpha\hat{M}} \begin{pmatrix} e^{\frac{1}{6}\omega_Q^{(1)}t} & 0 & 0 \\ 0 & e^{-\frac{1}{3}\omega_Q^{(1)}t} & 0 \\ 0 & 0 & e^{\frac{1}{6}\omega_Q^{(1)}t} \end{pmatrix} \\
\hat{U}(t) &= \begin{pmatrix} e^{\frac{-i}{6}\omega_Q^{(1)}t}\nu(t) & -e^{\frac{i}{3}\omega_Q^{(1)}t}e^{-i\omega_z t}\upsilon^*(t) & -e^{\frac{-i}{6}\omega_Q^{(1)}t}\chi^*(t) \\ -e^{\frac{-i}{6}\omega_Q^{(1)}t}\upsilon^*(t) & e^{\frac{i}{3}\omega_Q^{(1)}t}\left(1-2e^{-i\omega_z t}\chi(t)\right) & e^{\frac{-i}{6}\omega_Q^{(1)}t}\upsilon(t) \\ -e^{\frac{-i}{6}\omega_Q^{(1)}t}\chi(t) & e^{\frac{i}{3}\omega_Q^{(1)}t}e^{i\omega_z t}\upsilon(t) & e^{\frac{-i}{6}\omega_Q^{(1)}t}\nu^*(t) \end{pmatrix}.
\end{aligned} \tag{3.63}$$

To gain a deeper understanding of Equation (3.63), let's consider the scenario where the system initially resides in a Zeeman eigenstate, $|1,+1\rangle$, of $\hat{I}_z$. In this case, $\upsilon(t)$ and $\chi(t)$, which represent the off-diagonal elements of $\hat{U}(t)$, correspond to the probability amplitudes for transitions from $|1,+1\rangle$ to $|1,0\rangle$ and from $|1,+1\rangle$ to $|1,-1\rangle$, respectively (with their respective amplitudes for the reverse processes being $\upsilon^*(t)$ and $\chi^*(t)$). The transition probability for either case can be calculated as follows:

$$\begin{aligned}
Prob._{|+1\rangle\to|0\rangle} &= = \left|\langle 1,0|U(t)|1,1\rangle\right|^2 \\
&= \upsilon(t)\upsilon^*(t) = \left|\upsilon(t)\right|^2.
\end{aligned} \tag{3.64}$$

By substituting the expression for $\upsilon(t)$ from Equation (3.33), we derive the following result:

$$Prob._{|+1\rangle\to|0\rangle} = \sin^2\theta(1-cos\alpha) - \frac{\sin^4\theta}{2}(1-cos\alpha)^2. \tag{3.65}$$

In a similar manner, we obtain:

$$Prob._{|+1\rangle\to|-1\rangle} = \left|\eta(t)\right|^2 = \frac{\sin^4\theta}{4}(1-\cos\alpha)^2. \tag{3.66}$$

Moreover, the unitary condition $U^\dagger(t)U(t) = \mathbb{1}$ implies that $|\nu(t)|^2 + |\upsilon(t)|^2 + |\chi(t)|^2 = 1$, so $|\nu(t)|^2$ is the probability that no transition occurs.

Chapter 4

Results and Discussion

In this chapter, we present and analyze the results of the two models introduced in Chapter 3, focusing on the dynamical behavior and thermodynamic properties of spin-1 quadrupolar systems under static and rotating magnetic fields. We explore the impact of both thermal and quantum fluctuations, the role of quadrupolar interactions, and the distribution of work in non-equilibrium processes. The results are discussed in terms of energy level dynamics, polarization, work distributions, and the characteristic function of the system.

This chapter is organized as follows: Section 4.1 discusses the results for the average polarization components. Section 4.2 presents the analysis of work distributions and their dynamics. Section 4.3 explores the dependence of average work on the frequency and duration of the process. Section 4.4 discusses Characteristic Function and Work Distribution, which provides insight into the statistical properties of the work distribution.

4.1 Average Polarization Components

In this section, we explore the average polarization components of spin-1 systems under two distinct models: one that ignores quadrupolar interactions (Model-1) and another that incorporate them (Model-2). By examining the time evolution of spin observables, we can elucidate the dynamics of these systems and their implications in various physical contexts.

The time evolution of any observable A can be described by the following expression:

$$\langle A \rangle_{th} = Tr\{\hat{U}^{\dagger}(t) A \hat{U}(t) \rho_{th}\}. \tag{4.1}$$

where Tr denotes the trace operation, $\hat{U}(t)$ represents the time-evolution operator, A is the observable, and ρ_{th} is the thermal density matrix.

To investigate the mean polarization components $\langle \hat{I}_x \rangle$, $\langle \hat{I}_y \rangle$, and $\langle \hat{I}_z \rangle$, we employ:

$$\langle \hat{I}_i \rangle = Tr\{U^{\dagger}(t) \hat{I}_i U(t) \rho_{th}\}. \tag{4.2}$$

where $\langle \hat{I}_i \rangle$ represents the mean value of the spin component $\hat{I}_i$ ($i = x, y, z$). All computations involve performing matrix multiplications using 3×3 matrices. The time evolution operator $U(t)$ governs how the system's state changes over time, and its Hermitian conjugate $U^{\dagger}(t)$ is used to track the evolution of the spin operators. By taking the trace of the matrix product $U^{\dagger}(t)\hat{I}_i U(t)$ with the initial thermal density matrix ρ_{th}, we can obtain the mean value $\langle \hat{I}_i \rangle$, which provides insights into the spin dynamics of the system. This analytical approach has applications in various fields, such as condensed matter physics [55], quantum information processing [9], and nuclear magnetic resonance spectroscopy [32], where understanding the behavior of spin observables is crucial.

Accordingly, in case of model 1 (where quadrupolar interactions are ignored)the mean polarization component in the z-direction will be

$$\begin{aligned}\langle \hat{I}_z \rangle &= tr\{U^\dagger(t)\hat{I}_z U(t)\rho_{th}\} \\ &= \frac{4f}{3+f^2}\Big(|\nu|^2 - |\chi|^2\Big) = \frac{4f}{3+f^2}\Big\{1 - \sin^2\theta(1-\cos\Omega t\gamma)\Big\}. \end{aligned} \tag{4.3}$$

In the same manner, the mean polarization along the x and y-axis will be

$$\langle \hat{I}_x \rangle = \frac{4f\sin\theta}{(3+f^2)}\Big\{\cos\theta\cos\omega_z t(1-\cos\alpha) - \sin\alpha\sin\omega_z t\Big\}. \tag{4.4}$$

$$\langle \hat{I}_y \rangle = \frac{4f\sin\theta}{(3+f^2)}\Bigg\{\cos\theta\cos\omega_z t(1-\cos\alpha) + \sin\alpha\sin\omega_z t\Bigg\}. \tag{4.5}$$

The evolution of these components leads to expressions detailing their behavior over time. At resonance, where $\sin\theta = 1$, they become

$$\langle \hat{I}_z \rangle = \frac{4f}{3+f^2}\cos(\Omega t\gamma). \tag{4.6}$$

$$\langle \hat{I}_x \rangle = \frac{-4f}{(3+f^2)}\Big\{\sin\alpha\sin\omega_z t\Big\}. \tag{4.7}$$

$$\langle \hat{I}_y \rangle = \frac{4f}{(3+f^2)}\Bigg\{\sin\alpha\sin\omega_z t\Bigg\}. \tag{4.8}$$

These equations (Equations (4.6)–(4.8)) describe a parametric curve in a sphere of radius, $R = \frac{4f}{3+f^2}$, which is the initial magnetization.

In the second **model**, we also utilize the same foundational equation for the time evolution of observables. However, we incorporate the effects of quadrupolar interactions in our analysis.

The mean polarization components are similarly defined, but now we also account for additional terms due to quadrupolar interactions, leading to:

$$\langle \hat{A}_Q \rangle = 4Rf\Bigg\{1 - 3\sin^2\theta(1-\cos\alpha) + \frac{3}{2}\sin^4\theta(1-\cos\alpha)^2\Bigg\}.$$

The expressions for $\langle \hat{I}_x \rangle$, $\langle \hat{I}_Y \rangle$ and $\langle \hat{I}_z \rangle$ remain consistent with those in Model-1, yielding:

$$\langle \hat{I}_x \rangle = \frac{4f\sin\theta}{(3+f^2)}\Big\{\cos\theta\cos\omega_z t(1-\cos\alpha) - \sin\alpha\sin\omega_z t\Big\}. \tag{4.9}$$

$$\langle \hat{I}_y \rangle = \frac{4f\sin\theta}{(3+f^2)}\Bigg\{\cos\theta\cos\omega_z t(1-\cos\alpha) + \sin\alpha\sin\omega_z t\Bigg\}. \tag{4.10}$$

$$\begin{aligned}\langle \hat{I}_z \rangle &= tr\{U^\dagger(t)\hat{I}_z U(t)\rho_{th}\} \\ &= \frac{4f}{3+f^2}\Big(|\nu|^2 - |\chi|^2\Big) = \frac{4f}{3+f^2}\Big\{1 - \sin^2\theta(1-\cos\Omega t\gamma)\Big\}. \end{aligned} \tag{4.11}$$

At resonance, where $\sin\theta = 1$, the expressions simplify to:

$$\begin{aligned}
\langle \hat{I}_z \rangle &= 4R\cos(\Omega t\gamma). \\
\langle \hat{I}_x \rangle &= -4R\sin\theta\Big(\sin\alpha\sin\omega_z t\Big). \\
\langle \hat{I}_y \rangle &= 4R\sin\theta\Big(\sin\alpha\cos\omega_z t\Big). \\
\langle \hat{A}_Q \rangle &= 2Rf\big(3\cos^2\alpha - 1\big).
\end{aligned} \tag{4.12}$$

Where we utilized the expression for $R = \frac{f}{3+f^2}$ which represents the initial magnetization of the system. This formulation allows us to analyze how the polarization components evolve over time, providing crucial insights into the dynamics of the spin-1 system under the specified conditions.

The analysis highlights significant differences in the polarization dynamics when quadrupolar interactions are considered versus when they are ignored. While both models offer insights into the behavior of spin-1 systems, the inclusion of quadrupolar interactions introduces additional complexity and potential shifts in energy levels.

The results indicate that quadrupolar interactions can affect the amplitude and phase of the polarization components, which may have implications for applications in quantum information processing, condensed matter physics, and nuclear magnetic resonance spectroscopy. Understanding these dynamics is crucial for advancing technologies that rely on spin-based phenomena, such as quantum computing and advanced imaging techniques.

4.2 Work Distributions and Their Dynamics in Spin-1 Nuclei Systems

The work performed in a non-equilibrium process is the difference between the energy measurements at the final and initial states:

$$W = E_f - E_i. \tag{4.13}$$

For our specific case of spin-1 nuclei, which is the three-state system, we can explore the possible work values in energy transformations. Two models are considered: one where quadrupolar interactions are ignored, and the other where they are incorporated.

In model-1, when quadrupolar interactions are not considered, the Hamiltonian at the initial time $t = 0$ is given by $\hat{H}_i = -\omega_0\hat{I}_z$, resulting in the initial energy eigenvalues: $E^i_{-1} = \omega_0$ for the state $|-1\rangle$, $E^i_0 = 0$ for the state $|0\rangle$ and $E^i_{+1} = -\omega_0$ for the state $|+1\rangle$. At an arbitrary time 't', the Hamiltonian becomes $\hat{H}_f = -\omega_0\hat{I}_z + B_1(\cos\theta\hat{I}_x + \sin\theta\hat{I}_y)$ with final energy eigenvalues: $E^f_{\pm} = \mp\sqrt{B_0^2 + B_1^2(t)}$ for $|\pm 1\rangle$, and $E_0 = 0$ for $|0\rangle$.

However, since $B_1 \ll B_0$, the final eigenvalues are very similar to the initial eigenvalues. Consequently, the three values of W are very close to zero. To simplify the discussion, let us suppose that the radio frequency field $B_1(t) = B_1(\cos\omega_z t, \sin\omega_z t, 0)$ always changes by a full period. That is, we assume that the final protocol time τ is given by

$$\tau = \frac{2\pi l}{\omega}, l = 1, 2, 3, \cdots. \tag{4.14}$$

Physically, this tells us that for ω being a very fast frequency, we measure the work W after a certain amount of complete cycles. In this case, $\hat{H}_f = \hat{H}_i$, which further implies that both the two measurements (the initial and final) may have the same energy spectrum: $E\pm = \mp\omega_0$ and $E_0 = 0$ in their respective states. Thus, we can obtain seven possibilities of work distributions for spin-1 nuclei in an effective magnetic field. These are:

$$\begin{aligned}
&(1) \qquad W = E_{+1} - E_{-1} = -2\omega_0 \Longrightarrow |-1\rangle \rightsquigarrow |+1\rangle \\
&(2) \qquad W = E_{-1} - E_{+1} = 2\omega_0 \Longrightarrow |+1\rangle \rightsquigarrow |-1\rangle \\
&(3) \qquad W = E_0 - E_{+1} = \omega_0 \Longrightarrow |+1\rangle \rightsquigarrow |0\rangle \\
&(4) \qquad W = E_{+1} - E_0 = -\omega_0 \Longrightarrow |0\rangle \rightsquigarrow |+1\rangle \\
&(5) \qquad W = E_{-1} - E_0 = \omega_0 \Longrightarrow |0\rangle \rightsquigarrow |-1\rangle \\
&(6) \qquad W = E_0 - E_{-1} = -\omega_0 \Longrightarrow |-1\rangle \rightsquigarrow |0\rangle \\
&(7) \qquad W = 0 \Longrightarrow |0\rangle \rightsquigarrow |0\rangle \text{or} |+1\rangle \rightsquigarrow |+1\rangle \text{or} |-1\rangle \rightsquigarrow |-1\rangle.
\end{aligned} \tag{4.15}$$

As we can understand from this illustration, the work required to flip the nuclei spin from its initial state of $|-1\rangle$ to $|+1\rangle$ is equal to $-2\omega_0$ while the work required to flip in the reverse is $2\omega_0$. On the other hand, the work performed to flip the nuclei spin from initial states of $|0\rangle$ to the final state of $|+\rangle$ is equal to $-\omega_0$ and that performed in the reverse is ω_0. Likewise, the work performed to flip the spin from initial states of $|-1\rangle$ to the final state of $|0\rangle$ is equal to $-\omega_0$ while that performed in the reverse is ω_0.

The probability of the above work distributions, Equation 4.15, can be calculated by using:

$$P(W) = \sum p_n^0 p_{m|n}^\tau \delta\Big(W - (E_m^\tau - E_n^0)\Big). \tag{4.16}$$

Accordingly, using Equations 3.8 and 3.33 the probabilities for the work distributions in Equation (4.15) are obtained as

$$\begin{aligned}
&(1) \qquad P(W = -2\omega_0) = \frac{1-2f+f^2}{3+f^2}|\chi(t)|^2 \Longrightarrow |-1\rangle \rightsquigarrow |+1\rangle \\
&(2) \qquad P(W = 2\omega_0) = \frac{1+2f+f^2}{3+f^2}|\chi(t)|^2 \Longrightarrow |+1\rangle \rightsquigarrow |-1\rangle \\
&(3) \qquad P(W = \omega_0) = \frac{1+f}{3+f^2}|\upsilon(t)|^2 \Longrightarrow |+1\rangle \rightsquigarrow |0\rangle \quad \text{or} \quad |0\rangle \rightsquigarrow |-1\rangle \\
&(4) \qquad P(W = -\omega_0) = \frac{1-f}{3+f^2}|\upsilon(t)|^2 \Longrightarrow |0\rangle \rightsquigarrow |+1\rangle \quad \text{or} \quad |-1\rangle \rightsquigarrow |0\rangle \\
&(5) \qquad P(W = 0) = \frac{(1-f^2)}{3+f^2}s(t) \Longrightarrow |0\rangle \rightsquigarrow |0\rangle \\
&(6) \qquad P(W = 0) = \frac{(1+f^2)}{3+f^2}|\nu(t)|^2 \Longrightarrow |+1\rangle \rightsquigarrow |+1\rangle \quad \text{or} \quad |-1\rangle \rightsquigarrow |-1\rangle.
\end{aligned} \tag{4.17}$$

where $s(t) = \Big(1 + 4|\chi(t)|^2 - 2e^{-i\omega_z t}\chi(t) - 2e^{i\omega_z t}\chi^*(t)\Big)$.

If $\omega_0 > 0$ it is more likely that the spin will be aligned parallel to the field. In such a case, $f > 0$ and this further adds $P(W = 2\omega_0) > P(W = -2\omega_0)$ and $P(W = \omega_0) > P(W = -\omega_0)$. This implies that it is more likely that the field will promote a flip from $|+1\rangle$ to $|-1\rangle$ or from $|+1\rangle$ to $|0\rangle$ (and from $|0\rangle$ to $|-1\rangle$) than the other way around.

On the other hand, when quadrupolar interactions are included, **Model-2** the initial Hamiltonian is $\hat{H}_i = -\omega_0 \hat{I}_z + \frac{1}{6}\omega_Q^{(1)} \hat{A}_Q$, and the energy eigenvalues at $t = 0$ are: $E^i_{-1} = \omega_0 + \frac{1}{6}\omega_Q^{(1)}$ for the state $|-1\rangle$, $E^i_0 = -\frac{1}{3}\omega_Q^{(1)}$ for the state $|0\rangle$ and $E^i_{+1} = -\omega_0 + \frac{1}{6}\omega_Q^{(1)}$ for the state $|+1\rangle$.

At a later time t, the Hamiltonian becomes:

$$\hat{H}_f = -\omega_0 \hat{I}_z + \frac{1}{6}\omega_Q^{(1)} \hat{A}_Q - \omega_1(\cos\theta \hat{I}_x + \sin\theta \hat{I}_y). \tag{4.18}$$

The final energy eigenvalues in the respective states are similar to the initial ones, with three work values close to zero. Assuming the radio frequency field completes a full period change, the protocol time is again $\tau = \frac{2\pi l}{\omega}, l = 1, 2, 3, \cdots$.

In this case, the energy spectrum for the respective states is: $E_{\pm} = \mp\omega_0 + \frac{1}{6}\omega_Q^{(1)}$ and $E_0 = -\frac{1}{3}\omega_Q^{(1)}$.

Accordingly, the seven possible work distributions for the case quadrupolar interactions are considered will be obtained as:

$$\begin{aligned}
&(1) \qquad W = E_{+1} - E_{-1} = -2\omega_0 \Longrightarrow |-1\rangle \rightsquigarrow |+1\rangle \\
&(2) \qquad W = E_{-1} - E_{+1} = 2\omega_0 \Longrightarrow |+1\rangle \rightsquigarrow |-1\rangle \\
&(3) \qquad W = E_0 - E_{+1} = \omega_0 - \frac{1}{2}\omega_Q^{(1)} \Longrightarrow |+1\rangle \rightsquigarrow |0\rangle \\
&(4) \qquad W = E_{+1} - E_0 = -\omega_0 + \frac{1}{2}\omega_Q^{(1)} \Longrightarrow |0\rangle \rightsquigarrow |+1\rangle \\
&(5) \qquad W = E_{-1} - E_0 = \omega_0 + \frac{1}{2}\omega_Q^{(1)} \Longrightarrow |0\rangle \rightsquigarrow |-1\rangle \\
&(6) \qquad W = E_0 - E_{-1} = -\omega_0 - \frac{1}{2}\omega_Q^{(1)} \Longrightarrow |-1\rangle \rightsquigarrow |0\rangle \\
&(7) \qquad W = 0 \Longrightarrow |0\rangle \rightsquigarrow |0\rangle \text{or} |+1\rangle \rightsquigarrow |+1\rangle \text{or} |-1\rangle \rightsquigarrow |-1\rangle
\end{aligned} \tag{4.19}$$

The probabilities of these work distributions, Equation 4.19, will be given as:

$$\begin{aligned}
&(1) \qquad P(W = -2\omega_0) = \frac{R}{f}\Big(1 - 2f + f^2\Big)|\chi(t)|^2 \\
&(2) \qquad P(W = 2\omega_0) = \frac{R}{f}\Big(1 + 2f + f^2\Big)|\chi(t)|^2 \\
&(3) \qquad P(W = \omega_0 - \frac{1}{2}\omega_Q^{(1)}) = \frac{R}{f}\Big(1 + 2f + f^2\Big)|\upsilon(t)|^2 \\
&(4) \qquad P(W = -\omega_0 + \frac{1}{2}\omega_Q^{(1)}) = \frac{R}{f}\Big(1 - f^2\Big)|\upsilon(t)|^2 \\
&(5) \qquad P(W = \omega_0 + \frac{1}{2}\omega_Q^{(1)}) = \frac{R}{f}\Big(1 - f^2\Big)|\upsilon(t)|^2 \\
&(6) \qquad P(W = -\omega_0 - \frac{1}{2}\omega_Q^{(1)}) = \frac{R}{f}\Big(1 - 2f + f^2\Big)|\upsilon(t)|^2 \\
&(7) \qquad P(W = 0) = \frac{R}{f}\Big\{(1 + f^2)|\nu(t)|^2 + (1 - f^2)s_1(t)\Big\}
\end{aligned} \tag{4.20}$$

where $s_1(t) = \Big(1 + 4|\chi(t)|^2 - 2e^{-i\omega_z t}\chi(t) - 2e^{i\omega_z t}\chi(t)^*(t)\Big)$.

In both **models**, the work distributions for spin-1 nuclei in non-equilibrium processes are explored. **Model-1**, where quadrupolar interactions are ignored, yields symmetric work distributions, while **Model-2**, with quadrupolar interactions, introduces asymmetry in the probabilities. Both models highlight the dependence of work distributions on external magnetic fields and spin dynamics, with seven possible work values corresponding to different spin transitions.

4.2.1 Dependence of Average Work on Frequency and Time

In cases where $P(W)$ is not explicitly known, the average work performed during the transformation can be computed by using

$$\langle W \rangle = \langle \hat{H}_f \rangle_{t=\tau} - \langle \hat{H}_i \rangle_{t=0}. \tag{4.21}$$

In computing the expectation values of quantities related to the energy of the system, we may always use the unperturbed case (where a nucleus of spin-1 is only in the static, strong and uniform magnetic field, $\hat{B}_0$), for the reason that we expect the result, which we match with what we know from measurements in the unperturbed condition. Particularly, in our case of the spin-1 system in a strong static magnetic field, $\mathbf{B}_0$ (applied in the direction of the z-axis) and where a weak alternating magnetic field, $\mathbf{B}_1$, is applied along the perpendicular direction to the axis of rotation (z-axis) we use $\hat{H}_0 = -\omega_0 \hat{I}_z$ as a Hamiltonian operator in unperturbed conditions.

The mean value of the Hamiltonian in the absence of any perturbation to the system can be expressed as:

$$\langle \hat{H}_0 \rangle = \langle -\omega_0 \hat{I}_z \rangle = -\omega_0 \langle \hat{I}_z \rangle. \tag{4.22}$$

But since we already explicitly obtained the probability distribution of work, $P(W)$, for both models we considered in our study, it is possible to compute the average work, $\langle W \rangle$, from the definition:

$$\langle W \rangle = \sum_w w P(W = w). \tag{4.23}$$

where the sum extends over all possible values of w.

In **model-1** where we ignored the role of quadrupolar interactions, for the work distribution given in Equation (4.15) and the corresponding probability distributions given in Equation (4.17), the average work will be given as:

$$\begin{aligned}
\langle W \rangle &= \sum_{W=E_m^f - E_n^i} W P(W) \\
&= 2\omega_0 \Big(\frac{1+2f+f^2}{3+f^2} \Big) |\chi(t)|^2 - 2\omega_0 \Big(\frac{1-2f+f^2}{3+f^2} \Big) |\chi(t)|^2 + 2\omega_0 \Big(\frac{1+f}{3+f^2} \Big) |\upsilon(t)|^2 \\
&\quad -2\omega_0 \Big(\frac{1-f}{3+f^2} \Big) |\upsilon(t)|^2 + 0 \times \Big\{ 2(1+f^2)|\nu(t)|^2 + (1-f^2)\big(1 + 4|\chi(t)|^2 - 2e^{-i\omega_z t}\chi(t) \\
&\quad -2e^{i\omega_z t}\chi^*(t)\big) \Big\} \\
\langle W \rangle &= \frac{4\omega_0 f}{3+f^2} \Big\{ \upsilon(t)|^2 + 2|\chi(t)|^2 \Big\} \\
&= \frac{4f\omega_0}{3+f^2} \sin^2\theta \Big\{ 1 - \cos(\Omega\tau) \Big\}.
\end{aligned} \tag{4.24}$$

By substituting $\sin\theta = \frac{B_1}{\Omega}$, the average work at time 't' is given by:

$$\langle W\rangle = \frac{4f\omega_0}{3+f^2}\frac{B_1^2}{\Omega^2}\Big\{1-\cos(\Omega\tau)\Big\}. \tag{4.25}$$

The amplitude multiplying the average work is proportional to the initial magnetization: $R = \frac{f}{3+f^2}$ and to the ratio, $\frac{B_1^2}{\Omega^2}$. The average work, therefore, oscillates indefinitely with frequency, Ω. This is the consequence of the fact that the evolution operator is unitary. This resembles the known Lorentzian function, representing a sharp peak at the resonance frequency ($\omega = \omega_0$), which becomes sharper for smaller values of B_1. The maximum possible work occurs at resonance:

$$\langle W\rangle_{max} = \frac{4\omega_0 f}{3+f^2}. \tag{4.26}$$

In **Model 2**, with quadrupolar interactions included, the average work is modified by the quadrupolar interaction parameter $\omega_Q^{(1)}$. By using the expression for the work distribution in Equation (4.19) and the corresponding probabilities in (4.20), the average work becomes:

$$\langle W\rangle = \frac{4\omega_0 f}{3+f^2}\Big\{|\upsilon(t)|^2+2|\chi(t)|^2\Big\} - \frac{2\omega_Q^{(1)}f^2}{3+f^2}|\upsilon(t)|^2. \tag{4.27}$$

Further substituting for $\upsilon(t)$ and $\chi(t)$ will yields:

$$\begin{aligned}\langle W\rangle \;=\; & 4R\omega_0\sin^2\theta\Big\{1-\cos(\Omega\tau\gamma)\Big\}+2Rf\omega_Q^{(1)}\Big\{\frac{\sin^4\theta}{2}\Big(1-\cos(\Omega\tau\gamma)\Big)^2 \\ & -\sin^2\theta\Big(1-\cos(\Omega\tau\gamma)\Big)\Big\}\end{aligned} \tag{4.28}$$

Again by substituting for $\sin\theta = \frac{B_1}{\Omega}$, this can be further simplified as

$$\langle W\rangle = 4RB_0\frac{B_1^2}{\Omega^2}\Big(1-\cos(\Omega\tau\gamma)\Big)\Big\{1-\frac{\omega_Q^{(1)}f}{2B_0}\Big\{1-\frac{B_1^2}{2\Omega^2}\Big(1-\cos(\Omega\tau\gamma)\Big)\Big\}\Big\} \tag{4.29}$$

The expressions provided here in Equation (4.29) is the average work $\langle W\rangle$ done on the spin-1 system during the consideration of quadrupolar interactions. The maximum attainable work is achieved at resonance and can be quantified as follows:

$$\langle W\rangle = 4R\Big(\omega_0-\frac{f}{2}\omega_Q^{(1)}\Big). \tag{4.30}$$

Average Work as a Function of Frequency

By utilizing the assumption from equation (4.14), the average work in equation (4.25), which results from neglecting quadrupolar interactions, can be expressed as:

$$\langle W\rangle = \frac{4f\omega_0}{3+f^2}\frac{B_1^2}{\Omega^2}\Big\{1-\cos(\frac{2\pi l}{\omega}\Omega)\Big\}. \tag{4.31}$$

This result is similar to that obtained in the spin-half case discussed in reference [46], although it includes the additional multiplicative term $\Big\{1-\cos(\frac{2\pi l}{\omega}\Omega)\Big\}$.

By substituting for $\Omega = \sqrt{(\omega - B_0)^2 + B_1^2}$ and rearranging the terms, we can derive the full expression for the mean work as:

$$\langle W \rangle = \frac{4fB_0}{3+f^2}\frac{B_1^2}{(\omega - B_0)^2 + B_1^2}\left\{1 - \cos\left(\frac{2\pi l}{\omega}\sqrt{(\omega - B_0)^2 + B_1^2}\right)\right\} \tag{4.32}$$

$$\begin{aligned} \frac{\langle W \rangle}{4RB_0} &= \frac{\left(B_1/B_0\right)^2}{(\omega/B_0 - 1)^2 + (B_1/B_0)^2}\left\{1 - \cos\left(\frac{2\pi l}{\omega/B_0}\sqrt{(\omega/B_0 - 1)^2 + (B_1/B_0)^2}\right)\right\} \\ &= \left(\frac{K_1}{K_3}\right)^2\left\{1 - \cos(\frac{2\pi l K_3}{K_2})\right\} \end{aligned} \tag{4.33}$$

where we have used the notations:

$$K_1 = \frac{B_1}{B_0}; K_2 = \frac{\omega}{B_0}; k_3 = \sqrt{(K_2 - 1)^2 + K_1^2}; R = \frac{f}{3+f^2}. \tag{4.34}$$

The results in Equation (4.33) are illustrated in 4.1 for various values of l, while maintaining a fixed ratio of the externally applied fields, $\frac{B_1}{B_0}$. The resonance condition occurs when $K_2 = \frac{\omega}{B_0} = 1$. The dependence of $\langle W \rangle_l$ on the angular frequency ω is complex but meaningfully relates to the duration l of the protocol.

The average work $\langle W \rangle_l$ exhibits a notable dependence on the duration 'l' of the protocol, with distinct behaviors observed at different time scales. For small values of 'l', as shown in 4.1a–c, the average work remains relatively modest, even near resonance. As frequency ω increases, $\langle W \rangle_l$ gradually rises, reaching a peak near resonance, but this peak is not highly pronounced. After this point, the average work slowly decreases as the system returns to equilibrium. This gradual increase and decrease indicate a smooth transition of energy for short protocol durations, where the system does not have sufficient time to fully respond to the resonance condition. The relatively low magnitude of the work in this regime suggests that the system's energy absorption is limited when the protocol is brief.

In contrast, for larger values of 'l', the behavior of $\langle W \rangle_l$ becomes much more pronounced. As seen in 4.1d–f, especially for $l = 1000$ in 4.1f, the average work sharply rises as the system approaches resonance, reaching a distinct maximum exactly at resonance. For these larger l values, the system has more time to respond to the driving frequency, leading to a sharper and more significant increase in the work near resonance. Once the maximum is reached, the average work exhibits rapid oscillations as ω varies, reflecting the system's enhanced sensitivity to the frequency in this regime. This sharp rise and rapid fluctuation underscore the critical role of the protocol duration in determining the system's energy dynamics, with longer protocols allowing for more pronounced resonance effects and greater energy absorption.

To estimate the upper limit on the number of cycles for radio frequency (RF) oscillations without violating the assumption of an isolated system, we consider an energy relaxation time of approximately 3 seconds. Assuming a period of 1 ms for the RF oscillations, performing a thousand cycles would take about 1 second [56], well within the 3-second limit, ensuring safe operation. We can deduce that, for the spin-1 nuclei system, the change in free energy ΔF is zero when $H_f = H_i$, indicating that the free energy depends solely on the Hamiltonian at the initial or final state. This leads to the conclusion that $\langle W \rangle_l \geq 0$, meaning the average work always exceeds the free energy. However, caution is warranted regarding individual work realizations, as cases like $W = -\omega$ and $W = -2\omega$ may violate

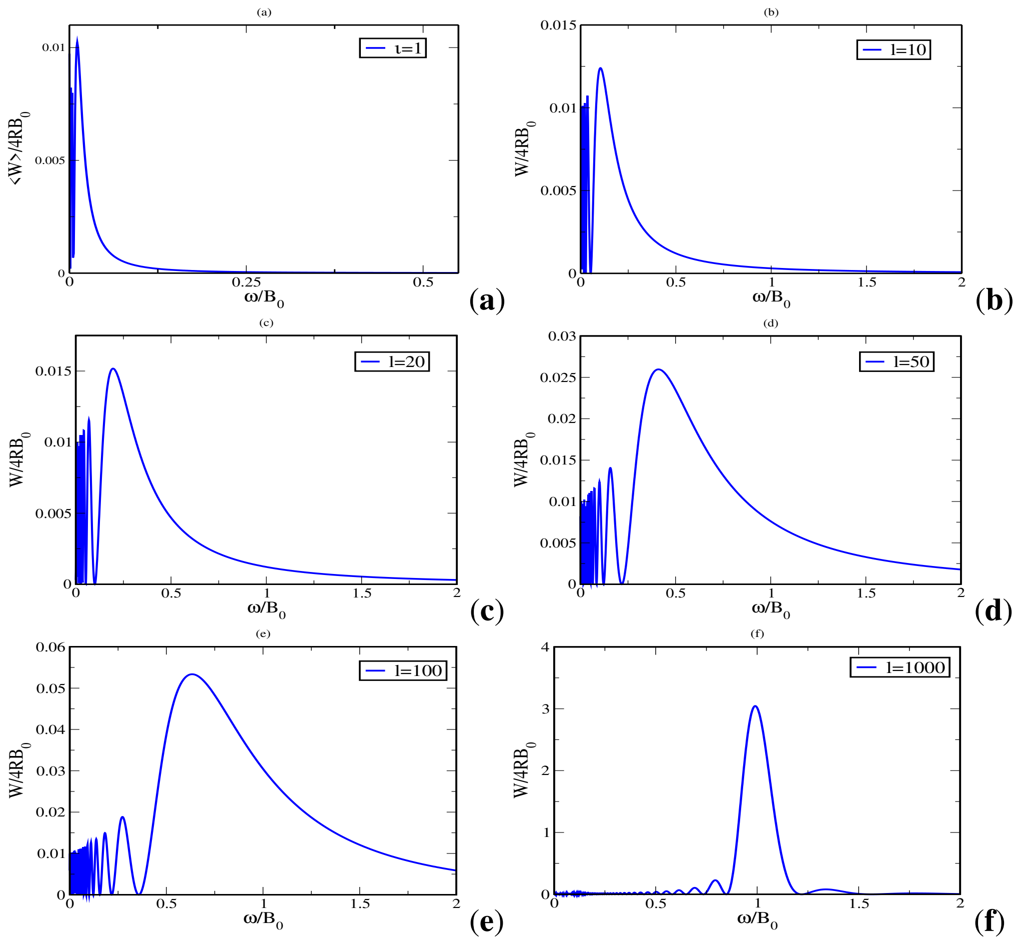


Figure 4.1: Average work $\frac{\langle W\rangle}{4RB_0}$ vs. $\frac{\omega}{B_0}$ computed using Equation (4.35) for fixed value $\frac{B_1}{B_z} = 0.01$.

the condition $W \geq \Delta F$, suggesting that while average work respects thermodynamic laws, individual instances may not.

Furthermore, when incorporating quadrupolar interactions in **model 2** by substituting $\Omega = \sqrt{(\omega - B_0)^2 + B_1^2}$ and setting $\gamma = 1$, we can present the complete expression for Equation (4.29) as follows:

$$\frac{\langle W\rangle}{4RB_0} = \left(\frac{K_1}{K_3}\right)^2\left(1-\cos\left(\frac{2\pi l K_3}{K_2}\right)\right)\left\{1-\frac{\omega_Q^{(1)} r}{2B_0}\left\{1-\frac{1}{2}\left(\frac{K_1}{K_3}\right)^2\left(1-\cos\left(\frac{2\pi l K_3}{K_2}\right)\right)\right\}\right\} \quad (4.35)$$

In the given expression, we have employed the following notations:

$$K_1 = \frac{\omega_1}{\omega_0}; K_2 = \frac{\omega}{\omega_0}; K_3 = \sqrt{(K_2-1)^2 + K_1^2}; R = \frac{r}{3+r^2} \quad (4.36)$$

The findings presented in Equation (4.35) are visualized in Figure 4.2, where various values of l and a fixed ratio of externally applied fields ($\frac{B_1}{B_0}$) are considered. The resonance condition is reached when $K_2 = \frac{\omega}{B_0} = 1$. Upon analyzing the figure, it becomes apparent that the relationship between $\langle W\rangle_l$ (average work) and the angular frequency ω is intricate, yet it exhibits a meaningful dependency on the duration (l) of the implemented protocol. In general, the work performed experiences a sharp increase as it approaches the resonance condition, signifying a notable correlation.

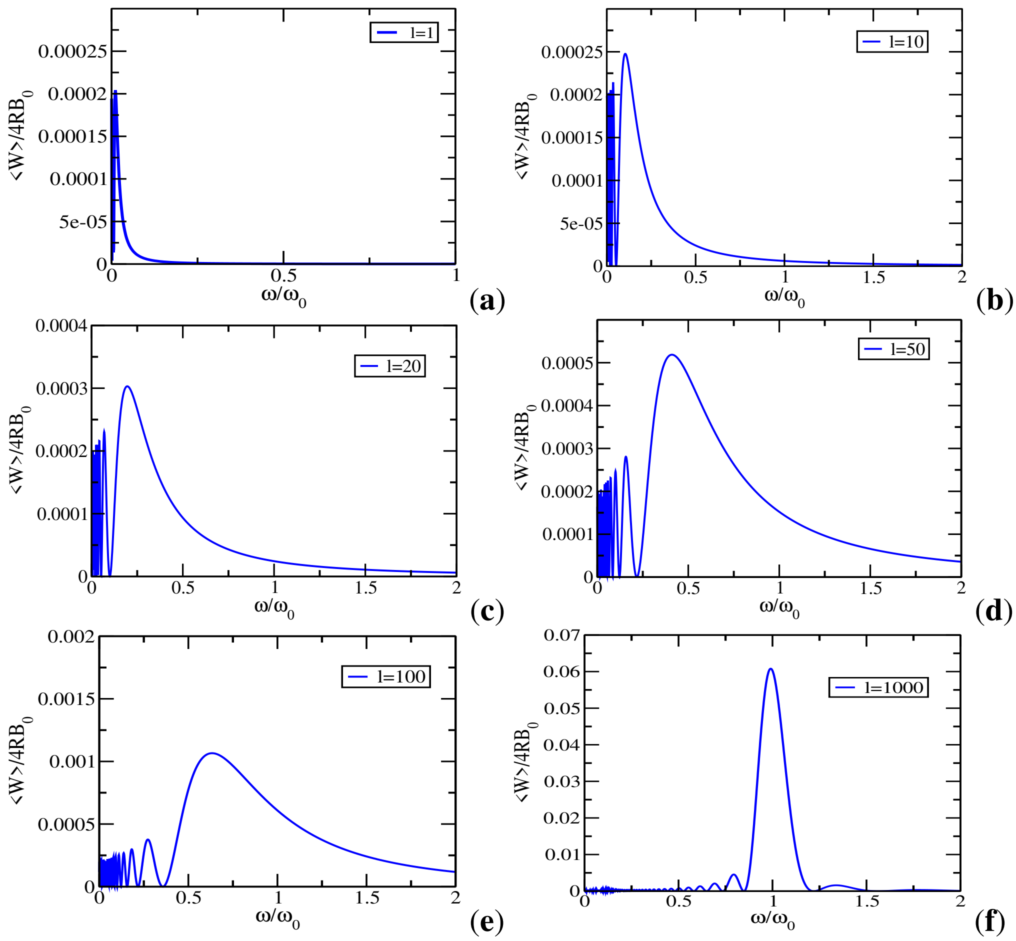


Figure 4.2: Average work $\frac{\langle W \rangle}{4RB_0}$ vs. $\frac{\omega}{B_0}$ computed using Equation (4.35) for fixed value $\frac{B_1}{B_z} = 0.01$.

Figure 4.2 $\left(\text{see } a - e\right)$ illustrate that, for small values of l, the average work initially rises with the angular frequency ω, approaching the resonance value. However, it then gradually declines, returning to the initial equilibrium state before reaching the resonance value. Conversely, for a large value of l, the average work experiences a sharp increase near the resonance value of $\frac{\omega}{B_0} = 1$ and reaches its maximum at resonance. This behavior is explicitly depicted in Figure 4.2f for $l = 1000$. In such instances, the oscillation becomes rapid as ω is varied.

Figure 4.2 in our study appears similar to the one presented in 4.1. However, upon closer examination, we notice a difference in the amplitude of the average work. Although the manner in which the average work varies with the ratio of frequencies remains the same, the amplitude of the average work is smaller in 4.2. This suggests that when considering the quadrupolar interaction, there is a delay or lag in the average work. To illustrate this, we can compare the average work ratio to the initial magnetization.

The free energy of the spin-1 nuclei system can be inferred as follows, considering our selected time τ in Equation (4.14) where $\hat{H}_f = \hat{H}_i$. Consequently, the change in free energy (ΔF) is determined to be 0, indicating that the free energy solely depends on the Hamiltonian measured at either the initial or final state. In this scenario, Equation (4.35) aligns with the inequality $\langle W \rangle_l \geq \Delta F$, which can now be expressed as $\langle W \rangle_l \geq 0$. Thus, it is always expected that the average work surpasses the free energy. However, caution must be exercised when considering individual realizations of the work distribution. For instance, cases where $W = -\omega \pm \frac{1}{2}\omega_Q^{(1)}$ and $W = -2\omega$ do not satisfy the aforementioned condition ($W \geq \Delta F$). This further implies that individual realizations may indeed violate the second law, while the average work remains unaffected.

The average work as a function of time

To provide a comprehensive understanding, we can also explore the average work as a function of time without relying on the assumption presented in Equation (4.14). In cases where $P(W)$ is not explicitly known, the average work done during the transformation can still be computed using alternative methods, defined as:

$$\langle W \rangle = \langle \hat{H}_f \rangle_{t=\tau} - \langle \hat{H}_i \rangle_{t=0}. \tag{4.37}$$

The general formula for $\langle W \rangle_t$ involves calculating the difference between the average energy at time t (when the protocol is deactivated) and the average energy at the initial time, $t = 0$ (immediately before the protocol was initiated).

Therefore, in the case of **model-1**, where we have ignored the quadrupolar interactions, using Equations (3.11) and (4.22) the average work as a function of time will be

$$\begin{aligned} \langle W \rangle_t &= \langle H(t) \rangle_t - \langle H_0 \rangle_{t=0} \\ &= -B_0 \langle I_z \rangle_t - B_1 \{ \langle I_x \rangle \cos \omega t + \langle I_y \rangle \sin \omega t \} - (-B_0 \langle I_z \rangle_{t=0}). \end{aligned} \tag{4.38}$$

Substituting for $\langle I_z \rangle, \langle I_x \rangle$, and $\langle I_y \rangle$ from Equations(4.11, 4.4 and 4.10), respectively, and simplifying the equation, yields us:

$$\begin{aligned} \frac{\langle W \rangle}{4RB_0} &= \left(\frac{K_1}{K_3} \right)^2 \Bigg\{ \Big(1 - \cos(B_0 K_3 t) \Big) - \frac{K_2 - 1}{K_3} \cos \omega t \Big(1 - \cos(B_0 K_3 t) \Big) (\cos \omega t + \sin \omega t) \\ &\quad + \sin(B_0 K_3 t) \sin \omega t \Big(\sin \omega t - \cos \omega t \Big) \Bigg\}. \end{aligned} \tag{4.39}$$

This result is illustrated in Figure 4.3 for different values of our work parameter, $B_1(t)$ and the angular frequency, ω, by which the spin is precessing around the resonance value, $\omega = \omega_0$. As we can see from the figure, the average work oscillates with two characteristic periods: a fast oscillation of frequency ω and a slow oscillation of frequency $\omega_1 = B_1$. The closer the oscillation is to ω_0 the higher is the performance of the average work performed.

For the case of **Model 2** utilizing Equations (3.1) and (3.42), we can determine the average work as a function of time in a similar procedure to that of model 1 as follows:

$$\begin{aligned} \langle W \rangle_t &= \langle H(t) \rangle_t - \langle H_0 \rangle_{t=0} \\ &= \Big(-B_0 \langle I_z \rangle_t + \frac{1}{6} \omega_Q^{(1)} \langle \hat{A}_Q \rangle_t - B_1 \{ \langle I_x \rangle \cos \omega t + \langle I_y \rangle \sin \omega t \} \Big) \\ &= -\Big(-B_0 \langle I_z \rangle_{t=0} + \frac{1}{6} \omega_Q^{(1)} \langle \hat{A}_Q \rangle_{t=0} \Big). \end{aligned} \tag{4.40}$$

Now, by substituting for $\langle I_z \rangle$, $\langle I_x \rangle$, $\langle I_y \rangle$ and $\langle \hat{A}_Q \rangle$ from Equations ((4.11) and 4.4) respectively, and simplifying the equation, we will have

$$\langle W \rangle = 4RB_0 \frac{B_1^2}{\Omega^2} \Big(1 - \cos(\Omega \tau \gamma) \Big) \Big\{ 1 - \frac{\omega_Q^{(1)} f}{2B_0} \Big\{ 1 - \frac{B_1^2}{2\Omega^2} \Big(1 - \cos(\Omega \tau \gamma) \Big) \Big\} \Big\} \tag{4.41}$$

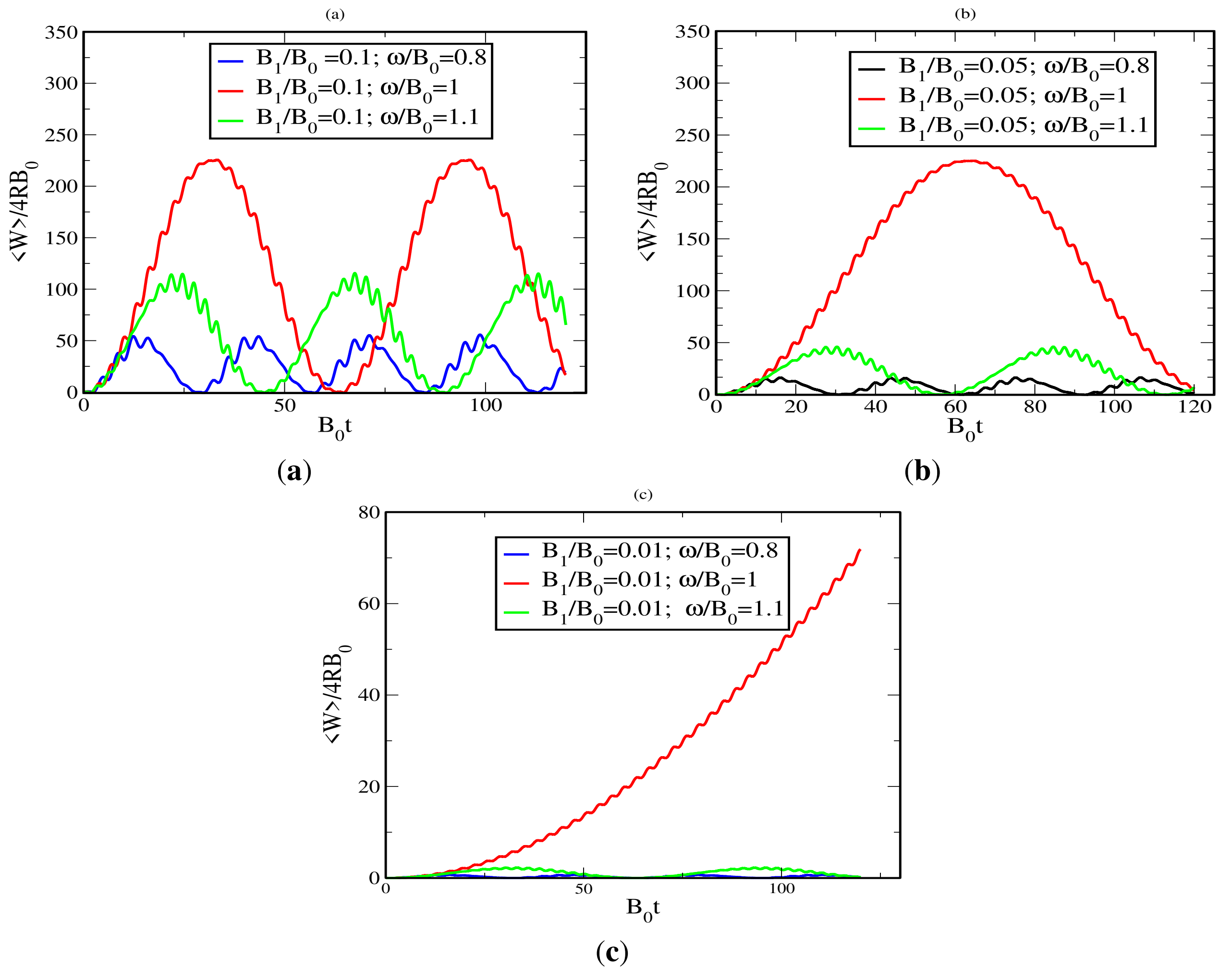


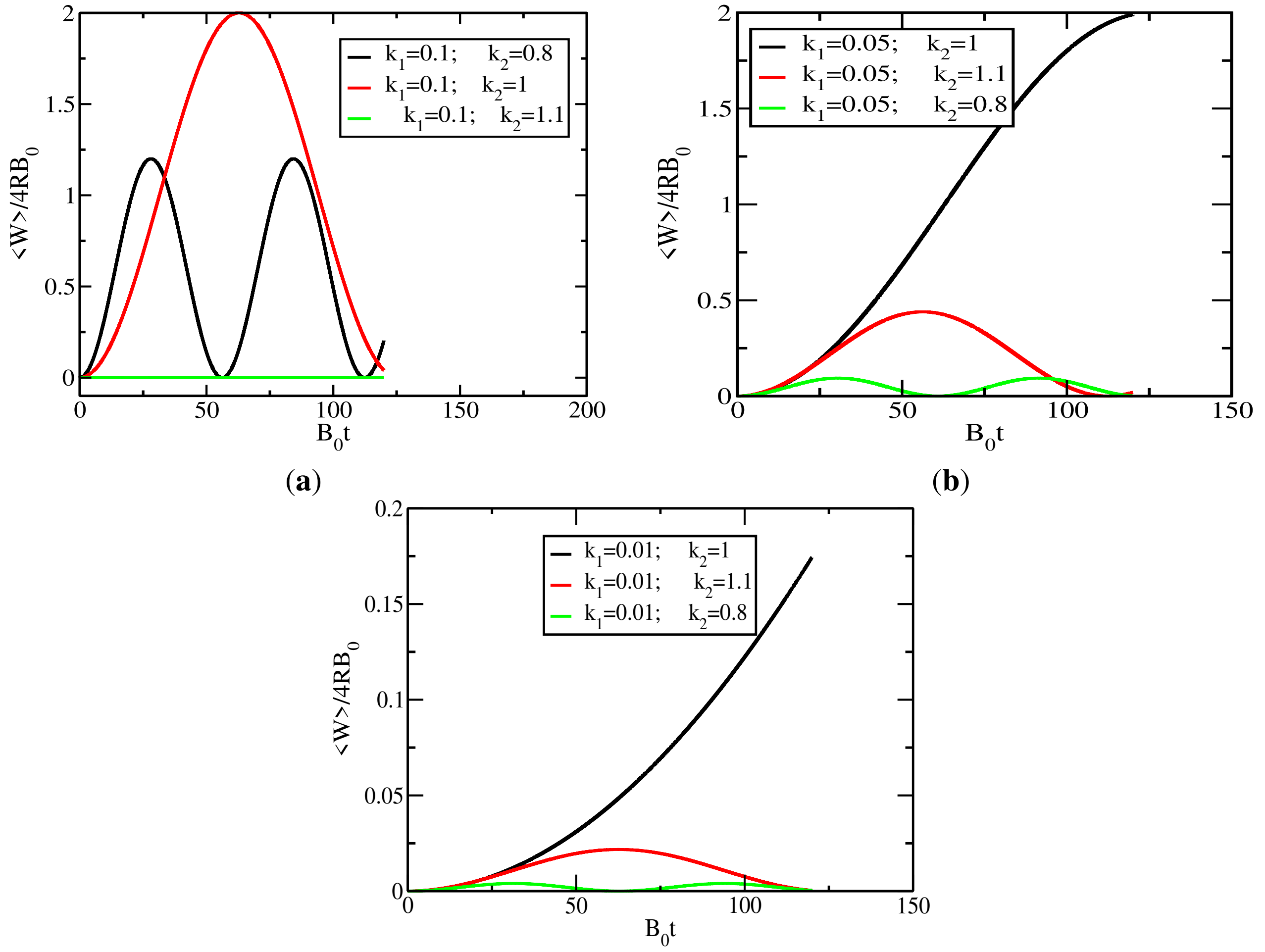
Figure 4.3: Average work computed by using Equation (4.39) $\left(\frac{\langle W\rangle}{4RB_0} \text{ vs. } B_0 t\right)$ for different values of $\frac{B_1}{B_0}$ and $\frac{\omega}{B_0}$.

$$\frac{\langle W\rangle}{4RB_0} = \left(\frac{K_1}{K_3}\right)^2\left(1-\cos(\frac{2\pi l K_3}{K_2})\right)\left\{1-\frac{\omega_Q^{(1)} f}{2B_0}\left\{1-\frac{1}{2}\left(\frac{K_1}{K_3}\right)^2\left(1-\cos(\frac{2\pi l K_3}{K_2})\right)\right\} +(1-k_2)\right\} \tag{4.42}$$

This equation models the normalized average work $\langle W\rangle$ as a function of time for a spin system, incorporating previously defined parameters K_1, K_2, and K_3 that represent various frequency ratios and nd using mathematical terms to capture the system's complex behavior, enabling accurate calculations of the average work.

Figure 4.3 demonstrates this outcome for various values of the work parameter, $B_1(t)$, and the angular frequency, ω, representing the precession of the spin around the resonance value, $\omega = \omega_0$. The graph reveals that the average work exhibits two distinct periods of oscillation: a rapid oscillation with a frequency of ω and a slower oscillation with a frequency of ω_1. Notably, the average work achieves better performance when the oscillation closely aligns with ω_0.

While our findings may bear resemblance to Figure 4.3, there are noteworthy distinctions. Specif-



(c)

Figure 4.4: Average work computed by using Equation (4.42) $\left(\frac{\langle W \rangle}{4RB_0} \text{ vs. } B_0 t\right)$ for different values of $\frac{B_1}{B_0}$ and $\frac{\omega}{B_0}$.

ically, when the frequency associated with the magnetic field aligns closely with the frequency of the assumed strong static magnetic field ($\hat{B}_0$) and ω exceeds ω_0, the quadrupolar interaction assumes greater importance in determining the resonance condition (see: 4.3a). In these instances, the quadrupolar interaction surpasses the influence of other parameters, establishing itself as the primary factor. This underscores the significance of accounting for quadrupolar interaction when the frequencies of the external work parameter and the static magnetic field are in close proximity.

4.3 Characteristic Function and Distribution of Work.

The change in energy within the total system characterizes the response of a quantum system, specifically the spin-1 nuclei, to an external magnetic field perturbation. Consequently, the characteristic function of the work distribution, which encompasses all statistical aspects of the work, can be expressed as follows:

$$G(u) = tr\{\hat{U}^\dagger(\tau) e^{ir\hat{H}_f} \hat{U}(\tau) e^{-ir\hat{H}_i} \rho_{th}\} \tag{4.43}$$

where $\hat{H}_i$ and $\hat{H}_f$- refers to the initial and final Hamiltonian respectively.

As we have mentioned in the past section, to calculate the the expectation value of the work distribution we use the unperturbed Hamiltonian, $\hat{H}_0$. Therefore, we replace both $\hat{H}_i$ and $\hat{H}_f$ by $\hat{H}_0$. In case where we have ignored the quadrupolar interactions the initial Hamiltonian is $\hat{H}_0 = -\omega_0 \hat{I}_z$, but while incorporating quadrupolar interactions it becomes: $\hat{H}_0 = -\omega_0 \hat{I}_z + \frac{1}{6}\omega_Q^{(1)} \hat{A}_Q$.

Then the characteristic function of the work done on the system for the **model 1** (see details in appendix A.4) will be:

$$G(u) = tr\Big(\hat{U}^\dagger(\tau) e^{-iu\omega_0 \hat{I}_z} \hat{U}(\tau) e^{iu\omega_0 \hat{I}_z} \rho_{th}\Big) \tag{4.44}$$

Substituting for $\hat{U}(t)$ from Eq. (3.32)and for ρ_{th} from Eq. (3.8) into Eq. (4.44) the characteristic function of work (**model 1**) in a more simplified form will be:

$$\begin{aligned} G(u) \quad = \quad & \frac{1}{3+f^2}\Big\{ \Big(|\nu|^2 + |\upsilon|^2 e^{iu\omega_0} + |\chi|^2 e^{2iu\omega_0}\Big)(1+2f+f^2) \\ & + \Big(1 - 2\chi e^{-i\omega_z t} - 2\chi^* e^{i\omega_z t} + 4|\chi|^2 + |\upsilon|^2 e^{-iu\omega_0} + |\upsilon|^2 e^{iu\omega_0}\Big)(1-f^2) \\ & + \Big(|\nu|^2 + |\upsilon|^2 e^{-iu\omega_0} + |\chi|^2 e^{-2iu\omega_0}\Big)(1-2f+f^2)\Big\} \end{aligned} \tag{4.45}$$

This can be rewritten in more useful form as:

$$\begin{aligned} G(u) \quad = \quad & \frac{1}{3+f^2}\Big\{ 2|\nu(t)|^2(1+f^2) + \Big(1 + 4|\chi(t)|^2 - 2\chi(t)e^{-i\omega_z t} - 2\chi^* e^{i\omega_z t}\Big)(1-f^2) + 2|\upsilon(t)|^2 e^{iu\omega_0}(1+f) \\ & + 2|\upsilon(t)|^2 e^{-iu\omega_0}(1-f) + |\chi(t)|^2 e^{2iu\omega_0}(1+2f+f^2) + |\chi(t)|^2 e^{-2iu\omega_0}(1-2f+f^2)\Big\} \end{aligned} \tag{4.46}$$

Similarly for **model 2** case, Then substituting for $\hat{U}(t)$ from Equation (3.63), for ρ_{th} from Equation 3.8 into Equation (4.44) the characteristic function of work, for the case of incorporating quadrupolar interactions (**model 2**), can be expressed in a more simplified form as follows:

$$\begin{aligned} G(u) \quad = \quad & \frac{1}{3+r^2}\Big\{ 2|\nu(t)|^2(1+r^2) + \Big(1 + 4|\chi(t)|^2 - 2\chi(t)e^{-i\omega_z t} - 2\chi^*(t)e^{i\omega_z t}\Big)(1-f^2) \\ & + |\upsilon(t)|^2 \Big[e^{iu\left(\omega_0 + \frac{\omega_Q^{(1)}}{2}\right)} + e^{-iu\left(\omega_0 - \frac{\omega_Q^{(1)}}{2}\right)} \Big](1-f^2) \\ & + \Big[|\upsilon(t)|^2 e^{iu\left(\omega_0 - \frac{\omega_Q^{(1)}}{2}\right)} + |\chi(t)|^2 e^{2iu\omega_0} \Big](1+2f+f^2) \\ & + \Big[|\upsilon(t)|^2 e^{-iu\left(\omega_0 + \frac{\omega_Q^{(1)}}{2}\right)} + |\chi(t)|^2 e^{-2iu\omega_0} \Big](1-2f+f^2)\Big\} \end{aligned} \tag{4.47}$$

Let's now investigate the connection between the probability distribution $P(W)$ and the characteristic function $G(u)$.

According to the definition of the characteristic function, we can establish the following connection:

$$G(u) = \langle e^{iuW} \rangle = \int_{-\infty}^{\infty} P(W) e^{iuW} dW \tag{4.48}$$

Subsequently, the characteristic function $G(u)$ can be represented using a power series expansion in terms of the statistical moments of work, as outlined below:

$$G(u) = \langle e^{iuW} \rangle = 1 + iu\langle W \rangle + \frac{(iu)^2}{2!}\langle W^2 \rangle + \frac{(iu)^3}{3!}\langle W^3 \rangle + \cdots \tag{4.49}$$

where

$$\langle W^n \rangle = (-i)^n \frac{\partial^n G(u)}{\partial u^n}|_{u=0} \tag{4.50}$$

4.3.1 The average and variance of the Work distribution

In this section, we compute the first and second moments of the work distribution and the corresponding variance for two models: Model 1, where quadrupolar interactions are neglected, and Model 2, where quadrupolar interactions are included. These models allow us to analyze how the inclusion of quadrupolar interactions affects the work statistics of a spin-1 system subjected to external magnetic fields.

Model 1: Neglecting Quadrupolar Interactions

In **Model 1**, where quadrupolar interactions are ignored, we can calculate the first and second moments of work, along with the variance by employing:

$$\langle W \rangle = (-i) \frac{\partial G(u)}{\partial u}|_{u=0} \tag{4.51}$$

Substituting for $G(u)$ from Eq. ((4.47)) into Eq. ((4.51)) and performing partial differentiating with respect to 'u' will yields:

$$\begin{aligned}
\langle W \rangle &= \frac{-i}{(3+f^2)} \Big\{ 2i\omega_0 |\upsilon|^2 e^{ir\omega_0}(1+f) - 2i\omega_0 |\upsilon|^2 e^{-ir\omega_0}(1-f) + 2i\omega_0 |\chi|^2 e^{2ir\omega_0}(1+2f+f^2) \\
&\quad -2i\omega_0 |\chi|^2 e^{-2ir\omega_0}(1-2f+f^2) \Big\} \\
&= \frac{\omega_0}{(3+f^2)} \Big\{ 2|\upsilon|^2(1+f) - 2|\upsilon|^2(1-f) + 2|\chi|^2(1+2f+f^2) - 2|\chi|^2(1-2f+f^2) \Big\}
\end{aligned}$$

Further simplification of this equation will yield:

$$\langle W \rangle = \frac{4f\omega_0}{(3+f^2)} \Big\{ |\upsilon|^2 + 2|\chi|^2 \Big\} \tag{4.52}$$

Then, by substituting for υ and χ the first moment of the work will become:

$$\langle W \rangle = \frac{4f\omega_0}{(3+f^2)} \sin^2\theta (1-\cos\alpha) \tag{4.53}$$

Again, substituting for $\alpha = \Omega\gamma t$, $\omega_0 = \gamma B_0$ and $\sin\theta = \frac{B_1}{\Omega}$ it can be rewritten as:

$$\langle W \rangle = \frac{4f\gamma B_0}{(3+f^2)} \frac{B_1^2}{\Omega^2} \Big(1 - \cos(\Omega\gamma t) \Big) \tag{4.54}$$

This is what we have already obtained in Eq. (4.62)

The second moment of work, $\langle W^2 \rangle$, can also be calculated as

$$\langle W^2 \rangle = \frac{\partial^2 G(u)}{\partial u^2}|_{u=0} = (-i) \frac{\partial \langle W \rangle}{\partial u}|_{u=0} \tag{4.55}$$

By substituting for $\langle W\rangle$ from Eq. (4.52) and performing differentiation with respect to 'r', the second moment of work can be expressed as:

$$\begin{aligned}\langle W^2\rangle &= \frac{(-i)^2}{(3+f^2)}\Big\{-2\omega_0^2|\upsilon|^2(1+f)-2\omega_0^2|\upsilon|^2(1-f)-4\omega_0^2|\chi|^2(1+2f+f^2)\\ &\quad -4\omega_0^2|\chi|^2(1-2f+f^2)\Big\}\\ &= \frac{4\omega_0{}^2}{(3+f^2)}\Big(|\upsilon|^2+2|\chi|^2(1+f^2)\Big) \qquad (4.56)\end{aligned}$$

Again, by substituting for υ and χ one can obtain:

$$\langle W^2\rangle = \frac{4\omega_0{}^2}{(3+f^2)}\sin^2\theta(1-\cos\alpha)+\frac{4\omega_0{}^2f^2}{(3+f^2)}\left(\frac{\sin^4\theta}{2}(1-\cos\alpha)^2\right) \qquad (4.57)$$

From the first moment of work obtained in Eq. (4.53) one can find its square, $\langle W\rangle^2$, as:

$$\langle W\rangle^2 = \frac{16f^2\omega_0^2}{(3+f^2)^2}\sin^4\theta(1-\cos\alpha)^2 \qquad (4.58)$$

As a consequence, the variance of the work distribution becomes

$$\begin{aligned}Var(W) &= \langle W^2\rangle-\langle W\rangle^2\\ &= \frac{4\omega_0{}^2}{(3+f^2)}\Big\{\sin^2\theta(1-\cos\alpha)+\frac{4\omega_0{}^2f^2}{(3+f^2)}\left(\frac{\sin^4\theta}{2}(1-\cos\alpha)^2\right)\\ &\quad -\frac{16\omega_0^2f^2}{(3+f^2)^2}\sin^4\theta(1-\cos\alpha)^2\Big\}\\ var(W) &= \frac{4\omega_0{}^2}{(3+f^2)}\left\{\sin^2\theta(1-\cos\alpha)+f^2\frac{(f^2-5)}{2(3+f^2)}\sin^4\theta(1-\cos\alpha)^2\right\} \qquad (4.59)\end{aligned}$$

Model 2: Incorporating Quadrupolar Interactions

In model 2 where quadrupolar interactions are incorporated, we can solve for the first and second moment of work, and the variance of work as follows. Specifically, the first moment of the work can be calculated by substituting Eqn. (4.47) into Eqn.(4.51) as follows:

$$\begin{aligned}\langle W\rangle &= (-i)\frac{\partial G(u)}{\partial u}|_{u=0}\\ &= \frac{1}{(3+f^2)}\Big\{\omega_Q^{(1)}|\upsilon(t)|^2(1-f^2)+\Big(|\upsilon(t)|^2[\omega_0-\frac{1}{2}\omega_Q^{(1)}]+2\omega_0|\chi(t)|^2\Big)(1+2f+f^2)\\ &\quad -\Big(|\upsilon(t)|^2[\omega_0+\frac{1}{2}\omega_Q^{(1)}]+2\omega_0|\chi(t)|^2\Big)(1-2f+f^2)\Big\}\\ \langle W\rangle &= 4R\omega_0\Big\{|\upsilon(t)|^2+2|\chi(t)|^2\Big\}-2Rf\omega_Q^{(1)}|\upsilon(t)|^2. \qquad (4.60)\end{aligned}$$

By replacing $\upsilon(t)$ and $\chi(t)$ with their corresponding values from Equation (3.33), the first moment of the work can be expressed as:

$$\langle W\rangle = 4R\omega_0\sin^2\theta(1-\cos\alpha)\Big\{1-\frac{f\omega_Q^{(1)}}{2\omega_0}\Big(1-\sin^2\theta(1-\cos\alpha)\Big)\Big\} \qquad (4.61)$$

Once again, after substituting $\alpha = \Omega t$, $\omega_0 = B_0$, $\gamma = 1$ and $\sin\theta = \frac{B_1}{\Omega}$, the expression can be rephrased as:

$$\langle W\rangle = 4RB_0\frac{B_1^2}{\Omega^2}\Big(1-\cos(\Omega\tau)\Big)\Big\{1-\frac{\omega_Q^{(1)}f}{2B_0}\Big\{1-\frac{B_1^2}{2\Omega^2}\Big(1-\cos(\Omega\tau)\Big)\Big\}\Big\} \tag{4.62}$$

Similarly, we can calculate the second moment of work, denoted as $\langle W^2\rangle$, using the following expression:

$$\begin{aligned}\langle W^2\rangle &= \frac{\partial^2 G(u)}{\partial u^2}|_{u=0} = (-i)\frac{\partial\langle W\rangle}{\partial u}|_{u=0}\\ &= \frac{4R{\omega_0}^2}{f}\Big(|\upsilon|^2+2|\chi|^2(1+f^2)-\frac{\omega_Q^{(1)}f}{\omega_0}|\upsilon|^2(1-\frac{\omega_Q^{(1)}}{4f\omega_0})\Big).\end{aligned} \tag{4.63}$$

Upon substituting the respective values of $\upsilon(t)$ and $\chi(t)$ from Equation (3.33), we arrive at the following result:

$$\begin{aligned}\langle W^2\rangle &= \frac{4R{\omega_0}^2}{f}\sin^2\theta(1-\cos\alpha)\Big\{1-\frac{f\omega_Q^{(1)}}{\omega_0}\Big(1-\frac{\omega_Q^{(1)}}{4f\omega_0}\Big)\\ &\quad -\frac{f\sin^2\theta}{2}(1-\cos\alpha)\Big(f-\frac{\omega_Q^{(1)}}{\omega_0}\Big(1-\frac{\omega_Q^{(1)}}{4f\omega_0}\Big)\Big)\Big\}\end{aligned} \tag{4.64}$$

Using the first moment of work obtained in Equation (4.53), we can determine its mean square, denoted as $\langle W\rangle^2$, by performing the necessary calculations. As a result we obtain

$$\begin{aligned}\langle W\rangle^2 &= 16R^2\omega_0^2\sin^4\theta(1-\cos\alpha)^2\Bigg\{1-\frac{f\omega_Q^{(1)}}{\omega_0}\Big(1-\frac{f\omega_Q^{(1)}}{4\omega_0}\Big)\\ &\quad +\frac{f\omega_Q^{(1)}}{2\omega_0}\sin^2\theta(1-\cos\alpha)\Big(1-\frac{f\omega_Q^{(1)}}{2\omega_0}\Big)+\frac{f^2\omega_Q^2}{16{\omega_0}^2}\sin^4\theta(1-\cos\alpha)^2\Bigg\}.\end{aligned} \tag{4.65}$$

Thus, the work distribution exhibits a variance characterized by

$$\begin{aligned}Var(W) &= \langle W^2\rangle-\langle W\rangle^2\\ &= \frac{4R{\omega_0}^2}{f}\sin^2\theta(1-\cos\alpha)\Bigg\{1-\frac{f}{\omega_0}\Big(1-\frac{\omega_Q^{(1)}}{4f\omega_0}\Big)\\ &\quad -\frac{R\sin^2\theta(1-\cos\alpha)}{8\omega_0^2 f}P(f)+\frac{2Rf^2\omega_Q^{(1)}}{\omega_0}\Big(1-\frac{f\omega_Q^{(1)}}{2\omega_0}\Big)\sin^4\theta(1-\cos\alpha)^2\\ &\quad +\frac{Rf^3\omega_Q^2\sin^6\theta}{4\omega_0^2}(1-\cos\alpha)^3\Bigg\}.\end{aligned} \tag{4.66}$$

where $P(f) = 8f^4{\omega_Q}^2+\frac{4f^3}{R}{\omega_0}^2(1-\frac{8R\omega_Q^{(1)}}{\omega_0})+\frac{4f^2}{R}{\omega_0}^2(8R+\frac{\omega_Q^{(1)}}{\omega_0})-\frac{{\omega_Q}^2 f}{R}$

This equation (4.66) breaks down the variance of the work distribution, $Var(W)$, in a quantum system. The first term relates to the mean work $\langle W\rangle$, while the subsequent terms account for higher-order moments and angular dependencies. The full expression represents the complete variance of the work distribution, which can offer insights into the energy fluctuations and dynamics of the quantum system.

The probability distribution of the work.

Finally, we determine the work probability distribution $P(W)$, which represents the complete distribution of work. To do this, we utilize the characteristic function $G(u)$ defined in Equation (4.49). By performing the inverse Fourier transform of the characteristic function $G(u)$, we can obtain the probability distribution function from the relation:

$$P(W) = \frac{1}{2\pi}\int_{-\infty}^{\infty} duG(u)e^{-iuW}. \tag{4.67}$$

Here, let we define the Dirac delta function given as:

$$\int_{-\infty}^{\infty} e^{iu(x-y)}du = \delta(y-x) \tag{4.68}$$

By substituting the expression for $G(u)$ from Equation (4.47), (obtained while ignoring quadrupolar interactions) into Equation (4.67) we will obtain the corresponding probability distribution of the work as follows:

$$\begin{aligned} P(W) \;=\; & \frac{1}{3+f^2}\Big\{2|\nu|^2(1+f^2)\delta(W) + \Big(1+4|\chi|^2 - 2\chi e^{-i\omega_z t} - 2\chi^* e^{i\omega_z t}\Big)(1-f^2)\delta(W) \\ & +2|\upsilon|^2(1+f)\delta(W-\omega_0) + 2|\upsilon|^2(1-f)\delta(W+\omega_0) \\ & +|\chi|^2(1+2f+f^2)\delta(W-2\omega_0) + |\chi|^2(1-2f+f^2)\delta(W+2\omega_0)\Big\}. \end{aligned} \tag{4.69}$$

In the same procedure, by substituting the expression for $G(u)$ from Equation (4.47), (obtained while considering quadrupolar interactions) into Equation (4.67) we will obtain the corresponding probability distribution of the work as follows:

$$\begin{aligned} P(W) \;=\; & \frac{1}{3+f^2}\Big\{2|\nu(t)|^2(1+f^2)\delta(W) + \Big(1+4|\chi(t)|^2 - 2\chi(t)e^{-i\omega_z t} - 2\chi^*(t)e^{i\omega_z t}\Big)(1-f^2)\delta(W) \\ & +|\upsilon(t)|^2(1-f^2)\delta\Big(W-\omega_0-\frac{1}{2}\omega_Q^{(1)}\Big) + |\upsilon(t)|^2(1-f^2)\delta\Big(W+\omega_0-\frac{1}{2}\omega_Q^{(1)}\Big) \\ & +|\upsilon(t)|^2(1+2f+f^2)\delta\Big(W-\omega_0+\frac{1}{2}\omega_Q^{(1)}\Big) + |\upsilon(t)|^2(1-2f+f^2)\delta\Big(W+\omega_0+\frac{1}{2}\omega_Q^{(1)}\Big) \\ & +|\chi(t)|^2(1+2f+f^2)\delta(W-2\omega_0) + |\chi(t)|^2(1-2f+f^2)\delta(W+2\omega_0)\Big\}. \end{aligned} \tag{4.70}$$

The probability distributions described by Equations (4.69) and (4.70) provides a detailed characterization of the work (W) done on the spin system during a nuclear magnetic resonance (NMR), revealing important information about the energy levels and transitions within the spin system. The different Dirac delta functions in the expression correspond to specific energy changes that can be related to fundamental properties of the spin system, such as the Zeeman splitting (ω_0) and the quadrupolar splitting ($\omega_Q^{(1)}$), allowing researchers to gain valuable insights into the quantum-mechanical behavior of the system for interpreting NMR spectra and understanding spin dynamics.

Consequently, when viewed as a random variable, the work can assume seven distinct values: $W = 0, W = \omega_0 + \frac{1}{2}\omega_Q^{(1)}, W = -\omega_0 + \frac{1}{2}\omega_Q^{(1)}, W = +\omega_0 - \frac{1}{2}\omega_Q^{(1)}, W = -\omega_0 - \frac{1}{2}\omega_Q^{(1)}, W = -2\omega_0$, and $W = 2\omega_0$.

Chapter 5

Summary and Conclusions

In this work, we developed a theoretical framework to analyze the quantum thermodynamic behavior of spin-1 nuclei under the influence of an externally applied work protocol. In particular, we focused on two models: Model 1, which ignores quadrupolar interactions, and Model 2, where quadrupolar interactions are included. Our aim was to study how these interactions influence the nuclear magnetic resonance (NMR) response of the system and to assess the impact of the externally imposed work parameter, a weak alternating radio frequency (R.F.) magnetic field, on the thermodynamic properties of the system.

In Model 1, we considered a spin-1 system subjected to a strong static magnetic field along the z-axis, which splits the energy levels of the nucleus into three distinct states: E_+, E_- and E_0. A weak alternating magnetic field $B_1(t)$ was applied perpendicular to the static field to induce transitions between these energy states. The first goal was to observe how the average work $\langle W \rangle$ and the variance of the work distribution behave as a function of the frequency ω of the R.F. field and the duration l of the applied protocol.

The results showed that for small protocol durations l, the average work $\langle W \rangle_l$ remained relatively small, even near resonance. As the frequency increased, $\langle W \rangle_l$ gradually rose, reaching a peak at resonance, before slowly decreasing back to equilibrium. For longer durations, however, the work sharply increased near resonance and exhibited a distinct maximum at the resonance frequency. This behavior indicated that the system's dynamics are governed mainly by the external magnetic fields, with the alternating field driving transitions between the energy states. The variance of the work distribution also revealed that fluctuations in the work are sensitive to both the frequency ω and the duration l, with larger fluctuations occurring as the system approaches resonance.

In Model 2, we introduced quadrupolar interactions, which arise from the non-spherical charge distribution of the spin-1 nuclei. These interactions added an extra term C_Q to the Hamiltonian, modifying the system's energy levels and dynamics. With the inclusion of quadrupolar interactions, the energy levels were further split, complicating the transitions between states driven by the R.F. field. The goal here was to assess how this additional interaction affects the average work and variance compared to the simpler case of Model-1.

The results demonstrated that the quadrupolar interaction introduces additional dependencies on the angles and strength of the applied fields. Specifically, the average work $\langle W \rangle$ in Model-2 exhibited sharper increases near resonance, and the work distribution was more sensitive to the frequency variation. The inclusion of quadrupolar interactions led to higher-order terms in the expressions for both the average work and its variance, reflecting more complex dynamics in the presence of these interactions. The variance of the work also increased more dramatically compared to Model 1, indicating that quadrupolar interactions introduce larger fluctuations in the system, particularly near resonance. This suggests that quadrupolar interactions play a significant role in governing the energy transitions and the overall thermodynamic behavior of the spin-1 nuclei.

By comparing Model 1 and Model 2, we demonstrated that quadrupolar interactions have a profound effect on the quantum thermodynamic behavior of spin-1 nuclei. In Model 1, where quadrupolar interactions are ignored, the system's dynamics are primarily dictated by the external magnetic fields, with the frequency of the alternating field playing a crucial role in driving energy transitions. In Model 2, the inclusion of quadrupolar interactions leads to more complex behavior, with sharper and more pronounced energy transitions near resonance, as well as larger fluctuations in the work distribution.

Overall, this study provides insights into the role of quadrupolar interactions in spin-1 systems and highlights the importance of considering these interactions when analyzing quantum thermodynamic properties. The results suggest that quadrupolar interactions significantly alter both the average work and the fluctuations in the system, particularly near resonance, making them essential to accurately describe the behavior observed in experiments. We recommend that future experimental studies investigate the influence of quadrupolar interactions in NMR and other quantum thermodynamic systems to further validate our theoretical findings.

Appendix A

Details of Mathematical Derivations

A.1 Time-Dependent to Time-Independent Schrödinger

Here we try to transform the time dependent schrodinger equation to that of time-independent one by using the rotating wave approximation method [57]. To do so let we consider the new time evolving operator, $\hat{U}'(t)$ given as:

$$\hat{U}'(t) = e^{i\omega_z t\hat{I}_z}\hat{U}(t) \tag{A.1}$$

To have an explicit form of the new time evolving operator, $\hat{U}'(t)$, we need to have the matrix form of $e^{i\omega_z t\hat{I}_z}$ as follows. Using the properties of pauli matrices for spin-1, and since $\hat{I}_z$ is already a diagonal matrix we have:

$$e^{i\omega_z t\hat{I}_z} = \begin{pmatrix} e^{i\omega_z t} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\omega_z t} \end{pmatrix} \tag{A.2}$$

Then an operator $\hat{I}_z$ that acts on the three Zeeman basis will yield:

(1)

$$\Longrightarrow e^{i\omega_z t\hat{I}_z}|1,1\rangle = \begin{pmatrix} e^{i\omega_z t} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\omega_z t} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} e^{i\omega_z t} \\ 0 \\ 0 \end{pmatrix} = e^{i\omega_z t}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = e^{i\omega_z t}|1,1\rangle \tag{A.3}$$

(2)

$$\Longrightarrow e^{i\omega_z t\hat{I}_z}|1,0\rangle = \begin{pmatrix} e^{i\omega_z t} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\omega_z t} \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = |1,0\rangle \tag{A.4}$$

(3)

$$\Longrightarrow e^{i\omega_z t\hat{I}_z}|1,-1\rangle = \begin{pmatrix} e^{i\omega_z t} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\omega_z t} \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ e^{-i\omega_z t} \end{pmatrix} = e^{-i\omega_z t}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = e^{-i\omega_z t}|1,-1\rangle \tag{A.5}$$

Thus, the transformation equation becomes

$$\begin{aligned} \hat{U}'(t)|n\rangle &= e^{i\omega_z t\hat{I}_z}\hat{U}(t)|n\rangle = e^{i\omega_z t\hat{I}_z}\hat{U}_+(t)|1,1\rangle + e^{i\omega_z t\hat{I}_z}\hat{U}_0(t)|1,0\rangle + e^{i\omega_z t\hat{I}_z}\hat{U}_-(t)|1,-1\rangle \\ \hat{U}'(t)|n\rangle &= e^{i\omega_z t}\hat{U}_+|1,1\rangle + \hat{U}_0|1,0\rangle + e^{-i\omega_z t}\hat{U}_-|1,-1\rangle \\ &= \hat{U}'_+(t)|1,1\rangle + \hat{U}'_0(t)|1,0\rangle + \hat{U}'_-(t)|1,-1\rangle. \end{aligned} \tag{A.6}$$

This indicates that

$$\begin{aligned} U_{+}(t) &= e^{-i\omega_z t}\hat{U}'_{+}(t) \\ U_{0}(t) &= \hat{U}'_{0}(t) \\ U_{-}(t) &= e^{i\omega_z t}\hat{U}'_{-}(t) \end{aligned} \tag{A.7}$$

and in matrix form it can be given as:

$$\begin{pmatrix} \hat{U}_{+}(t) \\ \hat{U}_{0}(t) \\ \hat{U}_{-}(t) \end{pmatrix} = \begin{pmatrix} e^{-i\omega_z t}\hat{U}'_{+}(t) \\ \hat{U}'_{0}(t) \\ e^{i\omega t}\hat{U}'_{-}(t) \end{pmatrix} \tag{A.8}$$

Now substituting for $\hat{U}_{+}(t), \hat{U}_{-}(t), \hat{U}_{0}(t)$ from Eq. (A.7) into Eq. (3.53) and implementing the method of differentiation by parts we will obtain:
(1)

$$i\frac{\partial \hat{U}_{+}(t)}{\partial t} = -\omega_0 \hat{U}_{+}(t) - \frac{\omega_1}{\sqrt{2}} e^{-i\omega_z t}\hat{U}_{0}(t)$$

$$i\frac{\partial \left(e^{-i\omega_z t}\hat{U}'_{+}(t)\right)}{\partial t} = -\omega_0 e^{-i\omega_z t}\hat{U}'_{+}(t) - \frac{\omega_1}{\sqrt{2}} e^{-i\omega_z t}\hat{U}'_{0}(t)$$

$$i\frac{\partial \left(e^{-i\omega_z t}\hat{U}'_{+}(t)\right)}{\partial t} = i\left\{-i\omega_z e^{-i\omega_z t}\hat{U}'_{+}(t) + e^{-i\omega_z t}\frac{\partial \hat{U}'_{+}(t)}{\partial t}\right\} = -\omega_0 e^{-i\omega_z t}\hat{U}'_{+}(t) - \frac{\omega_1}{\sqrt{2}} e^{-i\omega_z t}\hat{U}'_{0}(t)$$

$$\Longrightarrow e^{-i\omega_z t}\left\{\omega_z \hat{U}'_{+}(t) + i\frac{\partial \hat{U}'_{+}(t)}{\partial t}\right\} = \left\{-\omega_0 \hat{U}'_{+}(t) - \frac{\omega_1}{\sqrt{2}}\hat{U}'_{0}(t)\right\} e^{-i\omega_z t}$$

$$\Longrightarrow i\frac{\partial \hat{U}'_{+}(t)}{\partial t} = -(\omega_0 + \omega_z)\hat{U}'_{+}(t) - \frac{\omega_1}{\sqrt{2}}\hat{U}'_{0}(t) \tag{A.9}$$

(2)

$$i\frac{\partial \hat{U}'_{0}(t)}{\partial t} = -\frac{\omega_1}{\sqrt{2}}\left\{e^{i\omega_z t}e^{-i\omega_z t}\omega_0 \hat{U}'_{+}(t) - e^{-i\omega_z t}e^{i\omega_z t}\hat{U}'_{-}(t)\right\}$$

$$\Longrightarrow i\frac{\partial \hat{U}'_{0}(t)}{\partial t} = -\frac{\omega_1}{\sqrt{2}}\left\{\hat{U}'_{+}(t) + \hat{U}'_{-}(t)\right\} \tag{A.10}$$

(3)

$$i\frac{\partial \left(e^{i\omega_z t}\hat{U}'_{-}(t)\right)}{\partial t} = -\frac{\omega_1}{\sqrt{2}} e^{i\omega_z t}\hat{U}'_{0}(t) + \omega_0 e^{i\omega_z t}\hat{U}'_{-}(t)$$

$$i\frac{\partial \left\{e^{i\omega_z t}\hat{U}'_{-}(t)\right\}}{\partial t} = i\left\{i\omega_z e^{i\omega_z t}\hat{U}'_{-}(t) + e^{i\omega_z t}\frac{\partial \hat{U}'_{-}(t)}{\partial t}\right\} = \omega_0 e^{i\omega_z t}\hat{U}'_{-}(t) - \frac{\omega_1}{\sqrt{2}} e^{i\omega_z t}\hat{U}'_{0}(t)$$

$$e^{i\omega_z t}\left\{-\omega_z \hat{U}'_{-}(t) + i\frac{\partial \hat{U}'_{-}(t)}{\partial t}\right\} = \left\{\omega_0 \hat{U}'_{-}(t) - \frac{\omega_1}{\sqrt{2}}\hat{U}'_{0}(t)\right\} e^{i\omega_z t}$$

$$\Longrightarrow i\frac{\partial \hat{U}'_{-}(t)}{\partial t} = (\omega_0 + \omega_z)\hat{U}'_{-}(t) - \frac{\omega_1}{\sqrt{2}}\hat{U}'_{0}(t) \tag{A.11}$$

Hence, the matrix form of the modified Schrodinger equation becomes:

$$
\begin{aligned}
i\frac{\partial \psi'}{\partial t} &= \hat{H}'(t)\psi' \Longrightarrow i\frac{\partial \hat{U}'(t)}{\partial t} = \hat{H}'(t)\hat{U}'(t) \\
i\begin{pmatrix} \frac{\partial \hat{U}'_+(t)}{\partial t} \\ \frac{\partial \hat{U}'_0(t)}{\partial t} \\ \frac{\partial \hat{U}'_-(t)}{\partial t} \end{pmatrix} &= \begin{pmatrix} -\Big(\omega_0+\omega_z\Big)\hat{U}'_+(t) - \frac{\omega_1}{\sqrt{2}}\hat{U}'_0(t) \\ -\frac{\omega_1}{\sqrt{2}}\Big(\hat{U}'_+(t)+\hat{U}'_-(t)\Big) \\ -\frac{\omega_1}{\sqrt{2}}\hat{U}'_0(t) + \Big(\omega_0+\omega_z\Big)\hat{U}'_-(t) \end{pmatrix} \begin{pmatrix} \frac{\partial \hat{U}'_+(t)}{\partial t} \\ \frac{\partial \hat{U}'_0(t)}{\partial t} \\ \frac{\partial \hat{U}'_-(t)}{\partial t} \end{pmatrix} \\
i\frac{\partial \hat{U}'(t)}{\partial t} &= \left\{ -(\omega_0+\omega_z)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} - \omega_1 \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix} \right\}\hat{U}'(t) \qquad \text{(A.12)}
\end{aligned}
$$

This further gives

$$
i\frac{\partial \hat{U}'(t)}{\partial t} = \hat{H}'\hat{U}'(t) \qquad \text{(A.13)}
$$

where

$$
\hat{H}' = \{-(\omega_0+\omega_z)\hat{I}_z - \omega_1\hat{I}_x\} \qquad \text{(A.14)}
$$

Since $\hat{H}'$ is time-independent, the solution to the Eq. (A.13) can be easily calculated as follows:

$$
\begin{aligned}
\frac{\partial \hat{U}'(t)}{\partial t}) &= -i\hat{H}'\hat{U}'(t) \\
\int_{U'(0)}^{U'(t)} \frac{dU'}{U'} &= -i\hat{H}'\int_0^t dt \\
\ln \hat{U}'(t) - \ln \hat{U}'(0) &= \ln \frac{\hat{U}'(t)}{\hat{U}'(0)} = -i\hat{H}'t \\
\hat{U}'(t) &= \hat{U}'(0)e^{-i\hat{H}'t} \\
\hat{U}'(t) &= e^{-i\hat{H}'t} \qquad \text{(A.15)}
\end{aligned}
$$

A.2 The solution of the schrodinger equations

The full time evolution operator, $\hat{U}(t)$, in Eq. (3.59) can be rewritten as:

$$
\begin{aligned}
\hat{U}(t) &= e^{i\omega_z t\hat{I}_z}e^{-i\hat{H}'t} = e^{i\omega_z t\hat{I}_z}e^{i\alpha\hat{M}} \\
&= \begin{pmatrix} e^{i\omega_z t} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\omega_z t} \end{pmatrix} e^{i\alpha\hat{M}}. \qquad \text{(A.16)}
\end{aligned}
$$

To have in hand an explicit formula of $e^{i\alpha\hat{M}}$, we must apply the following trick. Since $\hat{M}$-is an operator of 3×3 matrix the exponential of it can be evaluated by using Taylor expansion as follows:

$$
e^{i\alpha\hat{M}} = \sum_{n=0}^{\infty}\frac{(i\alpha\hat{M})^n}{n!} = \hat{1} + i\alpha\hat{M} - \frac{\alpha^2\hat{M}^2}{2!} - i\frac{\alpha^3\hat{M}^3}{3!} + \frac{\alpha^4\hat{M}^4}{4!} + i\frac{\alpha^5\hat{M}^5}{5!} - \frac{\alpha^6\hat{M}^6}{6!} - \ldots.. \qquad \text{(A.17)}
$$

By collecting odd terms together and even terms together we will have

$$
e^{i\alpha\hat{M}} = \big(\hat{1} - \frac{\alpha^2\hat{M}^2}{2!} + \frac{\alpha^4\hat{M}^4}{4!} - \frac{\alpha^6\hat{M}^6}{6!} + \ldots\big) + i\Big(\alpha\hat{M} - \frac{\alpha^3\hat{M}^3}{3!} + \frac{\alpha^5\hat{M}^5}{5!} - \ldots\Big) \qquad \text{(A.18)}
$$

Since, $\hat{M}^2 - \hat{M}^2 = 0$, so adding it to the right side of Eq. (A.18) can not change the equation, rather helps us to have the mathematically known form of equation as follows:

$$e^{i\alpha\hat{M}} = \hat{1} - \hat{M}^2 + \hat{M}^2\Big(1 - \frac{\alpha^2}{2!} + \frac{\alpha^4\hat{M}^2}{4!} - \frac{\alpha^6\hat{M}^4}{6!} + ...\Big) + i\Big(\alpha\hat{M} - \frac{\alpha^3\hat{M}^3}{3!} + \frac{\alpha^5\hat{M}^5}{5!} - ...\Big) \quad \text{(A.19)}$$

Now using the matrix form of $\hat{I}_z$ and $\hat{I}_x$, $\hat{M}$ can be expressed as:

$$\begin{aligned}
\hat{M} &= \hat{I}_z\cos\theta + \hat{I}_x\sin\theta = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\cos\theta + \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix}\sin\theta \\
&= \begin{pmatrix} \cos\theta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\cos\theta \end{pmatrix} + \begin{pmatrix} 0 & \frac{\sin\theta}{\sqrt{2}} & 0 \\ \frac{\sin\theta}{\sqrt{2}} & 0 & \frac{\sin\theta}{\sqrt{2}} \\ 0 & \frac{\sin\theta}{\sqrt{2}} & 0 \end{pmatrix}
\end{aligned}$$

which further gives us

$$\hat{M} = \begin{pmatrix} \cos\theta & \frac{1}{\sqrt{2}}\sin\theta & 0 \\ \frac{1}{\sqrt{2}}\sin\theta & 0 & \frac{1}{\sqrt{2}}\sin\theta \\ 0 & \frac{1}{\sqrt{2}}\sin\theta & -\cos\theta \end{pmatrix} \quad \text{(A.20)}$$

Then, $\hat{M}^2$ can be obtained by performing the matrix multiplication, $\hat{M} \times \hat{M}$, of Eq. A.20 as follows:

$$\begin{aligned}
\hat{M}^2 &= \begin{pmatrix} \cos\theta & \frac{1}{\sqrt{2}}\sin\theta & 0 \\ \frac{1}{\sqrt{2}}\sin\theta & 0 & \frac{1}{\sqrt{2}}\sin\theta \\ 0 & \frac{1}{\sqrt{2}}\sin\theta & -\cos\theta \end{pmatrix}\begin{pmatrix} \cos\theta & \frac{1}{\sqrt{2}}\sin\theta & 0 \\ \frac{1}{\sqrt{2}}\sin\theta & 0 & \frac{1}{\sqrt{2}}\sin\theta \\ 0 & \frac{1}{\sqrt{2}}\sin\theta & -\cos\theta \end{pmatrix} \\
&= \begin{pmatrix} \cos^2\theta + \frac{1}{2}\sin^2\theta & \frac{\cos\theta\sin\theta}{\sqrt{2}} & \frac{1}{2}\sin^2\theta \\ \frac{\cos\theta\sin\theta}{\sqrt{2}} & \sin^2\theta & -\frac{\cos\theta\sin\theta}{\sqrt{2}} \\ \frac{1}{2}\sin^2\theta & -\frac{\cos\theta\sin\theta}{\sqrt{2}} & \cos^2\theta + \frac{1}{2}\sin^2\theta \end{pmatrix}
\end{aligned}$$

or

$$\hat{M}^2 = \begin{pmatrix} 1 - \frac{1}{2}\sin^2\theta & \frac{\cos\theta\sin\theta}{\sqrt{2}} & \frac{1}{2}\sin^2\theta \\ \frac{\cos\theta\sin\theta}{\sqrt{2}} & \sin^2\theta & -\frac{\cos\theta\sin\theta}{\sqrt{2}} \\ \frac{1}{2}\sin^2\theta & -\frac{\cos\theta\sin\theta}{\sqrt{2}} & 1 - \frac{1}{2}\sin^2\theta \end{pmatrix} \quad \text{(A.21)}$$

Similarly $\hat{M}^3$ and $\hat{M}^4$ can be derived as follows:

$$\begin{aligned}
\hat{M}^3 &= \hat{M}^2\hat{M} \\
&= \begin{pmatrix} 1-\frac{1}{2}\sin^2\theta & \frac{\cos\theta\sin\theta}{\sqrt{2}} & \frac{1}{2}\sin^2\theta \\ \frac{\cos\theta\sin\theta}{\sqrt{2}} & \sin^2\theta & -\frac{\cos\theta\sin\theta}{\sqrt{2}} \\ \frac{1}{2}\sin^2\theta & -\frac{\cos\theta\sin\theta}{\sqrt{2}} & 1-\frac{1}{2}\sin^2\theta \end{pmatrix} \begin{pmatrix} \cos\theta & \frac{1}{\sqrt{2}}\sin\theta & 0 \\ \frac{1}{\sqrt{2}}\sin\theta & 0 & \frac{1}{\sqrt{2}}\sin\theta \\ 0 & \frac{1}{\sqrt{2}}\sin\theta & -\cos\theta \end{pmatrix} \\
&= \begin{pmatrix} \cos\theta-\frac{1}{2}\cos\theta\sin^2\theta + \frac{1}{2}\cos\theta\sin^2\theta & \frac{\sin\theta}{\sqrt{2}}-\frac{\sin^3\theta}{2\sqrt{2}}+\frac{\sin^3\theta}{2\sqrt{2}} & \frac{1}{2}\cos\theta\sin^2\theta-\frac{1}{2}\cos\theta\sin^2\theta \\ \frac{\sin\theta}{\sqrt{2}}[\cos^2\theta+\sin^2\theta] & \frac{1}{2}\cos\theta\sin^2\theta-\frac{1}{2}\cos\theta\sin^2\theta & \frac{\sin\theta}{\sqrt{2}}[\cos^2\theta+\sin^2\theta] \\ \frac{1}{2}\cos\theta\sin^2\theta-\frac{1}{2}\cos\theta\sin^2\theta & \frac{\sin^3\theta}{2\sqrt{2}}+\frac{\sin\theta}{\sqrt{2}}-\frac{\sin^3\theta}{2\sqrt{2}} & -\frac{1}{2}\cos\theta\sin^2\theta-\cos\theta + \frac{1}{2}\cos\theta\sin^2\theta \end{pmatrix} \\
\hat{M}^3 &= \begin{pmatrix} \cos\theta & \frac{1}{\sqrt{2}}\sin\theta & 0 \\ \frac{1}{\sqrt{2}}\sin\theta & 0 & \frac{1}{\sqrt{2}}\sin\theta \\ 0 & \frac{1}{\sqrt{2}}\sin\theta & -\cos\theta \end{pmatrix} = \hat{M} \qquad \text{(A.22)}
\end{aligned}$$

From this we can obtain

$$\begin{aligned}
\hat{M}^4 &= \hat{M}^3\hat{M} = \hat{M}\hat{M} = \hat{M}^2 \\
&= \begin{pmatrix} 1-\frac{1}{2}\sin^2\theta & \frac{\cos\theta\sin\theta}{\sqrt{2}} & \frac{1}{2}\sin^2\theta \\ \frac{\cos\theta\sin\theta}{\sqrt{2}} & \sin^2\theta & -\frac{\cos\theta\sin\theta}{\sqrt{2}} \\ \frac{1}{2}\sin^2\theta & -\frac{\cos\theta\sin\theta}{\sqrt{2}} & 1-\frac{1}{2}\sin^2\theta \end{pmatrix} \qquad \text{(A.23)}
\end{aligned}$$

Now it is possible to conclude that $\hat{M}^{2n} = \hat{M}^2$ and $\hat{M}^{2n+1} = \hat{M}$. As a result Eq. (A.19) can be rewritten as:

$$e^{i\alpha\hat{M}} = \hat{1} - \hat{M}^2 + \hat{M}^2\Big(1-\frac{\alpha^2}{2!}+\frac{\alpha^4}{4!}-\frac{\alpha^6}{6!}+...\Big) + i\hat{M}(\alpha-\frac{\alpha^3}{3!}+\frac{\alpha^5}{5!}-\frac{\alpha^7}{7!}+...\Big) \qquad \text{(A.24)}$$

and again using the mathematical relations of the form:

$$\sin\alpha = \alpha - \frac{\alpha^3}{3!}+\frac{\alpha^5}{5!}-\frac{\alpha^7}{7!}+... \qquad \text{(A.25)}$$

$$\cos\alpha = 1 - \frac{\alpha^2}{2!}+\frac{\alpha^4}{4!}-\frac{\alpha^6}{6!}+... \qquad \text{(A.26)}$$

we do have

$$e^{i\alpha\hat{M}} = \hat{1} + i\hat{M}\sin\alpha - \Big(1-\cos\alpha\Big)\hat{M}^2 \qquad \text{(A.27)}$$

Then substituting Eqs. (A.20) and (A.21) into Eq. (A.27) we will have

$$e^{i\alpha\hat{M}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + i\sin\alpha \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ \frac{\sin\theta}{\sqrt{2}} & 0 & \frac{\sin\theta}{\sqrt{2}} \\ 0 & \frac{\sin\theta}{\sqrt{2}} & -\cos\theta \end{pmatrix} - \Big(1-\cos\alpha\Big)\hat{M}^2$$

Then by method of matrix addition

$$e^{i\alpha\hat{M}} = \begin{pmatrix} 1+i\cos\theta\sin\alpha & \frac{i\sin\theta\sin\alpha}{\sqrt{2}} & 0 \\ \frac{i\sin\theta\sin\alpha}{\sqrt{2}} & 1 & \frac{i\sin\theta\sin\alpha}{\sqrt{2}} \\ 0 & \frac{i\sin\theta\sin\alpha}{\sqrt{2}} & 1-i\cos\theta\sin\alpha \end{pmatrix} - (1-\cos\alpha) \begin{pmatrix} 1-\frac{1}{2}\sin^2\theta & \frac{\cos\theta\sin\theta}{\sqrt{2}} & \frac{1}{2}\sin^2\theta \\ \frac{\cos\theta\sin\theta}{\sqrt{2}} & \sin^2\theta & -\frac{\cos\theta\sin\theta}{\sqrt{2}} \\ \frac{1}{2}\sin^2\theta & -\frac{\cos\theta\sin\theta}{\sqrt{2}} & 1-\frac{1}{2}\sin^2\theta \end{pmatrix}$$

Again employing matrix addition and reordering terms will yield:

$$e^{i\alpha\hat{M}} = \begin{pmatrix} \frac{\sin^2\theta}{2} + \left(1 - \frac{\sin^2\theta}{2}\right)\cos\alpha & \frac{-\sin\theta}{\sqrt{2}}\Big(\cos\theta(1-\cos\alpha) & -\frac{\sin^2\theta}{2}(1-\cos\alpha) \\ +i\cos\theta\sin\alpha & -i\sin\theta\Big) & \\ \frac{-\sin\theta}{\sqrt{2}}\Big(\cos\theta(1-\cos\alpha) & 1-\sin^2\theta\,(1-\cos\alpha) & \frac{\sin\theta}{\sqrt{2}}\Big(\cos\theta(1-\cos\alpha) \\ -i\sin\theta\Big) & & +i\sin\theta\Big) \\ -\frac{\sin^2\theta}{2}(1-\cos\alpha) & \frac{\sin\theta}{\sqrt{2}}\Big(\cos\theta(1-\cos\alpha) & \frac{\sin^2\theta}{2} + (1-\frac{\sin^2\theta}{2})\cos\alpha \\ & +i\sin\theta\Big) & -i\cos\theta\sin\alpha \end{pmatrix} \tag{A.28}$$

Now, by substituting Eq. (A.28) into Eq. (A.16) we can express the full time evolution operator, $U\hat{(t)}$, as

$$\hat{U}(t) = e^{-i\omega_z t\hat{I}_z} e^{i\alpha\hat{M}} = \begin{pmatrix} \nu(t) & -e^{-i\omega_z t}\upsilon^*(t) & -\chi^*(t) \\ -\upsilon^*(t) & 1-2e^{-i\omega_z t}\chi(t) & \upsilon(t) \\ -\chi(t) & e^{i\omega_z t}\upsilon(t) & \nu^*(t) \end{pmatrix} \tag{A.29}$$

where we have used

$$\nu(t) = e^{-i\omega_z t}\left[\frac{\sin^2\theta}{2} + \left(1 - \frac{\sin^2\theta}{2}\right)\cos\alpha + i\cos\theta\sin\alpha\right]; \tag{A.30a}$$

$$\upsilon(t) = \frac{\sin\theta}{\sqrt{2}}\Big[\cos\theta(1-\cos\alpha) + i\sin\alpha\Big]; \tag{A.30b}$$

$$\chi(t) = e^{i\omega_z t}\left[\frac{\sin^2\theta}{2}(1-\cos\alpha)\right] \tag{A.30c}$$

On the other hand, we can find $\hat{U}^\dagger(t)$ as:

$$\hat{U}^\dagger(t) = \begin{pmatrix} \nu^*(t) & -\upsilon(t) & -\chi^*(t) \\ -e^{i\omega_z t}\upsilon(t) & 1-2e^{i\omega_z t}\chi^*(t) & e^{-i\omega_z t}\upsilon^*(t) \\ -\chi(t) & \upsilon^*(t) & \nu(t) \end{pmatrix} \tag{A.31}$$

A.3 Solving for Mean Polarizations

The mean value of any operator $\hat{A}$ can be given as

$$\langle\hat{A}\rangle = tr\{U^\dagger(t)\hat{A}U(t)\rho_{th}\} \tag{A.32}$$

For instance, we can compute for $\langle\hat{I}_z\rangle$, $\langle\hat{I}_x\rangle$ and $\langle\hat{I}_y\rangle$ as follows:

(1)

$$\begin{aligned} \langle\hat{I}_z\rangle &= tr\{U^\dagger(t)\hat{I}_z U(t)\rho_{th}\} \\ &= \frac{1}{D}tr\left\{\begin{pmatrix} \nu^* & -\upsilon & -\chi^* \\ -e^{i\omega_z t}\upsilon & 1-2e^{i\omega_z t}\chi^* & e^{-i\omega_z t}\upsilon^* \\ -\chi & \upsilon^* & \nu \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} \nu & -e^{-i\omega_z t}\upsilon^* & -\chi^* \\ -\upsilon^* & 1-2e^{-i\omega_z t}\chi & \upsilon \\ -\chi & e^{i\omega_z t}\upsilon & \nu^* \end{pmatrix}\begin{pmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{pmatrix}\right\} \\ &= \frac{1}{D}tr\begin{pmatrix} (\nu^*\nu - \chi\chi^*)A & (e^{i\omega_z t}\chi^*\upsilon - e^{-i\omega_z t}\nu^*\upsilon^*)B & 0 \\ (e^{-i\omega_z t}\upsilon^*\chi - e^{i\omega_z t}\upsilon\nu)A & 0 & (e^{i\omega_z t}\chi^*\upsilon - e^{-i\omega_z t}\nu^*\upsilon^*)C \\ 0 & (e^{-i\omega_z t}\upsilon^*\chi - e^{i\omega_z t}\upsilon\nu)B & -(\nu^*\nu - \chi\chi^*)C \end{pmatrix} \end{aligned} \tag{A.33}$$

where we have used $D = 3 + f^2$ and

$$A = (1 + 2f + f^2), \tag{A.34a}$$
$$B = (1 - f^2), \tag{A.34b}$$
$$C = (1 - 2f + f^2), \tag{A.34c}$$

Thus, the trace of the matrix above gives us:

$$\langle \hat{I}_z \rangle = \frac{1}{3+f^2}\{(|\nu|^2 - |\chi|^2)A + 0 - (|\nu|^2 - |\chi|^2)C\} \tag{A.35}$$

Then substituting back for A and C, will give us:

$$\begin{aligned}
\langle \hat{I}_z \rangle &= \frac{1}{3+f^2}\left\{(|\nu|^2 - |\chi|^2)(1+2f+f^2) + 0 - (|\nu|^2 - |\chi|^2)(1-2f+f^2)\right\} \\
&= \frac{1}{3+f^2}\left\{\left(|\nu|^2 - |\chi|^2\right)(2f) + 0 - \left(|\nu|^2 - |\chi|^2\right)(-2f)\right\} \\
\langle \hat{I}_z \rangle &= \frac{4f}{3+f^2}\left(|\nu|^2 - |\chi|^2\right)
\end{aligned} \tag{A.36}$$

Now using Eqs. (A.30) we can obtain $|\nu|^2$ and $|\chi|^2$ as:

$$\begin{aligned}
|\nu|^2 &= \nu(t)\nu^*(t) = e^{-i\omega_z t}\left[\frac{\sin^2\theta}{2} + \left(1 - \frac{\sin^2\theta}{2}\right)\cos\alpha + i\cos\theta\sin\alpha\right] \times \\
&\quad e^{i\omega_z t}\left[\frac{\sin^2\theta}{2} + \left(1 - \frac{\sin^2\theta}{2}\right)\cos\alpha - i\cos\theta\sin\alpha\right] \\
&= \frac{\sin^4\theta}{4} + \sin^2\theta\cos\alpha - \frac{\sin^4\theta\cos\alpha}{2} + \frac{\sin^4\theta\cos^2\alpha}{4} + \cos^2\theta \\
|\nu|^2 &= \frac{\sin^4\theta}{4}(1-\cos\alpha)^2 + \sin^2\theta\cos\alpha + \cos^2\theta
\end{aligned} \tag{A.37}$$

and

$$\begin{aligned}
|\chi|^2 &= \chi(t)\chi^*(t) = e^{i\omega_z t}\left[\frac{\sin^2\theta}{2}(1-\cos\alpha)\right] \times e^{-i\omega_z t}\left[\frac{\sin^2\theta}{2}(1-\cos\alpha)\right] \\
|\chi|^2 &= \frac{\sin^4\theta}{4}(1-\cos\alpha)^2
\end{aligned} \tag{A.38}$$

Then substituting these into Eq. (A.36) will yield:

$$\begin{aligned}
\langle \hat{I}_z \rangle &= \frac{4f}{3+f^2}\left(|\nu|^2 - |\chi|^2\right) = \frac{4f}{3+f^2}\left(\cos^2\theta + \sin^2\theta\cos\alpha\right) \\
&= \frac{4f}{3+f^2}\left(1 - \sin^2\theta + \sin^2\theta\cos\alpha\right) \\
\langle \hat{I}_z \rangle &= \frac{4f}{3+f^2}\left\{1 - \sin^2\theta(1-\cos\alpha)\right\}
\end{aligned} \tag{A.39}$$

where we have used $\cos^2\theta = 1 - \sin^2\theta$.

(2)

$$\begin{aligned}
\langle \hat{I}_x \rangle &= tr\{U^{\dagger}(t)\hat{I}_x U(t)\rho_{th}\} \\
&= \frac{1}{D} tr\left\{ \begin{pmatrix} \nu^* & -\upsilon & -\chi^* \\ -e^{i\omega_z t}\upsilon & 1-2e^{i\omega_z t}\chi^* & e^{-i\omega_z t}\upsilon^* \\ -\chi & \upsilon^* & \nu \end{pmatrix} \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} \nu & -e^{-i\omega_z t}\upsilon^* & -\chi^* \\ -\upsilon^* & 1-2e^{-i\omega_z t}\chi & \upsilon \\ -\chi & e^{i\omega_z t}\upsilon & \nu^* \end{pmatrix} \begin{pmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{pmatrix} \right. \\
&= \frac{1}{D} tr\left\{ \begin{pmatrix} \nu^* & -\upsilon & -\chi^* \\ -e^{i\omega_z t}\upsilon & 1-2e^{i\omega_z t}\chi^* & e^{-i\omega_z t}\upsilon^* \\ -\chi & \upsilon^* & \nu \end{pmatrix} \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} \nu A & -e^{-i\omega_z t}\upsilon^* B & -\chi^* C \\ -\upsilon^* A & (1-2e^{-i\omega_z t}\chi)B & \upsilon C \\ -\chi A & e^{i\omega_z t}\upsilon B & \nu^* C \end{pmatrix} \right\} \\
&= \frac{1}{D} tr\left\{ \begin{pmatrix} \nu^* & -\upsilon & -\chi^* \\ -e^{i\omega_z t}\upsilon & 1-2e^{i\omega_z t}\chi^* & e^{-i\omega_z t}\upsilon^* \\ -\chi & \upsilon^* & \nu \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} -\upsilon^* A & (1-2e^{-i\omega_z t}\chi)B & \upsilon C \\ (\nu-\chi)A & (e^{i\omega_z t}\upsilon - e^{-i\omega_z t}\upsilon^*)B & (\nu^*-\chi^*)C \\ -\upsilon^* A & (1-2e^{-i\omega_z t}\chi)B & \upsilon C \end{pmatrix} \right\}
\end{aligned}$$

As a result of further multiplication one can obtain:

$$\begin{aligned}
\langle \hat{I}_x \rangle &= \frac{1}{\sqrt{2}(3+f^2)} tr \begin{pmatrix} (s_1+s_1^*)A & s_2 B & 0 \\ s_2^* A & (s_4+s_4^*)B & s_3 C \\ 0 & s_3^* B & -(s_1+s_1^*)C \end{pmatrix} \\
\langle \hat{I}_x \rangle &= \frac{1}{\sqrt{2}(3+f^2)} \{(s_1+s_1^*)A + (s_4+s_4^*)B - (s_1+s_1^*)C\} \qquad \text{(A.40)}
\end{aligned}$$

where
$s_1 = \upsilon\chi - \nu\upsilon$ $s_2 = e^{-i\omega_z t}|\upsilon|^2 + 2e^{-i\omega_z t}|\chi|^2 - e^{i\omega_z t}\upsilon^2 - 2e^{-i\omega_z t}\nu^*\chi + \nu^* - \chi^*$
$s_3 = e^{-i\omega_z t}|\upsilon|^2 + 2e^{i\omega_z t}\chi^{*2} - e^{i\omega_z t}\upsilon^2 - 2e^{i\omega_z t}\chi^*\nu^* + \nu^* - \chi^*$
$s_4 = 2\upsilon\chi - 2e^{2i\omega_z t}\chi^*\upsilon$
Now substituting back for $A = 1+2f+f^2$, $B = 1-f^2$ and $C = 1-2f+f^2$ we will have

$$\langle \hat{I}_x \rangle = \frac{1}{\sqrt{2}(3+f^2)} \Big\{ 2f(s_1+s_1^*) + (s_1+s_1^*)(1+f^2) + (s_4+s_4^*)(1-f^2) - (-2f)(s_1+s_1^*) - (s_1+s_1^*)(1+f^2) \Big\}$$

$$\langle \hat{I}_x \rangle = \frac{1}{\sqrt{2}(3+f^2)} \Big\{ 4f(s_1+s_1^*) + (s_4+s_4^*)(1-f^2) \Big\} \qquad \text{(A.41)}$$

Again, substituting back for s_1, s_4 and using the fact that $\upsilon\chi = e^{2i\omega_z t}\chi^*\upsilon$ we will obtain

$$\begin{aligned}
\langle \hat{I}_x \rangle &= \frac{1}{\sqrt{2}(3+f^2)} \Big\{ 4f\Big[(\upsilon\chi - \upsilon\nu) + (\upsilon^*\chi^* - \upsilon^*\nu^*)\Big] + (\underbrace{2\upsilon\chi - 2\chi^*\upsilon e^{2i\omega_z t}}_{0} \\
&\quad + \underbrace{2\upsilon^*\chi^* - 2\chi\upsilon^* e^{-2i\omega_z t}}_{0})(1-f^2) \Big\} \\
&= \frac{4f}{\sqrt{2}(3+f^2)} \Big\{ (\upsilon\chi - \upsilon\nu) + (\upsilon^*\chi^* - \upsilon^*\nu^*) \Big\}
\end{aligned}$$

or

$$\langle \hat{I}_x \rangle = \frac{4f}{\sqrt{2}(3+f^2)} \Big\{ (\upsilon\chi + \upsilon^*\chi^*) - (\upsilon\nu + \upsilon^*\nu^*) \Big\} \qquad \text{(A.42)}$$

Then by substituting for $\upsilon(t), \nu(t)$ and $\chi(t)$ from Eqs. (A.30) we will have:

$$\begin{aligned}
\upsilon\chi &= \frac{\sin\theta}{\sqrt{2}}\Big[\cos\theta(1-\cos\alpha)+i\sin\alpha\Big]\times e^{i\omega_z t}\left[\frac{\sin^2\theta}{2}(1-\cos\alpha)\right] \\
&= \frac{\sin^3\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)^2\frac{e^{i\omega_z t}}{2}+i\frac{\sin^3\theta}{\sqrt{2}}\sin\alpha(1-\cos\alpha)\frac{e^{i\omega_z t}}{2} \qquad \text{(A.43a)} \\
\upsilon^*\chi^* &= \frac{\sin\theta}{\sqrt{2}}\Big[\cos\theta(1-\cos\alpha)-i\sin\alpha\Big]\times e^{-i\omega_z t}\left[\frac{\sin^2\theta}{2}(1-\cos\alpha)\right] \\
&= \frac{\sin^3\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)^2\frac{e^{-i\omega_z t}}{2}-i\frac{\sin^3\theta}{\sqrt{2}}\sin\alpha(1-\cos\alpha)\frac{e^{-i\omega_z t}}{2} \qquad \text{(A.43b)} \\
\nu\upsilon &= e^{-i\omega_z t}\left[\frac{\sin^2\theta}{2}+\left(1-\frac{\sin^2\theta}{2}\right)\cos\alpha+i\cos\theta\sin\alpha\right]\times\frac{\sin\theta}{\sqrt{2}}\Big[\cos\theta(1-\cos\alpha)+i\sin\alpha\Big] \\
&= \frac{\sin^3\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)^2\frac{e^{-i\omega_z t}}{2}-i\frac{\sin^3\theta}{\sqrt{2}}\sin\alpha(1-\cos\alpha)\frac{e^{-i\omega_z t}}{2} \\
&\quad +i\frac{\sin\theta}{\sqrt{2}}\sin\alpha e^{-i\omega_z t}-\frac{\sin\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)e^{-i\omega_z t} \qquad \text{(A.43c)} \\
\nu^*\upsilon^* &= e^{i\omega_z t}\left[\frac{\sin^2\theta}{2}+\left(1-\frac{\sin^2\theta}{2}\right)\cos\alpha-i\cos\theta\sin\alpha\right]\times\frac{\sin\theta}{\sqrt{2}}\Big[\cos\theta(1-\cos\alpha)-i\sin\alpha\Big] \\
&= \frac{\sin^3\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)^2\frac{e^{i\omega_z t}}{2}+i\frac{\sin^3\theta}{\sqrt{2}}\sin\alpha(1-\cos\alpha)\frac{e^{i\omega_z t}}{2} \\
&\quad -i\frac{\sin\theta}{\sqrt{2}}\sin\alpha e^{i\omega_z t}-\frac{\sin\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)e^{i\omega_z t} \qquad \text{(A.43d)}
\end{aligned}$$

By using the trigonometric relations of the form:

$$\sin\omega_z t = \left(\frac{e^{i\omega_z t}-e^{-i\omega_z t}}{2i}\right) \qquad \text{(A.44a)}$$

$$\cos\omega_z t = \left(\frac{e^{i\omega_z t}+e^{-i\omega_z t}}{2i}\right) \qquad \text{(A.44b)}$$

we will get:

$$\begin{aligned}
(\upsilon\chi+\upsilon^*\chi^*) &= \frac{\sin^3\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)^2\left(\frac{e^{i\omega_z t}+e^{-i\omega_z t}}{2}\right)-\frac{\sin^3\theta}{\sqrt{2}}\sin\alpha(1-\cos\alpha)\left(\frac{e^{i\omega_z t}-e^{-i\omega_z t}}{2i}\right) \\
(\upsilon\chi+\upsilon^*\chi^*) &= \frac{\sin^3\theta}{\sqrt{2}}\cos\theta\cos\omega_z t(1-\cos\alpha)^2-\frac{\sin^3\theta}{\sqrt{2}}\sin\alpha\sin\omega_z t(1-\cos\alpha) \qquad \text{(A.45a)} \\
(\upsilon\nu+\upsilon^*\nu^*) &= \frac{\sin^3\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)^2\left(\frac{e^{i\omega_z t}+e^{-i\omega_z t}}{2}\right)-\frac{\sin^3\theta}{\sqrt{2}}\sin\alpha(1-\cos\alpha)\left(\frac{e^{i\omega_z t}-e^{-i\omega_z t}}{2i}\right) \\
&\quad +2\frac{\sin\theta}{\sqrt{2}}\sin\alpha\left(\frac{e^{i\omega_z t}-e^{-i\omega_z t}}{2i}\right)-2\frac{\sin\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)\left(\frac{e^{i\omega_z t}+e^{-i\omega_z t}}{2}\right) \\
(\upsilon\nu+\upsilon^*\nu^*) &= \frac{\sin^3\theta}{\sqrt{2}}\cos\theta\cos\omega_z t(1-\cos\alpha)^2-\frac{\sin^3\theta}{\sqrt{2}}\sin\alpha\sin\omega_z t(1-\cos\alpha) \\
&\quad +2\frac{\sin\theta}{\sqrt{2}}\sin\alpha\sin\omega_z t-2\frac{\sin\theta}{\sqrt{2}}\cos\theta\cos\omega_z t(1-\cos\alpha) \qquad \text{(A.45b)}
\end{aligned}$$

Thus, the full expression of the polarization along x-axis can be expressed as:

$$\langle \hat{I}_x \rangle = \frac{4f}{\sqrt{2}(3+f^2)}\Big\{(\upsilon\chi + \upsilon^*\chi^*) - (\upsilon\nu + \upsilon^*\nu^*)\Big\}$$
$$= \frac{4f}{\sqrt{2}(3+f^2)}\Big\{\Big[\frac{\sin^3\theta}{\sqrt{2}}\cos\theta\cos\omega_z t(1-\cos\alpha)^2 - \frac{\sin^3\theta}{\sqrt{2}}\sin\alpha\sin\omega_z t(1-\cos\alpha)\Big] \quad \text{(A.46a)}$$
$$\Big[-\frac{\sin^3\theta}{\sqrt{2}}\cos\theta\cos\omega_z t(1-\cos\alpha)^2 + \frac{\sin^3\theta}{\sqrt{2}}\sin\alpha\sin\omega_z t(1-\cos\alpha) - 2\frac{\sin\theta}{\sqrt{2}}\sin\alpha\sin\omega_z t \quad \text{(A.46b)}$$
$$+2\frac{\sin\theta}{\sqrt{2}}\cos\theta\cos\omega_z t(1-\cos\alpha)\Big]\Big\}$$

$$\langle \hat{I}_x \rangle = \frac{4f\sin\theta}{(3+f^2)}\Big\{\cos\theta\cos\omega_z t(1-\cos\alpha) - \sin\alpha\sin\omega_z t\Big\} \quad \text{(A.47)}$$

(3) In the same manner to the above derivation of $\langle \hat{I}_x \rangle$:

$$\begin{aligned}
\langle \hat{I}_y \rangle &= tr\{U^\dagger(t)\hat{I}_y U(t)\rho_{th}\} \\
&= \frac{1}{D}tr\left\{\begin{pmatrix} \nu^* & -\upsilon & -\chi^* \\ -e^{i\omega_z t}\upsilon & 1-2e^{i\omega_z t}\chi^* & e^{-i\omega_z t}\upsilon^* \\ -\chi & \upsilon^* & \nu \end{pmatrix}\begin{pmatrix} 0 & \frac{-i}{\sqrt{2}} & 0 \\ \frac{i}{\sqrt{2}} & 0 & \frac{-i}{\sqrt{2}} \\ 0 & \frac{i}{\sqrt{2}} & 0 \end{pmatrix}\begin{pmatrix} \nu & -e^{-i\omega_z t}\upsilon^* & -\chi^* \\ -\upsilon^* & 1-2e^{-i\omega_z t}\chi & \upsilon \\ -\chi & e^{i\omega_z t}\upsilon & \nu^* \end{pmatrix}\begin{pmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{pmatrix}\right. \\
&= \frac{1}{D}tr\left\{\begin{pmatrix} \nu^* & -\upsilon & -\chi^* \\ -e^{i\omega_z t}\upsilon & 1-2e^{i\omega_z t}\chi^* & e^{-i\omega_z t}\upsilon^* \\ -\chi & \upsilon^* & \nu \end{pmatrix}\begin{pmatrix} 0 & \frac{-i}{\sqrt{2}} & 0 \\ \frac{i}{\sqrt{2}} & 0 & \frac{-i}{\sqrt{2}} \\ 0 & \frac{i}{\sqrt{2}} & 0 \end{pmatrix}\begin{pmatrix} \nu A & -e^{-i\omega_z t}\upsilon^* B & -\chi^* C \\ -\upsilon^* A & (1-2e^{-i\omega_z t}\chi)B & \upsilon C \\ -\chi A & e^{i\omega_z t}\upsilon B & \nu^* C \end{pmatrix}\right\} \\
&= \frac{1}{D}tr\left\{\begin{pmatrix} \nu^* & -\upsilon & -\chi^* \\ -e^{i\omega_z t}\upsilon & 1-2e^{i\omega_z t}\chi^* & e^{-i\omega_z t}\upsilon^* \\ -\chi & \upsilon^* & \nu \end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix} i\upsilon^* A & -i(1-2e^{-i\omega_z t}\chi)B & -i\upsilon C \\ i(\nu+\chi)A & -i(e^{i\omega_z t}\upsilon + e^{-i\omega_z t}\upsilon^*)B & -i(\nu^*-\chi^*)C \\ -i\upsilon^* A & i(1-2e^{-i\omega_z t}\chi)B & i\upsilon C \end{pmatrix}\right\}
\end{aligned}$$

Then the polarization along y-axis can be give in a simplified from as:

$$\begin{aligned}
\langle \hat{I}_y \rangle &= \frac{i}{\sqrt{2}(3+f^2)}tr\begin{pmatrix} (-s_1+s_1^*)A & s_2^* B & 0 \\ -s_2 A & (-s_4+s_4^*)B & s_3^* C \\ 0 & -s_3 B & (s_1-s_1^*)C \end{pmatrix} \\
&= \frac{i}{\sqrt{2}(3+f^2)}\Big\{(-s_1+s_1^*)A + (-s_4+s_4^*)B + (s_1-s_1^*)C\Big\} \qquad \text{(A.48)}
\end{aligned}$$

where

$s_1 = \upsilon\chi + \nu\upsilon$
$s_2 = e^{i\omega_z t}|\upsilon|^2 + e^{-i\omega_z t}\upsilon^{*2} + 2e^{i\omega_z t}|\chi|^2 + 2e^{i\omega_z t}\chi^*\nu - \nu - \chi$
$s_3 = e^{i\omega_z t}|\upsilon|^2 + e^{-i\omega_z t}\upsilon^{*2} + 2e^{-i\omega_z t}\chi^2 + 2e^{-i\omega_z t}\nu\chi - \nu - \chi$
$s_4 = 2\upsilon\chi - 2e^{2i\omega_z t}\chi^*\upsilon$

For the same reason to the case in $\langle \hat{I}_x \rangle$, $(-s_4+s_4^*) = 0$ and hence, by substituting for A, B and C, one will obtain:

$$\langle \hat{I}_y \rangle = \frac{i}{\sqrt{2}(3+f^2)}\Big\{(-s_1+s_1^*)(1+2f+f^2)+(-s_4+s_4^*)(1-f^2)+(s_1-s_1^*)(1-2f+f^2)\Big\}$$
$$= \frac{4fi}{\sqrt{2}(3+f^2)}\Big\{(-s_1+s_1^*)\Big\} \tag{A.49}$$

Again, substituting back for s_1, s_1^* will give us:

$$\langle \hat{I}_y \rangle = \frac{4fi}{\sqrt{2}(3+f^2)}\Big\{(-\upsilon\chi+\upsilon^*\chi^*)+(-\nu\upsilon+\nu^*\upsilon^*)\Big\} \tag{A.50}$$

But, by using Eqs. (A.43) one can obtain:

$$(-\upsilon\chi+\upsilon^*\chi^*) = -i\frac{\sin^3\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)^2\Big(\frac{e^{i\omega_z t}-e^{-i\omega_z t}}{2i}\Big)-i\frac{\sin^3\theta}{\sqrt{2}}\sin\alpha(1-\cos\alpha)\Big(\frac{e^{i\omega_z t}+e^{-i\omega_z t}}{2}\Big) \tag{A.51a}$$

$$(-\upsilon\nu+\upsilon^*\nu^*) = i\frac{\sin^3\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)^2\Big(\frac{e^{i\omega_z t}-e^{-i\omega_z t}}{2i}\Big)+i\frac{\sin^3\theta}{\sqrt{2}}\sin\alpha(1-\cos\alpha)\Big(\frac{e^{i\omega_z t}+e^{-i\omega_z t}}{2}\Big)$$
$$-2i\frac{\sin\theta}{\sqrt{2}}\sin\alpha\Big(\frac{e^{i\omega_z t}+e^{-i\omega_z t}}{2}\Big)-2i\frac{\sin\theta}{\sqrt{2}}\cos\theta(1-\cos\alpha)\Big(\frac{e^{i\omega_z t}-e^{-i\omega_z t}}{2i}\Big) \tag{A.51b}$$

As a result, $\langle \hat{I}_y \rangle$ will be:

$$\langle \hat{I}_y \rangle = \frac{4fi}{\sqrt{2}(3+f^2)}\Big\{(-\upsilon\chi+\upsilon^*\chi^*)+(-\upsilon\nu+\upsilon^*\nu^*)\Big\}$$
$$= \frac{4fi\cdot i}{\sqrt{2}\cdot\sqrt{2}(3+f^2)}\Big\{\Big(-\sin^3\theta\cos\theta\sin\omega_z t(1-\cos\alpha)^2-\sin^3\theta\sin\alpha\cos\omega_z t(1-\cos\alpha)\Big) \tag{A.52a}$$
$$+\Big(\sin^3\theta\cos\theta\sin\omega_z t(1-\cos\alpha)^2+\sin^3\theta\sin\alpha\cos\omega_z t(1-\cos\alpha)-2\sin\theta\sin\alpha\cos\omega_z t$$
$$-2\sin\theta\cos\theta\sin\omega_z t(1-\cos\alpha)\Big)\Big\}$$

$$\langle \hat{I}_y \rangle = \frac{4f\sin\theta}{(3+f^2)}\Big\{\cos\theta\cos\omega_z t(1-\cos\alpha)+\sin\alpha\sin\omega_z t\Big\} \tag{A.53}$$

A.4 Solving for Characteristic Function of the Work.

Then the characteristic function of the work done on/by the system can be calculated as follows:

$$G(r) = tr\{\hat{U}^\dagger(\tau)e^{irH_f}\hat{U}(\tau)e^{-irH_i}\rho_{th}\} = tr\{\hat{U}^\dagger(\tau)e^{-ir\omega_0\hat{I}_z}\hat{U}(\tau)e^{ir\omega_0\hat{I}_z}\rho_{th}\} \tag{A.54}$$

As usual, the matrix representation of the operator $\hat{I}_z$ is diagonal in the Zeeman basis, with the quantum numbers m = 1, 0, âˆ’1 on the diagonal, so that its exponentials can be given in matrix form as:

$$e^{-ir\omega_0\hat{I}_z} = \begin{pmatrix} e^{-ir\omega_0} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{ir\omega_0} \end{pmatrix} \tag{A.55}$$

Then substituting Eqs. (A.55), into Eq. (A.54) and substituting for $\hat{U}(t)$ from Eq. (A.29), for $\hat{U}^{\dagger}(t)$ from Eq. (A.31), for ρ_{th} from Eq. (3.8) into Eq. (A.54) the characteristic function can be rewritten as

$$G(r) = tr\left\{ \begin{pmatrix} \nu^* & -\upsilon & -\chi \\ e^{-i\omega t}\upsilon & 1-e^{i\omega t}\chi^* & e^{i\omega t}\upsilon^* \\ -\chi^* & \upsilon^* & \nu \end{pmatrix} \begin{pmatrix} e^{ir\omega_0} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-ir\omega_0} \end{pmatrix} \begin{pmatrix} \nu & e^{i\omega t}\upsilon^* & \chi \\ -\upsilon^* & 1-e^{-i\omega t}\chi & \upsilon \\ -\chi^* & e^{-i\omega t}\upsilon & \nu^* \end{pmatrix} D \right\} \tag{A.56}$$

where

$$D = e^{ir\omega_0 \hat{I}_z}\rho_{th} = \begin{pmatrix} e^{-ir\omega_0} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{ir\omega_0} \end{pmatrix} \begin{pmatrix} A & 0 & 0 \\ 0 & C & 0 \\ 0 & 0 & B \end{pmatrix} = \begin{pmatrix} e^{-ir\omega_0}A & 0 & 0 \\ 0 & C & 0 \\ 0 & 0 & e^{ir\omega_0}B \end{pmatrix}$$

for $A' = \frac{1+2f+f^2}{3+f^2}$, $C' = \frac{1-f^2}{3+f^2}$, $B' = \frac{1-2f+f^2}{3+f^2}$.

Then after long matrix multiplication of Eq. (A.56) we obtain:

$$\begin{aligned} G(r) &= \frac{1}{3+f^2} tr \begin{pmatrix} (1,1) & (1,0) & (1,-1) \\ (0,1) & (0,0) & (0,-1) \\ (-1,1) & (-1,0) & (-1,-1) \end{pmatrix} \\ &= \frac{1}{3+f^2}\Big\{(1,1)+(0,0)+(-1,-1)\Big\} \end{aligned} \tag{A.57}$$

Where

$$(1,1) = \Big(|\nu|^2 + |\upsilon|^2 e^{ir\omega_0} + |\chi|^2 e^{2ir\omega_0}\Big)(1+2f+f^2) \tag{A.58}$$

$$(1,0) = \Big(\nu^*\upsilon^* e^{i\omega t}e^{-ir\omega_0} - \chi\upsilon e^{-i\omega t}e^{ir\omega_0} + \upsilon\chi e^{-i\omega t} - \upsilon\Big)(1-f^2) \tag{A.59}$$

$$(1,-1) = \Big(-\nu^*\chi e^{-2ir\omega_0} - \upsilon^2 e^{-ir\omega_0} - \chi\nu^*\Big)(1-2f+f^2) \tag{A.60}$$

$$(0,1) = \Big(\upsilon\nu e^{-i\omega t} - \upsilon^* e^{ir\omega_0} + \chi^*\upsilon^* e^{i\omega t}e^{ir\omega_0} - \upsilon^*\chi^* e^{i\omega t}e^{2ir\omega_0}\Big)(1+2f+f^2) \tag{A.61}$$

$$(0,0) = \Big(|\upsilon|^2 e^{-ir\omega_0} + 1 - \chi e^{-i\omega t} - \chi^* e^{i\omega t} + |\chi|^2 + |\upsilon|^2 e^{ir\omega_0}\Big)(1-f^2) \tag{A.62}$$

$$(0,-1) = \Big(-\upsilon\chi e^{-i\omega t}e^{-2ir\omega_0} + \upsilon e^{-ir\omega_0} - \upsilon\chi^* e^{i\omega t}e^{-ir\omega_0} + \nu^*\upsilon^* e^{i\omega t}\Big)(1-2f+f^2) \tag{A.63}$$

$$(-1,1) = \Big(-\nu\chi^* e^{2ir\omega_0} - \upsilon^{*2}e^{ir\omega_0} - \chi^*\nu\Big)(1+2f+f^2) \tag{A.64}$$

$$(-1,0) = \Big(-\chi^*\upsilon^* e^{i\omega t}e^{-ir\omega_0} + \nu\upsilon e^{-i\omega t}e^{ir\omega_0} - \upsilon^*\chi e^{-i\omega t} + \upsilon^*\Big)(1-f^2) \tag{A.65}$$

$$(-1,-1) = \Big(|\nu|^2 + |\upsilon|^2 e^{-ir\omega_0} + |\chi|^2 e^{-2ir\omega_0}\Big)(1-2f+f^2) \tag{A.66}$$

Hence the characteristic function of work becomes

$$\begin{aligned} G(r) = \frac{1}{3+f^2}\Big\{ &\Big(|\nu|^2 + |\upsilon|^2 e^{ir\omega_0} + |\chi|^2 e^{2ir\omega_0}\Big)(1+2f+f^2) \\ &+\Big(1 - \chi e^{-i\omega t} - \chi^* e^{i\omega t} + |\chi|^2 + |\upsilon|^2 e^{-ir\omega_0} + |\upsilon|^2 e^{ir\omega_0}\Big)(1-f^2) \\ &+\Big(|\nu|^2 + |\upsilon|^2 e^{-ir\omega_0} + |\chi|^2 e^{-2ir\omega_0}\Big)(1-2f+f^2)\Big\} \end{aligned} \tag{A.67}$$

or in a more simplified form

$$G(r) = \frac{1}{3+f^2}\Big\{2|\nu|^2(1+f^2)+\Big(1+|\chi|^2-\chi e^{-i\omega t}-\chi^* e^{i\omega t}\Big)(1-f^2)+2|\upsilon|^2 e^{ir\omega_0}(1+f)$$
$$+2|\upsilon|^2 e^{-ir\omega_0}(1-f)+|\chi|^2 e^{2ir\omega_0}(1+2f+f^2)+|\chi|^2 e^{-2ir\omega_0}(1-2f+f^2)\Big\} \qquad \text{(A.68)}$$

Declaration

I hereby declare that this Ph.D. dissertation is my original work and has not been presented for a degree in any other university. All sources of material used for the Ph.D. dissertation have been duly acknowledged.

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References

[1] Janet Anders and Massimiliano Esposito. "Focus on quantum thermodynamics". In: *New J. Phys* **19**.1 (2017), p. 010201. DOI: 10.1088/1367-2630/19/1/010201.

[2] Ulf W Gedde and FE Helmholtz. *Essential classical thermodynamics*. Springer, 2020.

[3] John HS Lee and Krishnaswami Ramamurthi. *Fundamentals of thermodynamics*. CRC Press, 2022.

[4] Zi-Kui Liu. "Computational thermodynamics and its applications". In: *Acta Materialia* **200** (2020), pp. 745–792. DOI: 10.1016/j.actamat.2020.08.008.

[5] Alexander Schuckert et al. "Probing finite-temperature observables in quantum simulators of spin systems with short-time dynamics". In: *Physical Review B* **107**.14 (2023), p. L140410. DOI: 10.1103/PhysRevB.107.L140410.

[6] Jaime Aspas-Caceres et al. "Folding Free Energy Determination of an RNA Three-Way Junction Using Fluctuation Theorems". In: *Entropy* **24**.7 (2022), p. 895. DOI: 10.3390/e24070895.

[7] Nadia Guebli and Abdelaali Boudjemaa. "Quantum self-bound droplets in Bose-Bose mixtures: Effects of higher-order quantum and thermal fluctuations". In: *Physical Review A* **104**.2 (2021), p. 023310. DOI: 10.1103/PhysRevA.104.023310.

[8] Adel Kara Slimane, Phillipp Reck, and Geneviève Fleury. "Simulating time-dependent thermoelectric transport in quantum systems". In: *Physical Review B* **101**.23 (2020), p. 235413. DOI: 10.1103/PhysRevB.101.235413.

[9] Atharv Joshi, Kyungjoo Noh, and Yvonne Y Gao. "Quantum information processing with bosonic qubits in circuit QED". In: *Quantum Science and Technology* **6**.3 (2021), p. 033001. DOI: 10.1088/2058-9565/abe989.

[10] Carlos HS Vieira et al. "Exploring quantum thermodynamics with NMR". In: *Journal of Magnetic Resonance Open* **16** (2023), p. 100105. DOI: 10.1016/j.jmro.2023.100105.

[11] Paolo Solinas, Mirko Amico, and Nino Zanghi. "Measurement of work and heat in the classical and quantum regimes". In: *Physical Review A* **103**.6 (2021), p. L060202. DOI: 10.1103/PhysRevA.103.L060202.

[12] Akram Youssry et al. "Experimental graybox quantum system identification and control". In: *npj Quantum Information* **10**.1 (2024), p. 9. DOI: 10.1038/s41534-023-00795-5.

[13] Harry JD Miller and Janet Anders. "Time-reversal symmetric work distributions for closed quantum dynamics in the histories framework". In: *New Journal of Physics* **19**.4 (2017), p. 062001. DOI: 10.1088/1367-2630/aa703f.

[14] Santiago Hernandez-Gomez et al. "Experimental test of fluctuation relations for driven open quantum systems with an NV center". In: *New Journal of Physics* **23**.6 (2021), p. 065004. DOI: 10.1088/1367-2630/abfc6a.

[15] Santiago Hernández-Gómez et al. "Experimental test of exchange fluctuation relations in an open quantum system". In: *Physical Review Research* **2**.2 (2020), p. 023327. DOI: 10.1103/PhysRevResearch.2.023327.

[16] R Medeiros de Araújo et al. “Experimental study of quantum thermodynamics using optical vortices”. In: *Journal of Physics Communications* **2**.3 (2018), p. 035012. DOI: 10.1088/2399-6528/aab178.

[17] Kang-Da Wu et al. “Experimentally reducing the quantum measurement back action in work distributions by a collective measurement”. In: *Science Advances* **5**.3 (2019), eaav4944. DOI: 10.1126/sciadv.aav4944.

[18] Kaonan Micadei et al. “Experimental validation of fully quantum fluctuation theorems using dynamic Bayesian networks”. In: *Physical Review Letters* **127**.18 (2021), p. 180603. DOI: 10.1103/PhysRevLett.127.180603.

[19] Wei Cheng et al. “Experimental test of the Crooks fluctuation theorem in a single nuclear spin”. In: *Physical Review A* **109**.2 (2024), p. L020401.

[20] Wenquan Liu et al. “Experimental test of the Jarzynski equality in a single spin-1 system using high-fidelity single-shot readouts”. In: *Physical Review Letters* **131**.22 (2023), p. 220401. DOI: 10.1103/PhysRevLett.131.220401.

[21] Andrea Solfanelli, Alessandro Santini, and Michele Campisi. “Experimental verification of fluctuation relations with a quantum computer”. In: *PRX Quantum* **2**.3 (2021), p. 030353. DOI: 10.1103/PRXQuantum.2.030353.

[22] María García Díaz, Giacomo Guarnieri, and Mauro Paternostro. “Quantum work statistics with initial coherence”. In: *Entropy* **22**.11 (2020), p. 1223. DOI: 10.3390/e22111223.

[23] Kosuke Ito et al. “Generalized energy measurements and quantum work compatible with fluctuation theorems”. In: *Physical Review A* **99**.3 (2019), p. 032117. DOI: 10.1103/PhysRevA.99.032117.

[24] Konstantin Beyer, Kimmo Luoma, and Walter T Strunz. “Work as an external quantum observable and an operational quantum work fluctuation theorem”. In: *Physical Review Research* **2**.3 (2020), p. 033508. DOI: 10.1103/PhysRevResearch.2.033508.

[25] Tiago Debarba et al. “Work estimation and work fluctuations in the presence of non-ideal measurements”. In: *New Journal of Physics* **21**.11 (2019), p. 113002. DOI: 10.1088/1367-2630/ab4d9d.

[26] Frieder Conradt et al. “Electric-field fluctuations as the cause of spectral instabilities in colloidal quantum dots”. In: *Nano Letters* **23**.21 (2023), pp. 9753–9759. DOI: 10.1021/acs.nanolett.3c02318.

[27] Johan Åberg. “Fully quantum fluctuation theorems”. In: *Physical Review X* **8**.1 (2018), p. 011019. DOI: 10.1103/PhysRevX.8.011019.

[28] Gavin E Crooks. “Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences”. In: *Physical Review E* **60**.3 (1999), p. 2721. DOI: 10.1103/PhysRevE.60.2721.

[29] C Jarzynskia. “Nonequilibrium work relations: foundations and applications”. In: *The European Physical Journal B* **64** (2008), pp. 331–340. DOI: 10.1140/epjb/e2008-00254-2.

[30] Vikas Hassija et al. “Forthcoming applications of quantum computing: peeking into the future”. In: *IET Quantum Communication* **1**.2 (2020), pp. 35–41. DOI: 10.1049/iet-qtc.2020.0026.

[31] Frederik F Flöther. “The state of quantum computing applications in health and medicine”. In: *Research Directions: Quantum Technologies* **1** (2023), e10. DOI: 10.1017/qut.2023.4.

[32] Joseph B Lambert, Eugene P Mazzola, and Clark D Ridge. *Nuclear magnetic resonance spectroscopy: an introduction to principles, applications, and experimental methods*. John Wiley & Sons, 2019.

[33] Thomas Beth and Gerd Leuchs. *Quantum information processing*. Wiley Online Library, 2005.

[34] Tai L Chow. *Classical mechanics*. CRC press, 2024.

[35] Amnon Yariv. *An introduction to theory and applications of quantum mechanics*. Courier Corporation, 2013.

[36] Jiayang Zhou, Anqi Li, and Michael Galperin. “Quantum thermodynamics: Inside-outside perspective”. In: *Physical Review B* **109**.8 (2024), p. 085408. DOI: 10.1103/PhysRevB.109.085408.

[37] Andrei Nicolaide. *Electromagnetics. General Theory of the Electromagnetic Field. Classical and Relativistic Approaches*. Transilvania University Press, 2012.

[38] Michael Riordan. *The hunting of the quark: a true story of modern physics*. Plunkett Lake Press, 2019.

[39] Ethel J Ngen and Dmitri Artemov. “Advances in monitoring cell-based therapies with magnetic resonance imaging: future perspectives”. In: *International journal of molecular sciences* **18**.1 (2017), p. 198. DOI: 10.3390/ijms18010198.

[40] A Soare et al. “Experimental noise filtering by quantum control”. In: *Nature Physics* **10**.11 (2014), pp. 825–829. DOI: 10.1038/nphys3115.

[41] Malcolm H Levitt. *Spin dynamics: basics of nuclear magnetic resonance*. John Wiley & Sons, 2008.

[42] Paul Davidovits. *Physics in biology and medicine*. Elsevier, 2024.

[43] Brian M Dale, Mark A Brown, and Richard C Semelka. *MRI: Basic Principles and Applications*. John Wiley & Sons, 2015.

[44] JS Faulkner. *Modern Quantum Mechanics and Quantum Information*. IOP Publishing, 2021.

[45] Peter J Hore. *Nuclear magnetic resonance*. Oxford University Press, USA, 2015.

[46] Wellington L Ribeiro, Gabriel T Landi, and Fernando L Semião. “Quantum thermodynamics and work fluctuations with applications to magnetic resonance”. In: *American Journal of Physics* **84**.12 (2016), pp. 948–957. DOI: 10.1119/1.4964111.

[47] Alexander Kutsenko, Sergii Kovalenko, and Svitlana Kovalenko. “Generalization of the thermodynamic approach to multi-dimensional quasistatic processes”. In: *System research and information technologies* 1 (2023), pp. 62–77. DOI: 10.20535/SRIT.2308-8893.2023.1.05.

[48] Matteo Scandi et al. “Quantum work statistics close to equilibrium”. In: *Physical Review Research* **2**.2 (2020), p. 023377. DOI: 10.1103/PhysRevResearch.2.023377.

[49] Grzegorz Marcin Koczan. “Proof of Equivalence of Carnot Principle to II Law of Thermodynamics and Non-Equivalence to Clausius I and Kelvin Principles”. In: *Entropy* **24**.3 (2022), p. 392. DOI: 10.3390/e24030392.

[50] Peter Talkner, Eric Lutz, and Peter Hänggi. “Fluctuation theorems: Work is not an observable”. In: *Physical Review E—Statistical, Nonlinear, and Soft Matter Physics* **75**.5 (2007), p. 050102. DOI: 10.1103/PhysRevE.75.050102.

[51] Christopher Jarzynski. “Fluctuation relations and strong inequalities for thermally isolated systems”. In: *Physica A: Statistical Mechanics and its Applications* **552** (2020), p. 122077. DOI: 10.1016/j.physa.2019.122077.

[52] C Jarzynski. “Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach”. In: *PHYSICAL REVIEW E* **56**.5 (1997). DOI: 10.1103/PhysRevE.56.5018.

[53] Leslie E Ballentine. *Quantum mechanics: a modern development*. World Scientific Publishing Company, 2014.

[54] Arno Böhm. *Quantum mechanics: foundations and applications*. Springer Science & Business Media, 2013.

[55] Erik B Karlsson. “Internal dynamics in condensed matter, as studied by spin relaxation: some examples from 75 years”. In: *The European Physical Journal H* **47**.1 (2022), p. 4. DOI: 10.1140/epjh/s13129-021-00030-9.

[56] Adam D Wexler et al. “Nuclear magnetic relaxation mapping of spin relaxation in electrically stressed glycerol”. In: *ACS omega* **5**.35 (2020), pp. 22057–22070. DOI: 10.1021/acsomega.0c02059.

[57] Claude Cohen-Tannoudji, Bernard Diu, and Franck Laloë. *Quantum mechanics, volume 3: fermions, bosons, photons, correlations, and entanglement*. John Wiley & Sons, 2019.