Finite-time thermodynamic processes of a spin-one quantum electric dipole system

A Dissertation submitted to graduate programs in partial fulfillment
of the requirements for the degree of doctor of philosophy
in physics (statistical physics)

Addis Ababa University

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September

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Dedication:

To my beloved father Bassie Yassabie.

He had stimulated me to began my PhD study and he passed away in 2016 (2008 E.C).

and

To my brother Belay Bassie.

He accidentally passed away in 2020 (2012 E.C).

Table of Contents

List of Figures

Abstract

We take a collection of large non-interacting spin one particles, each having an electric dipole of magnitude D in contact with a heat reservoir at temperature T. We apply a strong static electric field, E_0, to the system along a z-axis causing three level split energy values. In addition to the strong electric field, applying a weak AC electric field in the xy−plane induced transitions between the three levels. Through a given protocol $\zeta(t)$, the system is taken from an initial thermodynamic equilibrium state $F(T, \tau_i)$ to a final non-equilibrium state with parameter ζ_f. We analytically obtain the expressions for the probability amplitudes for a transition from one particular initial state to the other two final states. This will enable us to find the work distributions of a finite-time process of taking the system from one initial state to either of the two final states of the three-level system. This finite-time non-equilibrium process will then enable us to extract equilibrium thermodynamic quantities like free energy from non-equilibrium process, which is what we call Jarzanski equality and its relation to the second law of thermodynamics. We obtain the possibilities of work distributions of the three-level system in the optimum condition for non-interacting particles. Besides, we empirically obtain the average work of the three-level system as a function of ω and time around the optimum frequency, where ω is the frequency of AC electric field.

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Chapter 1

Introduction

> "[...] everything appears to indicate that out of the classical theory the great principles of thermodynamics will not only maintain intact their central position in the quantum theory but will perhaps even extend their influence."
>
> *Max Planck*

Thermodynamics provides macroscopic descriptions of the states of complex systems and their behaviours when they interact or are constrained under various circumstances. It was originally developed to accord with macroscopic systems [1, 2] and is thus based on the idea that a handful of macroscopic variables, such as volume, pressure, and temperature, are enough to completely describe a system. Classical thermodynamics used these macroscopic variables to characterize the thermodynamic state of the system at near equilibrium, and use them to model the exchange of energy functions such as work and heat in keeping with the thermodynamic laws. Equilibrium thermodynamics is a systematic thought of the transfer of matter and energy in systems as they pass from one thermodynamic equilibrium state to another. On the other hand, non-equilibrium thermodynamics is concerned with physical systems that are far from thermodynamic equilibrium, but can be characterized in terms of non-equilibrium state variables which represent an extrapolation of the variables used to define the system in thermodynamic equilibrium. This implies that non-equilibrium thermodynamics is mainly concerned with the transport process and the rate of chemical reactions [3]. Notwithstanding, the beginning of the atomic theory understood the changes in the underlying small world to be continually fluctuating with the chaos and randomness of the small-world. Statistical mechanics is thus developed as a theory that links microscopic variables to macroscopic variables. Since one consistently deals with a large number of particles, the relative fluctuations become insignificant, so that thermodynamic measurements consistently concur very well with expected values of the microscopic fluctuating quantities that are an effect of the law of large numbers.

Equilibrium statistical mechanics is a very well-established and successful theory, where its formalism provided a powerful means to explain how the macroscopic properties of many-body systems at thermal equilibrium arise from the microscopic interactions that occur among their constituent particles. Its fundamental outcome is the Gibbs formula for the canonical ensemble [4]-[6] which mainly employed the approach for equilibrium statistical mechanics [4, 5] to provide a fundamental bridge between microscopic theory and thermodynamic measurements for any equilibrium situations. Unlike that of equilibrium statistical mechanics [4, 5], with its well-established foundation, a similar widely-accepted framework for non-equilibrium statistical mechanics [7] remains elusive because a handful of parameters used in thermodynamics no longer help to know the whole dynamics of the system.

In the study of statistical mechanics, we mainly focus on the ensemble of a large number of small systems where the relative fluctuations, ever-existing at the atomic level, becomes negligible for the reason that macroscopically the quantum fluctuations which is the temporary appearance of energetic particles out of empty space, as allowed by the uncertainty principle [8], can not be measured. So the measurement we experience at the macroscopic level takes place by averaging the fluctuations taking place at the microscopic level. In statistical mechanics, this averaging is done by implementing the law of large numbers [9]. Thus statistical thermodynamics relates the microscopic properties of individual atoms and molecules to the macroscopic measurements. This means the emergence of statistical thermodynamics with the advancement of atomic and molecular theories supplement classical thermodynamics with an interpretation of the microscopic interactions between individual particles [10, 11]. Indeed, talking about the average behavior of a given ensemble of small systems in statistical mechanics is probabilistic in the sense that as we intend to study deeply the dynamics of the system where micro-state changes always exist fluctuationing around the average value. These fluctuations near mean value have resulted as systems deviate randomly from its average state, which occurs in a system at equilibrium. This type of fluctuation is known as thermal fluctuation which becomes larger and more recurrent as the temperature increases and also decreases as the temperature of the system approaches absolute zero. These fluctuations are used as the source of noise in many systems. The random forces that give inflation to thermal fluctuations are a source of both diffusion and dissipation. The confronting effects of random drift and resistance to drift are associated by the fluctuation-dissipation theorem [12]. Thermal fluctuations play a major role in phase transitions [7] and chemical kinetics [3].

One of the puzzles in quantum idea today is to show how the well-studied properties of a few particles change into a statistical theory from which recent macroscopic quantum thermodynamic laws arise. This challenge is addressed by the appearing field of quantum thermodynamics which has grown rapidly over the last few decades. Quantum thermodynamics emerges as a theory aimed to interrelate the microscopic (atomic and molecular) theory to macroscopic measurements. This implies that quantum thermodynamics plays an ongoing dialogue between the two independent theories: thermodynamics and quantum mechanics. As one of a recent rapidly growing theory, quantum thermodynamics deals with the emergence of thermodynamic laws from inherent quantum mechanical theories. It differs from quantum statistical mechanics [13] in its emphases on the dynamical process out of equilibrium. In addition, there is a quest for the quantum thermodynamic idea to be relevant for a single individual quantum system. This new theory is fueled by new, highly controlled quantum experiments [14]-[20], the discovery of more powerful methods [21], and the development of new literature tools [22]-[28]. For instance, the newly developed novel theoretical approaches that help as tools for the development of quantum thermodynamics are non-equilibrium thermodynamics or stochastic thermodynamics [29] and quantum information theory [27, 28]. Therefore, quantum thermodynamics is a newly emerging research field. The aim of the realm is to extend standard thermodynamics [1] to non-equilibrium statistical mechanics [30] of small systems. So, researchers look for non-equilibrium conditions to incorporate the whole of quantum effects in this realm.

Quantum thermodynamics is fuelled by current equilibration experiments [14] in cold atomic and other physical systems, the opening of new numerical methods [21], and the discovery of basic theoretical relationships in non-equilibrium statistical physics and quantum information theory [31]-[36]. With ultrafast experimental mastery of quantum systems and engineering of small setting pushing the limits of conventional thermodynamics, the key intention of quantum thermodynamics is the extension of basic thermodynamics to incorporate quantum effects and small ensemble sizes. Apart from the academic chase to clear up basic processes in nature, it is expected that the industrial commitment for miniaturization of technologies to the nanoscale will benefit from an understanding of quantum thermodynamic processes. Obtaining an accurate awareness of how quantum fluctuations compete with thermal fluctuations is essential for us to be able to adapt existing technologies to operate at ever-decreasing scales, and to uncover new technologies that may harness quantum thermodynamic features.

Different outlooks have emerged in quantum thermodynamics, due to the multidisciplinary nature of the realm, and each provides various intuition. For instance, the study of thermalization has been approached by quantum information idea from the viewpoint of typicality and entanglement, and by many-body physics with a dynamical method. Also, the current study of quantum thermal machines, initially approached from a quantum optics outlook [37]-[39], has since received significant input from many-body physics, fluctuation relations, and linear response approaches [40, 41]. These designs further contrast with studies on thermal machines based on quantum information-theoretic approaches [42]-[47]. The variation in viewpoints on the identical issues has also meant that there are theories within quantum thermodynamics where general agreement is yet to be established.

Different investigators explore a brief overview of quantum thermodynamics. However, it is arduous to cover the analysis as long as the area of the realm is in rapid progress and has different features. A few topics have been deeply considered for several years and faithful reviews are available in the area. Thus are cited in classical non-equilibrium thermodynamics [48], fluctuation relations [49], non-asymptotic quantum information theory [50], quantum engines [51], equilibration and thermalisation [52, 53], and a recent quantum thermodynamics review focussing on quantum information theory techniques [54]. Other reviews of interest discuss Maxwell's demon and the physics of forgetting [55, 56] and thermodynamic aspects of information [57]. These investigations encourage scholars to take on board the insights gained from different ways of thought to fit together bits of the puzzle to create an overall united framework of quantum thermodynamics.

Research on the non-equilibrium dynamics of quantum systems has deeply produced valuable statements on the thermodynamics of small-scale systems undergoing quantum mechanical progresses [7, 9, 21], [26]-[28], [49], [58]. Fundamental examples are produced by the Crooks and Jarzynski relations [31, 32, 64]: taking into account fluctuations in nonequilibrium dynamics, such relations connect equilibrium properties of thermodynamical applicability with explicit nonequilibrium features. Recent advancements in experimental techniques allow one to measure and control systems at the level of single molecules and atoms [61, 62]. They use quantum theory to characterize systems at the atomic level since quantum mechanics is a fundamental theory in physics that characterizes nature at a small scale of energy levels of atoms and subatomic particles. Assumptions in thermodynamics can be formulated from quantum mechanical theory as an approximation valid at large (macroscopic) scale. In the real world, it is impractical to isolate a particular quantum system, in which we are interested, from its environments. Thus, in order to faithfully represent the real dynamical evolution of physical systems, we must consider the influence of the external environment upon the system's dynamics. Even though the recent advancement in experimental work done on the small systems is effective, we are unable to track either theoretically or experimentally, the dynamical evolution of the full system-plus-environment. This is because the random fluctuations introduced in small systems become valuable and must be incorporated in the explanation of the full system's dynamics. These random fluctuations in small systems may influence thermodynamic quantities like work and heat. A number of authors have proposed definitions of work and derived fluctuation theorems for quantum systems in contact with general thermal environments [22, 23], [32]-[66]. The great insight into the properties of non-equilibrium processes could be gained by treating work as a random variable [31, 64]. Over time, studies began to look for related conclusions in quantum systems, both for unitary [23] and open [60] quantum dynamics. Recently, in addition to the thermal fluctuations, one more has intrinsically quantum fluctuations, best to a very richer platform to work with. Therefore, one may question how much this rate fluctuation can affect thermodynamic quantities such as heat and work. The investigations were inspired by the remarkable upgrading of the past decade in the experimental control of atoms and photons, especially in the subject such as magnetic resonance, ultra-cold atoms, and quantum optics. The first experimental evidence of fluctuation theorems in small systems has only newly been used, using nuclear magnetic resonance [15] and trapped ions [61].

In this work, we take a collection of large non-interacting spin-one particles, each having an electric dipole of magnitude D in contact with a heat reservoir at temperature T. We apply an external static electric field, E_0, to the system along a z-axis causing three level split energy values. In addition, we apply a weak AC electric field in the $xy-$plane which induces transitions between the three level energy states acting as a control parameter for a finite-time process. Accordingly, the system will start from an initial thermodynamic equilibrium state, $F(T,0)$, evolve according to a specific protocol, $\zeta(t)$, until time τ and its non-equilibrium state $F_{non-equil}(T,\tau)$ recorded/ measured. This cyclic process will be repeated for a large number of times which will allow us to find the distribution of work performed by the external agent. We will examine different properties of the work distribution.

The organization of the rest of the thesis is as follows: in Chapter 2 we present as an exercise the formulation of the thermodynamically reversible processes of classical electric dipole and spin-one quantum electric dipole systems; in Chapter 3 we describe the particular procedure of carrying out the finite-time cyclic process, formulate the time evolution of the system and define the way to get expectation values of measurable quantities; in Chapter 4 taking the finite-time cyclic process of our system we evaluate the probability distribution of work, find its mean value and characteristic function and study the behavior of average work as a function of time. Finally, in Chapter 5, the current study of the work is summarized and a conclusion given.

Chapter 2

Thermodynamically reversible processes of classical and spin-one quantum electric dipole systems

A system confined in a region can interact with the rest of the external world either by exchange of its constituent parts (open system) or by other forms of coupling where its constituent parts are fixed (closed system). For a closed system one can further simplify the situation where the system is fairly isolated but weakly coupled with the external world. From now on we will limit our scope to such closed system.

The first section of this Chapter will present the classical thermodynamics of a weakly interacting large collection of electric dipoles in an external electric field and find the expressions for its internal energy, U, free energy, F, entropy, S, etc. Quasi-static processes such as heat and work exchanges with the surrounding world and first law of thermodynamics will be explained. The second section of this Chapter will introduce the quantum thermodynamics version of a weakly interacting spin-one quantum electric dipole. In this section, taking such system as a thermodynamic system in an external electric field in contact with a heat reservoir we find the expressions for U, F,

S, etc.. Lastly, quasi-static processes of heat and work exchanges of the system with the surrounding along with the first law of thermodynamics will be formulated.

2.1 Classical electric dipole

Consider a large collection of classical electric dipoles that are very weakly interacting with each other placed in a confined region. Imagine each dipole to be sitting on a fixed lattice but free to orient itself in any direction. Let us now apply an external electric field of magnitude E_0 along, say z-axis. In addition, we let the collection to be in contact with a heat bath of temperature T. We take identical electric dipoles of magnitude D. If this system is left alone for a long enough time, it will then be in a well defined equilibrium state such that its internal energy U, free energy F, partition function Z can be quantified in terms of T, D and E_0.

We take a large number, N, of identical electric dipoles subjected to electric field $\vec{E_0}$. The internal (potential) energy U of the system equals to

$$U = -\sum_{i=1}^{N} \vec{D}_i \cdot \vec{E_0}, \tag{2.1}$$

where $\vec{D}_i$ is the electric dipole vector of the i^{th} dipole. If the system exchanges energy in the form of heat, δQ, with the bath we can relate it with its specific heat capacity such that

$$\delta Q = C_E dT, \tag{2.2}$$

where δQ is a small amount of heat which causes an increase in the temperature of the system by dT. The proportionality constant C_E is the heat capacity of the system at constant electric field.

The interaction of the system due to a change in electric field and temperature of a heat bath can be related by the conservation of energy. So, the formulation of first law of thermodynamics becomes

$$dU = \delta W + \delta Q, \tag{2.3}$$

where the infinitesimal exchange of energy in the form of work, δW, is

$$\delta W = -\sum_{i=1}^{N} \vec{D}_i \cdot d\vec{E}_0. \tag{2.4}$$

The internal energy of a classical electric dipole system depends on its orientation with respect to the electric field. We can describe this orientation with the two angles θ and ϕ of a spherical coordinate system that is located at the center of each dipole, where the z-axis of the spherical coordinate system is chosen to be parallel to the electric field $\mathbf{E}_0$. The internal energy Eq. ((2.1)) can then be written as

$$U = -\sum_{i}^{N} DE_0 \cos(\theta_i). \tag{2.5}$$

The partition function Z_1 for a single dipole will be a sum of Boltzmann's factor over all possible energy states Eq. ((2.5)), which means a sum over all possible orientations (θ_i, ϕ) of the classical electric dipole such that $0 \le \theta_i \le \pi$ and $0 \le \phi \le 2\pi$. The partition function Z_1 for a single classical electric dipole is

$$Z_1 = \sum_{states} e^{-\beta U(states)} = \iint d\Omega e^{\beta DE_0 \cos(\theta_i)} \tag{2.6}$$

where $d\Omega$ is a solid angle which equals to $\sin(\theta_i) d\theta_i d\phi$. Since the classical electric dipole described in the infinitesimal solid angle $d\Omega$ is centered on (θ_i, ϕ), the partition function of a single classical electric dipole becomes

$$Z_1 = 4\pi \frac{\sinh(\beta DE_0)}{\beta DE_0}. \tag{2.7}$$

If the system has large collection of classical electric dipoles N, the partition function Z_N of all the electric dipoles becomes

$$Z_N = [Z_1]^N = \left[4\pi \frac{\sinh(\beta DE_0)}{\beta DE_0}\right]^N. \tag{2.8}$$

The free energy is given by

$$F = -k_B T lnZ_N = k_B T N ln\left[\beta D E_0\right] - k_B T N ln\left[4\pi \sinh(\beta D E_0)\right], \tag{2.9}$$

where k_B is the Boltzmann constant and $\beta = \frac{1}{k_B T}$.

The mean energy $\bar{E}$, which is the internal energy of the system is given by

$$\bar{E} = -\frac{\partial lnZ_N}{\partial \beta}. \tag{2.10}$$

Using Eq. (2.8) and Eq. (2.10) the mean energy will then be

$$\bar{E} = -N\left[D E_0 \coth(\beta D E_0) - \frac{1}{\beta}\right]. \tag{2.11}$$

The entropy, S, of the system which is given by $-\frac{\partial F}{\partial T}$ takes the expression

$$S = k_B N\left\{\ln\left[\frac{4\pi \sinh(\beta D E_0)}{\beta D E_0}\right] + 1 - \beta D E_0 \coth(\beta D E_0)\right\}. \tag{2.12}$$

An infinitesimal change in entropy, dS, at constant electric field, E_0, of the system due to change in temperature, dT is given by

$$dS = \left(\frac{\partial S}{\partial T}\right)_{E_0} dT = \frac{k_B N}{T}\left[1 + (\beta D E_0)^2[1 - \coth^2(\beta D E_0)]\right] dT. \tag{2.13}$$

Finally, using Eq. (2.2) and Eq. (2.13) we arrive at a relation

$$dS = \frac{\delta Q}{T}, \tag{2.14}$$

where

$$C_{E_0} = k_B N\left[1 + (\beta D E_0)^2[1 - \coth^2(\beta D E_0)]\right].$$

Hence, the infinitesimal exchange of energy of the system in the form of heat, δQ, from Eqs. (2.14) and (2.13) becomes

$$\delta Q = k_B N\left[1 + (\beta D E_0)^2[1 - \coth^2(\beta D E_0)]\right] dT. \tag{2.15}$$

For an infinitesimal change in free energy, dF, of the system due to small change in electric field dE_0 can be defined from Eq. (2.9) so that

$$dF = \left(\frac{\partial F}{\partial E_0}\right)_T dE_0 = -\frac{Nk_BT}{E_0}\left[\beta DE_0 \coth(\beta DE_0) - 1\right]dE_0 \tag{2.16}$$

which is equivalent to the infinitesimal work, δW,

$$\delta W = -\frac{Nk_BT}{E_0}\left[\beta DE_0 \coth(\beta DE_0) - 1\right]dE_0. \tag{2.17}$$

The sum of infinitesimal of heat and work exchanges of the system is the total change in its internal, dU, which is the first law of thermodynamic, i.e.

$$dU = \delta Q + \delta W. \tag{2.18}$$

In the next section, we consider a collection of very weakly interacting spin-one quantum electric dipoles and formulate the quantum thermodynamic version of the system under equilibrium reversible process.

2.2 Spin-one quantum electric dipole

Consider a system of large number, N, of quantum particles that are very weakly interacting with each other. Let us take these quantum particles to be charged and have spin-one. Each of these particles can be in any one of the three quantum states labeled by the quantum number m, where $m = \pm 1$ and 0.

In the presence of the applied external electric field the energy of each spin - one particle will split into three-level energy values. Each energy state of the system depends on the orientation of spin-one particle with respect to the applied electric field. Therefore, each spin - one particle has the same energy magnitude in the state $m = 1$ (spin alignment parallel to electric field) and the state $m = -1$ (spin alignment anti-parallel to electric field). But in state $m = 0$ (spin alignment perpendicular to electric field) the

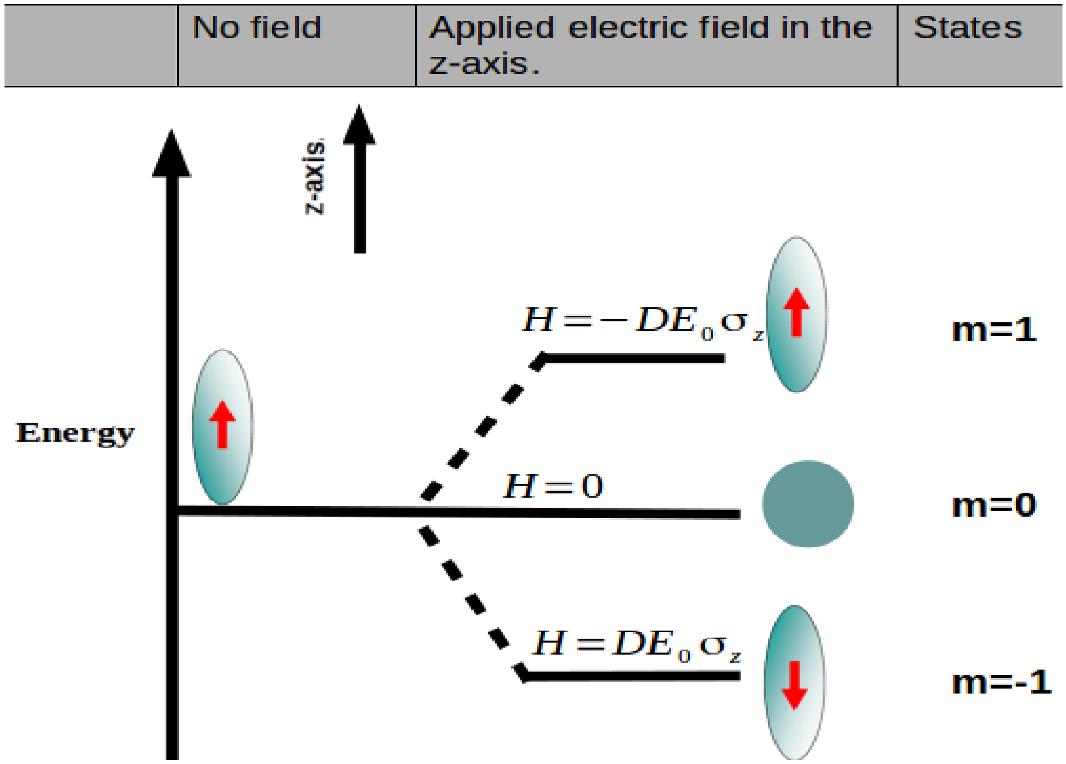


Figure 2.1: Possible states of single spin-one quantum electric dipole under an external electric field.

energy value equals to zero. Figure (2.1) illustrates the three possible energy states of a single quantum electric dipole under an external electric field $\mathbf{E}_0$.

The Hamiltonian, H, for each quantum electric dipole induced by an external electric field $\mathbf{E}_0$ along the $z$axis can be defined as

$$H_{single} = -\mathbf{D} \cdot \mathbf{E}_0, \tag{2.19}$$

where $\mathbf{D}$ is the quantum electric dipole which takes one of the three possible states.

The total Hamiltonian of the system containing large number, N, of identical quantum electric dipoles subjected to external electric field $\mathbf{E}_0$ becomes

$$H_N = -\sum_{i=1}^{N} \mathbf{D}_i \cdot \mathbf{E}_0, \tag{2.20}$$

where $\mathbf{D}_i$ is the dipole state of the i^{th} quantum particle. In addition to the external electric field the system is assumed to be in contact with a heat reservoir at a constant temperature of T. The Gibbs thermal density operator ρ_{th}, for the system is given by

$$\rho_{th} = \frac{e^{-\beta H_N}}{Z_N}, \tag{2.21}$$

where the partition function is

$$Z_N = \left[1 + 2\cosh(\beta D E_0)\right]^N, \tag{2.22}$$

and $\beta = \frac{1}{Tk_B}$, k_B is the Boltzmann constant. The density operators are successful in explaining the thermal equilibrium states of such system.

Average (internal) energy of the system can be expressed as

$$\bar{E} = -\frac{\partial ln Z_N}{\partial \beta}. \tag{2.23}$$

Using Eq. (2.22) and Eq. (2.23) the mean internal energy will then be

$$\langle U \rangle = \bar{E} = -\frac{2NDE_0 \sinh(\beta D E_0)}{1 + 2\cosh(\beta D E_0)}. \tag{2.24}$$

We need to identify the work, δW, performed by the system as $\mathbf{E}_0$ is changed slightly to $\mathbf{E}_0 + d\mathbf{E}_0$. In this infinitesimal change of electric field, the system's energy level also changes. Then, the exchange of energy in the form of work can be described as

$$\delta W = -\sum_{i=1}^{N} \mathbf{D}_i \cdot d(\mathbf{E}_0). \tag{2.25}$$

On the other hand, the system exchanges energy in the form of infinitesimal heat, δQ, with the bath relating its heat capacity at constant electric field, Ξ_E, and temperature change, dT, such that

$$\delta Q = \Xi_E dT. \tag{2.26}$$

In thermodynamics, the conservation of energy is expressed as

$$dU = \delta Q + \delta W. \tag{2.27}$$

This separation of change of average energy, dU, into two terms admit for an interesting physical explanation.

An infinitesimal change $d\langle U\rangle$, in the mean energy can arise in two ways: either (i) in the infinitesimal change in energy state caused by change in external field ($d\mathbf{E}_0$) at constant temperature of the system or (ii) in the infinitesimal change in temperature of the system dT, caused by heat exchange of the system with the reservoir.

Let us start from the free energy $F = -k_B T \ln Z_N$ of the system, which is given by

$$F = -k_B T N \ln\left(1 + 2\cosh(\beta D E_0)\right). \tag{2.28}$$

In this process, we notice that a change in the free energy, dF, of the system at constant temperature is

$$dF = \left(\frac{\partial F}{\partial E_0}\right)_T dE_0. \tag{2.29}$$

Using Eq.(2.28) we obtain

$$dF = -\frac{2ND\sinh(\beta D E_0)}{1 + 2\cosh(\beta D E_0)} dE_0. \tag{2.30}$$

This is precisely the infinitesimal amount of work exchange δW, of the system

$$dF = -\frac{2ND\sinh(\beta D E_0)}{1 + 2\cosh(\beta D E_0)} dE_0 = \delta W. \tag{2.31}$$

The free energy change is used to measure the work done by the system in a quasi-static isothermal process.

The entropy, S, of the system which is given by $-\frac{\partial F}{\partial T}$ takes the expression

$$S = k_B N\left[\ln[1 + 2\cosh(\beta D E_0)] - \frac{2\beta D E_0 \sinh(\beta D E_0)}{1 + 2\cosh(\beta D E_0)}\right]. \tag{2.32}$$

We find the infinitesimal change in entropy, dS, at a constant electric field of the system to be

$$dS = \left(\frac{\partial S}{\partial T}\right)_{E_0} dT = \frac{2N\beta D^2 E_0^2}{T^2}\left[\frac{\cosh(\beta DE_0)}{1+2\cosh(\beta DE_0)} - \frac{2\sinh^2(\beta DE_0)}{\left(1+2\cosh(\beta DE_0)\right)^2}\right]dT. \tag{2.33}$$

Finally, using Eqs. (2.26) and (2.33) we arrive at a relation

$$dS = \frac{\delta Q}{T}, \tag{2.34}$$

where the heat capacity at constant electric field is

$$\Xi_{E_0} = \frac{2N\beta D^2 E_0^2}{T}\left[\frac{\cosh(\beta DE_0)}{1+2\cosh(\beta DE_0)} - \frac{2\sinh^2(\beta DE_0)}{\left(1+2\cosh(\beta DE_0)\right)^2}\right].$$

This relation holds only for quasi-static processes. Hence, the infinitesimal exchange of energy of the system in the form of heat, δQ, using Eqs.(2.34) and (2.33) becomes

$$\delta Q = \frac{2N\beta D^2 E_0^2}{T}\left[\frac{\cosh(\beta DE_0)}{1+2\cosh(\beta DE_0)} - \frac{2\sinh^2(\beta DE_0)}{\left(1+2\cosh(\beta DE_0)\right)^2}\right]dT. \tag{2.35}$$

This Chapter has reviewed the equlibrium statistical thermodynamics of reversible processes for particular simple classical and quantum systems. The following two chapters cover the part of the work we have been concentrating in this study: finite-time thermodynamic processes of a spin-one quantum electric dipole system. The last Chapter gives summary and conclusion.

Chapter 3

Non-equilibrium processes of spin-one quantum electric dipole system

The spin-one quantum electric dipole closed and simple system we have studied in the previous Chapter will be subjected to repeated similar observations/measurements. The system starts from an initial thermodynamic equilibrium state followed by a particular mode of operation (control parameter) that spans for a fixed time interval and its state recorded (measured) at the end. Identical mode of operations where the system starts from the same initial thermodynamic equilibrium state, undergoes through the finite process and its state recorded at the end repeatedly. A large enough collection of such measurements allows us to determine the equilibrium thermodynamic state function of the system at the end of the fixed time interval such as its free energy.

One crucial point about our system is that it must be *very weakly* interacting with the heat bath. This will prevent the system from exchanging its energy in the form of heat. On the other hand, the system will be subjected to a strong and weak electric field in order for it to exchange its energy in the form of work.

In the following sections, we will first introduce the procedure to carry out the cyclic finite-time process (section (3.1)). The second section will formulate and solve the time evolution of the system's dynamics for two kinds of weak field orientations. The third section will determine the expectation value of measurable quantities such as spin polarization at the end of the non-equilibrium process.

3.1 The cyclic finite-time process

We attach our system to the heat bath and apply a strong electric field, E_0, along z-axis. After the system stayed enough time to equilibrate with the heat bath, we switch on a weak AC electric field in a particular direction that lasts for a given amount of time. The weak AC field is the control parameter, $\zeta(t)$, that will act on the system to evolve and make all possible transitions up to time τ. The zig-zag path shown in blue color line in Fig (3.1) depicts the protocol $\zeta(t)$. The dynamics of the system subjected to the AC field will terminate after the span of time τ at the end of which the final non-equilibrium state, $F_{non-equil}$, measured (recorded). After removing the AC field, but keeping the heat bath and strong electric field in tact, we let the system relax to its final equilibrium state, $F(T,\tau)$. The path from the non-equilibrium state at time τ (open circle $F_{non-equil}$) to the final equilibrium state (solid circle, $F(T,\tau)$) is shown in red color line in Fig. (3.1). Once the final equilibrium state is attained, the system will be taken to return back to its initial equilibrium state in a quasi-static process. The reverse path of taking the system from its final equilibrium state to its initial equilibrium state is shown in pink color line in Fig (3.1).

Once the system has returned to its initial thermodynamic equilibrium state, we initiate the weak AC field in the given direction for the same given span of time τ, measure its final non-equilibrium state at the end, let it relax to its final equilibrium state and, ultimately, return to its initial equilibrium state in a quasi-static process. This cyclic process will be performed repeatedly until we get enough data to find the expectation values of any measurable quantities.

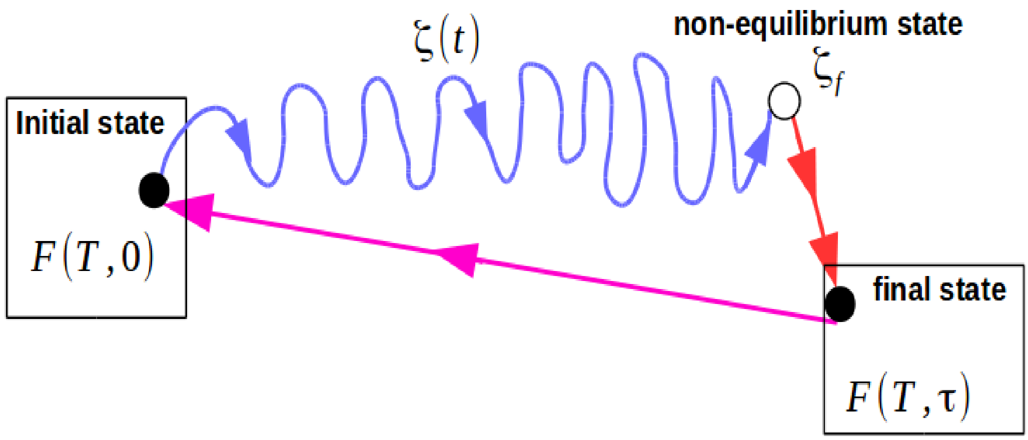


Figure 3.1: Cyclic finite-time process. Over the protocol $\zeta(t)$, the system is taken from an original equilibrium state $F(T,0)$ to a final non-equilibrium state with parameter ζ_f (blue color line). After the process is performed, the system will eventually relax from the non-equilibrium state to the final equilibrium state $F(T,\tau)$ (red color line). The reverse path will take the system from its final equilibrium state to its initial equilibrium state in a quasi-static process (pink color line).

One important quantity of interest is the amount of work, W, performed by the system during this finite-time process. Each measurement of W will, in principle, take different value during each observation. Having a large enough set of measurements will then enable us to relate it to the change in free energy, ΔF, of the system. In 1997, Jarzyanski discovered an equality relation between the work and the change in free energyΔF [31, 64] which is given by

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}. \tag{3.1}$$

Note that $\Delta F = F(T,\tau) - F(T,0)$. The above equality is now called Jarzyanski equality.

A consequence of this equality leads to a relation between W and ΔF such tat

$$\langle W \rangle \geq \Delta F. \tag{3.2}$$

3.2 The time evolution of the system

The system of spin-one particles in contact with the heat bath kept at constant temperature T is placed under a strong static electric field E_0 in the z direction, together with a weak oscillating field $E_I(t) = b \sin \omega t \sigma_\alpha$ in a certain direction σ_α yet to be fixed. This weak field plays the role of the work parameter of the system. We will neglect spin-spin interactions between the particles and consider only the coupling of the three-level system with the electric field. The Hamiltonian describing the response of a single spin to the two fields is given by

$$H(t) = -E_0 \sigma_z - E_I(t) \sigma_\alpha. \tag{3.3}$$

where the direction of σ_α is yet to be fixed.

For non-equilibrium process, we can describe the work of the system by requiring detailed knowledge of the dynamics of the system and how it is coupled to the heat bath. In the non-equilibrium processes, we assume that the system's coupling to the heat bath is very weak so that no heat is exchanged with the surrounding. This situation is actually encountered very often in experiments since many systems are only weakly coupled to the bath. It also simplifies considerably the description of the problem because it makes the entire dynamics unitary.

When the weak field, i.e. the protocol of the system is switched on at $t = 0$ it has an initial state with Hamiltonian $H_i = H(\zeta_i)$ in thermal equilibrium with the heat reservoir at a temperature T. So the initial state of the system is expressed by using the Gibbs density matrix in Eq.2.21.

Let E_n^i and $|n\rangle$ denote the eigenvalues and eigenvectors of the Hamiltonian $H_i = H(\zeta_i)$. Then the state $|n\rangle$ is obtained with probability

$$P_n = \frac{e^{-\beta E_n^i}}{Z}. \tag{3.4}$$

We immediately initiate the protocol changing ζ from $\zeta(0) = \zeta_i$ to $\zeta(\tau) = \zeta_f$ according to some pre-defined function $\zeta(t)$. Due to the very weak coupling of our system with the heat bath, the evolution of the system is unitary. The state of the system at any given time t is given by

$$|\psi(t)\rangle = U(t)|n\rangle \tag{3.5}$$

where $U(t)$ is the unitary time-evolution operator, which satisfies Schr$\ddot{o}$dinger's equation ($\hbar = 1$)

$$i\frac{\partial U}{\partial t} = H(t)U,\ U(0) = 1. \tag{3.6}$$

At the end of the finite-time process of span τ, we measure the energy of the system once again. The Hamiltonian at the end of the process, $H_f = H(\zeta_f)$, will be in a given energy level E_m^f and eigenvector $|m\rangle$. The probability that we now measure an energy E_m^f is

$$|\langle m|\psi(\tau)\rangle|^2 = |\langle m|U(\tau)|n\rangle|^2, \tag{3.7}$$

which can be interpreted as the conditional probability that a system initially in $|n\rangle$ will be found in $|m\rangle$ after a time τ .

In order to study the out-of-equilibrium properties of this system, we must know the initial thermal state, ρ_{th}, expressed in Eq. 2.21 and the time evolution operator, $U(t)$, which is a solution of the Schr$\ddot{o}$dinger equation expressed in Eq. 3.6. Its initial state is given by the thermal density matrix, ρ_{th},

$$\rho_{th} = \frac{e^{-\beta H_i}}{Z}, \tag{3.8}$$

where Z is the partition function and $\beta = \frac{1}{T}$ with Boltzmann constant k_B taken as 1.

The Hamiltonian H_i is described in Eq. (2.19), on any occasion this is true, the equivalent matrix exponential $e^{\frac{-H_i}{T}}$ can be evaluated by exponentiating the eigenvalues

$$e^{\frac{-H_i}{T}} = \begin{pmatrix} e^{\frac{E_0}{T}} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{\frac{-E_0}{T}} \end{pmatrix}. \tag{3.9}$$

The trace of this matrix is called the partition function of the system, $Z = tr(e^{\frac{-H}{T}}) = 1 + 2\cosh(\frac{E_0}{T})$.

The thermal density matrix can be written in a convenient way as

$$\rho_{th} = \begin{pmatrix} \frac{e^{\frac{E_0}{T}}}{Z} & 0 & 0 \\ 0 & \frac{1}{Z} & 0 \\ 0 & 0 & \frac{e^{\frac{-E_0}{T}}}{Z} \end{pmatrix}. \tag{3.10}$$

We can rewrite the thermal density matrix in the form of

$$\rho_{th} = \begin{pmatrix} \frac{1-f}{2} & 0 & 0 \\ 0 & \frac{f}{1-2\sinh(\frac{E_0}{T})} & 0 \\ 0 & 0 & \frac{1+f}{2} - \frac{f}{1-2\sinh(\frac{E_0}{T})} \end{pmatrix}, \tag{3.11}$$

where $f = \frac{1-2\sinh(\frac{E_0}{T})}{1+2\cosh(\frac{E_0}{T})}$.

Fig.3.2 describes a single spin-one particle in the presence of both the strong and weak AC electric field. This weak AC electric field applied to the spin promotes transitions from one particular initial state to the other two final states. With a large collection of such weakly interacting spin-one particles subjected to the strong and weak fields one can imagine how complex the dynamics of the system's evolution can be.

Next, we obtain the analytical solution of the Schr$\ddot{o}$dinger equation for time-dependent Hamiltonian, which is exceptionally possible. Fortunately, in our case one may obtain

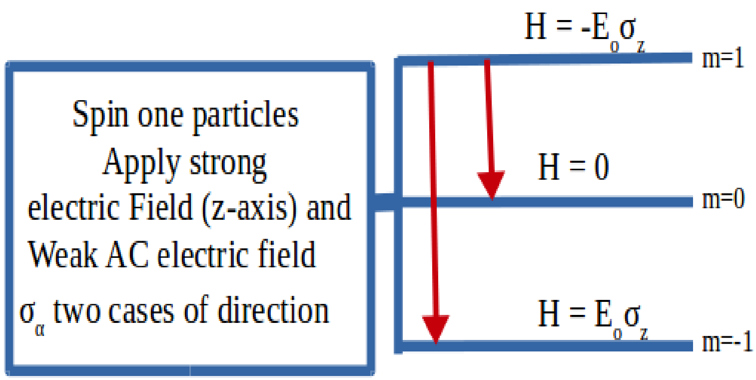


Figure 3.2: The model of the three-level system coupled to the strong and weak AC electric field

an approximate solution valid when $E_I \ll E_0$. In our study, we try to find the solution by considering two cases. In the first case, we take the direction of the weak electric field to be along the z axis. In the second case, we take the direction of the weak electric field to be rotating in the xy-plane.

3.2.1 Case 1: Weak field parallel to z direction

The work protocol is enforced by applying a very small field of amplitude E_I along the z-direction with frequency ω. Therefore, the work parameter ζ defined by the field is $\mathbf{E}_I = E_I e^{-i\omega t}\sigma_z$. The total Hamiltonian of the system now becomes

$$H = -E_0\sigma_z - E_I e^{-i\omega t}\sigma_z. \tag{3.12}$$

This weak field plays a central role in the perturbation of the system, which, even if extremely weak, may still promote transitions between the states. To make progress, we must now compute the approximate solution of the time-evolution operator $U(t)$ defined by

$$i\frac{\partial U(t)}{\partial t} = HU(t), \tag{3.13}$$

with in $U(0) = 1$. Let us first part define a new operator that is

$$U(t) = e^{i\omega t\sigma_z}\tilde{U}(t). \tag{3.14}$$

Substituting Eq. (3.14) into Eq. (3.13), one finds that $\tilde{U}$ must obey the modified Schr$\ddot{o}$dinger equation

$$i\frac{\partial \tilde{U}(t)}{\partial t} = (H + \omega\sigma_z)\tilde{U} = \tilde{H}\tilde{U}(t), \tag{3.15}$$

where

$$\tilde{H} = (\omega - E_0)\sigma_z - E_I(\cos\omega t - i\sin\omega t)\sigma_z. \tag{3.16}$$

Therefore, from Eq. (3.16), we have two distinct types of terms, one time-independent and the other oscillating with frequency ω. We take only the time independent part. Then, after neglecting any time-dependent terms from the expression in Eq. (3.16), we are left only with the much simpler Hamiltonian

$$\tilde{H} = \Omega\sigma_z, \tag{3.17}$$

where $\Omega = \omega - E_0$. From the modified Schr$\ddot{o}$dinger expression (Eq. 3.15),

$$\tilde{U}(t) = e^{-i\Omega\sigma_z t}, \tag{3.18}$$

where $\tilde{U}(0) = 1$. Therefore, the expression for the full time-evolution defined in Eq. (3.14), becomes

$$U(t) = e^{i\omega t\sigma_z}e^{-i\Omega\sigma_z t}. \tag{3.19}$$

To write an explicit formula for $U(t)$, we must first compute the matrix exponential of $e^{-i\Omega\sigma_z t}$. The operator series expansion of $e^{-i\Omega\sigma_z t}$ can be expressed as

$$e^{-i\Omega\sigma_z t} = \mathbb{1} - i\Omega t\sigma_z + \frac{(i\Omega t\sigma_z)^2}{2} - \frac{(i\Omega t\sigma_z)^3}{6} + \frac{(i\Omega t\sigma_z)^4}{4!} - \frac{(i\Omega t\sigma_z)^5}{5!} + \frac{(i\Omega t\sigma_z)^6}{6!} - .... \tag{3.20}$$

By rewriting Eq. (3.20), we have

$$e^{-i\Omega\sigma_z t} = \mathbb{1} + \sum_{n=1}^{\infty}(-1)^n\frac{(i\Omega t\sigma_z)^n}{n!}. \tag{3.21}$$

The summation expression expressed in Eq. (3.21) have two terms: even and odd.

For even terms:

$$-\frac{(\Omega t\sigma_z)^2}{2} + \frac{(\Omega t\sigma_z)^4}{4!} - \frac{(\Omega t\sigma_z)^6}{6!} + \frac{(\Omega t\sigma_z)^8}{8!} - .... = \sum_{n=1}^{\infty}(-1)^n\frac{(\Omega t\sigma_z)^{2n}}{(2n)!}.$$

For odd terms:

$$-i[\Omega t\sigma_z - \frac{(\Omega t\sigma_z)^3}{3!} + \frac{(\Omega t\sigma_z)^5}{5!} - \frac{(\Omega t\sigma_z)^7}{7!} + ...] = -i\sum_{n=0}^{\infty}(-1)^n \frac{(\Omega t\sigma_z)^{2n+1}}{(2n+1)!}.$$

By inserting the above two equations into Eq. (3.21) and reorganizing the terms, we obtain

$$e^{-i\Omega\sigma_z t} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} [\sum_{n=0}^{\infty}(-1)^n \frac{(\Omega t)^{2n}}{(2n)!} - 1] - \begin{pmatrix} i & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -i \end{pmatrix} \sum_{n=0}^{\infty}(-1)^n \frac{(\Omega t)^{2n+1}}{(2n+1)!}, \tag{3.22}$$

where

$$\sigma_z^{2n} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{3.23}$$

and

$$\sigma_z^{2n+1} = \sigma_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{3.24}$$

Eq. (3.22) can be simplified to take the form

$$e^{-i\Omega\sigma_z t} = \begin{pmatrix} \cos\Omega t - i\sin\Omega t & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \cos\Omega t + i\sin\Omega t \end{pmatrix}. \tag{3.25}$$

Finally, we write the time-evolution operator as

$$U(t) = e^{i\omega t\sigma_z} \begin{pmatrix} u(t) & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & u^*(t) \end{pmatrix}, \tag{3.26}$$

where

$$u(t) = \cos\Omega t - i\sin\Omega t. \tag{3.27}$$

From the time evolution matrix expression, the square of the magnitude of off-diagonal elements represent the transition probability per unit time for jump to occur. From

Eq. (3.26), we see that there is **no transition** probability per unit time for jump to occur. Hence, when the weak AC field acts along z-axis, there will be **no transition** probability at all.

3.2.2 Case 2: Weak field perpendicular to z-direction

The work protocol is enforced by applying a very small field of amplitude E_I rotating in the xy-plane with frequency ω. Therefore, the work parameter ζ is defined by the field $\mathbf{E}_I = \mathbf{E}_I(\cos\omega t, \sin\omega t, 0)$. The total Hamiltonian of the system now becomes

$$H = -E_0\sigma_z - \mathbf{E}_I(\sigma_x \cos\omega t + \sigma_y \sin\omega t). \tag{3.28}$$

This weak field plays a central role in the perturbation of the system, which, even if extremely weak, may still promote transitions between the states. We now compute the time evolution operator $U(t)$ defined by

$$i\frac{\partial U(t)}{\partial t} = HU(t), \tag{3.29}$$

with in $U(0) = 1$. We first define a new operator, given by the relation

$$U(t) = e^{i\omega t\sigma_z}\tilde{U}(t). \tag{3.30}$$

Substituting Eq. (3.30) into Eq. (3.29), one finds that $\tilde{U}$ must obey the modified Schr$\ddot{o}$dinger equation

$$i\frac{\partial \tilde{U}(t)}{\partial t} = (H + \omega\sigma_z)\tilde{U} = \tilde{H}\tilde{U}(t), \tag{3.31}$$

where

$$\tilde{H} = (\omega - E_0)\sigma_z - \mathbf{E}_I(\sigma_x \cos\omega t + \sigma_y \sin\omega t). \tag{3.32}$$

Therefore, from the expression (3.32), we have two distinct types of terms, one time-independent and the other oscillating with frequency ω. The system consists of a single spin placed with a static electric field in the z direction, together with a weak oscillating field $\mathbf{E}_I = A\sin\omega t$ oscillating with frequency ω in the xy direction, which plays the role of the work parameter ζ. Now the expression (3.32) can be rewritten as

$$\tilde{H} = (\omega - E_0)\sigma_z - A(\sigma_x \sin\omega t\cos\omega t + \sin\omega t\sin\omega t\sigma_y). \tag{3.33}$$

Using the relations

$$\sin(\alpha+\beta) = \sin\alpha\cos\beta + \cos\alpha\sin\beta$$

and

$$\cos(\alpha+\beta) = \cos\alpha\cos\beta + \sin\alpha\sin\beta$$

in Eq. 3.33 gives us

$$\tilde{H} = (\Omega\sigma_z - b\sigma_y) - b(\sigma_x\sin 2\omega t - \sigma_y\cos 2\omega t), \tag{3.34}$$

where $\Omega = \omega - E_0$ and $b = \frac{A}{2}$. After neglecting any time-dependent terms from the expression in Eq. (3.34), we are left only with the much simpler Hamiltonian, which is

$$\tilde{H} = \Omega\sigma_z - b\sigma_y. \tag{3.35}$$

Thus, we can apply the trick to our issue by writing Eq. (3.35) as

$$\tilde{H} = \Omega_r(\sigma_z\cos\theta - \sigma_y\sin\theta) \tag{3.36}$$

where

$$\Omega_r = \sqrt{\Omega^2 + b^2} \text{ and } \tan\theta = \frac{b}{\Omega}. \tag{3.37}$$

The full time-evolution operator relation expression, defined in (3.30), becomes

$$U(t) = e^{i\omega t\sigma_z}e^{-i\tilde{H}t}. \tag{3.38}$$

To write an explicit formula for the full time-evolution $U(t)$, we must first compute the matrix exponential of $e^{-i\tilde{H}t}$. Therefore, the exponential matrix can be written as

$$e^{-i\tilde{H}t} = e^{-i\Omega_r(\sigma_z\cos\theta - \sigma_y\sin\theta)t} = e^{-i\Omega_r t\cos\theta\sigma_z}e^{i\Omega_r t\sin\theta\sigma_y} \tag{3.39}$$

Then, the series expansion of exponential matrix operator of $e^{-i\Omega_r t\cos\theta\sigma_z}$ can be expressed as

$$e^{-i\Omega_r t\cos\theta\sigma_z} = \mathbb{1} - i\Omega_r t\cos\theta\sigma_z + \frac{(i\Omega_r t\cos\theta\sigma_z)^2}{2} - \frac{(i\Omega_r t\cos\theta\sigma_z)^3}{3!} + \frac{(i\Omega_r t\cos\theta\sigma_z)^4}{4!} - \frac{(i\Omega_r t\cos\theta\sigma_z)^5}{5!} + \frac{(i\Omega_r t\cos\theta\sigma_z)^6}{6!} - \frac{(i\Omega_r t\cos\theta\sigma_z)^7}{7!} + ... \tag{3.40}$$

By rewriting Eq. (3.40), we have

$$e^{-i\Omega_r t\cos\theta\sigma_z} = \mathbb{1} + \sum_{n=1}^{\infty}(-1)^n \frac{(i\Omega t\cos\theta\sigma_z)^n}{n!} \tag{3.41}$$

The expression in Eq. (3.41) have two terms: even and odd.

For even terms:

$$-\frac{(\Omega_r t\cos\theta\sigma_z)^2}{2} + \frac{(\Omega_r t\cos\theta\sigma_z)^4}{4!} - \frac{(\Omega_r t\cos\theta\sigma_z)^6}{6!} + \frac{(\Omega_r t\cos\theta\sigma_z)^8}{8!} - \frac{(\Omega_r t\cos\theta\sigma_z)^{10}}{10!} + \frac{(\Omega_r t\cos\theta\sigma_z)^{12}}{12!} - ...... = \sum_{n=1}^{\infty}(-1)^n \frac{(\Omega_r t\cos\theta\sigma_z)^{2n}}{(2n)!}$$

For odd terms:

$$-i[\Omega_r t\cos\theta\sigma_z - \frac{(\Omega_r t\cos\theta\sigma_z)^3}{3!} + \frac{(\Omega_r t\cos\theta\sigma_z)^5}{5!} - \frac{(\Omega_r t\cos\theta\sigma_z)^7}{7!} + \frac{(\Omega_r t\cos\theta\sigma_z)^9}{9!} - \frac{(\Omega_r t\cos\theta\sigma_z)^{11}}{11!}...] = -i\sum_{n=0}^{\infty}(-1)^n \frac{(\Omega_r t\cos\theta\sigma_z)^{2n+1}}{(2n+1)!}$$

By inserting the above two expressions into Eq. (3.40) and reorganizing the terms, we obtain

$$e^{-i\Omega_r t\cos\theta\sigma_z} = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} + \begin{pmatrix}1&0&0\\0&0&0\\0&0&1\end{pmatrix}[\sum_{n=0}^{\infty}(-1)^n \frac{(\Omega_r t\cos\theta)^{2n}}{(2n)!} - 1] - \begin{pmatrix}i&0&0\\0&0&0\\0&0&-i\end{pmatrix}\sum_{n=0}^{\infty}(-1)^n \frac{(\Omega_r t\cos\theta)^{2n+1}}{(2n+1)!}, \tag{3.42}$$

where

$$\sigma_z^{2n} = \begin{pmatrix}1&0&0\\0&0&0\\0&0&1\end{pmatrix}, \tag{3.43}$$

and

$$\sigma_z^{2n+1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{3.44}$$

By simplifying the exponential matrix of Eq. (3.42) we can have

$$e^{-i\Omega_r t\cos\theta\sigma_z} = \begin{pmatrix} \cos(\Omega_r t\cos\theta) - i\sin(\Omega_r t\cos\theta) & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \cos(\Omega_r t\cos\theta) + i\sin(\Omega_r t\cos\theta) \end{pmatrix}. \tag{3.45}$$

Rewriting Eq. (3.45) as

$$e^{-i\Omega_r t\cos\theta\sigma_z} = \begin{pmatrix} e^{-i\Omega_r t\cos\theta} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{i\Omega_r t\cos\theta} \end{pmatrix}. \tag{3.46}$$

The operator series expansion of exponential matrix of $e^{i\Omega_r t\sin\theta\sigma_y}$ can be expressed as

$$e^{i\Omega_r t\sin\theta\sigma_y} = \mathbb{1} + \sum_{n=1}^{\infty}(-1)^n \frac{(i\Omega_r t\sin\theta\sigma_y)^n}{n!} \tag{3.47}$$

Follow the same procedure expressed above and using the relations

$$\sigma_y^{2n} = \frac{1}{2}\begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix}$$

and

$$\sigma_y^{2n+1} = \sigma_y = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

to obtain the exponential matrix of Eq. (3.47). Then, we find the exponential matrix expression in the form

$$\begin{aligned} e^{i\Omega_r t\sin\theta\sigma_y} = \frac{1}{2}\begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 1 & 0 & -1 \\ 0 & 2 & 0 \\ -1 & 0 & 1 \end{pmatrix}\sum_{n=1}^{\infty}(-1)^n \frac{(i\Omega_r t\sin\theta)^{2n}}{(2n)!} \\ + \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}\sum_{n=1}^{\infty}(-1)^n \frac{(i\Omega_r t\sin\theta)^{2n+1}}{(2n+1)!}. \end{aligned} \tag{3.48}$$

By simplifying Eq. (3.48), we have

$$e^{i\Omega_r t\sin\theta\sigma_y} = \frac{1}{2}\begin{pmatrix} 1+\cos(\Omega_r t\sin\theta) & \sqrt{2}\sin(\Omega_r t\sin\theta) & 1-\cos(\Omega_r t\sin\theta) \\ -\sqrt{2}\sin(\Omega_r t\sin\theta) & 2\cos(\Omega_r t\sin\theta) & \sqrt{2}\sin(\Omega_r t\sin\theta) \\ 1-\cos(\Omega_r t\sin\theta) & -\sqrt{2}\sin(\Omega_r t\sin\theta) & 1+\cos(\Omega_r t\sin\theta) \end{pmatrix} \tag{3.49}$$

Substituting Eq. (3.46) and Eq. (3.49) into Eq. (3.39) to obtain exponential matrix of $e^{-i\tilde{H}t}$ and after some mathematical manipulation we have

$$e^{-i\tilde{H}t} =$$

$$\frac{1}{2}\begin{pmatrix} e^{-i\Omega_r t\cos\theta}(1+\cos(\Omega_r t\sin\theta)) & e^{-i\Omega_r t\cos\theta}\sqrt{2}\sin(\Omega_r t\sin\theta) & e^{-i\Omega_r t\cos\theta}(1-\cos(\Omega_r t\sin\theta)) \\ -\sqrt{2}\sin(\Omega_r t\sin\theta) & 2\cos(\Omega_r t\sin\theta) & \sqrt{2}\sin(\Omega_r t\sin\theta) \\ e^{i\Omega_r t\cos\theta}(1-\cos(\Omega_r t\sin\theta)) & -e^{i\Omega_r t\cos\theta}\sqrt{2}\sin(\Omega_r t\sin\theta) & e^{i\Omega_r t\cos\theta}(1+\cos(\Omega_r t\sin\theta)) \end{pmatrix} \tag{3.50}$$

After organizing and rearranging the terms we get the time-evolution operator

$$U(t) = \begin{pmatrix} u(t) & y^*(t) & w^*(t) \\ -v^*(t) & x(t) & v(t) \\ w(t) & -y(t) & u^*(t) \end{pmatrix}, \tag{3.51}$$

where the amplitude probabilities can be expressed as:

$$u(t) = e^{i\omega t\sigma_z} e^{-i\Omega_r t\cos\theta}\frac{1}{2}\{1+\cos(\Omega_r t\sin\theta)\}, \tag{3.52}$$

$$v(t) = e^{i\omega t\sigma_z}\frac{\sqrt{2}}{2}\sin(\Omega_r t\sin\theta), \tag{3.53}$$

$$w(t) = e^{i\omega t\sigma_z} e^{i\Omega_r t\cos\theta}\frac{1}{2}\{1-\cos(\Omega_r t\sin\theta)\}, \tag{3.54}$$

$$y(t) = e^{i\omega t\sigma_z} e^{-i\Omega_r t\cos\theta}\frac{\sqrt{2}}{2}\sin(\Omega_r t\sin\theta), \tag{3.55}$$

$$x(t) = e^{i\omega t\sigma_z}\cos(\Omega_r t\sin\theta). \tag{3.56}$$

To get a better physical interpretation of this result, consider the situation where the system initially starts in the eigenstate $|1,1\rangle$ of σ_z . Then $y^*(t)$ and $w^*(t)$, being the off-diagonal elements of $U(t)$, describe the probability amplitude for a transition from $|1,1\rangle \to |1,0\rangle$ or $|1,-1\rangle$ (the amplitude for the reverse transition processes are $v^*(t)$ and $w(t)$). Moreover, the unitarity condition $U^\dagger(t)U(t) = \mathbb{1}$ also implies that

$$|u(t)|^2 + |y(t)|^2 + |w(t)|^2 = 1,$$

$$2|v(t)|^2 + |x(t)|^2 = 1,$$

$$2|y(t)|^2 + |x(t)|^2 = 1,$$

and

$$|u(t)|^2 + |v(t)|^2 + |w(t)|^2 = 1.$$

Then, the expressions $|u(t)|^2$ and $|x(t)|^2$ are the probabilities for no transitions to occur.

From Eq. (3.53), Eq. (3.54) and Eq. (3.55) we also see that the off-diagonal elements of $U(t)$ is proportional to $\sin\theta$, which is, therefore, the characteristics of a physical connotation to the angle θ [defined in Eq.(3.37)] as representing the transition probability. This probability reaches a maximum precisely at an optimum condition ($\Omega = 0$), as we intuitively expect. In fact, at optimum condition, we obtain the simpler formulas

$$u(t) = e^{i\omega t\sigma_z}\frac{1}{2}\{1 + \cos(b^2 t)\} \tag{3.57}$$

$$v(t) = e^{i\omega t\sigma_z}\frac{\sqrt{2}}{2}\sin(b^2 t) \tag{3.58}$$

$$w(t) = e^{i\omega t\sigma_z}\frac{1}{2}\{1 - \cos(b^2 t)\} \tag{3.59}$$

$$y(t) = e^{i\omega t\sigma_z}\frac{\sqrt{2}}{2}\sin(b^2 t) \tag{3.60}$$

$$x(t) = e^{i\omega t\sigma_z}\cos(b^2 t) \tag{3.61}$$

In this condition, the transition probabilities, $|v(t)|^2$, $|w(t)|^2$ and $|y(t)|^2$ achieve maximum value. Hence, when the weak oscillating field is applied along xy-plane **transitions do occur**.

3.3 The expectation value of measurable quantities

To illustrate the physics behind Eq. (3.51), let us examine the time evolution of $\langle\sigma_x\rangle$, $\langle\sigma_y\rangle$, $\langle\sigma_z\rangle$. The general formula for the time evolution of any operator, A, is given by

$$\langle A\rangle = tr\{U^\dagger(t) A U(t)\rho_{th}\}, \tag{3.62}$$

where ρ_{th} is given by Eq. (3.11), $U(t)$ is given by Eq. (3.51), and

$$U^{\dagger}(t) = \begin{pmatrix} u^*(t) & -v(t) & w^*(t) \\ y(t) & x^*(t) & -y^*(t) \\ w(t) & v^*(t) & u(t) \end{pmatrix}, \tag{3.63}$$

where $u(t)$, $v(t)$, $y(t)$, $x(t)$, and $y(t)$ are expressed in Eq. (3.51). Now, we obtain the time evolution of the polarization components in the three different directions, $\langle\sigma_i\rangle$, where $i = x, y, z$. All estimations are reduced to the multiplication of 3×3 matrices. By using Eq. (3.62), we can obtain the polarization component in the z direction:

$$\langle\sigma_z\rangle = tr\begin{pmatrix} (u^*u - ww^*)\{\frac{1-f}{2}\} & (u^*y^* - w^*y)\{\frac{f}{k}\} & 0 \\ (yu - y^*w)\{\frac{1-f}{2}\} & 0 & (yw^* + y^*u^*)\{\frac{1-f}{2} - \frac{f}{k}\} \\ 0 & (wy^* + yu)\frac{f}{k} & (ww^* - uu^*)\{\frac{1+f}{2} - \frac{f}{k}\} \end{pmatrix} \tag{3.64}$$

where $k = 1 - 2\sinh(\frac{E_0}{T})$. By simplifying Eq.(3.64), and inserting the expression of u, w, f, and k, we have

$$\langle\sigma_z\rangle = (ww^* - u^*u)f + \frac{f}{k}(u^*u - ww^*) = \frac{2\cos(\Omega_r t\sin(\theta))\sinh(\frac{E_0}{T})}{1 + 2\cosh(\frac{E_0}{T})}. \tag{3.65}$$

The time evolution component along the x direction, $\langle\sigma_x\rangle$ can be obtain using Eq. (3.62), which is given by

$$\langle\sigma_x\rangle = \frac{1}{\sqrt{2}}tr\begin{pmatrix} (-v^*\gamma - v\Gamma)\{\frac{1-f}{2}\} & (x\gamma - v\zeta)\{\frac{f}{k}\} & 0 \\ (x^*\Gamma + v^*\zeta)\{\frac{1-f}{2}\} & (x^*\zeta - x\zeta)\{\frac{f}{k}\} & (x^*\gamma - x\zeta)\{\frac{1-f}{2} - \frac{f}{k}\} \\ 0 & (x\Gamma + v^*\zeta)\frac{f}{k} & (v\Gamma + v^*\gamma)\{\frac{1+f}{2} - \frac{f}{k}\} \end{pmatrix} \tag{3.66}$$

where $\gamma = u^* + w^*$, $\zeta = y^* - y$, $\Gamma = u + w$. By simplifying Eq. (3.66), we have the polarization of $\langle\sigma_x\rangle$:

$$\langle\sigma_x\rangle = \frac{1}{\sqrt{2}}[v^*(u^*+w^*)+v(u+w))f + \frac{f}{k}\{x^*(y^*-y)-x(y^*-y)-v(u+w)-v^*(u^*+w^*)\}]. \tag{3.67}$$

By rewritten Eq. (3.67) using the expression of u, w, v, y, x, f, and k, we have

$$\langle\sigma_x\rangle = -\frac{2\sin(\Omega_r t\sin(\theta))\cos(\Omega_r t\cos(\theta))\sinh(\frac{E_0}{T})}{1 + 2\cosh(\frac{E_0}{T})}. \tag{3.68}$$

In a similar way, using Eq.(3.62) we can obtain the polarization of $\langle\sigma_y\rangle$, which is given by

$$\langle\sigma_y\rangle = \frac{i}{\sqrt{2}} tr \begin{pmatrix} \Gamma(k^* - k)\{\frac{1-f}{2}\} & (x\gamma - v\zeta)\{\frac{f}{k}\} & 0 \\ (x^*\Gamma + v^*\zeta)\{\frac{1-f}{2}\} & \Lambda.C\{\frac{f}{k}\} & (x^*\gamma - x\zeta)\{\frac{1-f}{2} - \frac{f}{k}\} \\ 0 & (x\Gamma + v^*\zeta)\frac{f}{k} & [k(w+u) + k^*(w^* - u^*)]\{\frac{1+f}{2} - \frac{f}{k}\} \end{pmatrix} \tag{3.69}$$

where $\Gamma = u - w$, $\Lambda = y^* + y$, $C = x^* + x$. By simplifying Eq. (3.69), we have

$$\begin{aligned} \langle\sigma_y\rangle = \frac{i}{\sqrt{2}}[vw + \frac{v^*}{2}[u - w + w^* - u^*] + \frac{f}{2}(2uv + wv^* - uv^* + v^*w^* + v^*u^*) \\ + \frac{f}{k}\{(y^* - y)(x^* - x) - [v(w+u) - v^*(w^* - u^*)]\}] \end{aligned} \tag{3.70}$$

Rewriting Eq. (3.70) using the expression of u, w, v, y, x, f, and k, we get

$$\langle\sigma_y\rangle = -\frac{2\sin(\Omega_r t\cos(\theta))\sin(\Omega_r t\sin(\theta))\sinh(\frac{E_0}{T})}{1 + 2\cosh(\frac{E_0}{T})} \tag{3.71}$$

The full expressions using Eqs. (3.52)-(3.56) are somewhat bulky. Instead, let us look at the optimum case, where $u(t)$, $v(t)$, $y(t)$, $x(t)$, and $y(t)$ are given by Eqs. (3.57)-(3.61). In this case we obtain the dynamics of the three-level system of spins. Thus, we have the simplified form

$$\langle\sigma_z\rangle = -f[\cos(b^2t) - \frac{1}{k}\cos(b^2t)] = -\frac{2\cos(b^2t)\sinh(\frac{E_0}{T})}{1 + 2\cosh(\frac{E_0}{T})} \tag{3.72}$$

$$\langle\sigma_x\rangle = \frac{2f}{\sqrt{2}}[\sin(b^2t) + \frac{1}{k}\sin(b^2t)] = -\frac{2\sin(b^2t)\sinh(\frac{E_0}{T})}{1 + 2\cosh(\frac{E_0}{T})} \tag{3.73}$$

$$\langle\sigma_y\rangle = 0 \tag{3.74}$$

The expectation values of measurable quantities at the optimum condition expresse in Eqs.(3.72) - (3.74), which is the possible expected value of the result of the measurable quantities. In this optimum condition, the measurable quantity of the polarization, $\langle\sigma_y\rangle$, expressed in Eq. (3.74) has zero probability of occurring.

Chapter 4

Exploring the work distribution properties of spin-one system in different ways

Consider a similar finite-time cyclic process of our system where one starts from an initial thermodynamic equilibrium state at $t = 0$ and ends at a non-equilibrium state after a fixed time interval $t = \tau$. During this time interval the external agent performs work on the system. This work can be interpreted as a stochastic variable. We are dealing with a quantum system that is weakly interacting subjected to the strong and weak fields. This interpretation of work becomes essential since fluctuations become significant. In addition to the thermal fluctuations, the system also has a strong contribution from quantum fluctuations. These fluctuations are related to the fact that in order to access the amount of work performed on the system, one must measure its energy and therefore collapse the wave-function. When this happens the system can tend to explore different states with different probabilities. In this study we are mainly concerned with quantum systems, so that both thermal and quantum fluctuations are to be taken in to consideration. Thus, in such system we take a large enough collection of measurements that allows us to determine the distribution of work, the average work, the characteristic function, etc.

In the first section of this Chapter, we will obtain the probability distribution of work and figure out the possible distributions of work of the three-level system. The second section of this Chapter will evaluate the average work of the three-level system and formulate characteristic function and distribution of work of the system's dynamics. The last section of this Chapter will determine the average work of the three-level system as a function of time of the non-equilibrium process.

4.1 Work distribution of the three-level system-the case of a single representative spin-one particle

The system of spin-one particles in contact with a heat bath kept at constant temperature T and an external strong static electric field, E_0, along the z direction together with a weak field perpendicular to the z direction is applied. We begin our study of the considered system by defining a two point energy function which is the difference of the two point energy measurement of the system given by

$$W = E_m^f - E_n^i. \tag{4.1}$$

Due to the very weak interaction of the system with the heat bath heat can not be exchanged with the surrounding. But, any change in the energy function of the system must be related to the work performed by the external agent. We denote the energy recorded in the first measurement to be E_n^i while the energy recorded in the second measurement to be E_m^f. Both energies E_n^i and E_m^f are fluctuating quantities which change during each realization of the measurement. The first measurement of energy E_n^i value is random due to thermal variations (fluctuations) while the second measurement of energy, E_m^f, value is random due to quantum variations (fluctuations).

As a result, W can be treated as a random variable, encompassing both thermal and quantum fluctuations during each realization of the measurement. From Eq. (4.1) we recognize that work is a quantity which requires two measurements to be accessed. This reflects to the fact that work is not the system property, but rather the result of a process performed on the system.

Since the collection of the particles are assumed to be weakly interacting with each other compared to each particle's interaction with the external field, we can take the state of each particle to be determined by the interaction Hamiltonian with the external fields. Hence the study of our system can boil down to simply observing/recording the state of a single representative spin-one particle. And that is what we will do in the following work.

Each spin-one particle has three energy states and one can figure out all possible values of work, W. At time $t = 0$ the Hamiltonian is $H_i = -E_0\sigma_z$ so the initial energy eigenvalues can take one of the following three: $E^i_{\pm 1} = \mp E_0$ and $E^i_0 = 0$. At some other arbitrary time the Hamiltonian is $H(t) = -E_0\sigma_z - E_I(t)\sigma_x$ so the final instantaneous eigenvalue takes any one of the following: $E^f_{\pm 1} = \mp\sqrt{E_0^2 + E_I^2(t)}$ and $E^f_0 = 0$. From here, there are nine possible values of W:

$$W = E^f_m - E^i_m, \tag{4.2}$$

where $m = \pm 1$ and 0.

In order to simplify the discussion, let us suppose that we choose the protocol such that $E_I = b\sin(\omega t)$ always changes by a full period. That is, we assume that the final protocol time τ is an integral multiple of the period of the weak field, i.e.

$$\tau = \frac{2\pi l}{\omega},\ l = 1, 2, 3, ... \tag{4.3}$$

This is physically quite reasonable. After all, ω is supposed to be a very fast frequency and therefore we imagine always measuring the work after a certain amount of complete cycles. As a result, the value of work need to be fluctuating about zero.

With this choice $H_f = H_i$ we study the quantum thermodynamic properties of a three-level system, so they have energy spectrum $E_{m=\pm1} = \mp E_0$ and $E_{m=0} = 0$. Then, we obtain the following possible distributions of work of the single particle in the system:

$$\begin{aligned}
W &= E_{-1} - E_1 = 2E_0 \Longrightarrow 1 \rightsquigarrow -1 \\
W &= E_1 - E_{-1} = -2E_0 \Longrightarrow -1 \rightsquigarrow 1 \\
W &= E_0 - E_1 = -E_0 \Longrightarrow 1 \rightsquigarrow 0 \\
W &= E_1 - E_0 = E_0 \Longrightarrow 0 \rightsquigarrow 1 \\
W &= E_{-1} - E_0 = E_0 \Longrightarrow 0 \rightsquigarrow -1 \\
W &= E_0 - E_{-1} = -E_0 \Longrightarrow -1 \rightsquigarrow 0 \\
W &= E_0 - E_0 = 0 \Longrightarrow 0 \rightsquigarrow 0 \\
W &= E_1 - E_1 = 0 \Longrightarrow 1 \rightsquigarrow 1 \\
W &= E_{-1} - E_{-1} = 0 \Longrightarrow -1 \rightsquigarrow -1
\end{aligned} \tag{4.4}$$

In the first case, the spin initially was found in state $m = 1$ at $t = 0$ and then found in state $m = -1$ at $t = \tau$. The second case, correspond to the reverse process of the first case. In the third case, the spin state changes from state $m = 1$ to the state $m = 0$ and the fourth correspond to the reverse process of the third state. The fifth and sixth cases, correspond to the transition of state $m = 0(-1)$ to the state $m = -1(0)$ respectively. The last three expression correspond to no state transition at all.

We obtain the probability distribution of work, $P(W)$, by using the definition

$$P(W) = \sum_{n,m} |\langle m|U(\tau)|n\rangle|^2 P_n \delta[W - (E_m^f - E_n^i)], \tag{4.5}$$

where $\delta(x)$ is the Dirac's delta function and $x = W - (E_m^f - E_n^i)$. This expression is explained in words as the sum over all allowed events, weighted by their probabilities, and catalogue the terms according to the values of $E_m^f - E_n^i$.

For instance, the case $W = 2E_0$ means a transition from quantum state $m = 1$ to quantum state $m = -1$. From Eq. ((3.11)) we have the initial probability $P_1 = (1 - f)/2$, whereas the the transition probability is $|m = -1|U(\tau)|m = 1|^2 = |w(\tau)|^2$. Therefore, we obtain the transition probabilities as:

$$
\begin{aligned}
P(W = 2E_0) &= [\frac{1-f}{2}]|w(\tau)|^2 \\
P(W = -2E_0) &= [\frac{1+f}{2} - \frac{f}{1 - 2\sinh(E_0/T)}]|w(\tau)|^2 \\
P(W = -E_0) &= [\frac{1-f}{2}]|y(\tau)|^2 \\
P(W = E_0) &= [\frac{f}{1 - 2\sinh(E_0/T)}]|v(\tau)|^2 \\
P(W = E_0) &= [\frac{f}{1 - 2\sinh(E_0/T)}]|v(\tau)|^2 \\
P(W = -E_0) &= [\frac{1+f}{2} - \frac{f}{1 - 2\sinh(E_0/T)}]|y(\tau)|^2 \\
P(W = 0) &= 1 - \{(1 - \frac{f}{1 - 2\sinh(E_0/T)})|w(\tau)|^2 + \\
&\quad [\frac{1-f}{2} + \frac{f}{1 - 2\sinh(E_0/T)}]|y(\tau)|^2\} \\
P(W = 0) &= 1 - \{(1 - \frac{f}{1 - 2\sinh(E_0/T)})|v(\tau)|^2\} \\
P(W = 0) &= 1 - \{(1 - \frac{f}{1 - 2\sinh(E_0/T)})|w(\tau)|^2 + (\frac{1+f}{2})|v(\tau)|^2\}
\end{aligned}
\tag{4.6}
$$

If $E_0 > 0$ it is more likely that the spin will be found in state $m = 0$. In this case $f > 0$ so that $P(W = 2E_0) > P(W = E_0)$. This means that it is more likely that the field will promote a flip from state $m = 0$ to state $m = 1$ than the other way around.

4.2 Average work of the three-level system

Once we know the probability distribution of work, $P(W)$, we can get the average work of each representative spin-one particle from the definition:

$$\langle W \rangle = \sum_{W} W P(W). \tag{4.7}$$

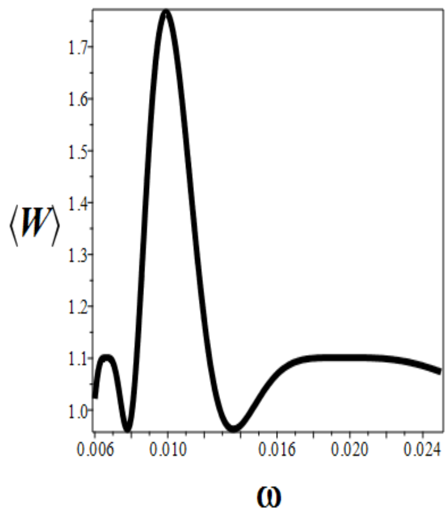
Using Eq.(4.7) we obtain the average work, $\langle W \rangle$, of the three-level system to be equal to

$$\begin{aligned}\langle W \rangle = &(2E_0)P(W=2E_0) + (-2E_0)P(W=-2E_0) + (-E_0)P(W=-E_0) + (E_0)P(W=E_0) \\ &+ (E_0)P(W=E_0) + (-E_0)P(W=-E_0).\end{aligned} \tag{4.8}$$

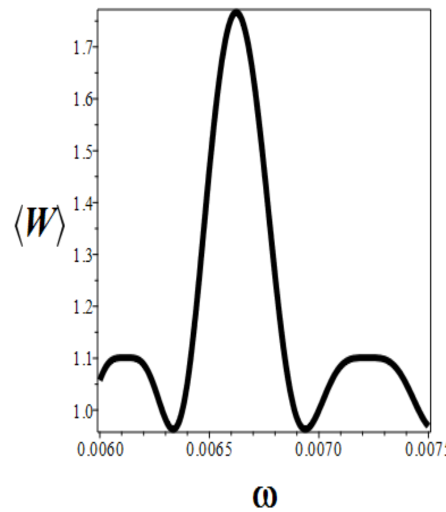
Using Eq.(4.6) and Eq.(4.7) we obtain the simplified average work of the three-level system as

$$\begin{aligned}\langle W \rangle = &\frac{E_0\left[-4\left(\sin(\Omega_r t\sin(\theta))\right)^4\cosh(\frac{E_0}{T}) + 2\left(-1+\cos(\Omega_r t\sin(\theta))\right)^2\sin(\frac{E_0}{T})\right]}{8+16\cosh(\frac{E_0}{T})} \\ &+ \frac{E_0\left(1+cos(\Omega_r t\sin(\theta))\right)^4}{8+16\cosh(\frac{E_0}{T})}.\end{aligned} \tag{4.9}$$

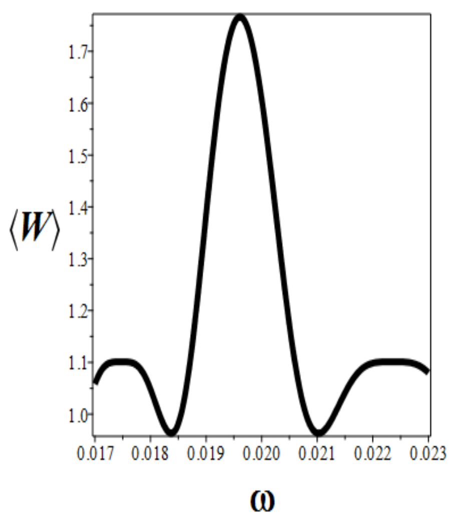
Figures 4.1, 4.2 and 4.3 are the plots of average work vs frequency of the three-level system for different values of b/E_0 and l in a narrow window of frequency. In the plots we use the temperature of the bath to be $300K$. As we see the plots the dependence of $\langle W \rangle$ on ω is quite complicated - highly non-linear- and depends sensitively on the duration l of the protocol and the static electric field. From the plots we see the dependence of average work on the strength of strong static electric field and the parameter, l. In the presence of strong static electric field the system performs a maximum average work around the optimum condition. In this optimum condition, the maximum average work of the system depends on the strength of the static electric field. In this



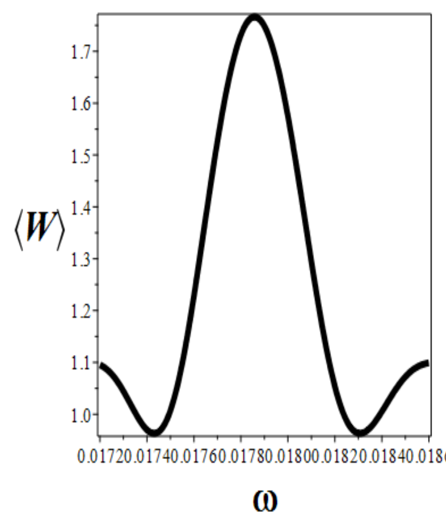
(a) Average work vs ω at $l = 1$



(b) Average work vs ω at $l = 4$

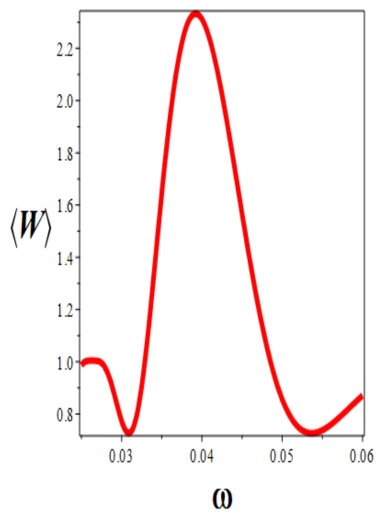


(c) Average work vs ω at $l = 8$

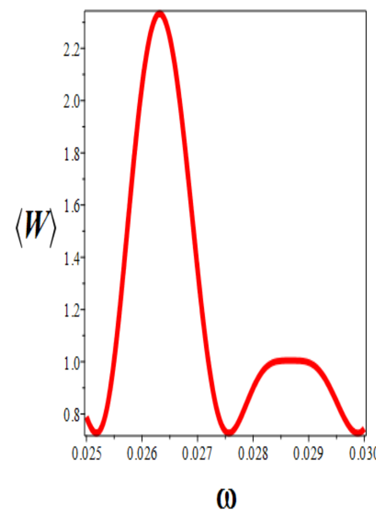


(d) Average work vs ω at $l = 20$

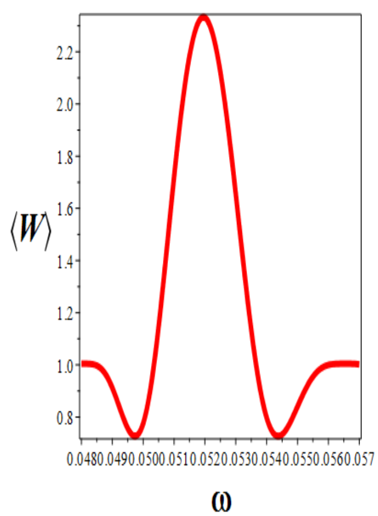
Figure 4.1: The plot of average work as function of ω at the values of $E_0 = 1\ eV$, $b = 0.01E_0$, $T = 300K$ and different values of l.



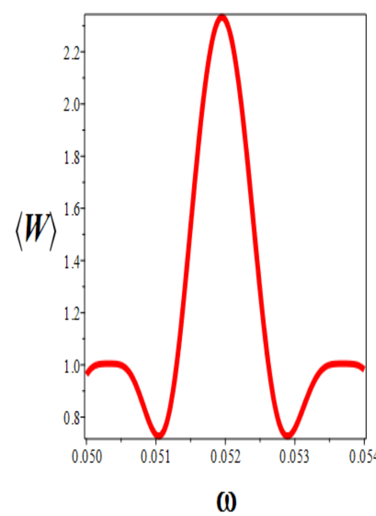
(a) Average work vs ω at $l = 1$



(b) Average work vs ω at $l = 4$

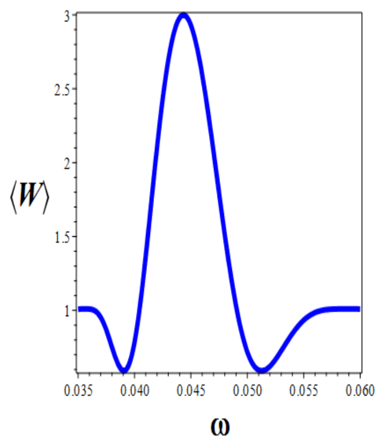


(c) Average work vs ω at $l = 8$

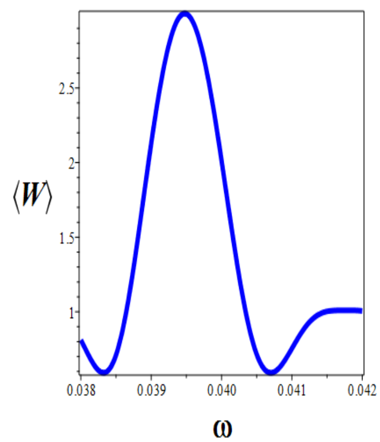


(d) Average work vs ω at $l = 20$

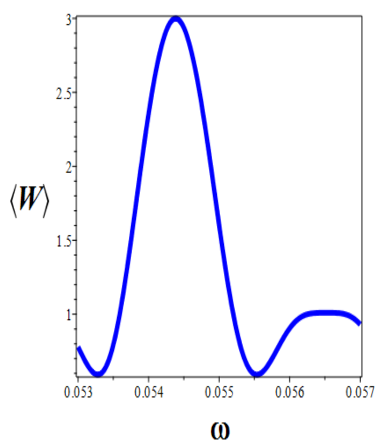
Figure 4.2: The plot of average work as function of ω at the values of $E_0 = 2\ eV$, $b = 0.01E_0$, $T = 300K$ and different values of l.



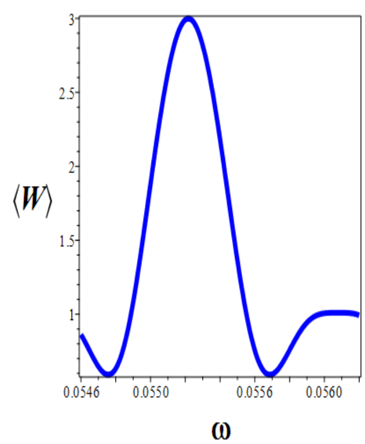
(a) Average work vs ω at $l = 1$



(b) Average work vs ω at $l = 4$



(c) Average work vs ω at $l = 8$



(d) Average work vs ω at $l = 20$

Figure 4.3: The plot of average work as function of ω at the values of $E_0 = 3\ eV$, $b = 0.01E_0$, $T = 300K$ and different values of l.

condition, the performed average work increases as the static electric field increases. But in a certain value of the parameter, l, we have a similar behavior of the average work. As we increase the value of the parameter, l, of the system we see a sharp dependence of the average work with frequency, ω, being maximum at the optimum condition. In general, the work performed increases close to the optimum condition, but for certain value of l it may be very small exactly at optimum condition.

4.2.1 Characteristic function and distribution of work

In general, there are a large number of allowed energy levels in most systems and therefore an even larger number of allowed energy discrepancies within it. Therefore, the total number of valid values in W tends to be very large. It is actually simple to deal with the characteristic function. Therefore, the characteristic function, $G(r)$, described as the Fourier transform of the original distribution is given by

$$G(r) = \langle e^{irW} \rangle = \int_{-\infty}^{\infty} P(W) e^{irW} dW. \tag{4.10}$$

We can attain a distribution of work, $P(W)$, which gives the probability that a certain amount of work is performed during the process. Therefore, using Eq. (4.10), we can find the inverse Fourier transform of $G(r)$ to be

$$P(W) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(r) e^{-irW} dr. \tag{4.11}$$

Using Eqs. (4.5) and (4.10) we can write the characteristic function $G(r)$ as

$$\begin{aligned}
G(r) &= \sum_{n,m} |\langle m|U(\tau)|n\rangle|^2 P_n e^{ir(E_m^f - E_n^i)} \\
&= \sum_{n,m} \langle n|U^\dagger e^{irE_m^f}|m\rangle\langle m|U e^{-irE_n^i} P_n|n\rangle, \\
&= \sum_{n,m} \langle n|U^\dagger e^{irH_f}|m\rangle\langle m|U e^{-irH_i}\rho_{th}|n\rangle \\
&= tr\{U^\dagger(\tau) e^{irH_f} U(\tau) e^{-irH_i}\rho_{th}\}.
\end{aligned}$$

Therefore,

$$G(r) = tr\{U^\dagger(\tau) e^{irH_f} U(\tau) e^{irH_i}\rho_{th}\}. \tag{4.12}$$

This equation describes the characteristic function and is expressed as the trace of a product of operators. For that reason, we conclude that the characteristic function does not have a very important physical meaning

Using Eq. (4.12), we achieve the Jarzynski equality by using the definition of characteristic function indicated in Eq. (4.10) and setting $r = i\beta$. This allows us to obtain

$$G(i\beta) = \langle e^{-\beta W} \rangle.$$

On the other hand, considering the initial state of Gibbs density matrix of the three-level system and Eq.(4.12) we have

$$G(i\beta) = \frac{1}{Z_i} tr(U^\dagger e^{-\beta H_f} U) = \frac{1}{Z_i} tr(e^{-\beta H_f}) = \frac{Z_f}{Z_i}. \tag{4.13}$$

Since $Z = e^{-\beta F}$, we obtain the statistical average $e^{-\beta W}$ of the Jarzynski equality as:

$$G(i\beta) = \langle e^{-\beta W} \rangle = e^{-\beta \Delta F}. \tag{4.14}$$

In our derivation, we assume that the evolution is unitary. This result used to interpret non-equilibrium statistical mechanics is what we call Jarzynski equality and it holds for a process performed far from equilibrium. Therefore, we acquire the Jarzynski relation when the system is coupled to a heat bath throughout the process with out considering the speed of the process.

4.2.2 Moments of the work

It is possible to express the characteristic function in a way that makes its physical interpretation more transparent, and which is also more convenient to perform certain computations. The idea is to use the Heisenberg representation. Given an arbitrary operator, $A(t)$, in the Schr$\ddot{o}$dinger picture we define its Heisenberg picture version as

$$\tilde{A}(t) = U^\dagger(t) A(t) U(t). \tag{4.15}$$

In particular,

$$\tilde{H_i} = \tilde{H}(0) = H_i,$$

$$\tilde{H_f} = \tilde{H}(\tau) = U^\dagger(\tau) H_f U(\tau).$$

Moreover, given an arbitrary operator A, we define the thermal average of this operator as

$$\langle A \rangle_{th} = tr(A \rho_{th}). \tag{4.16}$$

We can rewrite the characteristic function from Eq. (4.10) as

$$G = \langle e^{ir\tilde{H}_f} e^{-ir\tilde{H}_i} \rangle_{th}. \tag{4.17}$$

This formula has the structure of a Greens function for two operators, a quantity which appears often in quantum physics.

From the characteristic function we extract all statistical moments of the random variable W simply from differentiating G. The idea can be achieved by expanding the basic definition of the characteristic function expressed in Eq. (4.10) in a power series form in r. Therefore,

$$G(r) = \langle e^{irW} \rangle = 1 + ir\langle W \rangle - \frac{r^2}{2}\langle W^2 \rangle - i\frac{r^3}{6}\langle W^3 \rangle + ... \tag{4.18}$$

From the result we see that the statistical moment $\langle W^n \rangle$ appears as the expansion term of order r^n. Hence, knowing $G(r)$, we may obtain the n-th moment of W as

$$\langle W^n \rangle = (-i)^n \frac{\partial G(r)}{\partial r^n}|_{r=0}. \tag{4.19}$$

We may also obtain formulas for the various moments based on expectation values of the quantum mechanical operators. This is accomplished by expanding Eq. ((4.16)) in a power series in r and comparing it with Eq. ((4.19)). We then find:

$$\langle W \rangle = \langle \tilde{H}_f - \tilde{H}_i \rangle_{th}, \tag{4.20}$$

$$\langle W^2 \rangle = \langle \tilde{H}_f^2 + \tilde{H}_i^2 - 2\tilde{H}_f \tilde{H}_i \rangle_{th}, \tag{4.21}$$

$$\langle W^3 \rangle = \langle \tilde{H}_f^3 - 3\tilde{H}_f \tilde{H}_i^2 - 3\tilde{H}_f^2 \tilde{H}_i - \tilde{H}_i^3 \rangle_{th}, \tag{4.22}$$

etc. The first moment may be written more simply as

$$\langle W \rangle = \langle H_f \rangle_\tau - \langle H_i \rangle_0, \tag{4.23}$$

where we used the fact that $\langle A \rangle_t = tr[U^\dagger(t) A U(t) \rho_{th}]$. Hence, the first moment of W is quite simple to express as the difference between the average energy at time τ and the average energy at time 0, which is intuitive.

4.3 Average work of the three-level system as a function of time

The average work as a function of time of the three-level system can be given by the formula:

$$\langle W\rangle_t = \langle H_f\rangle_\tau - \langle H_i\rangle_0. \tag{4.24}$$

When calculating the expected values of quantities related to the system energy at the time $t = 0$, we can use the initial Hamiltonian $H_0 = -E_0\sigma_z$ instead of the whole time dependent Hamiltonian $H(t)$ in Eq. ((3.34)). So, we have

$$\langle H_i\rangle_0 = -E_0\langle\sigma_z\rangle = E_0 f[1-\frac{1}{k}]. \tag{4.25}$$

The Hamiltonian at time t is given by

$$H(t) = -E_0\sigma_z - 2b\sin\omega t\sigma_x. \tag{4.26}$$

The average Hamiltonian of the system at any given time can be found from Eq. (3.62) where $A = H(t)$

$$\langle H_f\rangle_\tau = -E_0\langle\sigma_z\rangle - 2b\sin\omega t\langle\sigma_x\rangle \tag{4.27}$$

Thus

$$\langle W\rangle_t = -E_0\langle\sigma_z\rangle - 2b\sin\omega t\langle\sigma_x\rangle - E_0 f[1-\frac{1}{k}] \tag{4.28}$$

Using Eqs. (3.65) and (3.68) substitute in to Eq.(4.28) and rearranging it we obtain the average work of the three-level system as a function of time to be

$$\begin{aligned}\langle W\rangle_t = &-\frac{2E_0\cos(\Omega_r t\sin(\theta))\sinh\left(\frac{E_0}{T}\right)}{1+2\cosh\left(\frac{E_0}{T}\right)} - \frac{E_0\left(1-2\sinh\left(\frac{E_0}{T}\right)\right)\left(1-\frac{1}{1-2\sinh\left(\frac{E_0}{T}\right)}\right)}{1+2\cosh\left(\frac{E_0}{T}\right)}\\ &+\frac{4b\sin(\omega t)\sin(\Omega_r t\sin(\theta))\cos(\Omega_r t\cos(\theta))\sinh\left(\frac{E_0}{T}\right)}{1+2\cosh\left(\frac{E_0}{T}\right)};\end{aligned} \tag{4.29}$$

where $f = \frac{1-2\sinh(\frac{E_0}{T})}{1+2\cosh(\frac{E_0}{T})}$. By simplifying Eq. (4.29) and rearranging the term, we get

$$\langle W \rangle_t = \frac{4[b\sin(\omega t)\sin(\Omega_r t\sin(\theta))\cos(\Omega_r t\cos(\theta)) - \frac{E_0}{2}(\cos(\Omega_r t\sin(\theta)) - 1)]\sinh\left(\frac{E_0}{T}\right)}{1 + 2\cosh\left(\frac{E_0}{T}\right)} \tag{4.30}$$

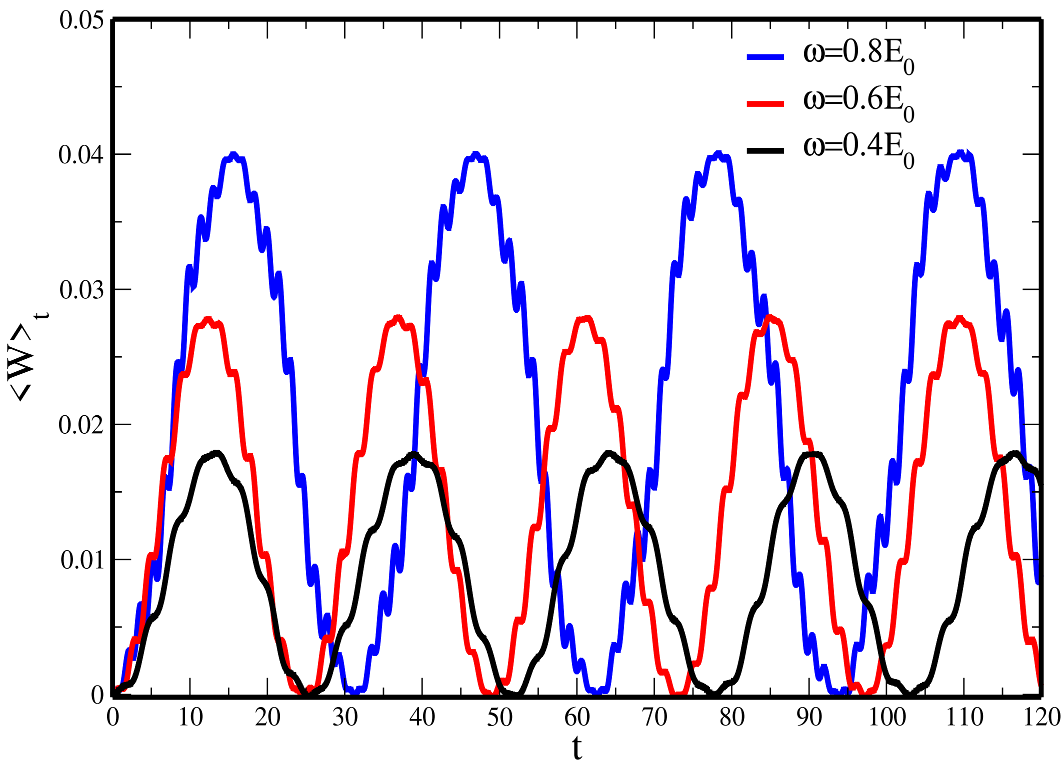


Figure 4.4: The average work as a function of time for the values of $E_0 = 3\ eV$, $2.5\ eV$ and $2\ eV$ and the values of $b = 0.1E_0$.

Figure (4.4) shows three plots where E_0 takes values of $3\ eV$, $2.5\ eV$ and $2\ eV$ while ω correspondingly takes $0.8E_0$, $0.6E_0$, $0.4E_0$, respectively for $b = 0.1E_0$. The temperature of the heat bath is taken to be $300K$. All the three plots show oscillatory behavior where the values of the average work as a function of time takes between zero and maximum value. The higher E_0 is the higher is the corresponding maximum value. One also observables two time scales: fast and slow oscillations, where the fast oscillation should be related with ω while the slow oscillation should be related to the value of b.

The slow time scale enslaves the dynamics and, as such, is responsible for governing the oscillatory nature of average work as a function of time.

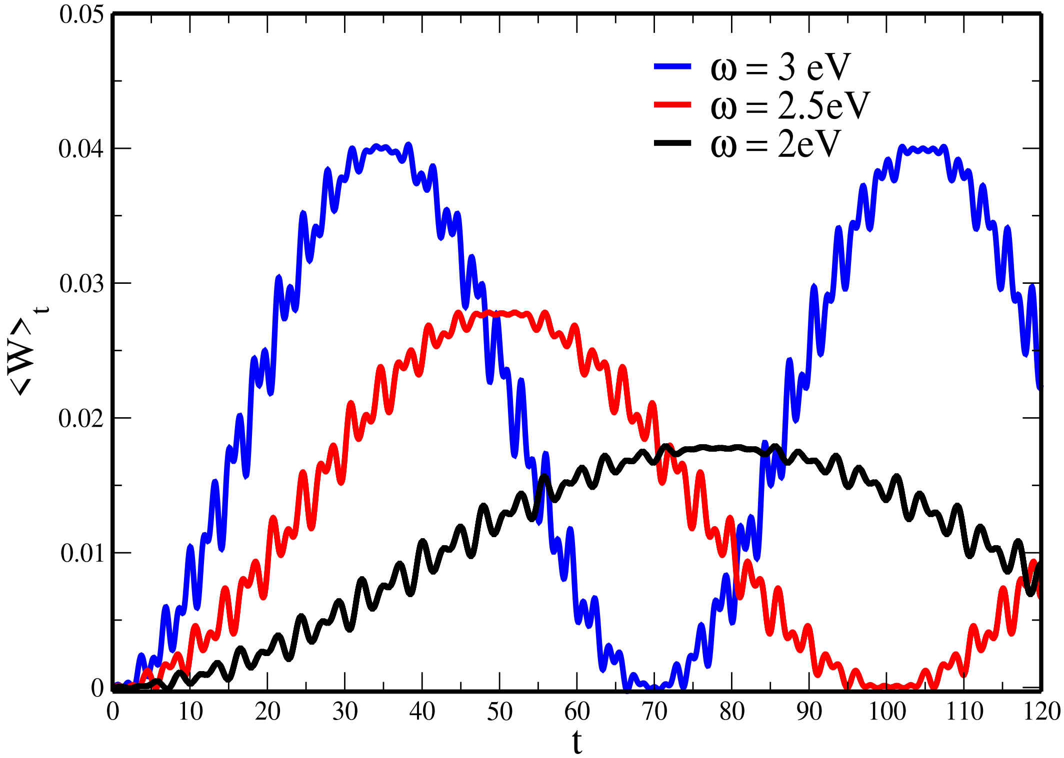


Figure 4.5: The average work as a function of time when $\omega = E_0$ for the values of $E_0 = 3$ eV, 2.5 eV and 2 eV and the values of $b = 0.1E_0$.

Figure (4.5) shows another three plots where E_0 takes values of 3 eV, 2.5 eV, and 2 eV while ω takes corresponding fixed values of E_0 respectively for $b = 0.1E_0$. Temperature, T, is again taken to be $300K$. The plots here show clearly the fast and slow oscillations. The fast time scale corresponds to $\omega = E_0$ while the slow time scale corresponds to $b = 0.1E_0$. In addition, the slow oscillation determines the oscillatory behavior of average work as a function of time. In addition, we observe that for large value of E_0 we get correspondingly large value of average work.

Chapter 5

Summary and conclusion

In this Chapter we summarize and give a brief conclusion of our work. As an exercise we first gave an illustration of reversible processes of classical and quantum electric dipole systems and evaluated their corresponding thermodynamic functions such as internal energy, free energy and entropy. We took the interaction of the two systems with a heat bath and with an external electric field and derived their infinitesimal heat and work exchanges. The relation of these energy exchange quantities with the conservation law of energy lead to the first law of thermodynamics.

As a non-equilibrium cyclic process we considered a spin-one system in contact with a heat bath and immersed in a strong electric field start from a thermodynamic equilibrium state. A weak AC electric field is immediately switched on it for a span of finite time τ and its non-equilibrium free energy at the end measured. After relaxing our system to its final equilibrium state, bring it back to its initial equilibrium state in a quasi-static process we repeated the cyclic process for a large number of times. This repeated measurement gave us a distribution of work by the external agent on the system.

We modelled this procedure of finite-time process, managed to get the probability of work distribution and evaluated its different properties such as the mean work, the characteristic function, Jarzynski equality and average work as a function of time.
This work has charted out a new scope yet to be explored. As pointed out by the famous physicist Max Planck, thermodynamics will be the guiding and connecting principle forging ahead the new unchartered emerging field of non-equilibrium phenomenon and beyond.

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DECLARATION

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

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Place and time of submission: Addis Ababa University, September 2020

This PhD dissertation has been submitted for examination with my approval as University advisor.

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