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Master Thesis

Master thesis

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Chapter 1

Introduction

1.1 Coherence and Excitation Transport

In this chapter, we aim to explain the phenomena of long coherences (lifetimes) and the excitation transport of light on a microtubule. The proposed model takes the following approach:

- The microtubule is modeled as a cylindrical structure consisting of nodes. Each node represents an atom, which is modeled as a two-level system. The number of atoms, N_{atoms}, is determined by the number of chains (n_{chains}) and the number of rings (n_{rings}), assuming fixed positions for these nodes.

- The system is restricted to a single excitation.

- A time-dependent coupling to an electric field is proposed, which may be either classical or quantum in nature. This coupling is intended to facilitate spectroscopy.

- Two types of Lindblad operators are introduced to model dissipation processes. Specifically:

  1. Spontaneous decay
  2. Dephasing

The Lindblad operators introduced to model the spontaneous decay and dephasing processes for each individual atom are defined as follows:

$$C_{\text{decay}}^{(i)} = \sqrt{\gamma_0}\, \sigma_-^{(i)}, \tag{1.1}$$

$$C_{\text{dephase}}^{(i)} = \sqrt{\gamma_\phi}\, \sigma_z^{(i)}, \tag{1.2}$$

where:

- $C_{\text{decay}}^{(i)}$ describes the spontaneous decay of the i-th atom, with a rate given by γ_0.

- $C_{\text{dephase}}^{(i)}$ describes the dephasing of the i-th atom, with a rate given by γ_ϕ.

- $\sigma_-^{(i)}$ is the lowering operator for the i-th atom, and $\sigma_z^{(i)}$ is the Pauli z-operator for the i-th atom.

1.2   Motivation

It is widely assumed that one of the crucial tasks currently facing quantum theorists is to understand and characterize the behaviour of realistic quantum systems. In any experiment, a quantum system is subject to noise and decoherence due to the unavoidable interaction with its surroundings. The theory of open quantum systems aims at developing a general framework to analyze the dynamical behaviour of systems that, as a result of their coupling with environmental degrees of freedom, will no longer evolve unitarily. [1]

2DES> [2], [3], [4]

NONlinear Optics> [5], [6]

Spectroscopy investigates the interaction between matter and electromagnetic radiation, offering a means to analyze composition and structure. Central to this analysis is the understanding of how molecules respond to specific frequencies of light, revealing information about their energy levels and bonding. Key concepts include wavelength (λ), wavenumber ($\bar{\nu}$), and frequency (ν). Wavelength, the distance between successive wave crests, is typically measured in nanometers or micrometers. Wavenumber, expressed in inverse centimeters (cm^{-1}), represents the number of waves per unit distance and is directly proportional to energy, defined as $\bar{\nu} = 1/\lambda$ (where λ is in cm). Frequency, the number of wave cycles per second, is measured in Hertz (Hz), and the angular frequency (ω) is related to frequency by $\omega = 2\pi\nu$. The relationship between angular frequency and wavenumber is given by $\omega = 2\pi c\bar{\nu}$, where c is the speed of light.

Next, I converted all units into femtoseconds (fs^{-1}), which is commonly used in time-domain spectroscopy.

Spectrometers are instruments designed to measure the intensity of light as a function of wavelength or frequency.

Different types of spectrometers are employed for various regions of the electromagnetic spectrum. Notably, UV-Vis spectrometers analyze absorption and transmission of ultraviolet and visible light, while infrared (IR) spectrometers measure the absorption of infrared light, providing insights into molecular vibrations. Nuclear Magnetic Resonance (NMR) spectrometers probe the magnetic properties of atomic nuclei, revealing molecular structure.

Chapter 2

Derivation of the Redfield Equation

The following derivation is part of [7]

2.1 Derivation from microscopic dynamics

The most common derivation of the Redfield master equation is based on open quantum theory. We will begin by discussing the general problem, where a small quantum system interacts with a larger environment. The total system Hilbert space $\mathcal{H}_T$ is divided into our system of interest, belonging to a Hilbert space $\mathcal{H}_S$, and the environment living in $\mathcal{H}_E$.

$$\mathcal{H}_T = \mathcal{H}_S \otimes \mathcal{H}_E. \tag{2.1}$$

The Redfield equation is then an effective motion equation for a this subsystem of interest S. The derivation can be found in several textbooks such as Breuer and Petruccione [8].

The evolution of the total system is given by the Liouville-Von Neumann equation, which represents the starting point of our derivation:

$$\dot{\rho}_T(t) = -i[H_T, \rho_T(t)], \tag{2.2}$$

where $\rho_T(t)$ is the density matrix of the total system, and H_T is the total Hamiltonian. Note that we used units where $\hbar = 1$. This equation can not be solved for arbitrary large enviroments. But as we are interested in the dynamics of the system without the environment, we trace over the environment degrees of freedom to obtain the reduced density matrix of the system $\rho(t) = \text{Tr}_E[\rho_T]$.

The total Hamiltonian can be separated as:

$$H_T = H_S \otimes \mathbb{1}_E + \mathbb{1}_S \otimes H_E + \alpha H_I, \tag{2.3}$$

where $H_S \in \mathcal{H}_S$, $H_E \in \mathcal{H}_E$, and $H_I \in \mathcal{H}_T$. H_I represents the interaction between the system and the environment with coupling strength α. The interaction term is typically decomposed as:

$$H_I = \sum_i S_i \otimes E_i, \tag{2.4}$$

where $S_i \in \mathcal{B}(\mathcal{H}_S)$ and $E_i \in \mathcal{B}(\mathcal{H}_E)$ are operators, that only act on the system and environment respectively.

The following requirements are to be fuildilled by the final derived Redfield equation:

- The equation should be linear in the system density matrix $\dot{\rho}_S(t) = F(\rho_S(t))$ (reduced equation of motion).

- The equation should be Markovian, meaning that the evolution of the system density matrix at time t only depends on the state of the system at time t and not on its past history $\dot{\rho}_S(t) = \rho_S(t)$.

- The equation should be trace-preserving, meaning that $\text{Tr}[\rho_S(t)] = \text{Tr}[\rho_S(0)]$ for all times t.

Unlike the Linblad equation it does not guarantee the complete (not even normal) positivity of the density matrix, which is a requirement for a physical state. So care has to be taken, when the Redfieldequation is useful. The equation will be valid in the weak coupling limit, meaning that the constant in the interaction Hamiltonian H_I fulfills $\alpha \ll 1$.

2.1.1   Interaction Picture

To describe the system dynamics, we move to the interaction picture where the operators evolve with respect to $H_S + H_E$. Any arbitrary operator O in the Schrödinger picture takes the form

$$\hat{O}(t) = e^{i(H_S+H_E)t}Oe^{-i(H_S+H_E)t}, \tag{2.5}$$

in the interaction picture, and depends on time. States now evolve only according to the interaction Hamiltonian H_I, and the Liouville-Von Neumann equation (Eq. (2.2)) changes to:

$$\dot{\hat{\rho}}_T(t) = -i\alpha[\hat{H}_I(t), \hat{\rho}_T(t)], \tag{2.6}$$

which can be formally integrated as:

$$\hat{\rho}_T(t) = \hat{\rho}_T(0) - i\alpha \int_0^t ds[\hat{H}_I(s), \hat{\rho}_T(s)]. \tag{2.7}$$

This equation will be inserted in Eq. (2.6):

$$\dot{\hat{\rho}}_T(t) = -i\alpha \left[\hat{H}_I(t), \hat{\rho}_T(0)\right] - \alpha^2 \int_0^t \left[\hat{H}_I(t), \left[\hat{H}_I(s), \hat{\rho}_T(s)\right]\right] ds, \tag{2.8}$$

which is not Morkovian, because of the intergal which sums up all the past. The step of integration and insertion can be repreated leading to a series expansion of the density matrix in the small parameter α:

$$\dot{\hat{\rho}}_T(t) = -i\alpha \underbrace{\left[\hat{H}_I(t), \hat{\rho}_T(0)\right]}_{(1)} - \alpha^2 \int_0^t \underbrace{\left[\hat{H}_I(t), \left[\hat{H}_I(s), \hat{\rho}_T(t)\right]\right]}_{(2)} ds + \mathcal{O}(\alpha^3). \tag{2.9}$$

where third order contributions (and higher) are neglected from now on. This can be justified in the weak coupling limit where $\alpha \ll 1$, which represents the "**Born**" approximation.

In this sense, the Redfield equation will be a second-order approximation of the actual dynamics. The weak coupling assumption does not hold universally and cannot be applied to all systems. For instance, it is often invalid in chemical or biological systems.

Remark, that Eq. (2.9) is still not Morkovian, because of the intergal over time. Since we are only interested in the dynamics of the system S, we will now take the partial trace over the environment degrees of freedom in Eq. (2.9).

2.1.2   Partial Trace

We now assume the whole system to be seperatable at $t = 0$ as a product state:

$$\hat{\rho}_T(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_E(0), \tag{2.10}$$

which means, that the two sub-systems only come into contact at $t = 0$ and there are no correlations. We take the interaction Hamiltonian Eq. (2.4), which has the same shape in the Interaction Picture into account. With this, the partial trace over the environment of the part (1) of Eq. (2.9) is given by:

$$\sum_i \text{Tr}_E\big[S_i \otimes E_i, \hat{\rho}_S(0) \otimes \hat{\rho}_E(0)\big] = \sum_i \big(S_i\hat{\rho}_S(0) - \hat{\rho}_S(0)S_i\big) \cdot \text{Tr}_E\big[E_i\hat{\rho}_E(0)\big], \tag{2.11}$$

where we used the cyclic property of the trace. We define the average of the bath degrees of freedom at zero temperature:

$$\langle E_i \rangle_0 \equiv \text{Tr}_E\big[E_i\hat{\rho}_E(0)\big]. \tag{2.12}$$

which results to zero, simplifying Eq. (2.9) to only the second part. This can always be justified when adding a zero to the total Hamiltonian:

$$H_T = H_S' + H_E + \alpha H_I', \tag{2.13}$$

where a new interaction and system Hamiltonian are introduced. The interaction Hamiltonian takes new environmental operators E_i' which are shifted by the average of the environment operators at time $t = 0$:

$$H_I' = \sum_i S_i \otimes E_i' = \sum_i S_i \otimes (E_i - \langle E_i \rangle_0). \tag{2.14}$$

The new system Hamiltonian is then given by the sum of the original system Hamiltonian shifted proportionally by the average of the environment operators at time $t = 0$:

$$H_S' = H_S + \alpha \sum_i S_i \langle E_i \rangle_0, \tag{2.15}$$

This however doesn't change the structure of the system dynamics. It only accounts for a redefinition of the energy levels ("a sort of renormalization"). This way the equation (2.11) results to zero and only the second part of the equation Eq. (2.9) remains.

$$\dot{\rho}_S(t) = -i\alpha[\hat{H}_I(t), \hat{\rho}_T(0)] - \alpha^2 \int_0^t ds \text{Tr}_E\big[\hat{H}_I(t), [\hat{H}_I(s), \rho_S(t) \otimes \rho_E]\big]$$
$$= -\alpha^2 \int_0^t ds \text{Tr}_E\big[\hat{H}_I(t), [\hat{H}_I(s), \rho_S(t) \otimes \rho_E]\big]. \tag{2.16}$$

In the follwoing, we will derive the final expression by calculating the environmental traces in the last equation.

2.1.3   Final Expression

Defining $s' = t - s$, we rewrite the second-order term as:

$$\dot{\rho}_S(t) = \alpha^2 \int_0^t ds \operatorname{Tr}_E \Big\{ \hat{H}_I(t) \big[\hat{H}_I(t-s)\hat{\rho}_T(t) - \hat{\rho}_T(t)\hat{H}_I(t-s) \big]$$

$$- \big[\hat{H}_I(t-s)\hat{\rho}_T(t) - \hat{\rho}_T(t)\hat{H}_I(t-s) \big] \hat{H}_I(t) \Big\}. \qquad (2.17)$$

A seperatability at all times is now assumed:

$$\hat{\rho}_T(t) = \hat{\rho}_S(t) \otimes \hat{\rho}_E(t), \qquad (2.18)$$

This assumtion has to be made even stronger later $\hat{\rho}_T(t) = \hat{\rho}_S(t) \otimes \hat{\rho}_E(0)$. Expanding Eq. (2.17), we obtain:

$$\dot{\rho}_T(t) = \alpha^2 \int_0^t ds \Big\{ \operatorname{Tr}_E \big[\hat{H}_I(t)\hat{H}_I(t-s)\hat{\rho}_T(t) \big] - \operatorname{Tr}_E \big[\hat{H}_I(t)\hat{\rho}_T(t)\hat{H}_I(t-s) \big] -$$

$$\operatorname{Tr}_E \big[\hat{H}_I(t-s)\hat{\rho}_T(t)\hat{H}_I(t) \big] + \operatorname{Tr}_E \big[\hat{\rho}_T(t)\hat{H}_I(t-s)\hat{H}_I(t) \big] \Big\}. \qquad (2.19)$$

Now, inserting the interaction Hamiltonian by tracking the operators at time $t - s$ with i' and at t with i, we have:

$$\dot{\rho}_T(t) = \alpha^2 \sum_{i,i'} \int_0^t ds \Big\{ \operatorname{Tr}_E \big[\hat{S}_i(t)\hat{S}_{i'}(t-s)\hat{\rho}_S(t) \otimes \hat{E}_i(t)\hat{E}_{i'}(t-s)\hat{\rho}_E(t) \big] -$$

$$\operatorname{Tr}_E \big[\hat{S}_i(t)\hat{\rho}_S(t)\hat{S}_{i'}(t-s) \otimes \hat{E}_i(t)\hat{\rho}_E(t)\hat{E}_{i'}(t-s) \big] -$$

$$\operatorname{Tr}_E \big[\hat{S}_{i'}(t-s)\hat{\rho}_S(t)\hat{S}_i(t) \otimes \hat{E}_{i'}(t-s)\hat{\rho}_E(t)\hat{E}_i(t) \big] +$$

$$\operatorname{Tr}_E \big[\hat{\rho}_S(t)\hat{S}_{i'}(t-s)\hat{S}_i(t) \otimes \hat{\rho}_E(t)\hat{E}_{i'}(t-s)\hat{E}_i(t) \big] \Big\}. \qquad (2.20)$$

Since the trace only acts on the environment, the system operators can be taken out of the trace, and we define the correlation functions:

$$C_{ij}(t-s) = \operatorname{Tr}_E \big[\hat{E}_i(t)\hat{E}_{i'}(t-s)\hat{\rho}_E(t) \big], \qquad (2.21)$$

such that:

$$\dot{\rho}_T(t) = \alpha^2 \sum_{i,i'} \int_0^t ds \Big\{ C_{ij}(t-s) \big[\hat{S}_i(t), \hat{S}_{i'}(t-s)\hat{\rho}_S(t) \big] + \text{H.c.} \Big\}. \qquad (2.22)$$

which is the desired form of the Redfield equation.

Note however, that the we have not used the strong condition $\hat{\rho}_T(t) = \hat{\rho}_S(t) \otimes \hat{\rho}_E(0)$ was not used yet. This however will make it possible to calculate the correlations Eq. (2.21), because we can assume that the enviroment is in a thermal equilibruium at a certain temperature. Because of the assumption this is the case for all times. It is equivalent to say that the environment is unaffected by the system. It is memoryless, because it is very big.

Chapter 3

Bath Correlation Functions

3.1 Bath Correlator

The general task of this chapter is to calculate the bath correlator, which is defined as:

$$C(\tau) = \langle B(\tau)B(0)\rangle, \tag{3.1}$$

where B is the bath operator, specified later. This correlator measures the operator B at two different times in the bath.

3.2 Useful Tools

3.2.1 Infinite Geometric Series

An infinite geometric series is expressed as:

$$S = a + ar + ar^2 + ar^3 + \cdots = \sum_{n=0}^{\infty} ar^n, \tag{3.2}$$

where a is the first term and r is the common ratio. For $|r| < 1$, the sum converges to:

$$S = \frac{a}{1 - r}. \tag{3.3}$$

Differentiating Eq. (3.3) with respect to r yields another useful series:

$$\sum_{n=0}^{\infty} nr^n = \frac{r}{(1 - r)^2}, \quad \text{for } |r| < 1. \tag{3.4}$$

3.2.2 Trace

For a bipartite system $A \otimes B$, the reduced density matrix of system A is obtained by tracing out system B:

$$\rho_A = \text{Tr}_B[\rho_{AB}], \tag{3.5}$$

where the partial trace over the subspace B is defined as:

$$\text{Tr}_B\left[\sum_{i,j,k,l} |a_i\rangle\langle a_j| \otimes |b_k\rangle\langle b_l|\right] = \sum_{i,j} |a_i\rangle\langle a_j|\text{Tr}\left[|b_k\rangle\langle b_l|\right] \tag{3.6}$$

The expectation value of an operator A in a system S is calculated as:

$$\langle A \rangle_S = \text{Tr}_S[\rho_S A] = \frac{1}{Z} \sum_n e^{-\beta E_n} A_{nn}, \tag{3.7}$$

where the inverse temperature β is defined as:

$$\beta = \frac{1}{k_B T}. \tag{3.8}$$

3.3 Harmonic Oscillators

A bosonic bath is modeled by an infinitely big set of harmonic oscillators, which we assume to be in thermal equilibrium. For such a system the thermal state is described by the Gibbs distribution:

$$\rho = \frac{e^{-\beta H}}{\text{Tr}\left[e^{-\beta H}\right]}, \quad H = \sum_k \hbar\omega_k \left(b_k^\dagger b_k + \frac{1}{2}\right), \quad E_k = \hbar\omega_k(n_k + \frac{1}{2}), \tag{3.9}$$

where ω_k is the frequency of the k-th mode, $b_k^\dagger$ and b_k are the creation and annihilation operators, respectively, and $n_k = \langle b_k^\dagger b_k \rangle$ is the expectation value of the number operator. The number operator is an eigenoperator to the number states $|k\rangle$ and the number n_k represents the number of excitations in that mode. The energy of the k-th mode E_k is directly related to this number.

3.3.1 Single Mode

For a single mode k harmonic oscillator $H = \hbar\omega_k b_k^\dagger b_k$ in thermal equilibrium at temperature T, the density matrix is given by:

$$\rho = \frac{e^{-\beta\hbar\omega_k b_k^\dagger b_k}}{Z_k}, \tag{3.10}$$

where ω_k is the constant frequency of the mode k. The partition function Z can be calculated by the geometric series:

$$Z_k \equiv \text{Tr}\left[e^{-\beta H}\right] = \sum_{m=0}^\infty \langle m|e^{-\beta\hbar\omega_k(n_k+\frac{1}{2})}|m\rangle = e^{-\beta\hbar\omega_k/2} \sum_{m=0}^\infty \langle m|m\rangle \delta_{km} e^{-\beta\hbar\omega_k n_k} = \frac{e^{-\beta\hbar\omega_k/2}}{1 - e^{-\beta\hbar\omega_k}}. \tag{3.11}$$

Using this, the expectation value of the number operator can be calculated:

$$n_k = \langle b_k^\dagger b_k \rangle_{\text{th}} = \text{Tr}\left[b_k^\dagger b_k \frac{e^{-\beta H}}{Z_k} \right] \tag{3.12}$$

$$= \frac{\text{Tr}\left[b_k^\dagger b_k e^{-\beta \hbar \omega_k b_k^\dagger b_k} \right]}{Z_k} \tag{3.13}$$

$$= \frac{\sum_{m=0}^{\infty} \langle m | b_k^\dagger b_k e^{-\beta \hbar \omega_k b_k^\dagger b_k} | m \rangle}{\frac{e^{-\beta \hbar \omega_k /2}}{1 - e^{-\beta \hbar \omega_k}}} \tag{3.14}$$

$$= \frac{e^{-\beta \hbar \omega_k}}{1 - e^{-\beta \hbar \omega_k}} \tag{3.15}$$

$$= \frac{1}{e^{\beta \hbar \omega_k} - 1}. \tag{3.16}$$

where we have used Eq. (3.4) in the last step. The partition function for the infinite set then generalizes to a product:

$$Z = \prod_k Z_k = \prod_k \frac{e^{-\beta \hbar \omega_k /2}}{1 - e^{-\beta \hbar \omega_k}}. \tag{3.17}$$

3.4 Bath Correlators

Now we turn to calculating the bath correlator. The bath operator B is defined as:

$$B = \sum_{n=1}^{\infty} c_n x_n, \tag{3.18}$$

where c_n are coupling constants and x_n are position operators. Note that in Sec. 2.1, the interaction Hamiltonian reduces such that only one bath correlator $C(\tau) \equiv C_{ii}(\tau)$ in Eq. (2.21) remains.

Expressing B in terms of creation and annihilation operators:

$$B(0) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{1}{2 m_n \omega_n}} (b_n + b_n^\dagger), \tag{3.19}$$

$$B(\tau) = \sum_{n=1}^{\infty} c_n \sqrt{\frac{1}{2 m_n \omega_n}} \left(b_n e^{-i \omega_n \tau} + b_n^\dagger e^{i \omega_n \tau} \right). \tag{3.20}$$

Substituting $B(\tau)$ and $B(0)$ into Eq. (3.1), we find:

$$C(\tau) = \left\langle \sum_{n=1}^{\infty} c_n \sqrt{\frac{1}{2 m_n \omega_n}} (b_n e^{-i \omega_n \tau} + b_n^\dagger e^{i \omega_n \tau}) \sum_{m=1}^{\infty} c_m \sqrt{\frac{1}{2 m_m \omega_m}} (b_m + b_m^\dagger) \right\rangle. \tag{3.21}$$

Similar calculations to Eq. (3.12) thermal expectation values can be calculated:

$$\langle b_n b_m^\dagger \rangle = \delta_{nm}(n_n + 1), \quad \langle b_n^\dagger b_m \rangle = \delta_{nm} n_n, \tag{3.22}$$

where n_k is the Bose-Einstein distribution:

$$n_k = \frac{1}{e^{\beta \omega_k} - 1}, \tag{3.23}$$

we obtain:

$$C(\tau) = \sum_{n=1}^{\infty} \frac{c_n^2}{2 m_n \omega_n} \left[(n_n + 1) e^{-i \omega_n \tau} + n_n e^{i \omega_n \tau} \right]. \tag{3.24}$$

3.4.1   Spectral Density Representation

The bath correlator can be expressed in terms of the spectral density $J(\omega)$, defined as:

$$J(\omega) = \pi \sum_{n=1}^{\infty} \frac{c_n^2}{2 m_n \omega_n} \delta(\omega - \omega_n). \tag{3.25}$$

With this, the bath correlator becomes:

$$C(\tau) = \int_0^{\infty} d\omega \frac{J(\omega)}{\pi} \left[(n(\omega) + 1) e^{-i \omega \tau} + n(\omega) e^{i \omega \tau} \right]. \tag{3.26}$$

3.4.2   Continuum Limit

As the frequencies $\{\omega_j\}$ become dense, the sum transitions to an integral:

$$\sum_{j=1}^{\infty} \quad \longrightarrow \quad \int d\omega' \, \rho(\omega'),$$

where $\rho(\omega')$ is the density of states. The coupling g_j becomes a function of frequency, $g(\omega')$, leading to:

$$J(\omega) = \rho(\omega) \, g(\omega)^2.$$

In this continuum limit, the bath correlator Eq. (3.24) becomes:

$$C(\tau) = \int_0^{\infty} d\omega \frac{J(\omega)}{\pi} \left[\coth\left(\frac{\beta \omega}{2} \right) \cos(\omega \tau) - i \sin(\omega \tau) \right]. \tag{3.27}$$

3.4.3   Ohmic Spectral Density

Source: Ulrich Weiss chapter 7.3: (*my interpretation: The Redfield equation is influenced by classical phenomenological models of dissipation*) For an Ohmic spectral density, the damping is frequency-independent, and the spectral density is given by:

$$J(\omega) \propto \gamma \omega, \tag{3.28}$$

where γ is the damping constant. To ensure physical behavior, a cutoff is introduced:

$$J(\omega) = \eta \frac{\omega^s}{\omega_c^{s-1}} e^{-\omega / \omega_c}, \tag{3.29}$$

where η is a dimensionless coupling constant, ω_c is the cutoff frequency, and s determines the type of spectral density (Ohmic for $s = 1$, sub-Ohmic for $s < 1$, and super-Ohmic for $s > 1$).

Chapter 4

Rabi Oscillations and Related Concepts

4.0.1 Density Matrix Formalism

The density matrix formalism provides a powerful framework to describe the dynamics of quantum systems, especially when dealing with mixed states or decoherence. The density matrix ρ is defined as:

$$\rho = |\psi\rangle\langle\psi|, \tag{4.1}$$

for pure states, and as a statistical mixture for mixed states. In this formalism, the diagonal elements represent populations and the off-diagonal elements represent coherences between states. Coherences are phase relations between different quantum states, which are crucial for interference. For example for a two level system a clear phase relation and a pure quantum state would have off diagonal elements of $\rho_{ij} = 1/2$. This state is often referred to as a coherent superposition of the two states.

When coupling a system to an environment, the environment is responsible for decoherence. The state evolves over time to a purely statistical mixture of states.

The time evolution of the density matrix is governed by the Liouville-von Neumann equation:

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}[H, \rho], \tag{4.2}$$

where H is the system Hamiltonian.

In the presence of decoherence or dissipation, the dynamics can be described using the Lindblad master equation:

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}[H, \rho] + \sum_k \mathcal{L}_k(\rho), \tag{4.3}$$

where $\mathcal{L}_k(\rho)$ are Lindblad operators modeling the interaction with the environment.

4.1 Rabi Oscillations

Rabi oscillations describe the coherent oscillatory behavior of a two-level quantum system interacting with a resonant electromagnetic field. This phenomenon is fundamental in quantum mechanics and quantum optics, with applications in quantum computing, spectroscopy, and atomic physics.

4.1.1   1. Schrödinger Picture

Consider a two-level system with states $|g\rangle$ (ground state) and $|e\rangle$ (excited state). The energy separation between the two states is given by:

$$\omega_0 = \frac{E_e - E_g}{\hbar}, \tag{4.4}$$

where E_e and E_g are the energies of the excited and ground states, respectively.

The system Hamiltonian is expressed as:

$$H_S = \hbar\omega_0 |e\rangle \langle e|. \tag{4.5}$$

The interaction of the system with a classical electromagnetic field $E(t)$ is described by the time-dependent interaction Hamiltonian:

$$H_{\text{int}}(t) = -\mu E(t) = -\left(\mu_{eg} |e\rangle \langle g| + \mu_{ge} |g\rangle \langle e|\right) E(t), \tag{4.6}$$

where μ_{eg} and μ_{ge} are the dipole matrix elements.

The total Hamiltonian of the system is then given by:

$$H(t) = H_S + H_{\text{int}}(t), \tag{4.7}$$

which combines the system's intrinsic energy and its interaction with the field.

Alternatively, the total Hamiltonian can be written in terms of Pauli matrices as:

$$H(t) = \frac{\hbar\omega_0}{2}\sigma_z + \hbar\Omega \cos(\omega_L t + \phi)\sigma_x, \tag{4.8}$$

where Ω is the Rabi frequency, proportional to the field amplitude and the dipole matrix element, ϕ, ω_L is the phase, frequency of the driving field respectively, and σ_z and σ_x are the Pauli matrices

The time evolution of the system is governed by the time dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H(t)|\psi(t)\rangle, \tag{4.9}$$

which describes the dynamics of the quantum state $|\psi(t)\rangle$ under the influence of the Hamiltonian $H(t)$.

4.1.2   Rotating Wave Approximation (RWA)

The rotating wave approximation simplifies the analysis of the Hamiltonian in Eq. (4.8). This approximation is valid when $\Omega \ll \omega_0$, allowing us to focus on the resonant interaction. The RWA reveals the essence of Rabi oscillations, where the population of the two levels oscillates with the Rabi frequency $\Omega_R = \sqrt{\Delta^2 + \Omega^2}$.

4.2   Applying the RWA Explicitly

Suppose the electric field is classical and oscillatory:

$$E(t) = E_0 \cos(\omega_L t + \phi) = \frac{E_0}{2}\left(e^{i\omega_L t + i\phi} + e^{-i\omega_L t - i\phi}\right) \tag{4.10}$$

Assuming $\mathbf{d} = \mu_{eg} \left|e\right\rangle \left\langle g\right| + \mathbf{d}_{ge} \left|g\right\rangle \left\langle e\right|$ and defining the Rabi frequency:

$$\hbar\Omega = -\mu_{eg} \cdot \mathbf{E}_0 \tag{4.11}$$

is the Rabi frequency, proportional to the field amplitude and the dipole matrix element.

Then the interaction Hamiltonian (4.6) becomes:

$$H_{\text{int}}(t) = \hbar\Omega \cos(\omega_L t + \phi)(\left|e\right\rangle \left\langle g\right| + \left|g\right\rangle \left\langle e\right|) \tag{4.12}$$

Now go to the interaction picture with a unitary transformation $U_0(t)$:

$$U_0(t) = e^{-iH_0 t/\hbar} = e^{-i\omega_0 t \left|e\right\rangle \left\langle e\right|} \tag{4.13}$$

The interaction Hamiltonian in the interaction picture is with Eq. (4.13):

$$H_{\text{int}}^{(I)}(t) = U_0^\dagger(t) H_{\text{int}}(t) U_0(t). \tag{4.14}$$

Under this transformation, the operators evolve as described in Eq. (4.12):

$$\left|e\right\rangle \left\langle g\right| \to e^{i\omega_0 t} \left|e\right\rangle \left\langle g\right|, \quad \left|g\right\rangle \left\langle e\right| \to e^{-i\omega_0 t} \left|g\right\rangle \left\langle e\right|. \tag{4.15}$$

which results in

$$H_{\text{int}}^{(I)}(t) = \hbar\Omega \cos(\omega_L t + \phi) \left(e^{i\omega_0 t} \left|e\right\rangle \left\langle g\right| + e^{-i\omega_0 t} \left|g\right\rangle \left\langle e\right| \right). \tag{4.16}$$

Rotating Frame Transformation

We now define the unitary transformation:

$$U_L(t) = e^{i\omega_L t \left|e\right\rangle \left\langle e\right|} = \begin{pmatrix} 1 & 0 \\ 0 & e^{i\omega_L t} \end{pmatrix} \tag{4.17}$$

that rotates the reference frame of the system to the rotating frame at frequency ω_L.

The transformed density matrix is:

$$\tilde{\rho}(t) = U_L^\dagger(t) \rho(t) U_L(t) \tag{4.18}$$

and in this frame, the total transformed Hamiltonian is:

$$\tilde{H}^I(t) = U_L^\dagger(t) H_{\text{int}}^I(t) U_L(t) - i\hbar U_L(t) \frac{d}{dt} U_L^\dagger(t) \tag{4.19}$$

The second term gives:

$$-i\hbar U_L^\dagger(t) \frac{d}{dt} U_L(t) = -\hbar\omega_L \left|e\right\rangle \left\langle e\right| \tag{4.20}$$

Thus:

$$\tilde{H}^I(t) = -\hbar\omega_L \left|e\right\rangle \left\langle e\right| + U_L^\dagger(t) H_{\text{int}}^I(t) U_L(t) \tag{4.21}$$

Transforming the Interaction Hamiltonian

In the rotating frame:

$$U_L^\dagger(t) \left|e\right\rangle \left\langle g\right| U_L(t) = e^{-i\omega_L t} \left|e\right\rangle \left\langle g\right|, \quad U_L^\dagger(t) \left|g\right\rangle \left\langle e\right| U_L(t) = e^{i\omega_L t} \left|g\right\rangle \left\langle e\right| \tag{4.22}$$

The interaction Hamiltonian becomes:

$$\tilde{H}_{\text{int}}(t) = -\hbar\Omega\cos(\omega_L t + \phi)\left(e^{i(\omega_0 - \omega_L)t}\,|e\rangle\,\langle g| + e^{-i(\omega_0 - \omega_L)t}\,|g\rangle\,\langle e|\right) \tag{4.23}$$

Rotating Wave Approximation (RWA)

We can use the identity:

$$\cos(\omega_L t + \phi) = \frac{1}{2}\left(e^{i(\omega_L t + \phi)} + e^{-i(\omega_L t + \phi)}\right) \tag{4.24}$$

Under RWA, drop fast-rotating terms $e^{\pm i 2\omega_L t}$, keeping only:

$$\tilde{H}_{\text{RWA}} = -\hbar\Delta\,|e\rangle\,\langle e| - \frac{E_0}{2}\left(\mu_{eg}\,|e\rangle\,\langle g| + \mu_{ge}\,|g\rangle\,\langle e|\right) \tag{4.25}$$

Equation of Motion

The von Neumann equation becomes:

$$\frac{d}{dt}\tilde{\rho}(t) = -\frac{i}{\hbar}[\tilde{H}_{\text{RWA}}, \tilde{\rho}(t)] + (\text{dissipation terms}) \tag{4.26}$$

To recover the entries of the original density matrix $\rho(t)$ from the evolved density matrix in the rotating frame $\tilde{\rho}(t)$, we use the inverse of the unitary transformation $U_L(t)$:

$$\rho(t) = U_L^{\dagger}(t)\tilde{\rho}(t)U_L(t) \tag{4.27}$$

where $U_L(t)$ and $U_L^{\dagger}(t)$ are given in Eq. (4.17).

Let the density matrices be:

$$\rho(t) = \begin{pmatrix} \rho_{gg}(t) & \rho_{ge}(t) \\ \rho_{eg}(t) & \rho_{ee}(t) \end{pmatrix}, \quad \tilde{\rho}(t) = \begin{pmatrix} \tilde{\rho}_{gg}(t) & \tilde{\rho}_{ge}(t) \\ \tilde{\rho}_{eg}(t) & \tilde{\rho}_{ee}(t) \end{pmatrix} \tag{4.28}$$

The recovery process is:

$$\rho(t) = \begin{pmatrix} 1 & 0 \\ 0 & e^{-i\omega_L t} \end{pmatrix}\begin{pmatrix} \tilde{\rho}_{gg}(t) & \tilde{\rho}_{ge}(t) \\ \tilde{\rho}_{eg}(t) & \tilde{\rho}_{ee}(t) \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & e^{i\omega_L t} \end{pmatrix} \tag{4.29}$$

Simplifying:

$$\rho(t) = \begin{pmatrix} \tilde{\rho}_{gg}(t) & e^{i\omega_L t}\tilde{\rho}_{ge}(t) \\ e^{-i\omega_L t}\tilde{\rho}_{eg}(t) & \tilde{\rho}_{ee}(t) \end{pmatrix} \tag{4.30}$$

Thus, the entries of the original density matrix $\rho(t)$ are related to the entries of the density matrix in the rotating frame $\tilde{\rho}(t)$ by:

$$\rho_{gg}(t) = \tilde{\rho}_{gg}(t)$$
$$\rho_{ee}(t) = \tilde{\rho}_{ee}(t)$$
$$\rho_{ge}(t) = e^{i\omega_L t}\tilde{\rho}_{ge}(t)$$
$$\rho_{eg}(t) = e^{-i\omega_L t}\tilde{\rho}_{eg}(t)$$

By moving to a rotating frame and neglecting rapidly oscillating terms, the effective Hamiltonian becomes:

$$H_{\text{RWA}} = \frac{\hbar\Delta}{2}\sigma_z + \frac{\hbar\Omega}{2}\sigma_x, \tag{4.31}$$

4.3 Applications and Implications

Rabi oscillations and the associated theoretical tools, such as the RWA and density matrix formalism, have wide-ranging applications:

- **Quantum Computing:** Rabi oscillations are used to implement quantum gates by precisely controlling the population of qubits.

- **Spectroscopy:** The Rabi frequency provides information about the interaction strength between light and matter.

- **Atomic Physics:** Understanding Rabi oscillations is essential for manipulating atomic states in experiments.

These concepts form the foundation for advanced topics in quantum mechanics and quantum technologies.

Step-by-Step Derivation of RWA in a Two-Level System (with Phase)

Step 5: Apply the Rotating Wave Approximation (RWA)

Use the identity:

$$\cos(\omega_L t + \phi) = \frac{1}{2} \left(e^{i(\omega_L t + \phi)} + e^{-i(\omega_L t + \phi)} \right) \tag{4.32}$$

The interaction terms become:

$$\frac{\hbar\Omega}{2} \left(e^{i(\omega_0 t + \omega_L t + \phi)} |e\rangle \langle g| + e^{i(\omega_0 t - \omega_L t - \phi)} |e\rangle \langle g| + \text{h.c.} \right) \tag{4.33}$$

Keep only the **slowly rotating terms** at frequency $\Delta = \omega_0 - \omega_L$, and drop the fast ones. The RWA Hamiltonian becomes:

$$H_{\text{RWA}} = \hbar\Delta |e\rangle \langle e| + \frac{\hbar\Omega}{2} \left(e^{i\phi} |e\rangle \langle g| + e^{-i\phi} |g\rangle \langle e| \right) \tag{4.34}$$

Step 6: Solve the Dynamics (Rabi Oscillations with Phase)

In matrix form, in the basis $\{|e\rangle, |g\rangle\}$:

$$H_{\text{RWA}} = \frac{\hbar}{2} \begin{pmatrix} 2\Delta & \Omega e^{i\phi} \\ \Omega e^{-i\phi} & 0 \end{pmatrix} \tag{4.35}$$

The phase ϕ does not change the **Rabi frequency**:

$$\Omega_R = \sqrt{\Delta^2 + \Omega^2} \tag{4.36}$$

But it **rotates the axis of Rabi oscillations** in the Bloch sphere — i.e., it changes the **initial direction** of the drive.

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