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DIPLOMOVÁ PRÁCE



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Theory of electron-phonon interaction in a model open quantum system

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V Praze dne

Jindřich Krčmář

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Abstrakt:

Cílem této práce je prozkoumat projekční operátorovou metodu odvození pohybových rovnic pro redukovanou matici hustoty a aplikovat je na modelový otevřený kvantový systém. Postupně přecházíme z kvantově mechanického modelu molekuly s jedním vibračním stupněm volnosti k příkladu otevřeného kvantového systému relevantního k teorii nelineární spektroskopie. V práci prezentujeme výsledky numerických simulací časové evoluce otevřeného kvantového systému provedených programem napsaným pro tento účel. Zvláště se zabýváme simulacemi řešení časově-bezkonvoluční zobecněné řídicí rovnice do druhého řádu poruchového rozvoje a ukazujeme, že za jistých okolností poskytuje exaktní řešení problému. Text také obsahuje odvození rekurentních relací pro Franck-Condonovy faktory pro nejobecnější případ dvou kvantových harmonických oscilátorů v jedné prostorové dimenzi, tedy transformační matici mezi dvěma bázemi $\mathcal{L}^2(\mathbb{R})$ prostoru určenými řešeními časově nezávislé Schrödingerovy rovnice příslušné těmto oscilátorům.

Klíčová slova: otevřený kvantový systém, projekční operátorová metoda, nelineární spektroskopie, kvantový harmonický oscilátor, Franck-Condonovy faktory

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Abstract:

The aim of this work is to investigate projection operator method of derivation of equations of motion for reduced density matrix and apply it to a model open quantum system. We gradually pass from quantum mechanical model

of a molecule with one vibrational degree of freedom to an example of open quantum system relevant in the theory of nonlinear spectroscopy. In the thesis we present results of numerical simulations of the time evolution of the open quantum system performed with a program written for this purpose. We are specially concerned with simulations of the solution of the time-convolutionless generalized master equation up to the a second order of the perturbation expansion, and we show that under certain conditions it provides an exact solution of the problem. The text also contains derivation of the recurrence relations for the Franck-Condon factors for the most general case of two quantum harmonic oscillators in one space dimension, i. e. transformation matrix between two bases of the $\mathcal{L}^2(\mathbb{R})$ space determined by the solutions of the time-independent Schrödinger equation appropriate for these oscillators.

Keywords: open quantum system, projection operator method, nonlinear spectroscopy, quantum harmonic oscillator, Franck-Condon factors

Chapter 1

Introduction

In quantum mechanics we very often describe a system like it was ideally isolated from its environment. Quantum mechanical theory, which goes beyond this approximation, is known as the theory of open quantum systems. The theory of open quantum system therefore involves the general quantum mechanical topics like quantum measurement process, decoherence or stochastic processes in quantum mechanics. As an example of a field, in which the theory of open quantum systems finds its applications, we could name nonlinear spectroscopy, theory of energy transfer processes (e.g. photosynthesis) and properties of semiconductors. In this work we are going to treat a model open quantum system closely related to the problems in molecular spectroscopy.

In the theory of open quantum system, the environment (for example heat bath) influences the system through coupling terms appearing in the equations of motion. One of the problems of the theory of open quantum systems is to obtain the equations of motion for the relevant - system part of the density matrix. In this thesis we are going to study one of the methods, which leads to the equations of motion for the system, the so-called projection operator technique.

The structure of the thesis is following: In the Chapter 2 we are going to discuss the necessary formalism for the treatment of the open quantum systems. In the first section of this chapter we will introduce quantum mechanical description of the harmonic oscillator stressing its application in light-matter interaction with a model two level molecule. This is going to lead us to the definition of the so-called Franck-Condon factors, which will play an important role in our model system. The recurrence formulas suitable for their computation are derived in Appendix A in detail. In the next section we are going to convert to the more common Dirac notation, which is going to be extensively used in the following chapters.

In the section 2.6 we are going to introduce statistical description of the quantum mechanical system by the density matrix. In this chapter we will also consider equations of motion for the reduced density operators in various forms using superoperator notation. In the last section of this chapter we will show the application of the Franck-Condon factors in transformations of operators and superoperators in different bases.

In the Chapter 3 we will continue with the general model of a system embedded in thermodynamic bath. We will introduce the concept of a two-layer bath and the appropriate two reductions of the total density matrix. In the first section of this chapter we will concentrate on the Hamiltonian of the model system. We are going to arrive at the Hamiltonian of the so-called spin boson model, in which the relevant system is represented by two electronic levels, and the bath is formed by infinitely many harmonic oscillators. In further section of this chapter you can find how is the description by the density operator used to solve some of the problems corresponding to light-matter interaction, and discuss the form of the initial condition, which is going to be used for the computer simulation. The influence of the environmental degrees of freedom in our open quantum system are going to be described by the relaxation tensor in the so-called Haken-Stroble-Reineker model (Ref. [7]).

In the Chapter 4 we will consider the projection operator techniques. We will derive basic equations of motion for the relevant part of the density matrix using the projection superoperators - in particular the Nakajima-Zwanzig equation and the time-convolutionless (TCL) form of the master equation. We will introduce the perturbation expansion in terms of the reduced density matrix in the interaction picture. Then we will treat the perturbation expansion for the time-convolutionless equation.

In the Chapter 5 we are going to deal with a particular application of the perturbation expansion of the TCL equation to our open quantum system. We are going to specify the concrete forms of the relevant Liouville superoperators used in the expansion. Further we will prove an important relation binding the reduced density operator in the interaction picture with the one in the Schrödinger picture. Further we will derive the analytical expression for the time dependence of the twice reduced density operator. In the last section we will concentrate on the derivation of the analytical solutions of the TCL equation up to the second order under some simplifying conditions.

Finally in the Chapter 6 we will present numerical simulations performed by a Fortran program written for this purpose and we will discuss numerical results. We will close this work by discussion of the obtained results.

Chapter 2

Model system and mathematical formalism

2.1 Quantum harmonic oscillator

2.1.1 Solution of time-independent Schrödinger equation

First of all we would like to make a brief reminder of quantum harmonic oscillator (possible to find in most of quantum mechanical textbooks). Let us discuss solutions of time-independent Schrödinger equation

$$E\psi(x) = \hat{H}_B\psi(x) = \left(\frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2\right)\psi(x), \quad (2.1)$$

where in m is the mass and ω is the resonance frequency of the oscillator. The \hat{H}_B is the Hamiltonian operator

$$\hat{H}_B = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 \quad (2.2)$$

of the quantum harmonic oscillator. It is well known, that solutions of this equation have discrete values of energy explicitly expressed as follows

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right), \quad (2.3)$$

where n can take values $0, 1, 2, \dots$ and ω is resonance frequency of the considered oscillator. In the present work we are going to work with exact, normalized solutions ψ_n for energy levels n

$$\psi_n(x) = \sqrt{\frac{1}{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right), \quad (2.4)$$

where H_n are Hermite polynomials

$$H_n(x) = (-1)^n e^{x^2} \left(\frac{d}{dx}\right)^n e^{-x^2}. \quad (2.5)$$

As one can see, the solution (2.4) would have more simple form using a new variable $\tilde{x} = \sqrt{\frac{m\omega}{\hbar}}x$. Then these solutions take a form

$$\psi_n(x) = \sqrt{\frac{1}{2^n n!}} \left(\frac{1}{\pi}\right)^{\frac{1}{4}} e^{-\frac{x^2}{2}} H_n(x), \quad (2.6)$$

where \tilde{x} is replaced by original x (in this work we are going to use frequently solutions of this form). This kind of transformation can be also understood as taking new harmonic oscillator with $m\omega = \hbar$.

2.1.2 Hermite polynomials

Hermite polynomials are solutions of the following differential equation

$$\frac{d}{dx}(e^{-x^2} \frac{d}{dx} H_n(x)) = -2ne^{-x^2} H_n(x). \quad (2.7)$$

It is possible to prove this using definition (2.5) by mathematical induction.

It follows from the definition (2.5) that even Hermite polynomials $H_{2n}(x)$ are even functions and odd Hermite polynomials $H_{2n+1}(x)$ are odd functions of x .

The Hermite polynomials satisfy the following recurrence relation

$$H_{n+1}(x) - 2xH_n(x) + 2nH_{n-1}(x) = 0. \quad (2.8)$$

Using this formula and letting the derivative act in the definition (2.5) you can prove the following formula

$$\frac{d}{dx} H_n(x) = 2nH_{n-1}(x). \quad (2.9)$$

Using the recurrence relation (2.8) in equation (2.6) we obtain recurrence relation for the solution of time-independent Schrödinger equation

$$\psi_n(x) = \sqrt{\frac{2}{n}} x \psi_{n-1}(x) - \sqrt{\frac{n-1}{n}} \psi_{n-2}(x), \quad (2.10)$$

which together with

$$\psi_0(x) = \left(\frac{1}{\pi}\right)^{\frac{1}{4}} e^{-\frac{x^2}{2}}, \quad (2.11)$$

$$\psi_1(x) = \sqrt{2}x\psi_0(x) \quad (2.12)$$

is sufficient to calculate $\psi_n(x)$ for every n .

2.1.3 Creation and annihilation operators

In the text we are going to make use of well known creation and annihilation operators. After the above mentioned transformation ($m\omega = \hbar$) these have a simple form

$$\hat{a} = \frac{1}{\sqrt{2}} \left(x + \frac{d}{dx} \right), \quad (2.13)$$

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}} \left(x - \frac{d}{dx} \right). \quad (2.14)$$

Creation and annihilation operators have the following properties

$$\hat{a}\psi_n(x) = \sqrt{n}\psi_{n-1}(x), \quad (2.15)$$

$$\hat{a}^\dagger\psi_n(x) = \sqrt{n+1}\psi_{n+1}(x), \quad (2.16)$$

$$\hat{a}\psi_0(x) = 0 \quad (2.17)$$

and satisfy the commutation relation:

$$[\hat{a}, \hat{a}^\dagger] = 1. \quad (2.18)$$

2.2 Excited and ground state of a molecule

Let us suppose a model molecule, in which the electrons belonging to the molecule are in state of lowest energy of the molecule - ground state. In our model we suppose that the ground state behaves as a quantum harmonic oscillator with energy levels

$$E_{gn} = E_g + \hbar\omega_g \left(n + \frac{1}{2} \right), \quad (2.19)$$

where ω_g is eigenfrequency of the ground state. The oscillator represents the internal nuclear motion of the molecule. Further we consider that electrons of the molecule may occur in the excited state approximated similarly with quantum harmonic oscillator with energy levels

$$E_{en} = E_e + \hbar\omega_e \left(n + \frac{1}{2} \right), \quad (2.20)$$

where ω_e is analogously eigenfrequency of the excited state.

Now we are going to discuss several expressions of $\psi_{en}(x)$. We can for example assume that the ground and excited states behave as harmonic oscillators with equilibrium positions shifted by x_0 with respect to each other. For simplicity we assume that the ground state has equilibrium position at $x = 0$ and the excited at $x = x_0$ and the eigenfrequencies are equal ($\omega_g = \omega_e$). From the physical point of view the corresponding probability distribution for every eigenstate of the Hamiltonian of the shifted harmonic oscillator has to be the same as for the original one shifted by x_0 . Thanks to this observation the solutions of the Schrödinger equation for the ground state ψ_{gn} and for the excited state ψ_{en} have the following form

$$\psi_{gn}(x) = \sqrt{\frac{1}{2^n n!}} \left(\frac{1}{\pi} \right)^{\frac{1}{4}} e^{-\frac{x^2}{2}} H_n(x) = \psi_{en}(x + x_0), \quad (2.21)$$

$$\psi_{en}(x) = \psi_{gn}(x - x_0), \quad (2.22)$$

where we used equation (2.4). We can also verify this by taking equation (2.1) with different term for the wave-function in the excited state namely $\frac{m\omega^2}{2}\hat{x}^2 \rightarrow \frac{m\omega^2}{2}(\hat{x} - x_0)^2$ and showing that equation (2.22) solve the new time-independent Schrödinger equation. This can be proven for example by substitution $x = \tilde{x} - x_0$ in the original equation.

We could also modify the assumption of wave-functions of the excited states saying that the equilibrium position of the excited state is the same as for ground state but the properties of harmonic oscillator are different, it has different mass m (probably not in the case of excitation, but for the sake of generality let us also include oscillators with different mass) and frequency ω . As we can see from the expression (2.4) this could be understood as modifying parameter $\lambda = \sqrt{\frac{m\omega}{\hbar}}$ in the solution. In this case the $\psi_{en}(x)$ has the form

$$\psi_{en}(x) = \sqrt{\frac{1}{2^n n!}} \left(\frac{\lambda^2}{\pi} \right)^{\frac{1}{4}} e^{-\frac{(\lambda x)^2}{2}} H_n(\lambda x) = \sqrt{\lambda} \psi_{gn}(\lambda x). \quad (2.23)$$

In the general case of one dimensional harmonic oscillator corresponding to the excited state using the same reasoning we would obtain

$$\psi_{en}(x) = \sqrt{\lambda}\psi_{gn}(\lambda(x - x_0)). \quad (2.24)$$

2.3 Franck-Condon factors - definition

Let us assume that at time $t = 0$ the molecule is described by a linear combination $\psi(x) = \sum_n c_n \psi_{gn}(x)$, and somehow driven to the excited state (the theory is going to be described later in section 3.5). What is its wave-function after excitation? We assume that right after excitation the wave-function is given by linear combination of $\psi_{en}(x)$ which have the same values at x as the original linear combination of $\psi_{gn}(x)$ (in so called Condon approximation). Our next aim is to determine coefficients of this linear combination.

The functions $\psi_{gn}(x)$ form a base of a $\mathcal{L}^2(\mathbb{R})$ space, therefore we can assume that we can express every function $\psi_{gn}(x)$ by a linear combination of the functions $\psi_{en}(x)$, i. e.

$$\psi_{gn}(x) = \sum_m c_{mn} \psi_{em}(x), \quad (2.25)$$

coefficients c_{mn} are called Franck-Condon (FC) factors . In other words FC factors form transformation matrix from one base of Hilbert space to another base of the same Hilbert space, in our case the Hilbert space is $\mathcal{L}^2(\mathbb{R})$. The two bases are solutions of time-independent Schrödinger equation for different harmonic oscillators. We can express $\psi(x)$ as follows

$$\psi(x) = \sum_n c_n \psi_{gn}(x) = \sum_{mn} c_n c_{mn} \psi_{em}(x) \quad (2.26)$$

and the coefficients are determined by the sum $\sum_n c_n c_{mn}$. We have reduced our problem of determining the wave function after excitation to determination of the FC factors.

Let us suppose a scalar product of equation (2.25) with $\psi_{em}(x)$. Thanks to orthonormality of functions $\psi_{en}(x)$ we can see that c_{mn} is scalar product of $\psi_{gn}(x)$ and $\psi_{em}(x)$

$$c_{mn} = \int_{-\infty}^{\infty} \psi_{em}^*(x) \psi_{gn}(x) dx \quad (2.27)$$

In this chapter we are going to show possible ways how to obtain c_{mn} for the cases described in the section 2.2.

2.4 Basic properties of the FC factors

Notice that the numbers c_{mn} are real in our case, because everything in the considered scalar product is composed of real numbers, the solutions are real functions. Further c_{mn} is usually not symmetric under interchange of m and n .

Another important property is, that matrix c_{mn} reduces to unit matrix in the case that the two basis are the same (the same harmonic oscillators). It expresses the fact that coefficients appropriate to some function in any base are determined unambiguously.

Because the solutions are normalized, the following equation holds

$$\int_{-\infty}^{\infty} \psi_{gk}^*(x) \psi_{gn}(x) dx = \delta_{kn}. \quad (2.28)$$

Using completeness arguments¹ we can rewrite the expression on the left hand side as

$$\int_{-\infty}^{\infty} \psi_{gk}^*(x) \psi_{gn}(x) dx = \sum_m \int_{-\infty}^{\infty} \psi_{gk}^*(x) \psi_{em}(x) dx \int_{-\infty}^{\infty} \psi_{em}^*(y) \psi_{gn}(y) dy. \quad (2.29)$$

But considering definition of c_{mn} (2.27) we can see that this is a matrix product

$$\sum_m c_{mk}^* c_{mn} = (c^\dagger c)_{kn} = \delta_{kn}, \quad (2.30)$$

therefore factors c_{mn} form a unitary matrix. The c is a shortcut for matrix with matrix elements c_{mn} and the symbol $(c^\dagger c)_{kn}$ is similarly a shortcut for the matrix element on the k -th row and the n -th column of the matrix product of the Hermitian conjugate of c and c . We are going to use such shortcuts in order to avoid too many indices and sums in the text.

Taking $k = n$ we obtain

¹The function $\psi_{gn}(x)$ is in $\mathcal{L}^2(\mathbb{R})$ space. Therefore it can be expanded in the base of functions $\psi_{en}(x)$. Thus $\psi_{gn}(x) = \sum_m c_m \psi_{em}(x)$. Considering scalar product of this equation gives $c_m = \int_{-\infty}^{\infty} \psi_{em}^*(y) \psi_{gn}(y) dy$. Putting this expression in the previous equation clarifies the rearrangement in equation (2.29).

$$\sum_m |c_{mn}|^2 = 1. \quad (2.31)$$

Thus in any such transformation matrix c_{mn} every column has to give the sum of squares of norms of numbers in the column equal to 1. In our case the matrix is of infinite order, therefore the terms in the sum has to satisfy the following consequence of the necessary condition of convergence

$$\lim_{m \rightarrow \infty} c_{mn} = 0. \quad (2.32)$$

By the same argumentation using $(cc^\dagger)_{kn} = \delta_{kn}$ we can also prove equations

$$\sum_n |c_{mn}|^2 = 1, \quad (2.33)$$

$$\lim_{n \rightarrow \infty} c_{mn} = 0. \quad (2.34)$$

The reader can find the calculation of the Franck-Condon factors in various cases in the Appendix A.

2.5 Converting to Dirac notation

In the previous text we have treated a molecule as a two level system with vibrational states. Before we proceed further to the statistical description of many such molecules in a heat bath, we are going to convert to the more common Dirac formalism. For this purpose we introduce the following basic equations

$$\psi_{gn}(x) = \langle g | \langle x | n \rangle | g \rangle, \quad (2.35)$$

$$\psi_{en}(x) = \langle e | \langle x | n_e \rangle | e \rangle, \quad (2.36)$$

where we treat the Hilbert space of our model system as a tensor product of a Hilbert space of a two level system with kets $|g\rangle$ appropriate to the ground state and $|e\rangle$ appropriate to the excited state, and the oscillator system with kets $|n\rangle$ ($n \in \{0, 1, 2, \dots\}$) appropriate to the oscillator system described above with wave-function $\psi_{gn}(x) = \langle x | n \rangle$. The kets $|n_e\rangle$ similarly have the wave-function $\psi_{en}(x) = \langle x | n_e \rangle$.

For the sake of brevity we define

$$|n\rangle|g\rangle = |ng\rangle, \quad (2.37)$$

$$|n_e\rangle|e\rangle = |ne\rangle. \quad (2.38)$$

The kets $|\alpha\rangle$ ($\alpha \in \{g, e\}$) form a complete orthonormal system of their Hilbert space and similarly kets $|n\rangle$ and $|n_e\rangle$. Kets $|n\rangle$ and $|n_e\rangle$ are related by the equation

$$|n\rangle = \sum_{m=0}^{\infty} |m_e\rangle \langle m_e|n\rangle = \sum_{m=0}^{\infty} |m_e\rangle \int_{-\infty}^{\infty} \psi_{em}^*(x) \psi_{gn}(x) dx = \sum_{m=0}^{\infty} c_{mn} |m_e\rangle, \quad (2.39)$$

where we have used the definition (2.27). By the way we can state another expression of the FC factors

$$c_{mn} = \langle m_e|n\rangle = \langle n|m_e\rangle. \quad (2.40)$$

Thus kets $|n\rangle|\alpha\rangle$ form an orthonormal base of our Hilbert space

$$\langle \beta|\langle m|n\rangle|\alpha\rangle = \delta_{n\alpha}^{m\beta}, \quad (2.41)$$

where we have introduced symbol $\delta_{n\alpha}^{m\beta}$ expressed by the usual Kronecker deltas as $\delta_{n\alpha}^{m\beta} = \delta_{mn} \delta_{\alpha\beta}$. We are going to use such symbols similarly for more indices. In further text the Greek indices always denote g or e and the Latin indices always denote the phonon states.

We are also going to make use of the creation and annihilation operators with properties

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle, \quad (2.42)$$

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \quad (2.43)$$

$$[\hat{a}, \hat{a}^\dagger] = 1. \quad (2.44)$$

In the Dirac formalism the Schrödinger equation has the following form

$$i\hbar \frac{d}{dt}|\psi\rangle = \hat{H}|\psi\rangle, \quad (2.45)$$

where $|\psi\rangle$ is state of the system and \hat{H} is the Hamiltonian operator of the system.

2.6 Statistical description and the density matrix

In this work we are going to treat system of many molecules in a bath instead of a single molecule. Standard quantum mechanical description of such systems makes use of the density matrix (for introduction to the density matrix theory is suitable for example Ref.[1]).

Let us summarize some of the most important properties of the density operator $\hat{\rho}$ of the density matrix. Compared to quantum mechanics describing the system by state $|\psi\rangle$, the density operator $\hat{\rho}$ treats the system like we had many such systems described by the set of states $|\psi_i\rangle$. Selecting randomly one of these systems, the probability to obtain the state $|\psi_i\rangle$ is p_i , where index i is taken from some set (let us suppose that the set is countable). The density operator is then given by

$$\hat{\rho} = \sum_i p_i |\psi_i\rangle \langle \psi_i|. \quad (2.46)$$

Let us define a trace of an operator \hat{A} acting on a Hilbert space spanned by base $|i\rangle$ (in the case of the treated system the i would be interchanged to two indices n and α , the base is composed from kets $|n\alpha\rangle$) as the following sum

$$Tr(\hat{A}) = \sum_i \langle i | \hat{A} | i \rangle. \quad (2.47)$$

Taking one of the states from the set $|\psi_i\rangle$, the probability of having some state is 1. As a consequence of this fact we can state the equation

$$Tr(\hat{\rho}) = 1. \quad (2.48)$$

Performing a measurement of the mean value of a measurable quantity corresponding to the operator \hat{A} on a system described by the density operator $\hat{\rho}$ is given by the equation

$$\langle \hat{A} \rangle = Tr(\hat{\rho} \hat{A}). \quad (2.49)$$

We can physically motivate such a description of our system for example assuming, that the molecules obey Boltzmann distribution law. We would come to the conclusion, that the probability to find a molecule in state $|gn\rangle$ is proportional to $e^{-\frac{E_{gn}}{kT}}$ and similarly for the excited state. It is also going to be useful to define matrix elements of the operator $\hat{\rho}$ denoted by $\rho_{m\alpha n\beta}$ as

$$\rho_{m\alpha n\beta} = \langle m\alpha | \hat{\rho} | n\beta \rangle. \quad (2.50)$$

Let us also introduce a so called reduced density matrix. We are going to denote the appropriate operator by $\hat{\sigma}$. To motivate consideration of such an operator let us assume a Hilbert space as a tensor product of a two Hilbert spaces - system with base of kets $|\alpha\rangle$, and another system with base of kets $|n\rangle$, which both are eigenstate of some operator of some measurable quantity. As an example of this general case could be considered our model of a molecule

described in section 2.5. Let us assume that we would like to measure in what state $|\alpha\rangle$ the system described by the density operator $\hat{\rho}$ is independently on state $|n\rangle$. Thus we would like to enumerate the sum

$$\langle\alpha|\hat{\sigma}|\alpha\rangle = \sum_n \langle\alpha|\langle n|\hat{\rho}|n\rangle|\alpha\rangle, \quad (2.51)$$

which defines the reduced density matrix. In our model system described earlier, the elements of the reduced density matrix $\langle g|\hat{\sigma}|g\rangle$ and $\langle e|\hat{\sigma}|e\rangle$ have thus the physical significance of probability for the molecule being found in the ground or excited states, respectively, no matter what vibrational state the molecule is in. Thus we define the reduced density operator $\hat{\sigma}$ by the equation

$$\hat{\sigma} = \sum_n \langle n|\hat{\rho}|n\rangle. \quad (2.52)$$

The time evolution of state $|\psi\rangle$ is given by the Schrödinger equation (2.45), and the description by the density operator preserves this evolution for every $|\psi_i\rangle$. The Schrödinger equation for the state $|\psi\rangle$ then implies the so called Liouville-von Neumann equation

$$i\hbar \frac{d}{dt} \hat{\rho} = [\hat{H}, \hat{\rho}]. \quad (2.53)$$

This equation can be rewritten in the superoperator notation as

$$i \frac{d}{dt} \hat{\rho} = \mathfrak{L}_0 \hat{\rho}, \quad (2.54)$$

and the \mathfrak{L}_0 we define as

$$\mathfrak{L}_0 \hat{\rho} = \frac{1}{\hbar} [\hat{H}, \hat{\rho}]. \quad (2.55)$$

Similarly to the case of matrix elements of the operators, we can define matrix elements of the superoperator \mathfrak{L}_0 denoted by $\mathfrak{L}_{0\,p\gamma q\delta}^{m\alpha n\beta}$ as

$$\mathfrak{L}_{0\,p\gamma q\delta}^{m\alpha n\beta} = \langle m\alpha | (\mathfrak{L}_0 |p\gamma\rangle \langle q\delta|) |n\beta\rangle. \quad (2.56)$$

If the superoperator \mathfrak{L}_0 is linear, we can express act of this superoperator on some operator \hat{B} using their matrix elements as

$$\langle m\alpha | \mathfrak{L}_0 \hat{B} |n\beta\rangle = (\mathfrak{L}_0 \hat{B})_{m\alpha n\beta} = \sum_{p\gamma q\delta} \mathfrak{L}_{0\,p\gamma q\delta}^{m\alpha n\beta} B_{p\gamma q\delta} \quad (2.57)$$

We can write a formal solution of the equation (2.54) as

$$\hat{\rho}(t) = e^{-i\mathfrak{L}_o t} \hat{\rho}(0), \quad (2.58)$$

where $\hat{\rho}(t)$ is the density operator at the time t , and the initial condition is chosen at the time equal to 0.

Let us now discuss the form of this equation in the interaction picture. The exponential of the superoperator in equation (2.58) is the known evolution superoperator, which we are going to denote as \mathfrak{U}_o , thus

$$\mathfrak{U}_o(t) = e^{-i\mathfrak{L}_o t}. \quad (2.59)$$

Further we are going to define the superoperator \mathfrak{U}_o^\dagger as

$$\mathfrak{U}_o^\dagger(t) = e^{i\mathfrak{L}_o t}. \quad (2.60)$$

Now we can define the density operator in the interaction picture by the equation

$$\hat{\rho}^I(t) = e^{i\mathfrak{L}_o t} \hat{\rho}(t) = \mathfrak{U}_o^\dagger(t) \hat{\rho}(t). \quad (2.61)$$

Finally, let us assume that instead of the \mathfrak{L}_o in (2.53) we have added some time independent interaction term \mathfrak{L}_I (let us note that the following equations would be true also in the case of time dependent \mathfrak{L}_I) changing the equation to

$$i \frac{d}{dt} \hat{\rho} = (\mathfrak{L}_o + \mathfrak{L}_I) \hat{\rho}. \quad (2.62)$$

Using the just mentioned definitions in this equation we can state the time evolution equation for the density operator in the interaction picture as

$$i \frac{d}{dt} \hat{\rho}^I(t) = \mathfrak{L}_I(t) \hat{\rho}^I(t), \quad (2.63)$$

where the $\mathfrak{L}_I(t)$ is defined by the equation

$$\mathfrak{L}_I(t) = e^{i\mathfrak{L}_o t} \mathfrak{L}_I e^{-i\mathfrak{L}_o t} = \mathfrak{U}_o^\dagger(t) \mathfrak{L}_I \mathfrak{U}_o(t). \quad (2.64)$$

The solution of the equation (2.63) is

$$\hat{\rho}^I(t) = e_{\leftarrow}^{-i \int_0^t \mathfrak{L}_I(\tau) d\tau} \hat{\rho}(0), \quad (2.65)$$

where $\hat{\rho}(0) = \hat{\rho}^I(0)$ and the $e_{\leftarrow}^{-i \int_0^t \mathfrak{L}_o \tau d\tau}$ is the well known positively time ordered exponential defined by the infinite sum

$$e_{\leftarrow}^{-i \int_0^t \mathfrak{L}_I(\tau) d\tau} = \mathbf{1} + (-i) \int_0^t \mathfrak{L}_I(\tau) d\tau + (-i)^2 \int_0^t \int_0^\tau \mathfrak{L}_I(\tau) \mathfrak{L}_I(\tau') d\tau d\tau' + \dots \quad (2.66)$$

2.7 Transformation matrices for the operators and the superoperators

It turned out to be useful in this work to work sometimes in the base $|n\alpha\rangle$ and sometimes in the base $|n\rangle|\alpha\rangle$. In this section we are going to define transformation operators and superoperators between these two bases. First of all consider the equation

$$(\langle m\alpha|)(|p\rangle|\gamma\rangle) = \delta_{ggm}^{\alpha\gamma p} + \delta_{ee}^{\alpha\gamma} c_{mp}, \quad (2.67)$$

where we have used the equation (2.40). We can define the elements $(\langle m\alpha|)(|p\rangle|\gamma\rangle)$ as a new matrix

$$c_{m\alpha p\gamma} = \delta_{ggm}^{\alpha\gamma p} + \delta_{ee}^{\alpha\gamma} c_{mp}. \quad (2.68)$$

Notice that it is clearly distinguished from the FC factors, because it has two more indices.

Let us define the matrix elements in the base $|n\rangle|\alpha\rangle$ of some operator \hat{A} as

$$\tilde{A}_{m\alpha n\beta} = \langle \alpha | \langle m | \hat{A} | n \rangle | \beta \rangle, \quad (2.69)$$

where we use the tilde to mark the operators in the base $|n\rangle|\alpha\rangle$. Using the completeness relation in this equation and the equation (2.68) we can state

$$\tilde{A}_{m\alpha n\beta} = \sum_{p\gamma q\delta} c_{p\gamma m\alpha} A_{p\gamma q\delta} c_{q\delta n\beta}. \quad (2.70)$$

This could motivate us to define superoperator \mathfrak{C} which transforms the operators from one base to another. The corresponding matrix elements are

$$\mathfrak{C}_{p\gamma q\delta}^{m\alpha n\beta} = c_{p\gamma m\alpha} c_{q\delta n\beta}, \quad (2.71)$$

and then

$$\tilde{A}_{m\alpha n\beta} = \sum_{p\gamma q\delta} \mathfrak{C}_{p\gamma q\delta}^{m\alpha n\beta} A_{p\gamma q\delta}. \quad (2.72)$$

The superoperator \mathfrak{C} is unitary as it is possible to prove using the definition; in other words

$$\mathfrak{C}\mathfrak{C}^T = \mathbf{1}. \quad (2.73)$$

Using this relation we can obtain the other transformation relation

$$A_{m\alpha n\beta} = \sum_{p\gamma q\delta} c_{m\alpha p\gamma} \tilde{A}_{p\gamma q\delta} c_{n\beta q\delta} \quad (2.74)$$

In the same way the superoperator \mathfrak{L}_o in base $|n\rangle|\alpha\rangle$ have the matrix elements defined by the equation

$$\tilde{\mathfrak{L}}_{op\gamma q\delta}^{m\alpha n\beta} = \langle m|\langle\alpha|(\mathfrak{L}_o|p\rangle|\gamma\rangle\langle q|\langle\delta|)|n\rangle|\beta\rangle, \quad (2.75)$$

where we again add the tilde to distinguish the superoperators in different bases. Using four times the completeness relation in the definition (2.56) and the equation (2.68) we find the equation

$$\mathfrak{L}_{op\gamma q\delta}^{m\alpha n\beta} = \sum_{m'\alpha'n'\beta'p'\gamma'q'\delta'} c_{m\alpha m'\alpha'} c_{n\beta n'\beta'} c_{p\gamma p'\gamma'} c_{q\delta q'\delta'} \tilde{\mathfrak{L}}_{op'\gamma'q'\delta'}^{m'\alpha'n'\beta'}. \quad (2.76)$$

We can rewrite this in a more compact form using the transformation superoperators \mathfrak{C} and \mathfrak{C}^T , because we can see in this equation their matrix elements. Let us therefore state another form of this equation

$$\mathfrak{L}_{op\gamma q\delta}^{m\alpha n\beta} = \sum_{m'\alpha'n'\beta'p'\gamma'q'\delta'} \mathfrak{C}_{m'\alpha'n'\beta'}^{Tm\alpha n\beta} \tilde{\mathfrak{L}}_{op'\gamma'q'\delta'}^{m'\alpha'n'\beta'} \mathfrak{C}_{p'\gamma'q'\delta'}^{p\gamma q\delta}. \quad (2.77)$$

The inverse relation we can obtain by multiplying this equation by superoperators \mathfrak{C} and \mathfrak{C}^T from the left and the right respectively.

Chapter 3

Model open quantum system

3.1 Hamiltonian of the model system

The Hamiltonian of a two level molecule with vibrational degree of freedom is

$$\hat{H} = \sum_{n=0}^{\infty} E_{gn}|n\rangle|g\rangle\langle g|\langle n| + E_{en}|n_e\rangle|e\rangle\langle e|\langle n_e|. \quad (3.1)$$

This forms a base of our Hilbert space in which the Hamiltonian operator \hat{H} is diagonal and has the form

$$\hat{H} = \sum_{n=0}^{\infty} \sum_{\alpha \in \{g,e\}} E_{\alpha n} |n\alpha\rangle\langle n\alpha|. \quad (3.2)$$

Let us rewrite the Hamiltonian operator to a different form, which clearly divides it in parts which act only on the electronic states $|\alpha\rangle$, the phonon states $|n\rangle$ and on both of them. We can make use of the Hamiltonian \hat{H}_B defined by equation (2.2) (replacing the ω by ω_g). Considering the definition (2.19) we can see that the Hamiltonian corresponding to the oscillator in the ground state can be written in the base of eigenstates of this Hamiltonian as

$$\sum_{n=0}^{\infty} E_{gn}|n\rangle|g\rangle\langle g|\langle n| = \left(\frac{\hat{p}^2}{2m} + \frac{m\omega_g^2}{2}\hat{x}^2 + E_g\right)|g\rangle\langle g| = (\hat{H}_B + E_g)|g\rangle\langle g|, \quad (3.3)$$

where we omit the subscript g in the m . Further we are going to define operators of the kinetic energy \hat{T} and the potential energy \hat{V}^g for the vibrational states in

the ground state by equations

$$\hat{T} = \frac{\hat{p}^2}{2m}, \quad (3.4)$$

$$\hat{V}^g = \frac{m\omega_g^2}{2}\hat{x}^2. \quad (3.5)$$

Thus we have

$$\sum_{n=0}^{\infty} E_{gn}|n\rangle\langle n| = (\hat{T} + \hat{V}^g + E_g)|g\rangle\langle g|. \quad (3.6)$$

In the same way we can rewrite the operator $E_{en}|n_e\rangle\langle n_e|$ as

$$\sum_{n=0}^{\infty} E_{en}|n_e\rangle\langle n_e| = (\hat{T} + \hat{V}^e + E_e)|e\rangle\langle e|, \quad (3.7)$$

having the operator \hat{V}^e defined by the equation

$$\hat{V}^e = \frac{m\omega_e^2}{2}(\hat{x} - x_0)^2, \quad (3.8)$$

where we omitted the subscript in m . Finally, we can rewrite the Hamiltonian \hat{H} in the form

$$\hat{H} = (\hat{T} + \hat{V}^g + E_g)|g\rangle\langle g| + (\hat{T} + \hat{V}^e + E_e)|e\rangle\langle e| = \quad (3.9)$$

$$= (\hat{T} + \hat{V}^g) + E_g|g\rangle\langle g| + E_e|e\rangle\langle e| + (\hat{V}^e - \hat{V}^g)|e\rangle\langle e|. \quad (3.10)$$

The part $\hat{T} + \hat{V}^g$ in this form is diagonal in electronic states, the part $E_g|g\rangle\langle g| + E_e|e\rangle\langle e|$ is diagonal in the phonon states $|n\rangle$ and the last part $(\hat{V}^e - \hat{V}^g)|e\rangle\langle e|$ acts on both Hilbert spaces.

We can further express this Hamiltonian in the form

$$\begin{aligned} \hat{H} = & (\hat{T} + \hat{V}^g) + E_g|g\rangle\langle g| + (E_e + Tr_B((\hat{V}^e - \hat{V}^g)\hat{W}_{eq}))|e\rangle\langle e| + \\ & + ((\hat{V}^e - \hat{V}^g) - Tr_B((\hat{V}^e - \hat{V}^g)\hat{W}_{eq}))|e\rangle\langle e|, \end{aligned} \quad (3.11)$$

where we define the operator \hat{W}_{eq} as

$$\hat{W}_{eq} = \frac{1}{Z_g} \sum_{n=0}^{\infty} e^{-\frac{E_{gn}}{kT}} |n\rangle\langle n|, \quad (3.12)$$

Now we are going to redefine the individual terms of the Hamiltonian. The mentioned \hat{H}_B reads

$$\hat{H}_B = \hat{T} + \hat{V}^g. \quad (3.13)$$

We further define

$$\hat{H}_S = E_g|g\rangle\langle g| + (E_e + Tr_B((\hat{V}^e - \hat{V}^g)\hat{W}_{eq}))|e\rangle\langle e|. \quad (3.14)$$

\hat{H}_S is the so called system Hamiltonian. Finally, the Hamiltonian which causes interaction between electronic and phonon states \hat{H}_{S-B} reads

$$\hat{H}_{S-B} = ((\hat{V}^e - \hat{V}^g) - Tr_B((\hat{V}^e - \hat{V}^g)\hat{W}_{eq}))|e\rangle\langle e|. \quad (3.15)$$

We subtracted the equilibrium average of the difference of the molecular potential energy from the interaction term in order to make sure that

$$Tr_B(\hat{H}_{S-B}\hat{W}_{eq}) = 0. \quad (3.16)$$

This relation will become important later. Let us also define

$$(\hat{V}^e - \hat{V}^g) - Tr_B((\hat{V}^e - \hat{V}^g)\hat{W}_{eq}) = \Delta\hat{V} \quad (3.17)$$

Consequently, the original Hamiltonian \hat{H} could be rewritten as

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{S-B}. \quad (3.18)$$

Accordingly the Liouville superoperator \mathfrak{L}_0 can be divided into three parts

$$\mathfrak{L}_0 = \mathfrak{L}_S + \mathfrak{L}_B + \mathfrak{L}_{S-B}, \quad (3.19)$$

where the superoperators are defined as

$$\mathfrak{L}_S = \frac{1}{\hbar} \left[\hat{H}_S, \hat{\rho} \right], \quad (3.20)$$

$$\mathfrak{L}_B = \frac{1}{\hbar} \left[\hat{H}_B, \hat{\rho} \right], \quad (3.21)$$

$$\mathfrak{L}_{S-B} = \frac{1}{\hbar} \left[\hat{H}_{S-B}, \hat{\rho} \right]. \quad (3.22)$$

Let us include in our model the environment of the molecule. The influence of the environment could be described by adding infinite amount of other quantum harmonic oscillators coupled to the vibrational states of the molecule to the

Hamiltonian \hat{H} as it was done for example in Ref. [3]. We are going to simplify the treatment introducing standard dimensionless coordinates (and momenta) as

$$\hat{X}_\alpha = \sqrt{\frac{m\omega_\alpha}{\hbar}}\hat{x}, \hat{P}_\alpha = \sqrt{\frac{1}{m\omega_\alpha\hbar}}\hat{p}, \quad (3.23)$$

and similarly for the bath harmonic oscillators

$$\hat{X}_n = \sqrt{\frac{m\omega_n}{\hbar}}\hat{x}_n, \hat{P}_n = \sqrt{\frac{1}{m\omega_n\hbar}}\hat{p}_n, \quad (3.24)$$

where the ω_n are frequencies of these oscillators.

Further let us discuss the case, when $\omega_e = \omega_g$ and $\hat{X}_\alpha = \hat{X} = \sqrt{\frac{m\omega_g}{\hbar}}\hat{x}$, $\hat{P}_\alpha = \hat{P} = \sqrt{\frac{1}{m\omega_g\hbar}}\hat{p}$. Let us denote the terms corresponding to the kinetic energy of the oscillators from the environment as \hat{T}_n and the potential energy terms as \hat{V}_n^α with meaning analogous to the operators \hat{T} and \hat{V}^α above. The complete Hamiltonian of a two level molecule with one vibrational degree of freedom in a multimode bath is going to be denoted as \hat{H}_ζ and defined by the equation

$$\hat{H}_\zeta = \left(\frac{\hbar\omega_g}{2}[(\hat{X} + \sum_k \hat{X}_k\kappa_k)^2 + \hat{P}^2] + E_g\right)|g\rangle\langle g| + \sum_{n=1}^{\infty}(\hat{T}_n + \hat{V}_n^g)|g\rangle\langle g| + \quad (3.25)$$

$$\left(\frac{\hbar\omega_g}{2}[(\hat{X} - X_0 + \sum_k \hat{X}_k\kappa_k)^2 + \hat{P}^2] + E_e\right)|e\rangle\langle e| + \sum_{n=1}^{\infty}(\hat{T}_n + \hat{V}_n^e)|e\rangle\langle e|, \quad (3.26)$$

where

$$X_0 = \sqrt{\frac{m\omega}{\hbar}}x_0. \quad (3.27)$$

We included the fact that the bath oscillators would also change their potential energy operators, therefore the superscripts g and e in the potential energy operators \hat{V}_n^α . We are going to split the Hamiltonian \hat{H}_ζ in the following parts

$$\hat{H}_{Bosc} = \frac{\hbar\omega_g}{2}[(\hat{X} + \sum_k \hat{X}_k\kappa_k)^2 + \hat{P}^2] + \sum_{n=1}^{\infty}(\hat{T}_n + \hat{V}_n^g), \quad (3.28)$$

$$\hat{H}_{Sosc} = E_g|g\rangle\langle g| + (E_e + \frac{\hbar\omega_g}{2}X_0^2)|e\rangle\langle e|, \quad (3.29)$$

$$\hat{H}_{S-Bosc} = (\hat{V}^e - \hat{V}^g - \hbar\omega_g X_0 \sum_k \hat{X}_k\kappa_k)|e\rangle\langle e|. \quad (3.30)$$

Consequently the total Hamiltonian could be rewritten as

$$\hat{H}_\zeta = \hat{H}_{Bosc} + \hat{H}_{Sosc} + \hat{H}_{S-Bosc}. \quad (3.31)$$

3.2 Density operators of the model system

Let us treat the density operator appropriate to our model open quantum system, which we are going to denote as $\hat{\zeta}$. This density operator is defined on the Hilbert space appropriate to the Hamiltonian \hat{H}_{ζ} . Analogously to the preceding cases, we can denote the base kets of this Hilbert space as $|nn_k\alpha\rangle$, where we added the n_k to include the infinite number of harmonic oscillators representing the environment of the molecule.

Following the discussion from the preceding section we can define the density matrix $\hat{\rho}$ as the reduced density matrix of the total density matrix $\hat{\zeta}$. In other words

$$\hat{\rho} = \sum_{n_k} \langle n_k | \hat{\zeta} | n_k \rangle. \quad (3.32)$$

And analogously we might be interested in the another density matrix $\hat{\sigma}$ defined by the equation

$$\hat{\sigma} = \sum_n \langle n | \hat{\rho} | n \rangle = Tr_B(\hat{\rho}),$$

which also defines the Tr_B . Accordingly we have something like three “layers” of our system. The total density operator $\hat{\zeta}$, the reduced density operator with respect to the phonon bath $\hat{\rho}$, and finally the density operator containing only the electronic states $\hat{\sigma}$. In the next section we are going to treat the first reduction from the density matrix $\hat{\zeta}$ to the density operator $\hat{\rho}$.

3.3 First reduction

In the electronic ground state, the dynamics is described by the Hamiltonian \hat{H}_{Bosc} (3.28). To obtain the dynamics of the density matrix $\hat{\rho}$, we are going to assume that the coupling to the environmental phonons is weak and the the relaxation of the energy is slow. Then we can use the so-called Haken-Stroble-Reineker model (Ref. [7]) and write down the equation of motion

$$i \frac{d}{dt} \langle g | \hat{\rho} | g \rangle = \langle g | (\mathfrak{L}_o + i\mathfrak{R}_{gggg}) \hat{\rho} | g \rangle, \quad (3.33)$$

where \mathfrak{R} is the so-called relaxation tensor. The explicit form of the \mathfrak{R} is going to be discussed in the next section. We would obtain similar equation for relaxation in the excited state, because it is another oscillator with the same coupling to

the environmental phonons. Thus

$$i \frac{d}{dt} \langle e | \hat{\rho} | e \rangle = \langle e | (\mathfrak{L}_o + i \mathfrak{R}_{eee}) \hat{\rho} | e \rangle.$$

There is also a part of the relaxation tensor responsible for dephasing emerging from the Hamiltonian \hat{H}_{S-Bosc} (3.30). Let us just note that the part containing the environmental phonon operators $-\hbar\omega_g X_0 \sum_k \hat{X}_k \kappa_k |e\rangle\langle e|$ is insensitive to the vibrational state of the system described by $\hat{\rho}$, and therefore we can assume its contribution to the relaxation dynamics of the form

$$\mathfrak{R}_{gege} = \mathfrak{R}_{egeg} = -\gamma, \quad (3.34)$$

independently on the phonon states the relaxation tensor acts on, γ is some constant.

The second reduction, which should lead us to the dynamics of the density operator $\hat{\sigma}$ is going to be treated in the Chapter 4.

3.4 Relaxation process

Let us discuss the equilibrium density $\hat{\rho}_{eq}^g$ matrix of our system. We are going to consider the case when the energy difference $E_e - E_g$ is big and the temperature of the heat bath T is so low, that in thermal equilibrium the molecules are approximately all in the ground state. Then the equilibrium density operator $\hat{\rho}_{eq}^g$ takes the form

$$\hat{\rho}_{eq}^g = \frac{1}{Z^g} \sum_{n=0}^{\infty} e^{-\frac{E_{gn}}{kT}} |ng\rangle\langle ng|, \quad (3.35)$$

where $Z^g = \sum_{n=0}^{\infty} e^{-\frac{E_{gn}}{kT}}$ is a partition function of the harmonic oscillator in the ground state, and we used the assumption that the system obeys the Boltzmann distribution law. By calculation of the trace this equation we can verify, that the density operator is normalized according to (2.48). As the reader may see (considering for example equations (3.2) and (2.53)), if we choose $\hat{\rho}(0) = \hat{\rho}_{eq}^g$, the density operator is invariant in time (as every density operator diagonal in the same base as the Hamiltonian).

In this section we would like to include into our model relaxation processes inside electronic states $|g\rangle$ and $|e\rangle$. For this purpose we suppose that these relaxation processes can be described by addition of the superoperator \mathfrak{R} introduced

in the previous section to the original Liouville superoperator \mathfrak{L}_0 obtaining from (2.54) the equation

$$i\frac{d}{dt}\hat{\rho} = (\mathfrak{L}_0 + i\mathfrak{R})\hat{\rho}. \quad (3.36)$$

The matrix elements (2.56) of the superoperator \mathfrak{L}_0 are

$$\hbar\mathfrak{L}_{0p\gamma q\delta}^{m\alpha n\beta} = \delta_{q\delta}^{n\beta} H_{m\alpha p\gamma} - \delta_{p\gamma}^{m\alpha} H_{q\delta n\beta}, \quad (3.37)$$

as is possible to directly verify using this result in equation (2.55). What are the matrix elements of the superoperator \mathfrak{R} ? First of all, we are going to consider how do the matrix elements of the $\hat{\rho}$ change in time under influence of relaxation. We are going to separate this influence into two parts - the diagonal (the elements $m = n, \alpha = \beta$ of $\rho_{m\alpha n\beta}$) and the off-diagonal elements (the other elements of $\rho_{m\alpha n\beta}$) and describe the time evolution by equations

$$\frac{d}{dt}\rho_{m\alpha n\beta} = \begin{cases} -K_{n\alpha n\alpha}\rho_{n\alpha n\alpha} + \sum_{p=0}^{\infty} \Gamma_{n\alpha p\alpha}\rho_{p\alpha p\alpha} & m = n, \alpha = \beta \\ -\gamma_{m\alpha n\beta}\rho_{m\alpha n\beta} & \text{the rest} \end{cases}, \quad (3.38)$$

where the matrices K , Γ and γ are constant. We are going to define these matrices in the way to fulfill the following demands

- The probability of finding the system in some state does not change in time - $\frac{d}{dt}\sum_{n\alpha}\rho_{n\alpha n\alpha} = 0$
- The elements of the density matrix asymptotically approaches to the density matrix of the equilibrium - $\hat{\rho}_{eq}^{\alpha} = \sum_{\alpha} \sum_{n=0}^{\infty} \frac{1}{\sum_{i=0}^{\infty} e^{-\frac{E_{\alpha i}}{kT}}} e^{-\frac{E_{\alpha n}}{kT}} |n\alpha\rangle\langle n\alpha| \Rightarrow \frac{d}{dt}\hat{\rho}_{eq}^{\alpha} = 0$
- The condition of the detailed balance is satisfied -

$$\rho_{eq}^{\gamma}{}_{m\alpha m\alpha}\Gamma_{n\alpha m\alpha} = \rho_{eq}^{\gamma}{}_{n\alpha n\alpha}\Gamma_{m\alpha n\alpha},$$

The first demand implies the equation

$$K_{n\alpha n\alpha} = \sum_{p=0}^{\infty} \Gamma_{p\alpha n\alpha}, \quad (3.39)$$

the second and the third demand is satisfied if

$$\gamma_{m\alpha n\beta} > 0, \quad (3.40)$$

$$\Gamma_{m\alpha n\alpha} = \tilde{k}_{\alpha}[(m+1)\delta_{mn-1} + me^{-\frac{\hbar\omega_{\alpha}}{kT}}\delta_{mn+1}], \quad (3.41)$$

where \tilde{k}_α is going to be a free parameter of our model (notice that for $\tilde{k}_\alpha = 0$ the relaxation tensor is 0). Notice, that the transitions between electronic states $|g\rangle$ and $|e\rangle$ are not involved in this model.

Motivated by the observation, that in the case when the coherences do not rise, the diagonal elements of the density matrix would decay like $e^{-K_{m\alpha m\alpha}t}$, and the off-diagonal elements $\rho_{m\alpha n\beta}$ would then go like

$$\sqrt{\rho_{m\alpha m\alpha}\rho_{n\beta n\beta}} \simeq e^{-\frac{1}{2}(K_{m\alpha m\alpha}+K_{n\beta n\beta})t},$$

we define

$$\gamma_{m\alpha n\beta} = \frac{1}{2}(K_{m\alpha m\alpha} + K_{n\beta n\beta}). \quad (3.42)$$

All the terms in (3.38) are defined, now we would like to express this equation as

$$\frac{d}{dt}\rho_{m\alpha n\beta} = \sum_{p\gamma q\delta} \mathfrak{R}_{p\gamma q\delta}^{m\alpha n\beta} \rho_{p\gamma q\delta}. \quad (3.43)$$

By substitution of $\mathfrak{R}_{p\gamma q\delta}^{m\alpha n\beta}$ into this equation it is possible to verify, that the correct matrix elements can be expressed as

$$\mathfrak{R}_{p\gamma q\delta}^{m\alpha n\beta} = -(1 - \delta_{\beta n}^{\alpha m})\gamma_{m\alpha n\beta}\delta_{p\gamma q\delta}^{m\alpha n\beta} + \delta_{\beta n}^{\alpha m}(-K_{m\alpha n\beta}\delta_{p\gamma q\delta}^{m\alpha n\beta} + \Gamma_{n\alpha p\alpha}\delta_{\gamma q\delta}^{\alpha p\alpha}). \quad (3.44)$$

Let us note that from the discussion in the preceding section it is clear that the matrix $\gamma_{m\alpha n\beta}$ could be in our model of multimode bath replaced by γ in the cases $\alpha \neq \beta$. In other words we would replace the matrix $\gamma_{m\alpha n\beta}$ by matrix $\gamma'_{m\alpha n\beta}$ defined as

$$\gamma'_{m\alpha n\beta} = \gamma_{m\alpha n\beta}\delta_{\alpha\beta} + \gamma(1 - \delta_{\alpha\beta}). \quad (3.45)$$

The γ is going to be treated as a new free parameter of our model. Closing this section we are going to remark that the solution of the equation (3.36) can be expressed as

$$\hat{\rho}(t) = e^{(-i\mathfrak{L}_o + \mathfrak{R})t}\hat{\rho}(0), \quad (3.46)$$

where $\hat{\rho}(0)$ is the initial condition, which we are going to take as equal to $\hat{\rho}_{ex}$. Matrix elements of the density operator $\hat{\rho}(t)$ can be calculated using ordinary matrix multiplication of the superoperators \mathfrak{L}_o and \mathfrak{R} , which emerge from Taylor expansion of the exponential of the superoperators.

3.5 The density operator and the light-molecule interaction

In this section we are going to use the density matrix description to treat the interaction of light with molecules in our model system. We are going to make use of the semi-classical description, which is possible to find for example in Ref. [2] in more detail. Thus we are going to describe the electromagnetic field classically, restricting ourselves to the transverse part of the electric field denoted by $\vec{E}(t)$. Let us note that the electric field is provided as function independent on the position, we use the so called dipole approximation (supposing that the wavelength of the field is much larger than the typical size of the molecule). In quantum mechanics, the influence of the electric field is then described an interaction Hamiltonian $-\vec{\hat{\mu}} \cdot \vec{E}(t)$ (further we are going to omit the arrows considering the resulting mean value of the scalar product as $E\hat{\mu}$). In our model system, the new Hamiltonian \hat{H}_{L-M} would thus read

$$\hat{H}_{L-M} = \hat{H} - \hat{\mu}E(t). \quad (3.47)$$

Passing over to density matrix description would lead us to redefine the super-operators \mathfrak{L}_0 and \mathfrak{L}_I in the form

$$\mathfrak{L}_0\hat{\rho} = \frac{1}{\hbar} [\hat{H}, \hat{\rho}], \quad (3.48)$$

$$\mathfrak{L}_I(t)\hat{\rho} = -\frac{1}{\hbar} [\hat{\mu}E(t), \hat{\rho}]. \quad (3.49)$$

The solution of the time evolution equation (2.63) is given by the equation (2.65).

The mean value of the dipole moment operator $\hat{\mu}$ corresponds to macroscopic polarization of the medium and it is important for calculation of the resulting absorption spectrum. Using the equation (2.49) and the already mentioned solution we obtain for the mean value of the dipole moment

$$\langle \hat{\mu} \rangle(t) = Tr(\hat{\rho}(t)\hat{\mu}) = Tr((e^{-i\mathfrak{L}_0 t} e_{\leftarrow}^{-i \int_0^t \mathfrak{L}_I(\tau) d\tau} \hat{\rho}(0))\hat{\mu}). \quad (3.50)$$

Another important factor in the calculation of the spectrum is a form of the dipole moment operator. In our model we are going to assume that the dipole moment operator is defined as

$$\hat{\mu} = d_{ge}|g\rangle\langle e| + d_{eg}|e\rangle\langle g|, \quad (3.51)$$

where $d_{ge} = d_{eg}^*$ (operators of measurable quantities in quantum mechanics are Hermitian).

In order to define a physically reasonable initial condition for our later treatment of the vibrational relaxation in the electronically excited state, we could also treat the time evolution of the density matrix itself

$$\hat{\rho}(t) = e^{-i\mathfrak{L}_0 t} e_{\leftarrow}^{-i \int_0^t \mathfrak{L}_I(\tau) d\tau} \hat{\rho}(0). \quad (3.52)$$

Let us expand the positive time ordered exponential in the equation (3.52). We obtain up to the first two orders in $\mathfrak{L}_I(\tau)$

$$\begin{aligned} \hat{\rho}(t) &= 1 - i \int_0^t d\tau \text{Tr}_B(\mathfrak{U}_0(t-\tau) \mathfrak{L}_I(\tau) \hat{\rho}_{eq}^g - \quad (3.53) \\ &- \int_0^t d\tau' \int_0^\tau d\tau \mathfrak{U}_0(t-\tau) \mathfrak{L}_I(\tau) \mathfrak{U}_0(\tau-\tau') \mathfrak{L}_I(\tau') \hat{\rho}_{eq}^g + \dots = \\ &= 1 + \frac{i}{\hbar} \int_0^t d\tau \mathfrak{U}_0(t-\tau) [\hat{\mu}, \hat{\rho}_{eq}^g] E(\tau) - \\ &- \frac{1}{\hbar^2} \int_0^t d\tau' \int_0^\tau d\tau \mathfrak{U}_0(t-\tau) [\hat{\mu}, \mathfrak{U}_0(\tau-\tau') [\hat{\mu}, \hat{\rho}_{eq}^g]] E(\tau') E(\tau) + \dots \end{aligned}$$

To simplify the treatment, let us assume a special form of $E(t)$ (in the so-called impulse limit), namely

$$E(t) = E_0 \delta(t + \epsilon), \quad (3.54)$$

where E_0 is a constant, $\delta(t)$ is the Dirac delta function, and ϵ is some infinitesimal positive number. Then we can rewrite our equation (in the limiting case $\epsilon \rightarrow 0$) as

$$\hat{\rho}(t) = 1 + \frac{i}{\hbar} \mathfrak{U}_0(t) [\hat{\mu}, \hat{\rho}_{eq}^g] E_0 - \quad (3.55)$$

$$- \frac{1}{\hbar^2} \mathfrak{U}_0(t) [\hat{\mu}, [\hat{\mu}, \hat{\rho}_{eq}^g]] E_0^2 + \dots \quad (3.56)$$

Let us now separately treat term with the first power of the E_0 and the term with the second power of the E_0 . From the definition of the commutator follows that the first power term reads

$$\frac{i}{\hbar} \mathfrak{U}_0(t) (\hat{\mu} \hat{\rho}_{eq}^g - \hat{\rho}_{eq}^g \hat{\mu}) E_0, \quad (3.57)$$

and the second power term reads

$$- \frac{1}{\hbar^2} \mathfrak{U}_0(t) (\hat{\mu}^2 \hat{\rho}_{eq}^g - 2\hat{\mu} \hat{\rho}_{eq}^g \hat{\mu} + \hat{\rho}_{eq}^g \hat{\mu}^2) E_0^2. \quad (3.58)$$

In these expressions we can see the time evolution of the operators $\hat{\mu}\hat{\rho}_{eq}^g\hat{\mu}$, $\hat{\mu}\hat{\rho}_{eq}^g$ or $\hat{\rho}_{eq}^g\hat{\mu}$. Terms like $\mathfrak{L}_o(t)\hat{\mu}\hat{\rho}_{eq}^g\hat{\mu}$ or $\mathfrak{L}_o(t)\hat{\rho}_{eq}^g\hat{\mu}$ appear in the above equation (2.58) if we consider in the equation $\hat{\mu}\hat{\rho}_{eq}^g\hat{\mu}$ or $\hat{\rho}_{eq}^g\hat{\mu}$ as the initial conditions.

We can use the definitions of $\hat{\rho}_{eq}^g$ and $\hat{\mu}$ (equations (3.35) and (3.51)) to write the operator $\hat{\mu}\hat{\rho}_{eq}^g\hat{\mu}$ as

$$\hat{\mu}\hat{\rho}_{eq}^g\hat{\mu} = \frac{1}{Z_g} \sum_{n=0}^{\infty} e^{-\frac{E_{gn}}{kT}} \hat{\mu}|ng\rangle\langle ng|\hat{\mu} = \frac{|d_{ge}|^2}{Z_g} \sum_{n=0}^{\infty} e^{-\frac{E_{gn}}{kT}} |e\rangle|n\rangle\langle n|\langle e|. \quad (3.59)$$

We find that this corresponds to population of electronically excited state. Similarly we can express $\hat{\mu}\hat{\rho}_{eq}^g$, as

$$\hat{\mu}\hat{\rho}_{eq}^g = \frac{d_{ge}}{Z_g} \sum_{n=0}^{\infty} e^{-\frac{E_{gn}}{kT}} |n\rangle|e\rangle\langle ng|, \quad (3.60)$$

$$\hat{\rho}_{eq}^g\hat{\mu} = \frac{d_{ge}^*}{Z_g} \sum_{n=0}^{\infty} e^{-\frac{E_{gn}}{kT}} |ng\rangle\langle n|\langle e|, \quad (3.61)$$

and we find that they correspond to optical coherences. Finally, with the use of the FC factors we obtain

$$(\hat{\mu}\hat{\rho}_{eq}^g\hat{\mu})_{mene} = |d_{ge}|^2 \sum_i \frac{Z_i^g}{Z_g} c_{mi}c_{ni}, \quad (3.62)$$

$$(\hat{\rho}_{eq}^g\hat{\mu})_{mgne} = d_{ge}^* \frac{Z_m^g}{Z_g} c_{nm}, \quad (3.63)$$

$$(\hat{\mu}\hat{\rho}_{eq}^g)_{nemg} = d_{ge} \frac{Z_m^g}{Z_g} c_{nm}. \quad (3.64)$$

Every of these operators are nonzero only in one of the possible combinations of α, β . To have normalization of the initial condition to unity we are going to point out the factors like d_{ge} . Let us conclude that the suitable initial condition for calculations (further denoted as $\hat{\rho}_{ex}$) could be defined by the following equations

$$\rho_{mgng}^{ex} = 0, \quad (3.65)$$

$$\rho_{mene}^{ex} = \sum_i \frac{Z_i^g}{Z_g} c_{mi}c_{ni}, \quad (3.66)$$

$$\rho_{mgne}^{ex} = \rho_{nemg}^{ex} = \frac{Z_m^g}{Z_g} c_{nm}, \quad (3.67)$$

where we have used symbol Z_i^g to denote the i -th element of the partition sum Z^g . Considering the trace of this density operator (and the relation (2.31))

$$\sum_m \rho_{meme}^{ex} = \sum_{im} \frac{Z_i^g}{Z^g} c_{mi} c_{mi} = \sum_i \frac{Z_i^g}{Z^g} = 1 \quad (3.68)$$

we can see, that the density operator $\hat{\rho}_{ex}$ is correctly normalized.

We might be interested also in the evaluation of the $\langle \hat{\mu} \rangle(t)$. Let us note that using the same argumentation we would obtain in the first power of E_0 the equation

$$\langle \hat{\mu} \rangle^{(1)}(t) = \frac{i}{\hbar} Tr(\hat{\mu} \mathfrak{L}_o(t) [\hat{\mu}, \hat{\rho}_{eq}^g]) E_0, \quad (3.69)$$

where the superscript (1) reminds that this is the term with the first power. We can see again the terms like $\mathfrak{L}_o(t) \hat{\rho}_{eq}^g \hat{\mu}$ motivating the choice of our initial condition.

Chapter 4

Projection operator method

4.1 Derivation of the equation of motion for the relevant part of the density matrix

In this chapter we are going to describe the projection operator techniques (POT). As a source of further information about POT could be recommended for example Ref. [4].

As the title prompts, the use of this technique is to derive the equations of motions for some projection of the total density matrix $\hat{\rho}$. To be concrete, let us suppose a superoperator \mathfrak{P} and a supplemental superoperator \mathfrak{Q} which have the ordinary features of the projection superoperators. These are summarized by the equations

$$\mathfrak{P} + \mathfrak{Q} = \mathbf{1}, \quad (4.1)$$

$$\mathfrak{P}^2 = \mathfrak{P}, \quad (4.2)$$

$$\mathfrak{Q}^2 = \mathfrak{Q}, \quad (4.3)$$

$$\mathfrak{P}\mathfrak{Q} = \mathfrak{Q}\mathfrak{P} = \mathbf{o}. \quad (4.4)$$

Further we are going to derive the equations of motion not for the original density operator $\hat{\rho}$ but for the density operator in the interaction picture $\hat{\rho}^I$ as they were described in section 2.6. For the sake of brevity we are going to omit the superscript I in the interaction picture density operator. Thus we can state the equation of motion as

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -i\mathfrak{L}_I(t)\hat{\rho}(t). \quad (4.5)$$

We are going to call the projection $\mathfrak{P}\hat{\rho}$ the relevant part of the density matrix and the projection $\mathfrak{Q}\hat{\rho}$ the irrelevant part of the density matrix. Letting these projection superoperators act on the equation of motion and assuming that the projection superoperators are time independent we obtain a pair of equations

$$\frac{\partial}{\partial t}\mathfrak{P}\hat{\rho}(t) = -i\mathfrak{P}\mathfrak{L}_I(t)\hat{\rho}(t), \quad (4.6)$$

$$\frac{\partial}{\partial t}\mathfrak{Q}\hat{\rho}(t) = -i\mathfrak{Q}\mathfrak{L}_I(t)\hat{\rho}(t). \quad (4.7)$$

Inserting the identity superoperator $\mathfrak{P} + \mathfrak{Q} = \mathbf{1}$ between the Liouville superoperator and the density matrices we get

$$\frac{\partial}{\partial t}\mathfrak{P}\hat{\rho}(t) = -i\mathfrak{P}\mathfrak{L}_I(t)\mathfrak{P}\hat{\rho}(t) - i\mathfrak{P}\mathfrak{L}_I(t)\mathfrak{Q}\hat{\rho}(t), \quad (4.8)$$

$$\frac{\partial}{\partial t}\mathfrak{Q}\hat{\rho}(t) = -i\mathfrak{Q}\mathfrak{L}_I(t)\mathfrak{P}\hat{\rho}(t) - i\mathfrak{Q}\mathfrak{L}_I(t)\mathfrak{Q}\hat{\rho}(t). \quad (4.9)$$

To obtain the equation of motion for the relevant part of the density matrix, we are going to solve the second equation and insert it into the first. The formal solution of the second equation is

$$\mathfrak{Q}\hat{\rho}(t) = \mathfrak{T}(t, 0)\mathfrak{Q}\hat{\rho}(0) - i \int_0^t ds \mathfrak{T}(t, s)\mathfrak{Q}\mathfrak{L}_I(s)\mathfrak{P}\hat{\rho}(s), \quad (4.10)$$

where $\hat{\rho}(0)$ is the initial condition, and where we introduce the superoperator $\mathfrak{T}(t, s)$ defined by the equation

$$\mathfrak{T}(t, s) = e_{\leftarrow}^{-i \int_s^t ds' \mathfrak{Q}\mathfrak{L}_I(s')}, \quad (4.11)$$

where we use the positively time ordered exponential introduced in the section 2.6. This superoperator is a solution of the differential equation

$$\frac{\partial}{\partial t}\mathfrak{T}(t, s) = -i\mathfrak{Q}\mathfrak{L}_I(t)\mathfrak{T}(t, s) \quad (4.12)$$

with the initial condition

$$\mathfrak{T}(s, s) = \mathbf{1}. \quad (4.13)$$

Inserting the equation (4.10) into the equation (4.8) we obtain the wanted equation of motion for the relevant part of the density matrix

$$\frac{\partial}{\partial t}\mathfrak{P}\hat{\rho}(t) = -i\mathfrak{P}\mathfrak{L}_I(t)\mathfrak{P}\hat{\rho}(t) - i\mathfrak{P}\mathfrak{L}_I(t)\mathfrak{T}(t, 0)\mathfrak{Q}\hat{\rho}(0) + \quad (4.14)$$

$$+ \mathfrak{P}\mathfrak{L}_I(t) \int_0^t ds \mathfrak{T}(t, s)\mathfrak{Q}\mathfrak{L}_I(s)\mathfrak{P}\hat{\rho}(s). \quad (4.15)$$

This equation, which is still exact, is known as the Nakajima-Zwanzig equation.

4.2 Time-convolutionless form of the master equation

The just derived Nakajima-Zwanzig equation contains the convolution in the last term, which complicates her solution. In this section we are going to show the way how to obtain a time-convolutionless form of the equation of motion for the relevant part of the density operator. For this purpose we introduce a superoperator $\mathfrak{H}(t, s)$ which solves the equation

$$\hat{\rho}(s) = \mathfrak{H}(t, s)(\mathfrak{P} + \mathfrak{Q})\hat{\rho}(t). \quad (4.16)$$

It is similar to the case of time evolution superoperator, but this superoperator propagates this system back in time. We may write

$$\mathfrak{H}(t, s) = e^{i \int_s^{\rightarrow} ds' \mathfrak{L}_I(s')}, \quad (4.17)$$

where the \rightarrow indicates the negative time ordering. Inserting the equation (4.16) into the equation (4.10) we obtain

$$\mathfrak{Q}\hat{\rho}(t) = \mathfrak{T}(t, 0)\mathfrak{Q}\hat{\rho}(0) - i \int_0^t ds \mathfrak{T}(t, s)\mathfrak{Q}\mathfrak{L}_I(s)\mathfrak{P}\mathfrak{H}(t, s)(\mathfrak{P} + \mathfrak{Q})\hat{\rho}(t). \quad (4.18)$$

For the sake of brevity we also introduce a superoperator $\Sigma(t)$ defined by the relation

$$\Sigma(t) = -i \int_0^t ds \mathfrak{T}(t, s)\mathfrak{Q}\mathfrak{L}_I(s)\mathfrak{P}\mathfrak{H}(t, s). \quad (4.19)$$

Using this superoperator in the previous equation we get

$$(\mathbf{1} - \Sigma(t))\mathfrak{Q}\hat{\rho}(t) = \mathfrak{T}(t, 0)\mathfrak{Q}\hat{\rho}(0) + \Sigma(t)\mathfrak{P}\hat{\rho}(t). \quad (4.20)$$

Let us suppose that the superoperator $\Sigma(t)$ can be inverted (it can be for small time t for example). Thus we may rewrite this equation as

$$\mathfrak{Q}\hat{\rho}(t) = (\mathbf{1} - \Sigma(t))^{-1}\mathfrak{T}(t, 0)\mathfrak{Q}\hat{\rho}(0) + (\mathbf{1} - \Sigma(t))^{-1}\Sigma(t)\mathfrak{P}\hat{\rho}(t). \quad (4.21)$$

It should be stressed that for large couplings or large t it may happen that the equation (4.20) could not be solved uniquely for $\mathfrak{Q}\hat{\rho}(t)$ such that the inverse of $(\mathbf{1} - \Sigma(t))$ does not exist.

Let us now insert the equation (4.21) into the equation (4.8)

$$\frac{\partial}{\partial t}\mathfrak{P}\hat{\rho}(t) = -i\mathfrak{P}\mathfrak{L}_I(t)\mathfrak{P}\hat{\rho}(t) - i\mathfrak{P}\mathfrak{L}_I(t)((\mathbf{1} - \Sigma(t))^{-1}\mathfrak{T}(t, 0)\mathfrak{Q}\hat{\rho}(0) + \quad (4.22)$$

$$\begin{aligned}
& +(\mathbf{1} - \Sigma(t))^{-1}\Sigma(t)\mathfrak{P}\hat{\rho}(t) = \\
& = -i\mathfrak{P}\mathfrak{L}_I(t)((\mathbf{1} - \Sigma(t))^{-1}\mathfrak{T}(t, 0)\mathfrak{Q}\hat{\rho}(0) - i\mathfrak{P}\mathfrak{L}_I(t)(\mathbf{1} - \Sigma(t))^{-1}\Sigma(t)\mathfrak{P}\hat{\rho}(t)) - \quad (4.23)
\end{aligned}$$

$$\begin{aligned}
& -i\mathfrak{P}\mathfrak{L}_I(t)(\mathbf{1} - \Sigma(t))^{-1}(\mathbf{1} - \Sigma(t))\mathfrak{P}\hat{\rho}(t) = \\
& = -i\mathfrak{P}\mathfrak{L}_I(t)((\mathbf{1} - \Sigma(t))^{-1}\mathfrak{T}(t, 0)\mathfrak{Q}\hat{\rho}(0) - i\mathfrak{P}\mathfrak{L}_I(t)(\mathbf{1} - \Sigma(t))^{-1}\mathfrak{P}\hat{\rho}(t)). \quad (4.24)
\end{aligned}$$

We can shorten this equation introducing the superoperators

$$\mathfrak{K}(t) = -i\mathfrak{P}\mathfrak{L}_I(t)(\mathbf{1} - \Sigma(t))^{-1}\mathfrak{P} \quad (4.25)$$

and

$$\mathfrak{J}(t) = -i\mathfrak{P}\mathfrak{L}_I(t)((\mathbf{1} - \Sigma(t))^{-1}\mathfrak{T}(t, 0)\mathfrak{Q}) \quad (4.26)$$

into the form

$$\frac{\partial}{\partial t}\mathfrak{P}\hat{\rho}(t) = \mathfrak{K}(t)\mathfrak{P}\hat{\rho}(t) + \mathfrak{J}(t)\mathfrak{Q}\hat{\rho}(0), \quad (4.27)$$

which is the desired time-convolutionless form of the master equation (We are going to call it further the TCL equation.).

4.3 Perturbation expansion for the TCL equation

In this section we are going to find the perturbation expansion for the equation of motion of the relevant part of the total density matrix. Because in the application of the perturbation expansion we are going to perform later, the irrelevant part of the density matrix at initial time is zero, let us restrict ourselves to the case

$$\mathfrak{Q}\hat{\rho}(0) = 0. \quad (4.28)$$

In this case the TCL equation (4.27) simplifies to

$$\frac{\partial}{\partial t}\mathfrak{P}\hat{\rho}(t) = \mathfrak{K}(t)\mathfrak{P}\hat{\rho}(t). \quad (4.29)$$

The perturbation expansion is going to be performed in orders of $\mathfrak{L}_I(t)$. First of all we are going to expand the term $(\mathbf{1} - \Sigma(t))^{-1}$ in

$$(\mathbf{1} - \Sigma(t))^{-1} = \mathbf{1} + \Sigma(t) + \Sigma^2(t) + \Sigma^3(t) + \dots$$

Inserting this expression into equation (4.25) we obtain

$$\mathfrak{K}(t) = -i\mathfrak{P}\mathfrak{L}_I(t)(\mathbf{1} + \Sigma(t) + \Sigma^2(t) + \Sigma^3(t) + \dots)\mathfrak{P}. \quad (4.30)$$

Let us restate the equation of motion for the relevant part as

$$\frac{\partial}{\partial t} \mathfrak{P} \hat{\rho}(t) = \sum_i \mathfrak{K}_i(t) \mathfrak{P} \hat{\rho}(t), \quad (4.31)$$

where the i denotes the order in $\mathfrak{L}_I(t)$ in the $\mathfrak{K}(t)$ we consider. Further expanding the $\Sigma(t)$ in orders of $\mathfrak{L}_I(t)$ we could show that the first several $\mathfrak{K}_i(t)$ terms are

$$\mathfrak{K}_1(t) = -i \mathfrak{P} \mathfrak{L}_I(t) \mathfrak{P}, \quad (4.32)$$

$$\mathfrak{K}_2(t) = - \int_0^t ds \mathfrak{P} \mathfrak{L}_I(t) \mathfrak{Q} \mathfrak{L}_I(s) \mathfrak{P}, \quad (4.33)$$

$$\mathfrak{K}_3(t) = i \mathfrak{P} \mathfrak{L}_I(t) \left(\int_0^t ds \mathfrak{Q} \mathfrak{L}_I(s) \mathfrak{P} \right)^2 + \quad (4.34)$$

$$+ i \mathfrak{P} \mathfrak{L}_I(t) \left[\int_0^t ds \int_0^s ds' (\mathfrak{Q} \mathfrak{L}_I(s) \mathfrak{Q} \mathfrak{L}_I(s') \mathfrak{P} - \mathfrak{Q} \mathfrak{L}_I(s') \mathfrak{P} \mathfrak{L}_I(s)) \mathfrak{P} \right]. \quad (4.35)$$

The higher order terms are also possible to obtain by this method. Let us mention the fact that the form of the $\mathfrak{K}_1(t)$ is possible to guess using the equation (4.6). Too see this, consider the derivative $\frac{\partial}{\partial t} \mathfrak{P} \hat{\rho}(t)$ at time 0. With our initial condition the equation (4.6) gives

$$\frac{\partial}{\partial t} \mathfrak{P} \hat{\rho}(0) = -i \mathfrak{P} \mathfrak{L}_I(0) \mathfrak{P} \hat{\rho}(0). \quad (4.36)$$

Because all the higher order terms of the perturbation theory vanish at time 0, the $\mathfrak{K}_1(t)$ has to be equal at time 0 to $-i \mathfrak{P} \mathfrak{L}_I(0) \mathfrak{P} \hat{\rho}(0)$.

Let us now discuss the case, when we can assume that

$$\mathfrak{P} \mathfrak{L}_I(t_1) \mathfrak{L}_I(t_2) \dots \mathfrak{L}_I(t_{2n+1}) \mathfrak{P} = 0. \quad (4.37)$$

Then the first order contribution $\mathfrak{K}_1(t)$ is zero. Further we can rewrite the second order contribution in the form

$$\mathfrak{K}_2(t) = - \int_0^t ds \mathfrak{P} \mathfrak{L}_I(t) \mathfrak{L}_I(s) \mathfrak{P}. \quad (4.38)$$

The $\mathfrak{K}_3(t)$ can be also simplified. Because $\mathfrak{Q} \mathfrak{P} = \mathfrak{o}$, the term containing

$$\left(\int_0^t ds \mathfrak{Q} \mathfrak{L}_I(s) \mathfrak{P} \right)^2 = \left(\int_0^t ds \mathfrak{Q} \mathfrak{L}_I(s) \right) \mathfrak{P} \mathfrak{Q} \left(\int_0^t ds \mathfrak{L}_I(s) \mathfrak{P} \right) \quad (4.39)$$

is zero, and because of the demand $\mathfrak{P}\mathfrak{L}(t_1)\mathfrak{L}(t_2)\dots\mathfrak{L}(t_{2n+1})\mathfrak{P} = 0$, and $\mathfrak{P}\mathfrak{L}_I(t)\mathfrak{Q} = \mathfrak{P}\mathfrak{L}_I(t)$, all the terms vanish, i. e.

$$\mathfrak{K}_3(t) = 0. \quad (4.40)$$

By similar argumentation we would find out that the fourth order contribution reads

$$\mathfrak{K}_4(t) = \mathfrak{P}\mathfrak{L}_I(t)\left[\int_0^t ds \int_0^s ds' \int_0^{s'} ds'' \mathfrak{L}_I(s)\mathfrak{L}_I(s')\mathfrak{L}_I(s'') - \right. \quad (4.41)$$

$$\left. - \mathfrak{L}_I(s)\mathfrak{P}\mathfrak{L}_I(s')\mathfrak{L}_I(s'') - \mathfrak{L}_I(s')\mathfrak{P}\mathfrak{L}_I(s)\mathfrak{L}_I(s'') - \mathfrak{L}_I(s'')\mathfrak{P}\mathfrak{L}_I(s')\mathfrak{L}_I(s)\right]\mathfrak{P}. \quad (4.42)$$

Chapter 5

The second reduction - expansion for the TCL equation

We have developed the model open quantum system and the perturbation expansion for the TCL equation in the preceding chapter. In this chapter we would like to show how would the POT work in our case. In the first section of this chapter we are going to discuss particular form of the Liouville superoperators. In the second section we are going to show the explicit expressions for the equation of motion in several orders of the interaction Liouville superoperator for a given projection superoperator. Further in the third section we are going to show relation between the reduced density matrix $\hat{\sigma}$ and the reduced density matrix in the interaction picture to simplify the obtained equations for the relevant part of the density matrix. In the fourth and the fifth section we are going to treat analytical solutions of the original equations of motion and also the TCL equation for several cases.

5.1 Liouville superoperators

We have already performed the first reduction, which led us to equation of motion containing only \mathfrak{L}_0 and the relaxation tensor \mathfrak{R} . The \mathfrak{L}_{S-B} part of the Liouville superoperator \mathfrak{L}_0 is going play a role of the interaction Liouville superoperator \mathfrak{L}_I . We are also going to separate the relaxation tensor \mathfrak{R} in several parts from reasons, which we are going to be clear later. Let us define the matrix elements of the relaxation superoperators \mathfrak{R}^g and \mathfrak{R}_e^g by equations

$$\mathfrak{R}_{p\gamma q\delta}^{g m\alpha n\beta} = \delta_{gg}^{\alpha\beta} (\mathfrak{R}_{p\gamma q\delta}^{mgng}), \quad (5.1)$$

$$\tilde{\mathfrak{R}}_{e\,p\gamma q\delta}^{g\,m\alpha n\beta} = \delta_{ee}^{\alpha\beta} (\mathfrak{R}_{p\gamma q\delta}^{mgng}), \quad (5.2)$$

where the tilde has the meaning explained in section 2.7. To conclude this section we are going to define the Liouville superoperators $\mathfrak{L}_I(t)$ and \mathfrak{L}_0 , which we are going to use in the TCL equation

$$\mathfrak{L}_0 = \mathfrak{L}_S + \mathfrak{L}_B + \mathfrak{R}^g + \mathfrak{R}_e^g, \quad (5.3)$$

$$\mathfrak{L}_I = \mathfrak{L}_{S-B} + \mathfrak{R} - \mathfrak{R}^g - \mathfrak{R}_e^g, \quad (5.4)$$

$$\mathfrak{L}_I(t) = e^{i\mathfrak{L}_0 t} \mathfrak{L}_I e^{-i\mathfrak{L}_0 t} = \mathfrak{U}_0^\dagger(t) \mathfrak{L}_I \mathfrak{U}_0(t), \quad (5.5)$$

where we instead of the addition of superscript I in the last equation denote the interaction picture by the time dependence of \mathfrak{L}_I . Let us note that we are going to specially treat the case of the relaxation tensor with the $\gamma'_{m\alpha n\beta}$ instead of the $\gamma_{m\alpha n\beta}$.

5.2 The equations of motion in the interaction picture

The last thing we need to do to use the TCL equation is to define the projection superoperator \mathfrak{P} . We are going to use the so called Argyres and Kelley projection superoperator (see for example Ref. [5]), which we define as

$$\mathfrak{P}\hat{\rho} = Tr_B(\hat{\rho})\hat{W}.$$

As we have already mentioned, the $\hat{\rho}$ denotes the density operator in the interaction picture, thus following the equation (2.52), which defines the reduced density operator $\hat{\sigma}$, we are going to define the reduced density operator in the interaction picture $\hat{\sigma}^I$ by the equation

$$\hat{\sigma}^I = Tr_B(\hat{\rho}). \quad (5.6)$$

Thus we can now state the perturbation expansion for the TCL equation as

$$\frac{\partial}{\partial t} \hat{\sigma}^I \hat{W} = -i\mathfrak{P}\mathfrak{L}_I(t)\hat{\sigma}^I \hat{W} - \int_0^t ds \mathfrak{P}\mathfrak{L}_I(t)\mathfrak{L}_I(s)\hat{\sigma}^I \hat{W} + \quad (5.7)$$

$$+ i\mathfrak{P}\mathfrak{L}_I(t) \left[\int_0^t ds \int_0^s ds' (\mathfrak{L}_I(s)\mathfrak{L}_I(s')\mathfrak{P} - \mathfrak{L}_I(s')\mathfrak{P}\mathfrak{L}_I(s)) \right] \hat{\sigma}^I \hat{W} \quad (5.8)$$

in the first three orders in $\mathfrak{L}_I(t)$. We have performed the second reduction of our system obtaining the equations of motion for the reduced density matrix $\hat{\sigma}^I$. In the next subsection we are going to show how is the $\hat{\sigma}^I$ connected with $\hat{\sigma}$. Thus we started with the total density matrix $\hat{\zeta}$, then we obtained the equations of motion for the reduced density matrix $\hat{\rho}$ and now we have performed the second reduction obtaining the equations of motion for the reduced density operator $\hat{\sigma}^I$.

5.3 Transformation of the reduced density matrix to the interaction picture

Let us now show the connection between the reduced density operator in the interaction picture and the ordinary one. We are going to consider the definition of the $\hat{\sigma}^I$ (5.6) and the definition of the interaction picture density matrix (2.61) (now denoted by the same symbol $\hat{\rho}$) and state the equation

$$\hat{\sigma}^I = Tr_B(e^{i\mathfrak{L}_0 t} \hat{\rho}). \quad (5.9)$$

Considering our form of the \mathfrak{L}_0 defined in the equation (5.3) we can show that the following equation holds

$$\hat{\sigma}^I = e^{i\mathfrak{L}_S t} Tr_B(\hat{\rho}) = e^{i\mathfrak{L}_S t} \hat{\sigma}. \quad (5.10)$$

To prove this, it is sufficient to prove the following equations

$$Tr_B(\mathfrak{L}_B \hat{\rho}) = 0, \quad (5.11)$$

$$Tr_B(\mathfrak{R}^g \hat{\rho}) = 0, \quad (5.12)$$

$$Tr_B(\mathfrak{R}_e^g \hat{\rho}) = 0, \quad (5.13)$$

because then in the expansion of the exponential in the equation (5.9) there are only terms \mathfrak{L}_S giving nonzero, these terms than form an exponential $e^{i\mathfrak{L}_S t}$. Because this exponential does not act on the phonon states, it can be interchanged with the Tr_B operand. The first equation follows from the diagonal form of \hat{H}_B , the second and the third equation follows from the equation (3.39). Therefore we can obtain the reduced density matrix from the knowledge of the reduced density equation in the interaction picture inverting the relationship (5.10).

5.4 Analytical solution of the equations of motion for the twice reduced density matrix

Considering the form of the superoperator \mathfrak{L}_S we can directly write down the transformation relation

$$\sigma_{\alpha\beta}(t) = e^{-\frac{i}{\hbar}(\langle\alpha|\hat{H}_S|\alpha\rangle - \langle\beta|\hat{H}_S|\beta\rangle)t} \sigma_{\alpha\beta}^I(t). \quad (5.14)$$

Let us also write down the analytical solution for the matrix elements of the reduced density matrix at time t . Using the expression (3.46) for the exact solution and the relations

$$Tr_B(\langle\alpha|\mathfrak{R}\hat{\rho}|\alpha\rangle) = 0, \quad (5.15)$$

$$Tr_B(\langle\alpha|\mathfrak{L}_o\hat{\rho}|\alpha\rangle) = 0, \quad (5.16)$$

we can see that the diagonal elements of the reduced density matrix $\hat{\sigma}$ are time independent, thus

$$\sigma_{\alpha\alpha}(t) = \sigma_{\alpha\alpha}(0). \quad (5.17)$$

We are going to use the initial condition (3.66), thus the elements are $\sigma_{gg}(t) = 0$ and $\sigma_{ee}(t) = 1$. We can also express the time dependence of the off-diagonal elements of $\hat{\sigma}$. From the equations (3.2), (3.38) and (3.36) follows that the matrix elements ρ_{mgne} satisfy the differential equation

$$\frac{d}{dt}\rho_{mgne}(t) = \left(-\frac{i}{\hbar}(E_{mg} - E_{ne}) - \gamma_{mgne}\right)\rho_{mgne}(t). \quad (5.18)$$

This equation has a solution

$$\rho_{mgne}(t) = e^{(-\frac{i}{\hbar}(E_{mg} - E_{ne}) - \gamma_{mgne})t} \rho_{mgne}(0). \quad (5.19)$$

Further using the relation (2.70) we can express the element σ_{ge} as

$$\sigma_{ge}(t) = \sum_{nq} \rho_{ngqe}(t) c_{qn} \quad (5.20)$$

and for the initial condition (3.66) we finally obtain

$$\sigma_{ge}(t) = \sum_{nq} e^{(-\frac{i}{\hbar}(E_{ng} - E_{qe}) - \gamma_{ngqe})t} \frac{Z_n^g}{Z} c_{qn} c_{qn}. \quad (5.21)$$

Because the reduced density matrix is Hermitian $\sigma_{ge}(t) = \sigma_{eg}^*(t)$, we have obtained analytical solutions for every element of the reduced density matrix $\sigma_{\alpha\beta}$.

We assumed the more complicated case, when the γ_{mgne} depends on the phonon indices. In the section 3.4 we noted that we can set $\gamma_{mgne} = \gamma_{meng} = \gamma$.

5.5 Simplifying and solving the TCL equation

We would like to show that the equation (5.7) leads to set of equations for matrix elements of the reduced density matrix in the interaction picture, which are independent for every element of the reduced density matrix. To see this, we consider Tr_B of this equation yielding

$$\frac{\partial}{\partial t} \hat{\sigma}^I = -i Tr_B(\mathfrak{L}_I(t) \hat{\sigma}^I \hat{W}) - Tr_B\left(\int_0^t ds \mathfrak{L}_I(t) \mathfrak{Q} \mathfrak{L}_I(s) \hat{\sigma}^I \hat{W}\right) + \quad (5.22)$$

$$+ i Tr_B(\mathfrak{L}_I(t) \int_0^t ds \int_0^s ds' (\mathfrak{Q} \mathfrak{L}_I(s) \mathfrak{Q} \mathfrak{L}_I(s') \mathfrak{P} - \mathfrak{Q} \mathfrak{L}_I(s') \mathfrak{P} \mathfrak{L}_I(s)) \hat{\sigma}^I \hat{W}). \quad (5.23)$$

Now notice that in the perturbation expansion, if we restrict ourselves to the electronic part of the Hilbert space, every term is composed of commutators with operators diagonal in the electronic states (for the case of zero relaxation term often denoted as $\hat{H}_I(t)$) and sometimes there also occur superoperators \mathfrak{R}^g and \mathfrak{R}_e^g . Because acting of a diagonal operator does not “mix” different matrix elements of the operators it acts on, and the superoperators \mathfrak{R}^g and \mathfrak{R}_e^g also do not cause transition between different electronic states, we can regard this equation as four independent equations for matrix elements $\hat{\sigma}^I$.

Thus we may rewrite this equation in the first two orders in a form

$$\frac{\partial}{\partial t} \sigma_{\alpha\beta}^I = -i \sum_{npq} (\tilde{\mathfrak{L}}_{I p\alpha q\beta}^{n\alpha n\beta}(t) \sigma_{\alpha\beta}^I \hat{W}_{pq}) - \quad (5.24)$$

$$- \sum_{npq r t p' q'} \left(\int_0^t ds \tilde{\mathfrak{L}}_{I p\alpha q\beta}^{n\alpha n\beta}(t) \tilde{\mathfrak{Q}}_{r\alpha t\beta}^{p\alpha q\beta} \tilde{\mathfrak{L}}_{I p' \alpha q' \beta}^{r\alpha t\beta}(s) \sigma_{\alpha\beta}^I W_{p' q'} \right), \quad (5.25)$$

or if we define $K_{1\alpha\beta}(t)$ and $K_{2\alpha\beta}(t)$ by the equations

$$K_{1\alpha\beta}(t) = -i \sum_{npq} (\tilde{\mathfrak{L}}_{I p\alpha q\beta}^{n\alpha n\beta}(t) W_{pq}), \quad (5.26)$$

$$K_{2\alpha\beta}(t) = - \sum_{npq r t p' q'} \left(\int_0^t ds \tilde{\mathfrak{L}}_{I p\alpha q\beta}^{n\alpha n\beta}(t) \tilde{\mathfrak{Q}}_{r\alpha t\beta}^{p\alpha q\beta} \tilde{\mathfrak{L}}_{I p' \alpha q' \beta}^{r\alpha t\beta}(s) W_{p' q'} \right), \quad (5.27)$$

we can rewrite the equation as

$$\frac{\partial}{\partial t} \sigma_{\alpha\beta}^I = (K_{1\alpha\beta}(t) + K_{2\alpha\beta}(t)) \sigma_{\alpha\beta}^I. \quad (5.28)$$

As we have already mentioned, the diagonal elements of the reduced density matrix are in our model time independent, thus we would expect that the functions $K_{1\alpha\alpha}(t)$ and $K_{2\alpha\alpha}(t)$ are 0 and they really are (it follows from the definition of $\tilde{\mathfrak{L}}_{I p\alpha q\beta}^{n\alpha n\beta}(t)$). We can also note that in the first order, following the definitions (5.3), (5.4), (5.5) and the diagonality of \hat{W} we can show that

$$\sum_{npq} (\tilde{\mathfrak{L}}_{I p g q e}^{n g n e}(t) W_{pq}) = \sum_{np} (e^{i\tilde{\mathfrak{L}}_0 t} \tilde{\mathfrak{K}} e^{-i\tilde{\mathfrak{L}}_0 t})_{p g p e}^{n g n e} W_{pp}. \quad (5.29)$$

Thus in the case with no relaxation, the first order contribution is zero or in other words all the terms $\mathfrak{P}\mathfrak{L}_I(t)\mathfrak{P}$ are zero. The only part of the relaxation tensor, which gives a nonzero contribution in the first order is the part responsible for decay of the off-diagonal (in electronic states) elements of the density matrix $\rho_{m\alpha n\beta}$.

From now on, we are going to suppose $\gamma_{mgne} = \gamma_{meng} = \gamma$. From the expression (5.21), we can see that the analytical solution is

$$\sigma_{ge}(t) = e^{-\gamma t} \sum_{nq} e^{-\frac{i}{\hbar}(E_{ng} - E_{qe})t} \frac{Z_n^g}{Z} c_{qn} c_{qn}. \quad (5.30)$$

To simplify the perturbation expansion we can suggest to assume $\gamma = 0$, solve the equations of motion from the TCL equation and then multiply the resulting $\sigma_{ge}(t)$ by factor $e^{-\gamma t}$.

In the case $\gamma = 0$, the equation (5.29) is zero, and therefore the first order of the perturbation theory (5.26) is zero as well. We can even prove (at least in the case $\omega_g = \omega_e$) that the condition (4.37) holds. From the equation (5.29) follows that

$$\mathfrak{P}\mathfrak{L}(t)\mathfrak{P}\hat{\rho} = 0.$$

We have already discussed that the terms $K_{n\alpha\alpha}(t)$ are zero thus (because of the Hermiticity) it is sufficient to prove that

$$\langle g | \mathfrak{P}\mathfrak{L}_I(t_1)\mathfrak{L}_I(t_2) \dots \mathfrak{L}_I(t_{2n+1})\mathfrak{P}\hat{\rho} | e \rangle = 0. \quad (5.31)$$

Using the definitions of the superoperators in this expression we would arrive at

$$\begin{aligned} & \langle g | \mathfrak{P}\mathfrak{L}_I(t_1)\mathfrak{L}_I(t_2) \dots \mathfrak{L}_I(t_{2n+1})\mathfrak{P}\hat{\rho} | e \rangle \sim \\ & \sim Tr_B(\hat{W}_{eq}\hat{D}_{2n+1}\Delta\hat{V}\hat{D}'_{2n+1} \dots \hat{D}_2\Delta\hat{V}\hat{D}'_2\hat{D}_1\Delta\hat{V}\hat{D}'_1)\sigma_{ge}\hat{W}_{eq}, \end{aligned} \quad (5.32)$$

where the symbol \sim denotes proportionality and the operators \hat{D}_{2n+1} , \hat{D}'_{2n+1} are some diagonal operators (in the base $|n\rangle$, dependent on times $t_1, t_2, \dots, t_{2n+1}$). From the definition of $\Delta\hat{V}$ (3.17) it follows that

$$\Delta\hat{V} \sim \hat{a} + \hat{a}^\dagger. \quad (5.33)$$

But then the expression contains trace over product of a diagonal matrices and odd products of the creation and annihilation operators, which is always zero, thus the statement $\mathfrak{P}\mathfrak{L}_1(t_1)\mathfrak{L}_1(t_2)\dots\mathfrak{L}_1(t_{2n+1})\mathfrak{P}\hat{\rho} = 0$ is proven. We have already shown in the section 4.3 that having this relationship, the $\mathfrak{K}_1(t)$ and the $\mathfrak{K}_3(t)$ are zero. Now let us calculate the non-vanishing $K_{2ge}(t)$ analytically using the equation (5.27). As we have already said, we can omit the \mathfrak{Q} and after some rearrangements we obtain

$$K_{2ge}(t) = -\frac{1}{\hbar^2}Tr_B\left(\int_0^t ds\Delta\hat{V}\Delta\hat{V}(s)\hat{W}_{eq}\right), \quad (5.34)$$

where

$$\Delta\hat{V}(s) = \hat{U}_B^\dagger(s)\Delta\hat{V}\hat{U}_B(s), \quad (5.35)$$

and

$$\hat{U}_B^\dagger(s) = e^{\frac{i}{\hbar}\hat{H}_B s}. \quad (5.36)$$

From the definition of the operator $\Delta\hat{V}$ follows that in our case

$$\Delta\hat{V} = -m\omega_g^2\hat{x}x_0 = -\hbar\omega_g\hat{X}X_0 = -\frac{\hbar\omega_g}{\sqrt{2}}X_0(\hat{a} + \hat{a}^\dagger),$$

where we made use of the creation and annihilation operators defined in section 2.5 and the dimensionless coordinates \hat{X} and X_0 defined by equations (3.23) and (3.27). We can express the $K_{2ge}(t)$ as

$$K_{2ge}(t) = -\frac{X_0^2}{2}\omega_g Tr_B\left(\int_0^t ds(\hat{a} + \hat{a}^\dagger)(\hat{a}(s) + \hat{a}^\dagger(s))\hat{W}_{eq}\right), \quad (5.37)$$

where the $\hat{a}(s)$ reads

$$\hat{a}(s) = \hat{U}_B^\dagger(s)\hat{a}\hat{U}_B(s), \quad (5.38)$$

and the $\hat{a}^\dagger(s)$ is Hermitian conjugate of this operator. After calculations considering the definition of \hat{W}_{eq} , the definition of $\hat{U}_B^\dagger(s)$, and the properties of the creation and annihilation operators we would obtain

$$K_{2ge}(t) = -i\frac{X_0^2}{2}\omega_g(1 - e^{i\omega_g t} - \bar{n}(e^{i\omega_g t} - e^{-i\omega_g t})), \quad (5.39)$$

where the \bar{n} is defined by the equation

$$\bar{n} = \sum_n \langle n | \hat{W}_{eq} | n \rangle n = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}. \quad (5.40)$$

Considering this relation in equation (5.28) and its consequence

$$\sigma_{ge}^I(t) = e^{\int_0^t K_{2ge}(s)} \sigma_{ge}^I(0), \quad (5.41)$$

we can after integration of the involved exponential functions write down the solution following from the second order expansion of the TCL equation

$$\sigma_{ge}^I(t) = e^{\frac{X_0^2}{2}((1+\bar{n})(e^{+i\omega_g t}-1)-i\omega_g t+\bar{n}(e^{-i\omega_g t}-1))} \sigma_{ge}^I(0). \quad (5.42)$$

We are going to show that at least for limiting case $T \rightarrow 0$, this solution is identical with the analytical solution (5.21). In the low temperature limit, when $Z_n^g = \delta_{n0}$, we can write down the analytical solution (in the considered case $\gamma = 0$)

$$\sigma_{ge}(t) = \sum_{nq} e^{-\frac{i}{\hbar}(E_{ng}-E_{qe})t} \frac{Z_n^g}{Z} c_{qn} c_{q0} = \sum_q e^{-\frac{i}{\hbar}(E_{0g}-E_{qe})t} c_{q0} c_{q0}. \quad (5.43)$$

Further using the relation (A.28) in this equation we have

$$\sigma_{ge}(t) = \sum_q e^{-\frac{i}{\hbar}(E_{0g}-E_{qe})t} e^{-\frac{X_0^2}{2}} \left(\frac{X_0^2}{2} \right)^q \frac{1}{q!}. \quad (5.44)$$

Passing to the interaction picture (equation (5.14)) and using the definitions of E_{ng} and E_{qe} we obtain

$$\sigma_{ge}^I(t) = \sum_q e^{i\omega_g q t - i\frac{X_0^2}{2}\omega_g t} e^{-\frac{X_0^2}{2}} \left(\frac{X_0^2}{2} \right)^q \frac{1}{q!} = \quad (5.45)$$

$$= e^{\frac{X_0^2}{2}(e^{i\omega_g t}-1-i\omega_g t)}. \quad (5.46)$$

This expression is equal to the expression (5.42) in the low temperature limit, when $\bar{n} = 0$ with our initial condition $\sigma_{ge}^I(0) = 0$. The solution of the TCL equation in the second order gives at least in the low temperature limit solution identical with the analytical solution.

Let us now discuss the special case case, when the frequencies of the oscillators are equal ($\omega_g = \omega_e$), and they have identical equilibrium position $X_0 = 0$. Then the operators \hat{V}^e and \hat{V}^g would take the form

$$\hat{V}^g = \frac{\hbar\omega_g}{2}\hat{X}^2, \quad (5.47)$$

$$\hat{V}^e = \frac{\hbar\omega_g}{2}\lambda^4\hat{X}^2, \quad (5.48)$$

where the $\lambda = \frac{\omega_g^2}{\omega_e^2}$ (we use the λ from the subsection A.4.1). By the same argumentation as in the preceding case we could prove that the relation $\mathfrak{P}\mathfrak{L}_I(t_1)\mathfrak{L}_I(t_2)\dots\mathfrak{L}_I(t_{2n+1})\mathfrak{P}\hat{\rho} = 0$ (valid also for nonzero temperatures). We are going to restrict ourselves to the case $T \rightarrow 0$. Then we can state the equation

$$\Delta\hat{V} = \frac{\hbar\omega}{4}(\lambda^4 - 1)((\hat{a} + \hat{a}^\dagger)^2 - 1). \quad (5.49)$$

Considering again in the same way the second order of the TCL equation we would obtain

$$\sigma_{ge}^I(t) = e^{\int_0^t K_{2ge}(s)}\sigma_{ge}^I(0) = e^{\frac{(\lambda^4-1)^2}{32}(e^{2i\omega_g t}-1-2i\omega_g t)}\sigma_{ge}^I(0). \quad (5.50)$$

Chapter 6

Results of the numerical simulations

6.1 Description of the used program

The program was written in Fortran 95. It can be compiled by standard Fortran compilers with no supplemental libraries. The Runge-Kutta method in the fourth order was used for the integration of systems of differential equations (description of these methods can be found for example in Ref. [6]) and for the evaluation of the integrals. To make the number of phonon states finite, a cutoff denoted in the program by N , was chosen. For the simulations the cutoff was chosen big enough to have negligible influence on the numerical simulations. This was tested by variation of the cutoff and observation of the differences in the resulting figures.

The program also contains a routine calculating the FC factors based on the recurrence formulas described in the subsection A.4.2 in the Appendix A. The routine calculates the matrix $c_{mn} \hat{=} \mathbf{C}(m, n)$ for given $\lambda \hat{=} \mathbf{W}0$ and $x_0 \hat{=} \mathbf{x}0$ with cutoff N .

The Runge-Kutta method of the fourth order is used to solve the equation (5.27) and to perform the integration with step denoted in the program as h_a . In the program, the matrix elements of the operators and the superoperators in different bases are distinguished instead of tilde by last letter w (for example $LLI \hat{=} \mathcal{L}_I$, $LLIw \hat{=} \tilde{\mathcal{L}}_I$). All the mathematical objects from this text are similarly marked in the program (for example the transformation superoperator $\mathfrak{C} \hat{=} CCC$).

6.2 Parameters of the model system

In this section we are going to discuss, what could be typical parameters of our model system to treat. From the definitions and (3.44) and (3.2) it is possible to see that we should specify parameters T - temperature of the bath, \tilde{k}_α - reorganization energy (with units of frequency), $E_g - E_e$ - energy difference of the ground and the excited state of the molecule, ω_g and ω_e vibrational eigenfrequencies of the molecule in the ground and excited state, respectively. To determine the FC factors, we should also add the values of λ and x_0 , as defined in the discussion in (A.4.1).

Because here we are not interested in a particular molecules, we are going to discuss only range of possible parameters relevant to “common” physical processes. We are going to consider temperature in range between 0 and 10^3K . Further, the energy difference $E_e - E_g$ is going to be in range of transitions appropriate to visible light. The energy of one phonon $\hbar\omega_g$. will be taken about 100 times smaller than than that of the optical transition. Visible light has the frequency ranging from 405 to 790 THz. The frequency ω_g is thus going to be one or two orders of magnitude under the frequency of visible light, thus in range about $2\pi(10^{12}$ to $10^{13})$ Hz. The ω_e is going to be taken equal or very similar to ω_g . In the next sections, we choose the frequency of light corresponding to the difference $E_e - E_g$ as 500 THz, thus the appropriate ω of the light is $\pi \text{ fs}^{-1}$. We consider the ω_g hundred times smaller, thus $\omega_g = \frac{\pi}{100} \text{ fs}^{-1}$.

Finally, we are going to discuss the reasonable range for parameters x_0 and λ . To obtain a reasonable guesses for these dimensionless parameters, we could use the definitions (A.72) and (A.73). For the x_0 we are going to choose some values in range between 0 and 2. The parameter λ is also going to taken between 0 and 2.

We are going to use the spectroscopic units, which follow from the demand

$$2\pi\hbar c = 1. \tag{6.1}$$

In these units it is usual to use inverse centimeter as unit of the energy, because

$$2\pi\hbar c = 1.98645 \times 10^{-23} \text{ J cm} \tag{6.2}$$

We have specified the range of parameters of our model and the results in particular cases are going to be discussed in the next section.

6.3 Numerical results for second order TCL equation

In this section we are going to discuss several figures obtained by the simulations with our Fortran program for various parameters. Everywhere in this section we are going to omit the superscript I writing $\hat{\sigma}$ instead of $\hat{\sigma}^I$. The parameters x_0 (in previous chapters sometimes denoted as X_0) and λ denote in this section the dimensionless parameters of the FC factors defined by the equations (A.73) and (A.72). The resulting figures do not depend on the energy difference $E_e - E_g$, therefore we are not going to mention the value of this difference. We have plotted the real part of the off-diagonal element σ_{ge} of the reduced density matrix in the interaction picture (interaction picture was chosen in order to avoid fast oscillations depending on the difference $E_e - E_g$). In all simulations mentioned in this section, the cutoff N was chosen equal to 11.

The temperature dependence of the time evolution of the $\sigma_{ge}(t)$ element of the reduced density matrix is presented in Figures 6.1 and 6.2. We have already proven that in the case of zero temperature, and $\omega_g = \omega_e$, the perturbation theory gives in the first two orders in $\mathfrak{L}_I(t)$ identical results as the analytical expression (5.21). Performing further numerical simulations we have observed this behavior also in higher temperatures. Therefore you can see in the figures only analytical solutions.

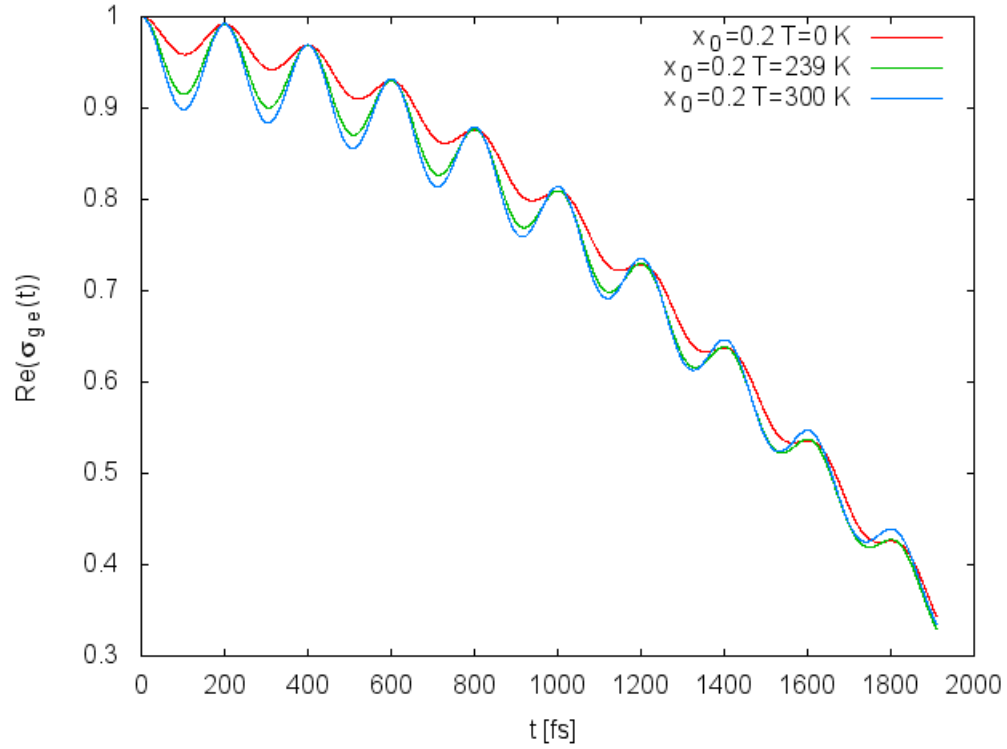


Figure 6.1: Real part of the matrix element σ_{ge} obtained by the numerical simulations. The parameters of the model system were chosen as $\hbar\omega_g = \hbar\omega_e \approx 166.78 \text{ cm}^{-1}$, $x_0 = 0, 2$, for the temperature $T \approx 0 \text{ K}$, $T \approx 239 \text{ K}$ and $T \approx 300 \text{ K}$. The results of the perturbation theory in the second order are identical with the results of the analytical calculation.

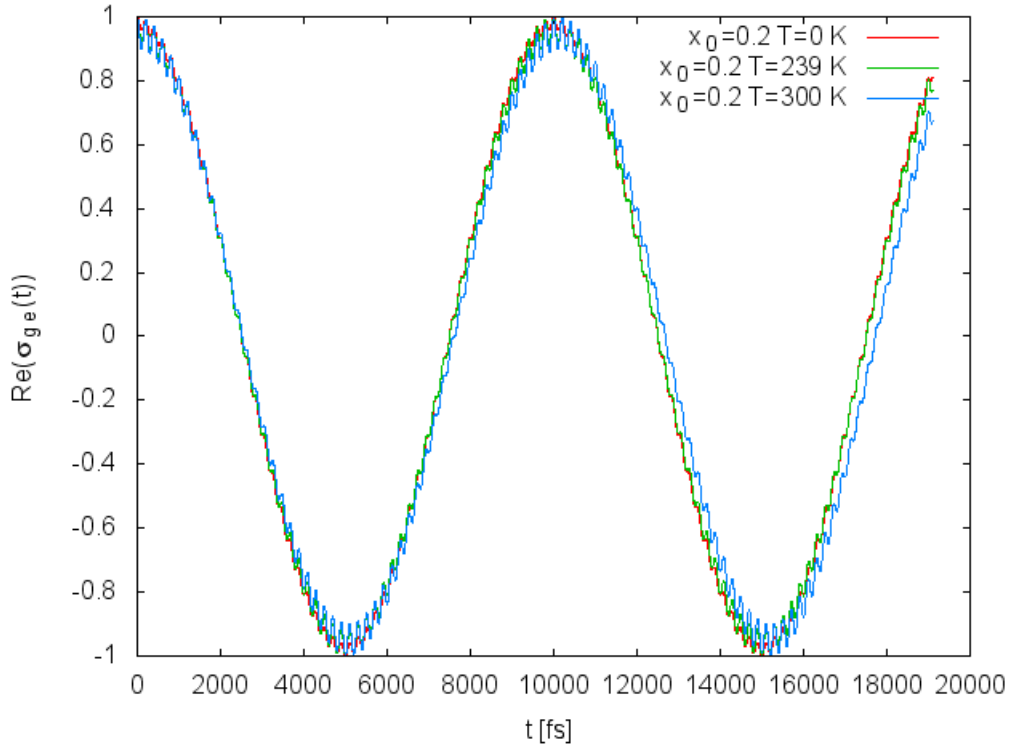


Figure 6.2: Real part of the matrix element σ_{ge} for the same parameters as the figure 6.1. The dynamics is presented in a time range 10 times larger than in Fig. 6.1.

In the Figs. 6.3 and 6.4 you can see the dependence of $\sigma_{ge}(t)$ on another parameter x_0 . As in the preceding case, the analytical solutions were identical with the solutions following from the second order perturbation theory.

The case of parameter $x_0 = 1, 2$, is shown in the Figs. 6.5 and 6.6. As we can see, the changes of the parameter x_0 lead to significant changes in the resulting dynamics.

Let us now discuss the case, when the oscillators have the same equilibrium position, but different frequencies. It turned out that the results of the second order perturbation of the TCL equation leads to different result than the analytical expression. The results are in the figures 6.7 and 6.8 for the temperature $T \approx 239$ K and in the Figs. 6.9 and 6.10 for the temperature $T \approx 0$ K.

Thus we can conclude that in the case of the shifted harmonic oscillators, the second order of TCL equation gives the solution reproducing the exact dynamics

of the system. In the case of oscillators with different frequencies, the second order perturbation theory gives time dependence, which is satisfactory only for very short times. Higher orders of the perturbation theory would be necessary to faithfully reproduce the exact dynamics.

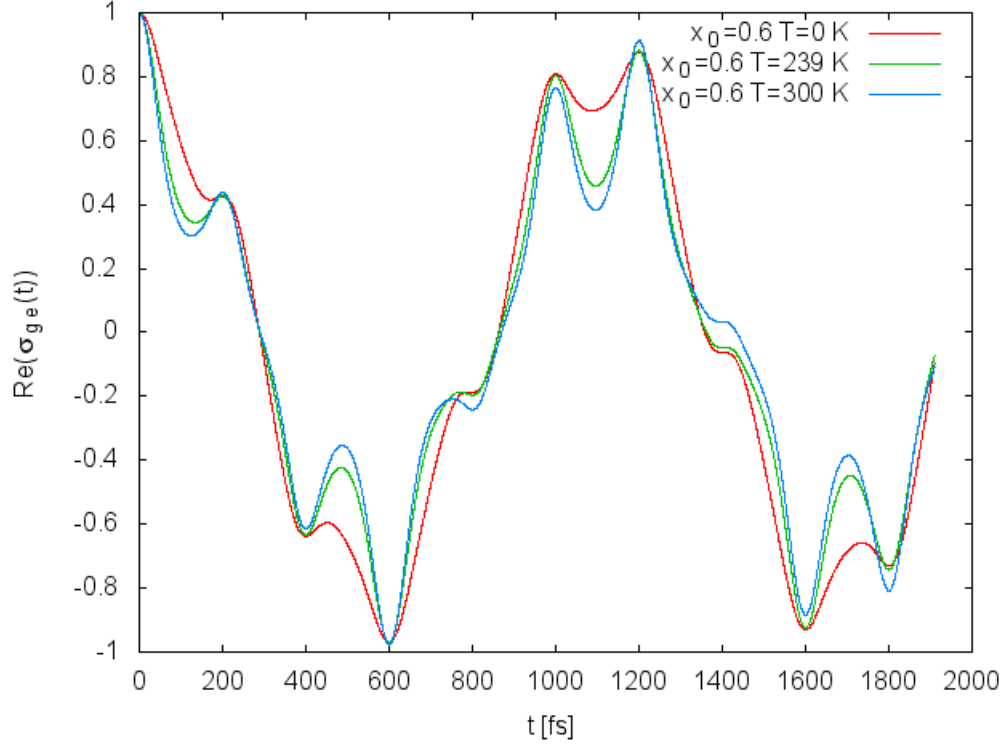


Figure 6.3: The parameters of the model system were chosen as $\hbar\omega_g = \hbar\omega_e \approx 166.78 \text{ cm}^{-1}$, $x_0 = 0,6$, for the temperature $T \approx 0 \text{ K}$, $T \approx 239 \text{ K}$ and $T \approx 300 \text{ K}$. The results of the perturbation theory in the second order are identical with the results of the analytical calculation.

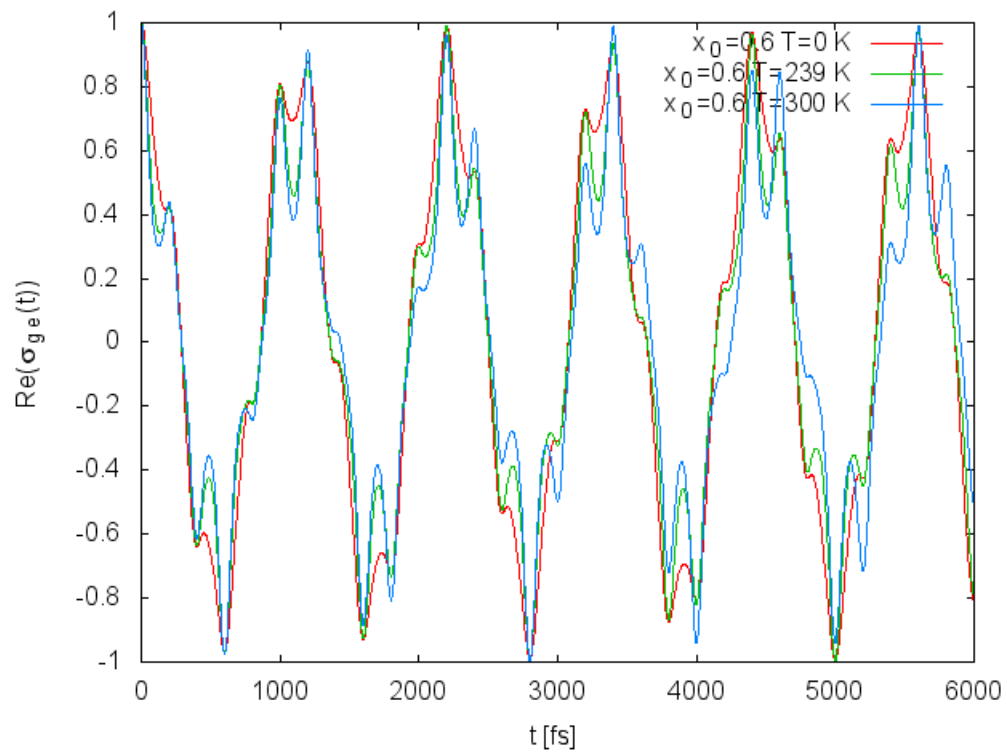


Figure 6.4: Same parameters as the Fig. 6.3. The time range of this figure is 10 times larger than in Fig. 6.3.

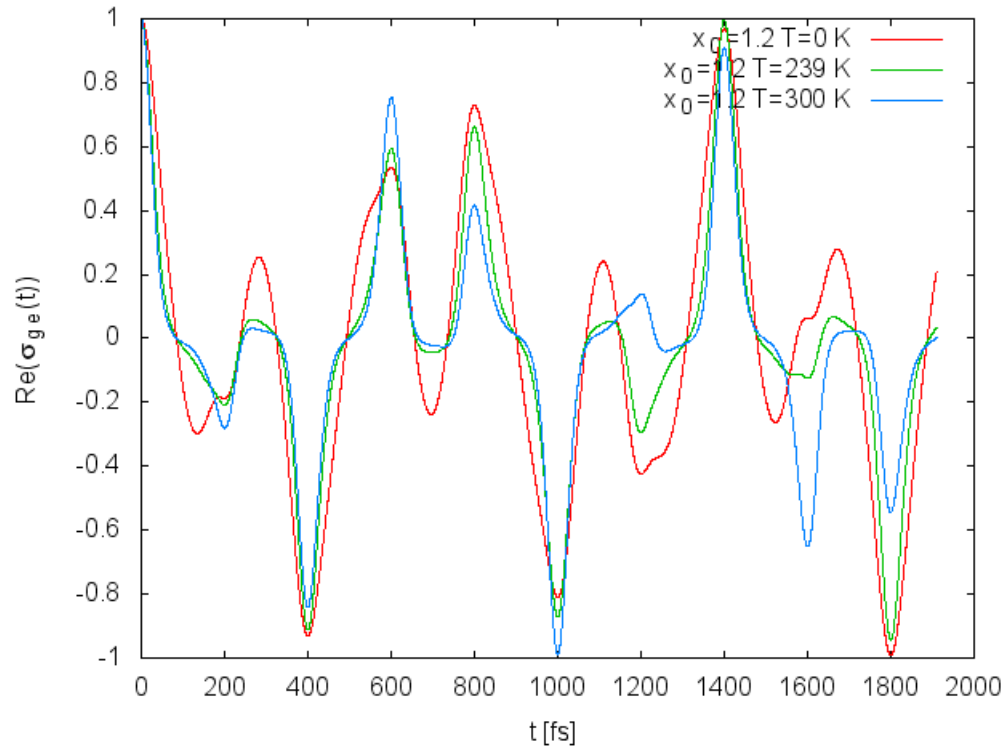


Figure 6.5: The parameters of the model system were chosen as $\hbar\omega_g = \hbar\omega_e \approx 166.78 \text{ cm}^{-1}$, $x_0 = 1, 2$, for the temperature $T \approx 0 \text{ K}$, $T \approx 239 \text{ K}$ and $T \approx 300 \text{ K}$. The results of the perturbation theory in the second order are identical with the results of the analytical calculation.

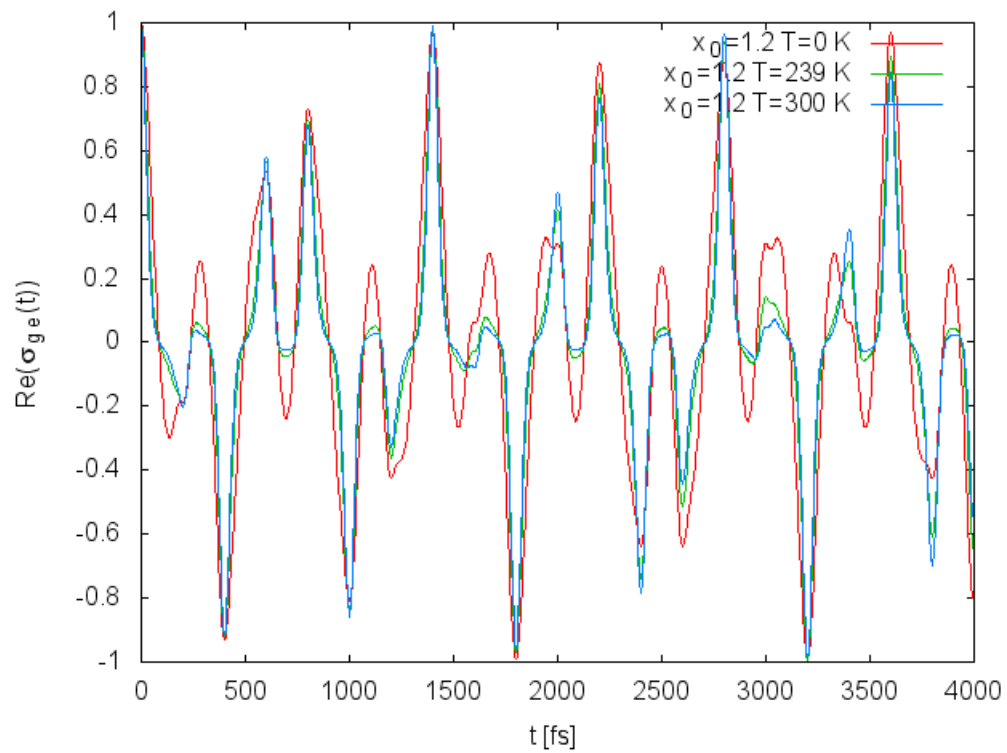


Figure 6.6: Same parameters as the Fig. 6.5. The time range of this figure is doubled with respect to Fig. 6.5.

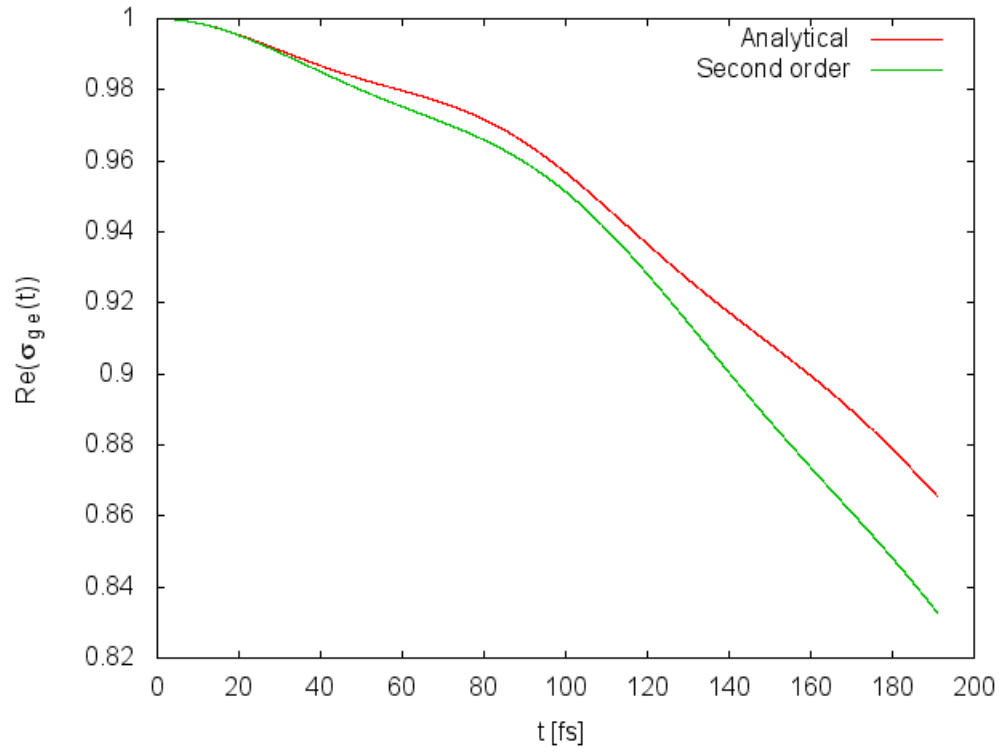


Figure 6.7: The parameters of the model system were chosen as $\hbar\omega_g \approx 166.78 \text{ cm}^{-1}$, $\hbar\omega_e = 1,1\hbar\omega_g$ $x_0 = 1,2$, $\lambda = \sqrt{\frac{\omega_e}{\omega_g}} \approx 1,05$ for the temperature $T \approx 239 \text{ K}$.

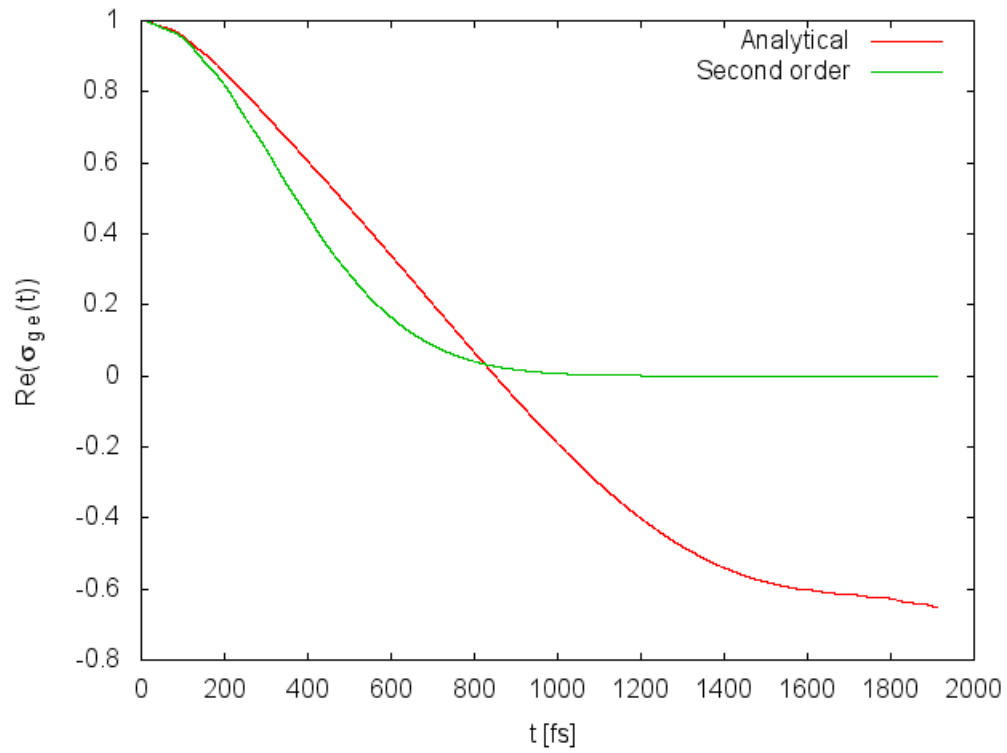


Figure 6.8: Same parameters as in Fig. 6.7. The time range of this figure is 10 times larger than in Fig. 6.7.

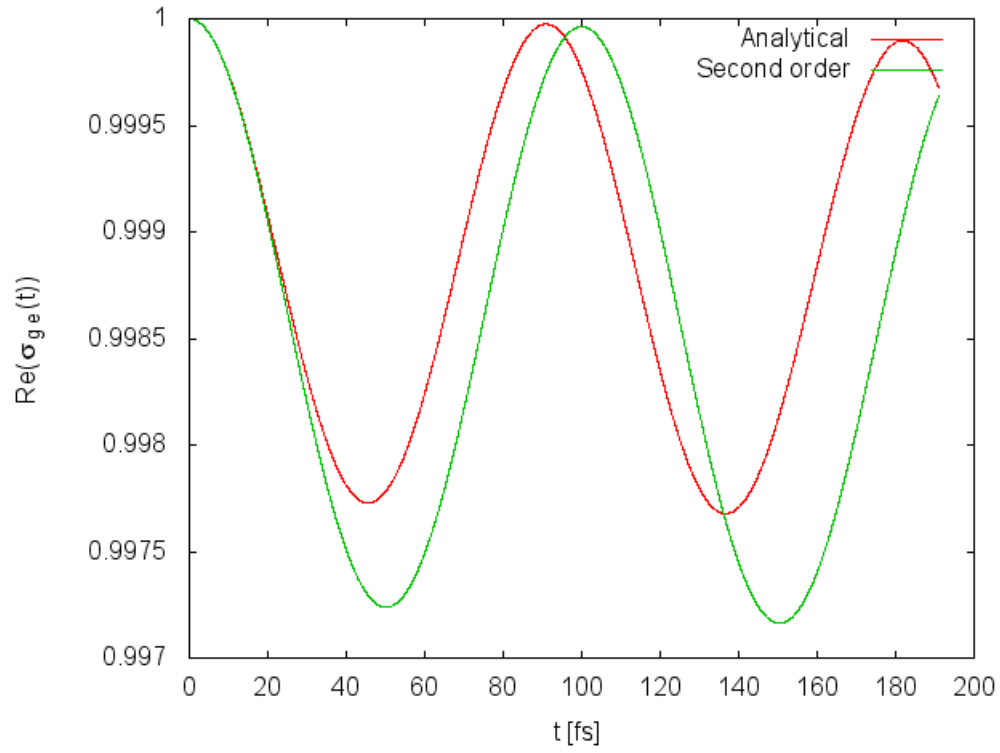


Figure 6.9: The parameters of the model system were chosen as $\hbar\omega_g \approx 166.78 \text{ cm}^{-1}$, $\hbar\omega_e = 1,1\hbar\omega_g$ $x_0 = 1,2$, $\lambda = \sqrt{\frac{\omega_e}{\omega_g}} \approx 1,05$ for the temperature $T \approx 0\text{K}$.

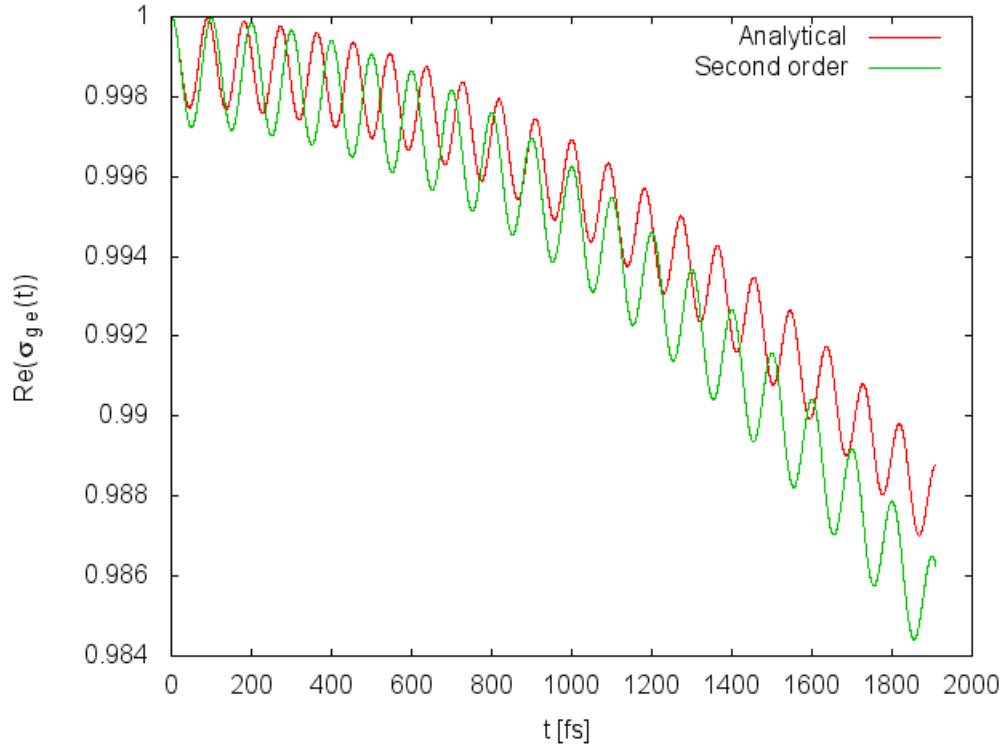


Figure 6.10: Same parameters as Fig. 6.9. The time range of this figure is 10 times larger than in Fig. 6.9.

6.4 Simulations of the relaxation processes

In this section we are going to discuss several plots of the exact numerical simulation of the relaxation process. We have assumed the equation of motion for the density operator $\hat{\rho}$ of the form (3.36) with $\gamma_{m\alpha n\beta}$ defined by equation (3.42). The first plot you can find in the figure 6.11. As you can see, the diagonal elements of the density matrix asymptotically approach the canonical equilibrium. The diagonal elements of the density matrix at time $t = 0$ are not identical with the equilibrium density matrix, because of the nontrivial FC factors $x_0 \neq 0$. In the figures we can observe, how big difference the transformation using the FC factors caused for the parameter $x_0 = 1, 2$.

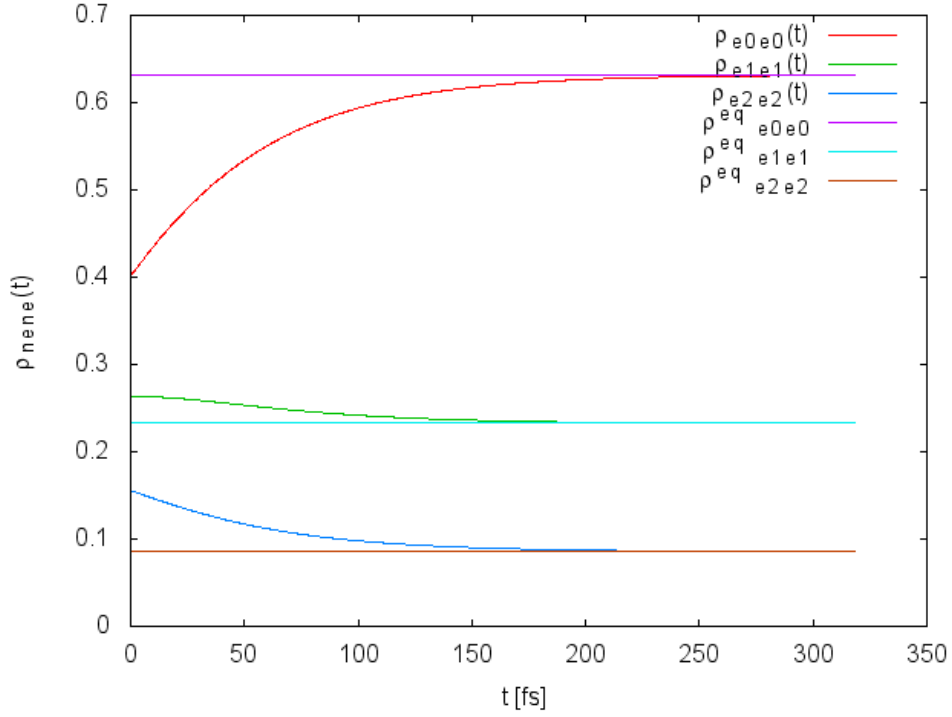


Figure 6.11: The parameters for the simulation of the relaxation process were chosen as $\tilde{k}_g\hbar = \tilde{k}_e\hbar = \hbar\omega_e = \hbar\omega_g \approx 166.78 \text{ cm}^{-1}$, $x_0 = 1, 2$, for the temperature $T \approx 239\text{K}$, $E_e - E_g = 100\hbar\omega_g \approx 16\,678 \text{ cm}^{-1}$, $x_0 = 1, 2$. In the figure you can see the time dependence of the first three diagonal elements in the excited state $\rho_{0e0e}(t)$, $\rho_{1e1e}(t)$, $\rho_{2e2e}(t)$ and the appropriate elements of the equilibrium density matrix $\rho_{eq\,0e0e}^e$, $\rho_{eq\,1e1e}^e$, $\rho_{eq\,2e2e}^e$.

As we discussed in section 3.4, the off-diagonal elements should decay to zero. The numerical simulation of this process is in the figure 6.12, which confirms this assumption. The cutoff N was chosen in all the figures in this section equal to 10.

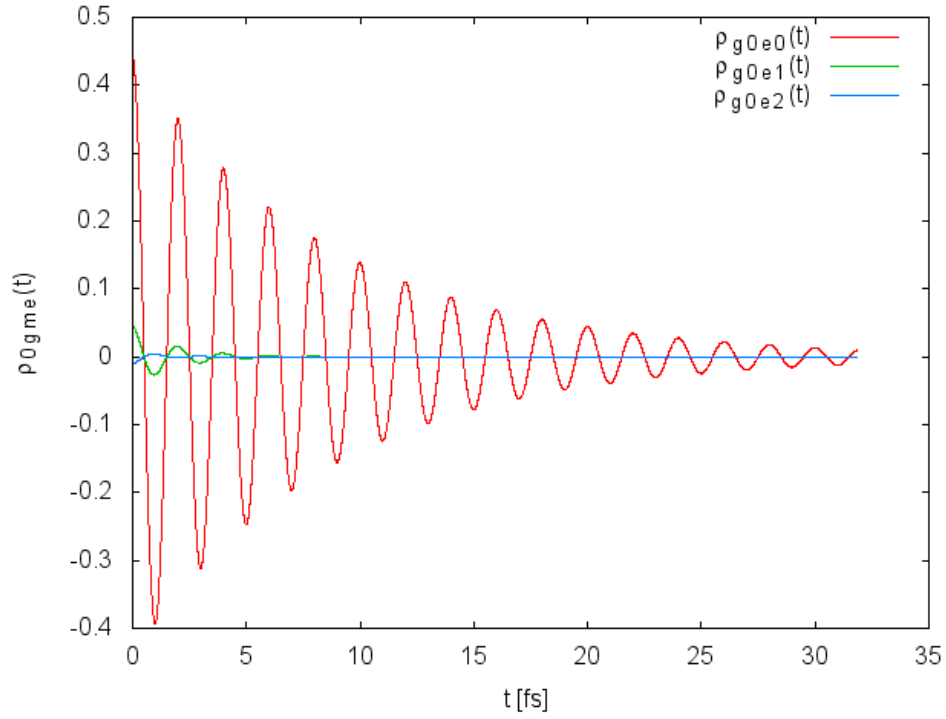


Figure 6.12: The parameters for the simulation of the relaxation process were chosen as $\frac{\tilde{k}_g}{10}\hbar = \frac{\tilde{k}_e}{10}\hbar = \hbar\omega_e = \hbar\omega_g \approx 166.78 \text{ cm}^{-1}$, $x_0 = 1, 2$, for the temperature $T \approx 239\text{K}$, $E_e - E_g = 100\hbar\omega_g \approx 16678 \text{ cm}^{-1}$, $x_0 = 1, 2$. In the figure you can see the time dependence of three off-diagonal elements of the density matrix $\rho_{0e0e}(t)$, $\rho_{0e1e}(t)$, $\rho_{0e2e}(t)$.

Chapter 7

Conclusion

In this work we have studied a two-level electronic system coupled to quantum harmonic oscillators an example of a model open quantum system. It turned out to be important to calculate the FC factors, which can be found in the Appendix A. Physically our model system can be understood as a two level molecule with one internal nuclear vibrational degree of freedom in a phonon bath. The phonon bath interacts directly only with the internal vibration of the molecule. We performed two formal reductions of the system. First reduction was performed with the help of Haken-Stroble-Reineker model (Ref. [7]), obtaining from equations of motion of $\hat{\zeta}$ the equations of motion for the reduced density matrix $\hat{\rho}$.

We derived basic equations of the projection operator technique and the perturbation expansion of the time-convolutionless equation and we applied these equations for the second reduction of our model system, passing to the twice reduced density operator $\hat{\sigma}$. In this way we could obtain a quasi exactly solvable open quantum system problem.

To obtain the desired reduced matrix $\hat{\sigma}$ from the time-convolutionless equation, we derived many helpful relations in Chapter 4. We showed that the the density operators $\hat{\sigma}$ and $\hat{\sigma}^I$ are related by equation (5.10). We also derived the exact, analytical time dependence of the $\hat{\sigma}$. We analytically solved the differential equations following from the time-convolutionless equation for the case of shifted harmonic oscillators with the same eigenfrequency up to the second order. For the special case of very low temperatures we showed that the second order leads to analytical solution of the equations of motion for the operator $\hat{\sigma}$.

Using our Fortran program we tested the quality of these equations up to the second order of the perturbation expansion of the time-convolutionless equation for an optical coherence. The results of the numerical simulations showed, that

the perturbation expansion to the second order of the time-convolutionless equation leads to exact time evolution of the coherence element of the reduced density matrix for the case of shifted harmonic oscillators with the same frequencies in arbitrary temperatures. For the cases of frequency shift, the perturbation theory in the second order led only to dependencies, which were exact only for small times. We also plotted the relaxation process of the density operator $\hat{\rho}$ obtaining the expected relaxation to equilibrium density operator.

The exactly solvable model of an open quantum system presented in this work can be used to investigate the validity of various perturbation schemes in general. We performed this study for the dynamics of an optical coherence which has a direct application in absorption spectroscopy. Further work is needed to develop understanding of the validity of these schemes e.g for population transfer and non-linear spectroscopy.

Appendix A

Calculation of the Franck-Condon factors

A.1 Recurrence relations for the Franck-Condon factors

For computational calculations it is useful to express Franck-Condon (further FC factors) factors by recurrence formulas which we are going to derive now. First of all we are going to consider the case of two harmonic oscillators with shifted equilibrium positions with wave-functions $\psi_{gn}(x)$ and $\psi_{en}(x)$ as described in section 2.2 by equations (2.21) and (2.22).

Let's start with definition of the FC factors using formula (2.22)

$$c_{mn} = \int_{-\infty}^{\infty} \psi_{em}^*(x) \psi_{gn}(x) dx = \int_{-\infty}^{\infty} \psi_{gm}(x - x_0)^* \psi_{gn}(x) dx \quad (\text{A.1})$$

Now we are going to make use of the Taylor expansion of $\psi_{gm}(x - x_0)$:

$$\psi_{gm}(x - x_0) = \left(1 - x_0 \frac{d}{dx} + \frac{(-x_0)^2}{2!} \frac{d^2}{dx^2} + \dots\right) \psi_{gm}(x) = e^{-x_0 \frac{d}{dx}} \psi_{gm}(x) \quad (\text{A.2})$$

It is possible to rewrite the operator $\frac{d}{dx}$ in this expression using definition relations (2.13) and (2.14)

$$\frac{d}{dx} = \frac{1}{\sqrt{2}} (\hat{a} - \hat{a}^\dagger). \quad (\text{A.3})$$

Therefore c_{mn} may be rewritten as

$$c_{mn} = \int_{-\infty}^{\infty} \left(e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)} \psi_{gm}(x) \right)^* \psi_{gn}(x) dx. \quad (\text{A.4})$$

Using the relation (2.16) we may rewrite this as

$$\int_{-\infty}^{\infty} \left(e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)} \psi_{gm}(x) \right) \frac{\hat{a}^\dagger}{\sqrt{n}} \psi_{gn-1}(x) dx \quad (\text{A.5})$$

$$= \frac{1}{\sqrt{n}} \int_{-\infty}^{\infty} \left(\hat{a} e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)} \psi_{gm}(x) \right) \psi_{gn-1}(x) dx, \quad (\text{A.6})$$

where we omitted the asterisk, because the function is real. We used integration by parts in this equation to change the creation operator to the annihilation operator acting on from the most left.

To proceed further we are going to use the special case of Campbell-Baker-Hausdorf formula

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}} e^{\hat{B}} e^{-\frac{1}{2}[\hat{A},\hat{B}]}, \quad (\text{A.7})$$

which is valid if $[\hat{A}, \hat{B}]$ commutes with \hat{A} and \hat{B} . In our case $\hat{A} = -\frac{x_0}{\sqrt{2}}\hat{a}$, $\hat{B} = \frac{x_0}{\sqrt{2}}\hat{a}^\dagger$ and $[\hat{A}, \hat{B}] = \frac{x_0^2}{2}[\hat{a}, \hat{a}^\dagger] = \frac{x_0^2}{2}$, where we used linearity of commutator and equation (2.18). The commutator $[\hat{A}, \hat{B}]$ is a multiple of identity operator, therefore the condition

$$\left[[\hat{A}, \hat{B}], \hat{A} \right] = \left[[\hat{A}, \hat{B}], \hat{B} \right] = 0 \quad (\text{A.8})$$

is satisfied and we can use the relation (A.7) in the equation (A.5). The operator identity in our case is

$$e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)} = e^{-\frac{x_0}{\sqrt{2}}\hat{a}} e^{\frac{x_0}{\sqrt{2}}\hat{a}^\dagger} e^{-\frac{x_0^2}{4}}. \quad (\text{A.9})$$

Now we can see that in the equation (A.5) we may express the act on the annihilation operator as follows

$$\hat{a} e^{-\frac{x_0}{\sqrt{2}}\hat{a}} e^{\frac{x_0}{\sqrt{2}}\hat{a}^\dagger} e^{-\frac{x_0^2}{4}} = e^{-\frac{x_0}{\sqrt{2}}\hat{a}} \hat{a} e^{\frac{x_0}{\sqrt{2}}\hat{a}^\dagger} e^{-\frac{x_0^2}{4}}, \quad (\text{A.10})$$

because the exponential $e^{-\frac{x_0}{\sqrt{2}}\hat{a}}$ commutes with \hat{a} . Using the identity

$$\hat{a}\hat{a}^{\dagger N} = \hat{a}^{\dagger N}\hat{a} + N\hat{a}^{\dagger N-1}, \quad (\text{A.11})$$

which can be proven with the aid of commutation relation (2.18), we may also rewrite the expression $\hat{a}e^{\frac{x_0}{\sqrt{2}}\hat{a}^\dagger}$ as follows

$$\begin{aligned} \hat{a}e^{\frac{x_0}{\sqrt{2}}\hat{a}^\dagger} &= \hat{a}\left(1 + \frac{x_0}{\sqrt{2}}\hat{a}^\dagger + \left(\frac{x_0}{\sqrt{2}}\right)^2 \frac{\hat{a}^{\dagger 2}}{2!} + \dots\right) = \left(1 + \frac{x_0}{\sqrt{2}}\hat{a}^\dagger + \left(\frac{x_0}{\sqrt{2}}\right)^2 \frac{\hat{a}^{\dagger 2}}{2!} + \dots\right)\hat{a} + \\ &+ \left(\frac{x_0}{\sqrt{2}} + \left(\frac{x_0}{\sqrt{2}}\right)^2 \hat{a}^\dagger + \left(\frac{x_0}{\sqrt{2}}\right)^3 \frac{\hat{a}^{\dagger 2}}{2!} + \dots\right). \end{aligned} \quad (\text{A.12})$$

This expression could be rewritten as

$$\hat{a}e^{\frac{x_0}{\sqrt{2}}\hat{a}^\dagger} = e^{\frac{x_0}{\sqrt{2}}\hat{a}^\dagger} \left(\hat{a} + \frac{x_0}{\sqrt{2}}\right). \quad (\text{A.13})$$

Using equations (A.9), (A.10), (A.11) we get

$$\hat{a}e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)} = e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)} \left(\hat{a} + \frac{x_0}{\sqrt{2}}\right). \quad (\text{A.14})$$

Let's use this expression in equation (A.5)

$$\frac{1}{\sqrt{n}} \int_{-\infty}^{\infty} \left(\hat{a}e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)}\psi_{gm}(x)\right)\psi_{g_{n-1}}(x) dx = \quad (\text{A.15})$$

$$= \frac{1}{\sqrt{n}} \int_{-\infty}^{\infty} \left(e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)} \left(\hat{a} + \frac{x_0}{\sqrt{2}}\right)\psi_{gm}(x)\right)\psi_{g_{n-1}}(x) dx \quad (\text{A.16})$$

Now we obtain the recurrence relation

$$c_{mn} = \frac{x_0}{\sqrt{2n}}c_{m_{n-1}} + \sqrt{\frac{m}{n}}c_{m-1_{n-1}}, \quad (\text{A.17})$$

if we use equation (2.15), definition (2.27) and realize that $e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)}\psi_{gm}(x) = \psi_{em}(x)$. For the special case $m = 0$ we obtain using the equation (2.17)

$$c_{0n} = \frac{x_0}{\sqrt{2n}}c_{0_{n-1}}. \quad (\text{A.18})$$

We could also consider equation

$$c_{mn} = \int_{-\infty}^{\infty} \left(e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)} \frac{\hat{a}^\dagger}{\sqrt{m}} \psi_{gm-1}(x) \right) \psi_{gn}(x) dx \quad (\text{A.19})$$

instead of equation (A.5) and then proceed in a very similar way proving the relationship

$$e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)} \hat{a}^\dagger = \left(\hat{a}^\dagger - \frac{x_0}{\sqrt{2}} \right) e^{-\frac{x_0}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)}, \quad (\text{A.20})$$

and then in the same way use the integration by parts to let the appropriate annihilation operator act on the $\psi_{gn}(x)$ and finally obtain recurrence relations

$$c_{mn} = \sqrt{\frac{n}{m}} c_{m-1n-1} - \frac{x_0}{\sqrt{2m}} c_{m-1n} \quad (\text{A.21})$$

$$c_{m0} = -\frac{x_0}{\sqrt{2m}} c_{m-10}. \quad (\text{A.22})$$

The recurrence relations we derived are sufficient to determine the whole matrix c_{mn} when we know c_{00} . If we knew c_{00} we could determine the first column of the matrix by relation (A.22) and the first row by relation (A.18) and the rest of the matrix by relation (A.17) or (A.21) one row by one. Now we are going to calculate c_{00} . It is possible to express the corresponding scalar product (see equation (2.27)) as follows

$$c_{00} = \int_{-\infty}^{\infty} \psi_{e0}^*(x) \psi_{g0}(x) dx = \int_{-\infty}^{\infty} \left(\frac{1}{\pi} \right)^{\frac{1}{2}} e^{-\frac{(x-x_0)^2}{2}} e^{-\frac{x^2}{2}} dx, \quad (\text{A.23})$$

where we made use of equations (2.27), (2.21), (2.22). Further we can simplify the expression

$$\int_{-\infty}^{\infty} \left(\frac{1}{\pi} \right)^{\frac{1}{2}} e^{-\frac{(x-x_0)^2}{2}} e^{-\frac{x^2}{2}} dx = \int_{-\infty}^{\infty} \left(\frac{1}{\pi} \right)^{\frac{1}{2}} e^{-\frac{(\sqrt{2}x - \frac{x_0}{\sqrt{2}})^2 - \frac{x_0^2}{2}}{2}} dx = e^{-\frac{x_0^2}{4}}, \quad (\text{A.24})$$

where we used the standard substitution method to calculate the Gaussian integral. The general formula to calculate such integrals provable by this method is

$$\int_{-\infty}^{\infty} e^{-ax^2+bx} dx = \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}}, \quad (\text{A.25})$$

which we will use later on ($a > 0$).

A.2 Resulting formulas

Finally using $c_{00} = e^{-\frac{x_0^2}{4}}$ we can summarize this section by recurrence relations suitable for calculation of the elements c_{mn}

$$c_{mn} = \frac{x_0}{\sqrt{2n}}c_{mn-1} + \sqrt{\frac{m}{n}}c_{m-1n-1}, \quad (\text{A.26})$$

$$c_{0n} = \frac{x_0}{\sqrt{2n}}c_{0n-1} = e^{-\frac{x_0^2}{4}} \left(\frac{x_0}{\sqrt{2}}\right)^n \frac{1}{\sqrt{n!}}, \quad (\text{A.27})$$

$$c_{m0} = -\frac{x_0}{\sqrt{2m}}c_{m-10} = e^{-\frac{x_0^2}{4}} \left(-\frac{x_0}{\sqrt{2}}\right)^m \frac{1}{\sqrt{m!}}. \quad (\text{A.28})$$

It should be noted that the obtained recurrence relations determine c_{mn} with all the properties derived in section 2.4. Taking $x_0 = 0$ the functions ψ_{gn} and ψ_{en} are the same, therefore the matrix should be matrix of an identity. Looking at the three equations above you can see that $c_{mn} = \delta_{mn}$ really satisfies the recurrence relations. Another example could be verification of the relationship (2.31) for the zero column

$$\sum_m |c_{m0}|^2 = \sum_m e^{-\frac{x_0^2}{2}} \left(\frac{x_0^2}{2}\right)^m \frac{1}{m!} = 1, \quad (\text{A.29})$$

where we made use of well known Taylor expansion of exponential. It is interesting to see that this could be also regarded as a way how to prove that $\sum_m \left(\frac{x_0^2}{2}\right)^m \frac{1}{m!} = e^{\frac{x_0^2}{2}}$. We are not going to prove in this text that the other properties are also satisfied.

A.3 FC factors for oscillators with different mass and frequency

A.3.1 The first three recurrence formulas

In this section we are going to calculate matrix c_{mn} for the case that the harmonic oscillators have the same equilibrium position but different mass and frequency, i. e. different $\lambda = \sqrt{\frac{m\omega}{\hbar}}$. From the definition of c_{mn} (2.27) and the expression

for $\psi_{en}(x)$ (2.24) we can get

$$c_{mn} = \int_{-\infty}^{\infty} \psi_{em}^*(x) \psi_{gn}(x) dx = \sqrt{\lambda} \int_{-\infty}^{\infty} \psi_{gm}(\lambda x) \psi_{gn}(x) dx. \quad (\text{A.30})$$

We can immediately calculate one half of the matrix c_{mn} if we realize that integral over odd function and symmetric interval with respect to $x = 0$ is zero and that the functions $\psi_{gn}(x)$ and $\psi_{en}(\lambda x)$ are even for n even and odd for n odd (as discussed in the first chapter). Therefore $c_{2m2n+1} = 0$ and $c_{2m+12n} = 0$, because in these cases we integrate product of an odd and of an even function, consequently odd functions and we can use this reasoning.

As in the preceding section we can obtain needed recurrence formulas by rearrangement certain integrals in different ways. First of all we are going to derive interesting relationship used in our calculation. Let us suppose a smooth function $f(x)$ and function $f(\lambda x)$. We can say that the function $f(\lambda x)$ is actually $f(x)$ with argument shifted by some x'

$$f(\lambda x) = f(x + x'), \quad (\text{A.31})$$

then we can make use of a Taylor expansion around point x

$$f(x + x') = \left(1 + x' \frac{d}{dx} + \frac{x'^2}{2!} \frac{d^2}{dx^2} + \dots \right) f(x). \quad (\text{A.32})$$

Now these equations are correct in the case that $x + x' = \lambda x$ or equivalently $x' = (\lambda - 1)x$, therefore we can finally write

$$f(\lambda x) = \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) f(x). \quad (\text{A.33})$$

Notice that the expression in the bracket is not an exponential of operator $(\lambda - 1)x \frac{d}{dx}$, because for operators equation $\hat{A}^N \hat{B}^N = (\hat{A} \hat{B})^N$ is generally not true against the case of numbers, when we would understand it as an exponential automatically. In our case this equation does not hold, so it is not an exponential of $(\lambda - 1)x \frac{d}{dx}$.

To calculate one of the recurrence relations we are going to consider following integral

$$\sqrt{2} \int_{-\infty}^{\infty} x \psi_{em}^*(x) \psi_{gn}(x) dx = \int_{-\infty}^{\infty} \psi_{em}^*(x) (\hat{a} + \hat{a}^\dagger) \psi_{gn}(x) dx =$$

$$= \sqrt{n}c_{mn-1} + \sqrt{n+1}c_{mn+1}, \quad (\text{A.34})$$

using the definitions (2.13), (2.14) of creation and annihilation operators and their properties acting on the base functions (2.15), (2.16). On the other hand we can rewrite the $\psi_{em}(x)$ function in this integral as in equation (A.30)

$$\sqrt{2} \int_{-\infty}^{\infty} x \psi_{em}^*(x) \psi_{gn}(x) dx = \sqrt{2\lambda} \int_{-\infty}^{\infty} x \psi_{gm}(\lambda x) \psi_{gn}(x) dx \quad (\text{A.35})$$

and then use the expression (A.33) for the case of $\psi_{gm}(\lambda x)$

$$\sqrt{2\lambda} \int_{-\infty}^{\infty} x \psi_{gm}(\lambda x) \psi_{gn}(x) dx = \quad (\text{A.36})$$

$$= \sqrt{2\lambda} \int_{-\infty}^{\infty} \left(x \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) \psi_{gm}(x) \right) \psi_{gn}(x) dx. \quad (\text{A.37})$$

Let us treat the emerging operator

$$x \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) \quad (\text{A.38})$$

Using commutation relation

$$\left[\frac{d}{dx}, x \right] = 1 \quad (\text{A.39})$$

and another commutation relation which follows from the mentioned one

$$x \left(\frac{d}{dx} \right)^N = \left(\frac{d}{dx} \right)^N x - N \left(\frac{d}{dx} \right)^{N-1}, \quad (\text{A.40})$$

the considered operator can be rewritten as

$$\begin{aligned} & x \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) = \\ & = \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) x - \end{aligned}$$

$$-(\lambda - 1)x \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right). \quad (\text{A.41})$$

By subtraction $x \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right)$ and rearrangement we can simplify this equation to the form

$$\begin{aligned} & x \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) = \\ & = \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) \frac{x}{\lambda}. \end{aligned} \quad (\text{A.42})$$

Now we can get back, use this operator equation in equation (A.36) and rewrite $\sqrt{2}x$ in terms of creation and annihilation operator

$$\begin{aligned} & \sqrt{2\lambda} \int_{-\infty}^{\infty} \left(x \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) \psi_{gm}(x) \right) \psi_{gn}(x) dx = \\ & = \sqrt{2\lambda} \int_{-\infty}^{\infty} \left(\left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) \frac{x}{\lambda} \psi_{gm}(x) \right) \psi_{gn}(x) dx = \\ & = \sqrt{\lambda} \int_{-\infty}^{\infty} \left(\left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) \frac{\hat{a} + \hat{a}^\dagger}{\lambda} \psi_{gm}(x) \right) \psi_{gn}(x) dx. \end{aligned} \quad (\text{A.43})$$

Letting the creation and annihilation operators act on the $\psi_{gm}(x)$ and using the relation (A.33) and definition of c_{mn} (A.30) we finally obtain

$$\sqrt{2} \int_{-\infty}^{\infty} x \psi_{em}^*(x) \psi_{gn}(x) dx = \frac{\sqrt{m}}{\lambda} c_{m-1n} + \frac{\sqrt{m+1}}{\lambda} c_{m+1n}. \quad (\text{A.44})$$

Comparing this equation and equation (A.34) we have the wanted recurrence relation

$$\sqrt{n} c_{mn-1} + \sqrt{n+1} c_{mn+1} = \frac{\sqrt{m}}{\lambda} c_{m-1n} + \frac{\sqrt{m+1}}{\lambda} c_{m+1n}. \quad (\text{A.45})$$

The derivation leads to this recurrence relation unless we take m and n equal to 0. Then we would obtain in the same way but using (2.17) the following recurrence relations

$$\sqrt{n}c_{0n-1} + \sqrt{n+1}c_{0n+1} = \frac{c_{1n}}{\lambda}, \quad (\text{A.46})$$

$$c_{m1} = \frac{\sqrt{m}}{\lambda}c_{m-10} + \frac{\sqrt{m+1}}{\lambda}c_{m+10}. \quad (\text{A.47})$$

A.3.2 Other recurrence formulas

By similar reasoning we are going to obtain another recurrence relations for c_{mn} . This time we are going to use integral

$$\sqrt{2} \int_{-\infty}^{\infty} \left(\frac{d}{dx} \psi_{em}(x) \right) \psi_{gn}(x) dx. \quad (\text{A.48})$$

By integration by parts we can prove that the integral is equal to

$$- \sqrt{2} \int_{-\infty}^{\infty} \psi_{em}(x) \frac{d}{dx} \psi_{gn}(x) dx. \quad (\text{A.49})$$

Further we can express the derivative (using definitions of creation and annihilation operators (2.13), (2.14)) as

$$\sqrt{2} \frac{d}{dx} = \hat{a} - \hat{a}^\dagger, \quad (\text{A.50})$$

use this operator equation in the integral and then (standardly using (A.30), (2.15), (2.16), (2.23)) get

$$\sqrt{2\lambda} \int_{-\infty}^{\infty} \left(\frac{d}{dx} \psi_{gm}(\lambda x) \right) \psi_{gn}(x) dx = -\sqrt{n}c_{mn-1} + \sqrt{n+1}c_{mn+1}. \quad (\text{A.51})$$

As before, we can rewrite the left hand side of the equation according to (A.33)

$$\sqrt{2\lambda} \int_{-\infty}^{\infty} \left(\frac{d}{dx} \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) \psi_{gm}(x) \right) \psi_{gn}(x) dx. \quad (\text{A.52})$$

We could treat with an operator of the form

$$\frac{d}{dx} \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) \quad (\text{A.53})$$

and then obtain the recurrence relation in a very similar way¹ but this time we are going to try different approach. Combining equations (2.13), (2.14), (2.15), (2.16), (2.17) and realizing that $\psi_{gn}(x) = \psi_n(x)$ we obtain relations

$$\frac{1}{\sqrt{2}} \left(x + \frac{d}{dx} \right) \psi_{gn}(x) = \sqrt{n} \psi_{gn-1}(x), \quad (\text{A.54})$$

$$\frac{1}{\sqrt{2}} \left(x - \frac{d}{dx} \right) \psi_{gn}(x) = \sqrt{n+1} \psi_{gn+1}(x), \quad (\text{A.55})$$

$$\frac{1}{\sqrt{2}} \left(x + \frac{d}{dx} \right) \psi_{g0}(x) = 0. \quad (\text{A.56})$$

Now we can interchange the variable x to λx and rewrite $\psi_{gn}(\lambda x)$ to $\psi_{en}(x)$ and use equation (2.23) having

$$\frac{1}{\sqrt{2}} \left(\lambda x + \frac{d}{\lambda dx} \right) \psi_{en}(x) = \sqrt{n} \psi_{en-1}(x), \quad (\text{A.57})$$

$$\frac{1}{\sqrt{2}} \left(\lambda x - \frac{d}{\lambda dx} \right) \psi_{en}(x) = \sqrt{n+1} \psi_{en+1}(x), \quad (\text{A.58})$$

$$\frac{1}{\sqrt{2}} \left(\lambda x + \frac{d}{\lambda dx} \right) \psi_{e0}(x) = 0. \quad (\text{A.59})$$

To simplify our notation let us define creation and annihilation operators for excited state

$$\hat{a}_e = \frac{1}{\sqrt{2}} \left(\lambda x + \frac{d}{\lambda dx} \right), \quad (\text{A.60})$$

$$\hat{a}_e^\dagger = \frac{1}{\sqrt{2}} \left(\lambda x - \frac{d}{\lambda dx} \right), \quad (\text{A.61})$$

which have the same properties acting on $\psi_{en}(x)$ as creation and annihilation operators have acting on $\psi_{gn}(x)$. Using these definitions and basic properties of

¹The appropriate operator relation would be $\frac{d}{dx} \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) = \left(1 + (\lambda - 1)x \frac{d}{dx} + \frac{((\lambda - 1)x)^2}{2!} \frac{d^2}{dx^2} + \dots \right) \lambda \frac{d}{dx}$.

creation and annihilation operators of excited state we can rewrite the integral (A.48) as

$$\begin{aligned}
\sqrt{2} \int_{-\infty}^{\infty} \left(\frac{d}{dx} \psi_{em}(x) \right) \psi_{gn}(x) dx &= \lambda \int_{-\infty}^{\infty} ((\hat{a}_e - \hat{a}_e^\dagger) \psi_{em}(x)) \psi_{gn}(x) dx = \\
&= \lambda \int_{-\infty}^{\infty} \left(\sqrt{m} \psi_{em-1}(x) - \sqrt{m+1} \psi_{em+1}(x) \right) \psi_{gn}(x) dx = \\
&= \lambda (\sqrt{m} c_{m-1n} - \sqrt{m+1} c_{m+1n}). \tag{A.62}
\end{aligned}$$

Comparing this equation with equation (A.51) we finally obtain the recurrence relation

$$- \sqrt{n} c_{mn-1} + \sqrt{n+1} c_{mn+1} = \lambda (\sqrt{m} c_{m-1n} - \sqrt{m+1} c_{m+1n}). \tag{A.63}$$

As in the previous case we have to consider the special cases when m or n equals to 0. The appropriate recurrence formulas are

$$c_{m1} = \lambda \sqrt{m} c_{m-10} - \lambda \sqrt{m+1} c_{m+10}, \tag{A.64}$$

$$- \sqrt{n} c_{0n-1} + \sqrt{n+1} c_{0n+1} = -\lambda c_{1n}. \tag{A.65}$$

We could now show that the 6 obtained recurrence formulas (A.45), (A.46), (A.47), (A.63), (A.64), (A.65) after several additions of equations and explicit expressions of some integrals defining c_{mn} are sufficient to determine the whole matrix c_{mn} , but this way there would arise an overlap with the following section, therefore we are going to end here in order to avoid repeating similar calculations.

A.4 General case of two oscillators in one space dimension

A.4.1 Calculation of recurrence formulas

In the previous sections we have derived recurrence formulas for the matrix c_{mn} in cases of shifted oscillators with respect to each other and oscillators with different mass and frequency. In this section we are going to obtain recurrence formulas for c_{mn} in the case of two general harmonic oscillators in one dimension and determine formulas to determine all elements of c_{mn} .

The behavior of harmonic oscillator is determined by three parameters - by mass m of the oscillating entity, by resonance frequency ω and by Cartesian coordinate of the equilibrium position x_0 . As discussed before, we can absorb the first two parameters into one parameter $\lambda = \sqrt{\frac{m\omega}{\hbar}}$, therefore we are left with two parameters for one harmonic oscillator. To stay within the same notation we are going to describe the two sets of appropriate solutions of Schrödinger equation described in the first chapter (see section 2.2) as

$$\psi_{gn}(x) = \sqrt{\frac{1}{2^n n!}} \left(\frac{\lambda_g^2}{\pi}\right)^{\frac{1}{4}} e^{-\frac{(\lambda_g(x-x_g))^2}{2}} H_n(\lambda_g(x-x_g)) = \sqrt{\lambda_g} \psi_n(\lambda_g(x-x_g)), \quad (\text{A.66})$$

$$\psi_{en}(x) = \sqrt{\frac{1}{2^n n!}} \left(\frac{\lambda_e^2}{\pi}\right)^{\frac{1}{4}} e^{-\frac{(\lambda_e(x-x_e))^2}{2}} H_n(\lambda_e(x-x_e)) = \sqrt{\lambda_e} \psi_n(\lambda_e(x-x_e)), \quad (\text{A.67})$$

where λ_g and x_g are the mentioned parameters for ground state and λ_e and x_e are the parameters for the excited state and we have used $\psi_n(x)$ defined by equation (2.6). Our task is to calculate the matrix c_{mn} , which has now the form (using the defining integral for c_{mn} (2.27))

$$c_{mn} = \int_{-\infty}^{\infty} \psi_{em}^*(x) \psi_{gn}(x) dx = \sqrt{\lambda_e \lambda_g} \int_{-\infty}^{\infty} \psi_m(\lambda_e(x-x_e)) \psi_n(\lambda_g(x-x_g)) dx. \quad (\text{A.68})$$

Now we are going to reduce number of parameters using substitution $x \rightarrow \lambda_g(x-x_g)$

$$\begin{aligned} c_{mn} &= \sqrt{\frac{\lambda_e}{\lambda_g}} \int_{-\infty}^{\infty} \psi_m\left(\frac{\lambda_e}{\lambda_g}x + \lambda_e(x_g - x_e)\right) \psi_n(x) dx = \\ &= \sqrt{\lambda} \int_{-\infty}^{\infty} \psi_m(\lambda(x-x_0)) \psi_n(x) dx, \end{aligned} \quad (\text{A.69})$$

where we use parameters $\lambda = \frac{\lambda_e}{\lambda_g}$ and $x_0 = \lambda_g(x_e - x_g)$. We have just obtained equation (2.24). In other words the matrix c_{mn} for the case of one harmonic oscillator in the origin with $\sqrt{\frac{m\omega}{\hbar}} = 1$ and the other with equilibrium position in x_0 and $\sqrt{\frac{m\omega}{\hbar}} = \lambda$ is the same as the general matrix c_{mn} we want to determine

in this section. Therefore in what follows we can consider

$$\psi_{gn}(x) = \psi_n(x), \quad (\text{A.70})$$

$$\psi_{en}(x) = \sqrt{\lambda}\psi_n(\lambda(x - x_0)) \quad (\text{A.71})$$

and then at the end of our calculations change the variables to

$$\lambda = \frac{\lambda_e}{\lambda_g}, \quad (\text{A.72})$$

and

$$x_0 = \lambda_g(x_e - x_g). \quad (\text{A.73})$$

As in the calculation in preceding section we are going to define creation and annihilation operators for the excited state. Repeating the same considerations, which led us to definitions (A.60) and (A.61) we would obtain

$$\hat{a}_e = \frac{1}{\sqrt{2}} \left(\lambda(x - x_0) + \frac{d}{\lambda dx} \right), \quad (\text{A.74})$$

$$\hat{a}_e^\dagger = \frac{1}{\sqrt{2}} \left(\lambda(x - x_0) - \frac{d}{\lambda dx} \right), \quad (\text{A.75})$$

which has the standard properties of creation and annihilation operators acting on $\psi_{en}(x)$.

To obtain the first three recurrence relations analogous to the relations in preceding section we consider an integral

$$\begin{aligned} \sqrt{2} \int_{-\infty}^{\infty} (x - x_0) \psi_{em}^*(x) \psi_{gn}(x) dx &= \int_{-\infty}^{\infty} \psi_{em}^*(x) (\hat{a} + \hat{a}^\dagger - \sqrt{2}x_0) \psi_{gn}(x) dx = \\ &= \sqrt{n}c_{mn-1} + \sqrt{n+1}c_{mn+1} - \sqrt{2}x_0c_{mn}, \end{aligned} \quad (\text{A.76})$$

where we have proceeded in the same way as in the preceding chapter. On the other hand we can rewrite this integral using \hat{a}_e and \hat{a}_e^\dagger

$$\begin{aligned} \sqrt{2} \int_{-\infty}^{\infty} (x - x_0) \psi_{em}^*(x) \psi_{gn}(x) dx &= \frac{1}{\lambda} \int_{-\infty}^{\infty} ((\hat{a}_e + \hat{a}_e^\dagger) \psi_{em}^*(x)) \psi_{gn}(x) \\ &= \frac{1}{\lambda} (\sqrt{m}c_{m-1n} + \sqrt{m+1}c_{m+1n}). \end{aligned} \quad (\text{A.77})$$

By comparison of the last two equations we have the recurrence relation

$$\sqrt{n}c_{mn-1} + \sqrt{n+1}c_{mn+1} - \sqrt{2}x_0c_{mn} = \frac{1}{\lambda}(\sqrt{m}c_{m-1n} + \sqrt{m+1}c_{m+1n}) \quad (\text{A.78})$$

and standardly considering the cases when m or n are equal to 0 we have

$$\sqrt{n}c_{0n-1} + \sqrt{n+1}c_{0n+1} - \sqrt{2}x_0c_{0n} = \frac{c_{1n}}{\lambda}, \quad (\text{A.79})$$

$$c_{m1} - \sqrt{2}x_0c_{m0} = \frac{1}{\lambda}(\sqrt{m}c_{m-10} + \sqrt{m+1}c_{m+10}) \quad (\text{A.80})$$

The next recurrence relations we are going to obtain considering this integral

$$\begin{aligned} -\sqrt{2} \int_{-\infty}^{\infty} \psi_{em}(x) \frac{d}{dx} \psi_{gn}(x) dx &= \int_{-\infty}^{\infty} \psi_{em}(x) (\hat{a}^\dagger - \hat{a}) \psi_{gn}(x) dx = \\ &= \sqrt{n+1}c_{mn+1} - \sqrt{n}c_{mn-1}, \end{aligned} \quad (\text{A.81})$$

where we have used standard rearrangements from preceding section. Further using integration by parts and operators \hat{a}_e and \hat{a}_e^\dagger we have

$$\begin{aligned} -\sqrt{2} \int_{-\infty}^{\infty} \psi_{em}(x) \frac{d}{dx} \psi_{gn}(x) dx &= \sqrt{2} \int_{-\infty}^{\infty} \left(\frac{d}{dx} \psi_{em}(x) \right) \psi_{gn}(x) dx = \\ &= \lambda \int_{-\infty}^{\infty} ((\hat{a}_e - \hat{a}_e^\dagger) \psi_{em}(x)) \psi_{gn}(x) dx = \lambda(\sqrt{m}c_{m-1n} - \sqrt{m+1}c_{m+1n}). \end{aligned} \quad (\text{A.82})$$

By comparison of these equations we finally obtain

$$-\sqrt{n}c_{mn-1} + \sqrt{n+1}c_{mn+1} = \lambda(\sqrt{m}c_{m-1n} - \sqrt{m+1}c_{m+1n}) \quad (\text{A.83})$$

and for the special cases when m or n are equal to 0 we have

$$c_{m1} = \lambda(\sqrt{m}c_{m-10} - \sqrt{m+1}c_{m+10}), \quad (\text{A.84})$$

$$-\sqrt{n}c_{0n-1} + \sqrt{n+1}c_{0n+1} = -\lambda c_{1n}. \quad (\text{A.85})$$

To close this subsection let us consider special case when $m = n = 0$, when we would obtain in the same way relations

$$c_{01} = -\lambda c_{10} \quad (\text{A.86})$$

and

$$c_{01} - \sqrt{2}x_0c_{00} = \frac{c_{10}}{\lambda}. \quad (\text{A.87})$$

Excluding c_{10} from these equations we have

$$c_{01} = \frac{\lambda^2\sqrt{2}x_0c_{00}}{1 + \lambda^2}. \quad (\text{A.88})$$

A.4.2 Determining c_{mn}

In this subsection we are going to use the recurrence relations to obtain expressions able to determine the matrix c_{mn} , which use only few elements of c_{mn} calculated explicitly as “initial conditions”.

To calculate the zero row of the matrix c_{mn} we can make use of the recurrence relations (A.79) and (A.85). Let's exclude from these equations c_{1n} . We get

$$\sqrt{n}c_{0n-1}(\lambda^2 - 1) + \sqrt{n+1}c_{0n+1}(\lambda^2 + 1) = \lambda^2\sqrt{2}x_0c_{0n}. \quad (\text{A.89})$$

We can see that it is sufficient to determine c_{00} and c_{01} , the other elements of the zero row is possible to determine one by one using this recurrence relation.

Similarly to obtain suitable recurrence relation to determine the zero column of the c_{mn} , we are going to exclude c_{m1} from equations (A.80) and (A.84) getting

$$\lambda\sqrt{2}x_0c_{m0} = \sqrt{m}c_{m-10}(\lambda^2 - 1) - \sqrt{m+1}c_{m+10}(\lambda^2 + 1). \quad (\text{A.90})$$

Thanks to this equation it is sufficient to calculate c_{00} and c_{10} to have the zero column.

Supposing we have calculated the zero column or the zero row we are now going to derive the recurrence relations, which would directly determine the whole matrix c_{mn} . Two solutions are offering, we can exclude from recurrence relations (A.78) and (A.83) c_{m-1n} to obtain recurrence relation which could determine c_{mn} row by row or c_{mn-1} and determine c_{mn} column by column. These expressions look this way in the first case

$$2\lambda\sqrt{m+1}c_{m+1n} = -\lambda^2\sqrt{2}x_0c_{mn} + \sqrt{n+1}c_{mn+1}(\lambda^2 - 1) + \sqrt{n}c_{mn-1}(\lambda^2 + 1) \quad (\text{A.91})$$

and this way

$$2\lambda\sqrt{n+1}c_{mn+1} = \sqrt{2}x_0\lambda c_{mn} + \sqrt{m}c_{m-1n}(\lambda^2 + 1) + \sqrt{m+1}c_{m+1n}(1 - \lambda^2) \quad (\text{A.92})$$

in the second case.

Thanks to relations (A.88) and (A.86) there is one number we have to calculate to obtain the matrix by recurrence formulas - c_{00} . We are going to calculate c_{00} using expression (A.69) and (2.6)

$$c_{00} = \sqrt{\lambda} \int_{-\infty}^{\infty} \psi_0(\lambda(x - x_0)) \psi_0(x) dx = \sqrt{\frac{\lambda}{\pi}} \int_{-\infty}^{\infty} e^{-\frac{(\lambda(x-x_0))^2}{2}} e^{-\frac{x^2}{2}} dx. \quad (\text{A.93})$$

This integral we can evaluate using (A.25) for $a = \frac{\lambda^2+1}{2}$, $b = x_0\lambda$

$$c_{00} = \sqrt{\frac{\lambda}{\pi}} \int_{-\infty}^{\infty} e^{-\frac{(\lambda(x-x_0))^2}{2}} e^{-\frac{x^2}{2}} dx = \sqrt{\frac{2\lambda}{\lambda^2+1}} e^{-\frac{x_0^2\lambda^4}{2(\lambda^2+1)}}. \quad (\text{A.94})$$

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