MASTER

On the reservoir model for CO2-laser amplification

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Abstract

In many technological applications, such as extreme ultraviolet lithography, high-intensity CO$_2$-laser pulses are used, which are created in a CO$_2$-laser amplification system. Research concerned with CO$_2$-laser amplification tries to describe the dynamics of such amplifications systems to be able to make predictions about its characteristics and performance. The system under consideration is a single plasma cell of the amplification system having a pre-mixture of CO$_2$-CO-N$_2$-He and infra-red radiation with a wavelength of 10.58 µm and 10.206 µm. This thesis provides an in-depth treatment of laser physics together with a derivation of the reservoir model for CO$_2$-laser amplification describing the evolution the infra-red CO$_2$-laser radiation through the system under consideration. Furthermore, a numerical implementation of the model in the PLASIMO code is used to simulate the evolution of the radiation through various cases, thereby showing its verification and the capabilities of the model.

**Keywords:** CO$_2$, laser, PLASIMO, reservoir model.
Preface

This thesis is written for my physics master performed in the Elementary Processes in Gas Discharges (EPG) group at the Physics Department of the Eindhoven University of Technology under the supervision of Jan van Dijk and Diana Mihailova (Plasma Matters B.V.). The modeling research of EPG involves the use of the PLASIMO code and directly involves Plasma Matters B.V. under the supervision of Diana Mihailova. The research at EPG and Plasma Matters B.V. is, among many other subjects, concerned with CO$_2$-laser amplification. This research is performed in close relation with partner ASML, which uses it in and investigates it for its application in extreme ultraviolet lithography. The research tries to describe the dynamics of a CO$_2$-laser amplification system to be able to make predictions about its characteristics and performance. The modeling research involves theoretical derivations and development of the model, together with the investigation and verification of the simulation results using its numerical implementation in PLASIMO. These parts of the research go hand in hand, and the people, next to myself, working on these aspects of the research, whom I worked with, are Diana Mihailova, Jan van Dijk, and Marc van Dort. This thesis provides an extensive and in-depth treatment of laser physics for the theoretical derivation of the reservoir model for CO$_2$-laser amplification from first principles. Furthermore, the evolution of CO$_2$-laser radiation pulses through a CO$_2$-N$_2$-He-CO laser plasma is investigated using its numerical implementation in the PLASIMO code, thereby showing its verification and the capabilities of the model.
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Introduction

"Waltzing Matilda, waltzing Matilda. You’ll go waltzing Matilda with me."

Rod Stewart

1.1 The development of CO₂-laser amplification

Lasers Lasers were invented in the early 1960’s and are now common devices in commercial and scientific environments. A laser produces light, which is different in both intensity and quality than any other source. It has, therefore, a vast variety of applications among a large part of the technological platform. Laser light is used as the carrier wave in long distance communication, while in the manufacturing industry it is mainly used for cutting and welding. In medicine lasers are used for eye surgery to the sealing of dental enamel, while in biology they are applied to holographic microscopy and pattern recognition.

Within this wide range of applications an important role is taken on by the carbon dioxide laser (CO₂-laser), which emits infra-red light. Using CO₂-lasers most nonmetallic materials can be cut, thereby for example increasing the cutting speed of garments. For laser surgery, potential advantages are the ability to cauterize and cut with minimum damage to adjacent tissue. The control of power and energy distribution makes a CO₂-laser preferable over ruby and neodymium.

Vibrational relaxation The behavior of a volume of gas in a sound field or gas flow can be described by the standard equations consisting of the conservation of mass, the conservation of momentum, the conservation of energy, and the equation of state. However, in many physical processes relaxation processes occur, such as in dielectric polarization, para-magnetism but also in molecular rotation and vibration. These relaxation processes are characterized by the change of a physical quantity followed by a slower process of equilibration of other physical quantities. The characteristic time for such a process is the relaxation time \( \tau \), giving an indication of the time in which stationary conditions are reached after the change of a physical quantity.

The process of vibrational relaxation can be illustrated as follows. If energy is supplied to a gas, the translational degrees of freedom (dofs) will take up this energy and the temperature of the gas will increase. This increased translational energy is not in equilibrium with the internal dofs, being the rotational and vibrational dofs. As a result, energy flows from the translational dofs to the internal dofs continuing until all dofs are in thermal equilibrium. This energy transfer between the different dofs occurs during molecular collisions.

In the study of vibrational excitation, by means of inelastic molecular collisions, the main difficulty lies in determining a solution for the system concerning the relative motion of two colliding molecules. More than the approximate solution of the Schrödinger equation, it is the lack of knowledge of the shape of the interaction potential curve of two molecules that increases the inaccuracy of the calculations as the transition probabilities are very sensitive to changes in the steepness of the interaction potential. To high-velocity collisions, such as electron-scattering,
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the Born approximation has been successfully applied. However, for slow molecular collisions it is less successful, because it considers incident and outgoing waves as simple plane waves. It does not take into account that at the point of closest approach, where the transitions are most effective, the waves are distorted and, therefore, it breaks down. It is possible to describe the relative motion of the center of mass of two molecules approximately with classical equations.

Another approach to this vibrational excitation problem is to use the Ehrenfest adiabatic principle. From its application it can be concluded that rotational excitation is much more effective than vibrational excitation, meaning that collisions are effective in the transfer of rotational energy but ineffective in that of vibrational energy. This is in agreement with theoretical and experimental evidence showing that the rotational dofs thermalize very rapidly compared to the vibrational dofs resulting in a very small relaxation time for rotational relaxation. This research has led to the establishment of the temperature dependence of the relaxation time. Fore these reasons, in studying vibrational relaxation, often both translational and rotational dofs are assumed to be fully thermalized and have no time delay for energy variation. The slower process of energy exchange, in which the vibrational dofs obtain their energy, is called the vibrational relaxation.

In the presence of relaxation processes in a gas the standard equations are not sufficient, because the internal energy of the gas cannot be expressed as a function of a single temperature. For a perfect gas the internal energy consists of the sum of translational energy, rotational energy, and vibrational energy. These energies depend on the corresponding translational temperature, rotational temperature, and vibrational temperature, which are not necessarily equal to each other. Due to a great interest in relaxation phenomena a large amount of experimental data is accumulated concerning the relaxation of pure gases and gas mixtures. The dependence of the relaxation time on the density over moderate ranges is, therefore, well known, however the dependence on temperature is not.

The theoretical treatment of the slow energy exchange process of vibrational relaxation is a fairly complicated process. The first generally accepted theoretical calculation on the vibrational relaxation time of gases gives the general character of the dependence of the relaxation time of a diatomic gas on the density and temperature. By assuming harmonic oscillations for a pure diatomic gas the lack of adjustment of the vibrational dofs, or vibrational relaxation, is described by the Landau-Teller equation,

$$\frac{dE_v(T_v)}{dt} = \frac{1}{\tau} \left( E_v(T_0) - E_v(T_v) \right).$$

Here, $E_v(T_v)$ is the momentary vibrational energy, $E_v(T_0)$ the vibrational energy if it were in thermal equilibrium with the other dofs, and $\tau$ the relaxation time constant of the gas. This equation states that the rate of restoration of the energy balance for the internal motion is proportional to the extend of the imbalance.

Energy is transferred between the different dofs during molecular collisions. The energy transfer rate is, therefore, inversely proportional to the number of collisions of a molecule per time unit $M$ which depends on the spatial number density. In addition, not every collision is equally effective in transferring energy quanta between dofs, such as in the case of a diatomic gas between the vibrational and translational dofs. Therefore, the relaxation time $\tau$ is proportional to the probability $P$ of that upon collision a quantum of energy is exchanged between, for example, the translational and vibrational dofs in such an energy transfer process. This leads to an expression for the relaxation time given by $\tau = \frac{1}{MP}$.

Quantum mechanical treatments in closed-form of the relative motion of two particles using a 1D solution for the collision of an atom with a molecule contributed to the description of the problem. In a relaxation process, however, the collisions occur between two molecules. With knowledge about the force constant between molecules a quantitative calculation of the vibrational relaxation times can be made using an exponential repulsion in a 1D model. The constants of the interaction potential can be determined by fitting the interaction potential to available data. The method is generally applicable to diatomic gases, gases with several vibrational dofs, and chemically nonreactive gas mixtures.
For gas mixtures with different types of molecules or polyatomic molecular gases the energy transfer can occur between different vibrational dofs as well as with the translational dofs. Each of these energy transfers is described by a separate relaxation time. If more vibrational modes, possibly being degenerate, are present the relaxation process becomes more complex. Therefore, equations more complicated than equation (1) must be used to describe the behavior of the gas. Furthermore, the theory describing the macroscopic behavior of gases with relaxation times, such as sound dispersion and absorption can be extended to include the more complex relaxation processes in polyatomic gases and gas mixtures [3]. The CO$_2$ molecule is especially interesting in this field of research as the energy quanta of the symmetric vibrational mode of CO$_2$ have approximately double the amount of energy of the bending mode [5] leading to a high probability for energy exchange.

**Lasing action**  Observations have shown [9] that the vibrational excitation of nitrogen N$_2$ is very effective under certain discharge conditions. In addition, the vibrational energy quanta of N$_2$ are very large relative to the average translational energy of the N$_2$ molecules, leading to a very large time constant for their thermal relaxation. Together these properties lead to the possibility of a very high population density of vibrationally excited N$_2$ molecules. The vibrational energy quanta of N$_2$, being $v_{N_2} = 2331$ cm$^{-1}$, and the energy of the first excited level of the asymmetric vibrational mode of CO$_2$ [0, 0, 1], being $v_2 = 2349$ cm$^{-1}$, are very close in value to each other. This leads to very fast energy transfer from the vibrationally excited N$_2$ molecules to the [0, 0, 1] vibrational state of CO$_2$, because the small energy discrepancy can easily be exchanged with the translational dofs. This mechanism led to the consideration [10] and realization [11] [12] [13] of laser action using a gas mixture of CO$_2$ and N$_2$, in which the [0, 0, 1] vibrational state of CO$_2$ is the upper lasing level.

The [1, 0, 0] vibrational state of CO$_2$, being the lower lasing level, is depopulated by a two-step process [14]. The energy quanta of the symmetric vibrational mode of CO$_2$, or valance mode, have approximately double the energy of the energy quanta of the bending mode of CO$_2$. During molecular collisions, therefore, there is a relatively large probability for this almost resonant energy to be transferred. One valance mode quantum can easily be transferred as two quanta into the bending modes of the colliding molecules. Hereafter, the relatively slow thermal relaxation of the bending modes to the translational motion completes the depopulation process. The rate of this slow process can be increased considerably by the addition of a small amount of water vapor [15]. The energy quanta of the vibration of the angle between the two O-H bonds in the H$_2$O molecule, which is the lowest vibrational frequency of 1596 cm$^{-1}$, is within an energy range of $kT$ of the energy of the vibrational state [1, 0, 0] of CO$_2$. Therefore, the CO$_2$ in the state [1, 0, 0] needs only a small amount of collisions with H$_2$O molecules to transfer its energy. The vibrationally excited H$_2$O molecule, in turn, needs only in the order of 10 collisions with other H$_2$O molecules to relax by transferring its energy to the translational modes [16] [17].

**Reservoir model**  The translational, rotational, and vibrational dofs are to a good approximation independent of each other if the motion of the molecule is not disturbed. By summing the separate contributions of the dofs the thermodynamic properties of a gas can be determined. The molecular motion is described quantum mechanically by the product of wave functions associated with each dof. The amplitudes of the vibrational motion of molecules are very small and may, therefore, considered to be in accordance with simple harmonic oscillatory motion. This is an excellent approximation for the thermal energy levels. The energies of various dofs are shown experimentally to be in thermal equilibrium with each other. Therefore, a mechanism for transferring energy between the dofs has to exist for the dofs to equilibrate after a distortion. This mechanism comes into play when the molecules are perturbed by a force field that interacts with various dofs, meaning that molecular collisions are essential to this energy transfer process. The molecular energy transfer from its motion as a whole to the internal modes of the molecule are considered by studying actual molecular collisions and not the simplified model of a collision between an atom and a molecule [18]. In doing so, a full set of equations for vibrational energy transfer
according to various intermolecular exchange probabilities can be derived. As the energy quanta of the translational and rotational dofs are very small this energy effectively is accessible and can be assumed to have a classical distribution. This is not the case for vibrational energy, which has a relatively large energy spacing between its levels. For example, the smallest vibrational quanta of CO$_2$ are that of the bending mode, which are greater than 3$K_T$ and, therefore, cannot be treated classically. As a result, at room temperature thermal vibrational excitation is only accessible to a small number of molecules, which mainly account for the slow rate of the process of vibrational relaxation.

The exchange of vibrational energy quanta within a vibrational mode is much faster than the transfer of these quanta to other vibrational modes, rotational dofs, and translation dofs [19]. For example, in CO$_2$-lasers the energy pump rate and the relaxation rate from a vibrational mode at a pressure of 1 Torr and a gas temperature of 300 °C is $\sim 10^4$ s$^{-1}$, while the quantum exchange rate in each mode is $\sim 10^{6}$-$10^7$ s$^{-1}$. Within a vibrational modes, therefore, a local thermal equilibrium is established leading to a Boltzmann distribution for the vibrational energy levels with a characteristic vibrational temperature. These vibrational temperatures will, in general, differ from each other and from the gas temperature. Furthermore, this thermal equilibrium within each vibrational mode will prevail even in the presence of foreign gases and a discharge, which occurs in a laser. In this way a very large set of rate equations for the populations of the vibrational levels, or species, in a gas mixture can be replaced by a small set of energy balance equations of the vibrational modes. This approach is valid only if the the rate of exchange of vibrational energy quanta within each vibrational mode is rapid. For this reason, the gas additives and impurities cannot much exceed the CO$_2$ concentration. Another limitation is imposed by the anharmonicity of the vibrations.

The so-called 5T-model consists of a self-contained set of non-linear differential equations, or reservoir equations, describing the time evolution of the energy densities stored in the dofs of a CO$_2$-N$_2$-He gas mixture. These equations describe the occurring energy transfer processes and are based on relations between the characteristic relaxation times of the constituents of the gas mixture. The basic quantities are the energy densities for translation $U_t$, rotation $U_r$, the vibrational symmetric stretch mode $U_1$ of CO$_2$, the vibrational bending mode $U_2$ of CO$_2$, the vibrational asymmetric stretch mode $U_3$ of CO$_2$, and the vibrational mode of N$_2$ $U_4$. The energy densities are divided into five distinct energy density reservoirs, three for the three vibrational modes of CO$_2$, one for the vibrational mode of N$_2$, and one for both all rotational and all translational dofs. The molecular vibrational dofs are modeled as harmonic oscillators. The population distribution of the vibrational levels of a vibrational mode is described by the Boltzmann distribution with a vibrational temperature $T_i$. The ro-translational reservoir is assumed to be in thermal equilibrium with the ambient temperature $T_0$, because of its fast relaxation time. The vibrational temperatures represent the effective temperature of a vibrational mode and giving enough time after a disturbance these will relax to the ro-translational or ambient temperature $T_0$. By knowing the vibrational temperatures the vibrational energy $E_i$ stored in vibrational modes and the population of a vibrational level of CO$_2$ and N$_2$ molecules can be determined. The energy densities are related to each other with appropriate rate equations describing the collisional energy transfer processes. Different terms in the reservoir equations, describing these different collisional processes, can be derived from different physical reasonings. In order to obtain a self-consistent model an overall energy balance should prevail. The system is modeled as interacting energy reservoirs, where each interaction is being described by an appropriate time constant. This time constant may be a function of the configuration of the system leading to non-linear behavior. The reservoir equations are written, essentially, in a linear form and all non-linearity is induced by the dependence of the relaxation rates on the system configuration.

**Amplification of CO$_2$-laser radiation** The internally consistent 5T-model [20] describing the dynamical behavior in the active medium of a fast-flow CO$_2$-laser are reformulated in their simplest and spatially uniform form [21]. In this way, the main properties of the temporal behavior of a CO$_2$-laser can be described, while the use of practically inaccessible physical quantities is
avoided leading to a transparent set of equations. The 5T-model is already applied to a variety of operational modes of the CO$_2$-laser, such as CW lasing and cavity dumping. Although the model has a large amount of simplifications, realistic results are obtained for relevant quantities, such as electro-optic conversion efficiency (CW), peak power (Q-switched), pulse repetition rate and duty cycle limitations. This strongly suggests that the formulation of the model, based on experimental and theoretical evidence, represents the overall kinetics of the molecular discharge very well and can reliably be used to predict laser performance at least for its upper limits.

The description of the energy transfer processes in the active medium of a fast-flow CO$_2$-laser has been subject to research covering a wide range of sophistication from simple four-level schemes to 3D computations of the vibrational energy distribution in the turbulent flow of a fast-flow CO$_2$-N$_2$-He discharge. The Boltzmann distribution is shown to be inadequate in the strong non-equilibrium conditions of a fast-flow laser suggesting that the vibrational energy densities are not related to vibrational temperatures, while an alternative Treanor distribution is inappropriate for this reservoir model.

Reservoir models are coupled with an equation that describes the time evolution of the population inversion of the lasing levels. The lower lasing level [0, 0, 0] of CO$_2$ and the upper lasing level [1, 0, 0] of CO$_2$ are connected through a 10.58 µm transition. It is assumed that the process of stimulated emission occurs between the lasing levels only. Furthermore, molecular dissociation is neglected and the reduced electric field $\mathbf{E} / N$, where $\mathbf{E}$ is the electric field and $N$ the number of neutral particles, is assumed constant in time and uniform in space. The average gas residence time $\tau_d$ and the rotational relaxation time $\tau_R$ are assumed to be constant. The 5T-model is also employed to predict the output-power pulse shape from a TEA-laser. Theoretical predictions are compared to experimental data for several gas mixtures, cavity configurations, and excitation levels. Furthermore, several techniques are found which provide high-power pulsed CO$_2$-lasers with extremely uniform gain media. As a result, these CO$_2$-lasers can emit highly reproducible output pulses. The detailed shape of these pulses and the time delay between the electrical discharge and the peak of the coherent emission depends heavily on the gas mixture and the pumping level. The time-dependent description for the laser gain is provided by the 5T-model for a CO$_2$-N$_2$-He system, which, in combination with a cavity intensity equation and appropriate pumping terms, can be used to accurately predict the characteristics and output-power pulse shape of high-power TEA-lasers.

The use of lasers as pulse amplifiers has been subject to research. The evolution of a pulse of radiation propagating through a medium with an inversion population inversion is described by non-linear time-dependent photon density transport equations. The continuity equations account for the effect of the radiation on the medium as well as that of the medium on the radiation. These photon transport equations, describing the growth of a pulse in an amplifier, can be solved in closed form for an arbitrary input pulse and an arbitrary distribution of inverted population. The amplification of pulses traversing a medium with a population inversion is given by the exponential law only in the limit of infinitesimal pulse width. For a finite pulse width the tail of the pulse encounters a medium which has been altered by its head. To account for this effect the amplification process is more complicated and must described by non-linear time-dependent radiation transfer equations.

**Admixtures** Carbon monoxide (CO) can be produced by the dissociation of CO$_2$. The populations of the vibrational levels in a CO$_2$-laser with an amplifying medium of CO$_2$-N$_2$-He-CO have been calculated and are described in literature. In the laser scheme the vibrational mode of N$_2$, the vibrational mode of CO, and the antisymmetric mode of CO$_2$ are excited by resonant electron-molecule collisions. These vibrational modes exchange energy through near-resonant molecular collisions, while the excitation of the bending and symmetric mode of CO$_2$ is ignored. The vibrational modes of CO$_2$ are assumed to relax in series, where each quantum of the antisymmetric mode decays to one quantum of the symmetric mode and one quantum of the bending mode. Other processes contributing to this
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Figure 1.1: The relevant vibrational levels of CO$_2$ and N$_2$ together with the lasing transitions. The symmetric, bending, and asymmetrical vibrational modes of CO$_2$ are indicated in this thesis by respectively the indices 1, 2, and 3, while vibrational mode of N$_2$ and CO are indicated by respectively the indices 4 and 5.

specific relaxation are shown to have a negligibly small probability $^{[14]}$. The symmetric mode energy relaxes into the bending mode, which is a nearly resonant process. The relaxation time of this process, therefore, is smaller than the relaxation of the bending modes into the translation. To greatly simplify the analysis the temperatures of the symmetric and bending modes can be assumed to be equal. The relevant vibrational levels of CO$_2$ and N$_2$ together with the lasing transitions are presented in Figure 1.1. The symmetric, bending and asymmetrical vibrational modes of CO$_2$ are indicated by respectively the indices 1, 2, and 3. The indices 4 and 5 are designated to respectively the vibrational mode of N$_2$ and CO.

Freely moving electrons within the medium excite the vibrational levels of both N$_2$ and CO. Hereafter, resonance energy transfer occurs from the vibrational energy of N$_2$ to the asymmetric mode of CO$_2$ and from the vibrational energy of CO to the asymmetric mode of CO$_2$ as well as the level $[1,1^1,0]$ of CO$_2$. Due to molecular collisions the vibrational energy in the CO$_2$ molecule is transferred to the bending modes. Hereafter, the bending mode energy relaxes into the translational dofs. Calculations show that a significant role is played by the CO molecules that can be formed in a discharge and that their presence can significantly influence the population inversion and the performance of the CO$_2$-laser $^{[35]}$. A similar thermodynamic analysis can be used to describe the effects of stimulated emission and compare the results with the measured saturated gain of a CO$_2$-laser.

Rotational relaxation  It is shown that even for 20 ns pulses on the $P(20)$ 10.6 $\mu$m transition at a pressure of 580 Torr not all rotational energy is available $^{[48]}$. This can be qualitatively explained by a simple model with a saturation energy depending on the pulse width $^{[45]}$. Research shows that based on a rate equation model the time constant for short-pulse energy extraction from all rotational levels in a CO$_2$-laser amplifier on a single $P(J)$ or $R(J)$ transition is larger than the rotational relaxation time by about $\frac{1}{k(J,T)}$. Here, $k(J,T)$ is the partition fraction of the transition levels at temperature $T$.

However, research on short-pulse energy extraction in CO$_2$-laser amplifiers shows that not all rotational energy is available for amplification $^{[48]}$. Vibrational re-pumping or decay in the CO$_2$-
1.1. THE DEVELOPMENT OF CO\textsubscript{2}-LASER AMPLIFICATION

Figure 1.2: Illustration of stimulated emission. In the initial state a photon with an energy equal to the energy difference between two molecular energy levels encounters the molecule. In the final state, through light-matter interaction the molecule transitions into the lower energy state, thereby emitting a photon with a wavelength and phase equal to the incident photon.

\( \text{N}_2\text{-He kinetics can be neglected at a time scale of 5 ns and a pressure of about 1 atm. Therefore, only the upper and lower vibrational levels together with their rotational sub-levels have to be considered for a short-pulse CO}_2\text{-laser amplifier. The rotational sub-levels within a vibrational level are coupled through collisions with a time constant of about 0.15-0.2 ns in typical CO}_2\text{-laser gas mixtures} \ [49] \ [50]. This implies that for a 1 to 2 ns pulse sufficient time is available for keeping the rotational levels thermalized so that the pulse can draw on the total rotational population. However, a rotational relaxation model \ [51] shows that this is not the case and not all rotational energy can be used for amplification. The time-scale for energy extraction from all the rotational sub-levels is longer than the rotational relaxation time by about a factor of \( \frac{1}{5} \), which physically can be thought of as the number of rotational levels if all had equal weight.}

Experimental verification of this rotational relaxation model comes from short-pulse energy extraction measurement on the Los Alamos Scientific Laboratory three-stage amplifier system \ [52]. The energy extraction from one, two and all three stages of amplification of nanosecond \( P(20) \) 10.6 \( \mu \)m pulses is in excellent agreement with the rate equation theory including the rotational relaxation model and beam expansion, where amplified pulse energies of up to 20 J in 1.5 ns were obtained.

Light Amplification by Stimulated Emission of Radiation (LASER) In order for radiation to amplify, energy has to be transferred from a medium to the electromagnetic field. Stimulated emission is the process which is responsible for this transfer of energy and, therefore, the amplification. This process occurs if the energy of a photon is equal to the energy difference between two states of a molecule. This leads to a light-matter interaction in which the molecule transitions to the lower energy state, thereby emitting a photon with a wavelength and phase equal to the incident photon, as illustrated in Figure 1.2. Stimulated absorption is the inverse process in which incident photons with an energy equal to the energy difference between two energy levels of a molecule are absorbed. This lead to a transition of the molecule to a higher energy state and causing a reduction of the radiation intensity. Upon interaction of these photons with CO\textsubscript{2} molecules in the particular lasing states the particular transitions presented in Figure 1.1 occur, thereby emitting or absorbing a photon.

The constituents of a medium, such as a gas mixture, interact in collisions, through which their state is able to change. Without any disturbances the gas mixture will thermalize towards thermal equilibrium. In thermal equilibrium the populations of the energy levels have a Boltzmann distribution, in which the upper lasing level, with the higher energy, has a smaller population than
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Figure 1.3: Illustration of Light Amplification by Stimulated Emission of Radiation (LASER) in a cavity between two mirrors, which increase the beam path length through the laser medium. After the initial stimulated emission the number of photons with equal wavelength and phase grows rapidly. The total reflection mirror reflects almost all laser light back into the cavity, while the output mirror transmits a small portion and reflects back the rest. This enables the laser to reach an equilibrium state in which the power levels on the inside and outside are constant.

This the fundamental principle of Light Amplification by Stimulated Emission of Radiation, or LASER. A typical laser is constructed with a gas filled tube with mirrors placed at opposite ends of the laser cavity. This creates a resonant cavity in which some of the emission is reflected back into the laser medium, thereby amplifying the radiation intensity through multiple stimulated emissions. Figure 1.3 illustrates this amplification that occurs with this increased path length in the resonant cavity due to the mirrors at each end. After the initial stimulated emission, two photons have equal energy, and therefore wavelength, and phase. These photons are likely to encounter excited particles, which will lead to more stimulated emissions. In this way the number of photons with equal wavelength and phase, produced by stimulated emission, grows rapidly. This increase is directly proportional to the distance the radiation travels through the laser medium. The magnitude of the amplification is indicated by the gain, which represents the amount of stimulated emission a photon creates per distance traveled through the laser medium. The mirrors enable the radiation to travel back and forth, thereby increasing the beam path length through the medium. Only photons propagating parallel to the cavity walls reflect from both mirrors,
therefore a narrowly focused beam is produced which is also an important characteristic of a laser. Each time the laser beam passes the cavity, the intensity grows until an equilibrium, or saturation, level is reached. One of the mirrors reflects almost all laser light back into the cavity, while the other mirror, the output mirror, transmits a small portion of the light and reflects back the rest. In the equilibrium state the laser power is higher on the inside of cavity than on the outside. This ratio can be varied by changing the transmittance of the output mirror. This function of the output mirror reflecting radiation back into cavity enables the laser to reach the equilibrium state in which the power levels on the inside and outside the laser become constant.

In order to obtain a positive population inversion the upper lasing level has to be populated, while the lower level has to be depopulated. Various different processes coming from various physical reasonings can be used to achieve this. Here, among others, electron pumping is used, in which high-energy electrons will excite the molecules, thereby populating the molecular excited states. Furthermore, the addition of $\text{N}_2$ leads to collisional processes with $\text{CO}_2$ molecules in which the upper lasing level is populated. Helium atoms will depopulate the lower lasing level by energy transfer through collisions.

**CO$_2$-laser amplification** In many technological applications, such as the process of extreme ultraviolet (EUV) lithography, high-intensity CO$_2$-laser pulses are used. Some technological applications require such high-intensity laser radiation that this cannot be produced by a single CO$_2$-laser. The CO$_2$-laser radiation has to be amplified in order to meet these demands. An illustration of a setup, in which such a CO$_2$-laser amplification system is used, to create EUV radiation for EUV lithography is presented in Figure 1.4. The process of creating EUV radiation starts in the sub-fab floor, where output pulses of the seed CO$_2$-laser are led into the amplification system. This CO$_2$-laser amplification system consists of multiple amplifiers in series and possibly a pre-amplifier, thereby amplifying the CO$_2$-laser pulses to the desired intensity. Depending on the particular design of the amplifiers a gas mixture, being the laser medium, can be flowing through the cavities, thereby constantly refreshing to optimize performance. The pulses from this CO$_2$-laser amplification system are led onto the fab floor through the beam transport. After passing laser focusing system the pulses hit a rapid-fire stream of molten tin droplets. Each tin droplet is first flattened by a pre-pulse and subsequently hit with a main pulse, which heats the droplet to create a plasma. EUV radiation emitted from this plasma is collected by a mirror and directed into the scanner.

### 1.2 Present work

**The system** The physical principles of such a CO$_2$-laser amplifier and a CO$_2$-laser are very similar such that a model describing their dynamics can be applied to both of these amplification systems. In order to describe the dynamics of such a CO$_2$-laser amplifier and a CO$_2$-laser, a portion of the laser medium is considered through which radiation is evolving. This so-called plasma cell is a region of the amplification medium, where radiation enters, hereafter amplifies, and finally exits. Multiple of these plasma cells in series represent the laser beam path through the laser medium of an entire amplifier or laser, or even an amplification system consisting of a laser with multiple amplifiers. Taking a single plasma cell as the system under consideration allows for a general description of the laser plasma dynamics together with the evolution of the radiation, which can be applied to both a CO$_2$-laser amplifier and a CO$_2$-laser.

The plasma cell, or amplification system, is modeled as a one-dimensional (1D) space through which radiation can propagate in the two opposite directions. The system contains a pre-mixture of CO$_2$-$\text{N}_2$-He-CO through which infra-red radiation with a wavelength of 10.58 $\mu$m and 10.206 $\mu$m, corresponding to the the $10^P20$ and $10^R26$ transitions of CO$_2$ molecules, is propagating.

**Research** The 5T-model [21] is coupled with an equation that describes the evolution of the photon densities [45]. To accurately simulate the evolution of the photon density, the model then is extended to account the second wavelength radiation and the admixture of CO. Furthermore,
Figure 1.4: Illustration of a setup used to create EUV radiation for EUV lithography. The process begins in the sub-fab floor, where two sets of different output pulses of the seed CO$_2$-laser are led into the amplification system. This CO$_2$-laser amplification system consists of multiple amplifiers in series and possibly a pre-amplifier, thereby amplifying the CO$_2$-laser pulses to the desired intensity. On the fab floor the pulses hit a rapid-fire stream of molten tin droplets. Each tin droplet is first flattened by a pre-pulse and subsequently hit with a main pulse, which heats the droplet to create a plasma from which the EUV radiation is emitted.
1.2. PRESENT WORK

in order to account for rotational relaxation a model describing this process incorporated. This leads to the reservoir model for CO$_2$-laser amplification, which is derived from first principles, describing the evolution of the photon density through the system under consideration. The numerical implementation of the model in the PLASIMO code is used to simulate various cases showing its verification and the capabilities of the model.

**Structure** A thorough description of laser plasmas involves various fields of physics, such as molecular dynamics, thermodynamics, statistical physics, quantum mechanics, quantum optics, and electrodynamics. A fundamental and in-depth treatment of laser plasmas and laser physics combines the theory of these fields of physics. The parts of these fields that are essential for the development and derivation of the reservoir model for CO$_2$-laser amplification are described in Chapter 2. In this chapter, the molecular dynamics of a general molecule are considered, which can be applied to the constituents of the gas mixture in an amplification system. Furthermore, the distribution of energy in a system is described for its application on the laser plasma populations. Finally, the fundamental mechanism of lasing action through light-matter interaction is treated. This theory is then applied in Chapter 4 to a CO$_2$-laser amplification system in order to describe its dynamics. In this chapter, the molecular dynamics are applied to the CO$_2$ molecule, as this molecule plays a central role in the dynamics of a CO$_2$-laser plasma. Furthermore, a theoretical derivation of the reservoir model is given from the first principles described in the previous chapter. Finally, this general model is then applied to the system under consideration leading to the reservoir model for CO$_2$-laser amplification. The numerical implementation of the model in PLASIMO is used in Chapter 4 to investigate the evolution of radiation pulses through the system under consideration. Various cases are presented showing the behavior of the system together with the capabilities of the model.
Background theory

"Look deep into nature, and then you will understand everything better."

Albert Einstein

In this chapter the essential parts from different field of physics for a fundamental and in-depth treatment of laser physics and laser plasmas are presented. This background theory is necessary for the development and derivation of the reservoir model for CO\textsubscript{2}-laser amplification described in the next chapter.

This chapter is divided into three sections. In section 2.1 the structure and dynamics of a general molecule are considered, serving as a basis for its application on the constituents of a laser plasma in chapter 3 and especially to a CO\textsubscript{2} molecule in section 3.1. In section 2.2 a general description for the distribution of energy and populations in a lasing system is presented. This is essential for the derivation of the reservoir model for CO\textsubscript{2}-laser amplification in chapter 3 and for the calculation of the lasing level populations in section 3.4. In section 2.3 the fundamental mechanism of light-matter interaction leading to lasing action is described. This is used for the description of the evolution of radiation in chapter 3 and the interaction of the laser plasma with the radiation in section 3.4.

2.1 Dynamics of a general molecule

In this section, the structure and dynamics of a general molecule are described. Firstly, the geometric structure and its general mathematical description are presented to have a fundamental description which applies to all molecules in the laser plasma. Hereafter, the rotation and vibration of molecules are described individually, while neglecting the interaction with each other and other types of motion. Modeling the rotation and vibration is essential in understanding and describing the molecular energy levels of the laser plasma molecules. Finally, the interaction of rotation and vibration, ro-vibration, is treated, which can be used for more accurate descriptions of the molecule.

2.1.1 Structure

Classification There are many different kinds of molecules differing, among others, in their shapes, sizes and constituents. Molecular symmetry is a theory, which classifies different kinds of molecules according to their geometry, or to be more precise on their symmetry. Molecular symmetry extends into chemistry, spectroscopy and valence theory. Usually group theory is the mathematical framework in which molecular symmetry is described. Group theory was developed in the early nineteenth century, but it was not until the 1920’s and 1930’s that it was applied to molecules and atoms. Molecular symmetry can predict many chemical properties, such as dipole moments, allowed transitions and molecular orbitals.
**Degrees of freedom**  In classical mechanics, a molecule is a system of atoms bound to each other with chemical bonds. These chemical bonds are, for example, bonds resulting from the electrostatic force or covalent bonds. The atom is composed of a nucleus surrounded by electrons. The nuclei of the molecule can be modeled as a system of interacting point particles. In three-dimensional space a point particle can move in three independent directions. Therefore, a point particle has three spatial degrees of freedom $f$, or in short dofs $f$. A system with $N$ point particles has thus $3N$ spatial dofs $f$. The movement of point particles can be restricted by a constraint. For example, the movement of two point particles can be dependent on each other, which means that two or more spatial dofs are not independent. An example of a constraint in a molecular model can be the constant displacement between two nuclei. As a result the set of dependent spatial dofs reduce smaller set of independent spatial dofs through these constraints.

The spatial motion of a molecule can be decomposed into translation, rotation and vibration. Translation is the motion of the center of mass of the molecule in the three independent spatial directions, for which there is a maximum of three translational dofs $f_t$. Rotation is the rotational motion about three perpendicular axes passing through the center of mass of the molecule, for which there is a maximum of three rotational dofs $f_r$. The number of rotational dofs $f_r$ depends on the geometry of the molecule. A mono-atomic molecule $^1$ has no rotation, so there are zero rotational dofs $f_r$ which account for its rotation. The rotation of a linear molecule is about two axes through its center of mass and perpendicular to the molecular axis. Rotation about the molecular axis does not result in a rotation of the molecule, because there is no moment of inertia $I$ associated with this motion. Therefore, the rotation of a linear molecule is described by two rotational dofs $f_r$. The rotation of a non-linear molecule is about three axes through its center of mass, so it is described by 3 rotational dofs $f_r$. An equivalent argument is that for a linear molecule rotation changes the spatial orientation of the molecular axis, which can be described by two dofs. For a non-linear molecule the spatial orientation of an axis is described by two dofs, while the rotation about this axis is described by a third dof. Vibration is the relative motion of the nuclei in the molecule with respect to each other, for which there are $3N - f_t - f_r$ vibrational dofs $f_v$. This vibrational motion can be very complex, Lissajous motion, consisting of angle-bending and bond-stretching. The vibration can, making some assumptions, be decomposed into a combination of so-called normal vibrations. A normal vibration is, in general, one in which all the nuclei undergo a harmonic motion, having the same frequency, move in phase, and can have different amplitudes. However, there are circumstances in which the vibration involves only a localized part of the molecule. In conclusion, the spatial dofs $f$ of a system of $N$ point particles consist of translational dofs $f_t$, rotational dofs $f_r$ and vibrational dofs $f_v$ and is given by,

$$f = f_t + f_r + f_v. \tag{2.1}$$

**Degrees of freedom of a diatomic molecule**  As an illustration of the usage of spatial dofs $f$ of a molecule, a diatomic molecule is considered. Diatomic molecules are chosen, because these exist, among others, in the considered gas mixture of this report. A diatomic molecule consists of two atoms and is therefore a linear molecule. If it consists of the same chemical elements it is homo-nuclear, otherwise it is hereto-nuclear. A diatomic molecule can be modeled as a system of $N = 2$ particles having a total of $f = 3N = 6$ spatial dofs. The translation of the center of mass is, as always in three dimensional space, described by $f_t = 3$ translational dofs. Along the internuclear axis of a diatomic molecule a symmetry axis exists. For homo-nuclear diatomic molecules there exists also a symmetry plane perpendicular to the internuclear axis through the center of mass of the molecule. As a result, the rotation is about two axes through its center of mass and described by $f_r = 2$ rotational dofs. The vibration of a diatomic molecule is then according to equation (2.1) described by $f_v = f - f_t - f_r = 1$ vibrational dof.

**Molecular wave equation**  The description of a molecule is established using quantum physics \[^{[55]}\]. The molecular dynamics can be described by the time-dependent Schrödinger equation \[^{[56]}\].

\[^{1}\text{A molecule consisting of a single atom.}\]
2.1. DYNAMICS OF A GENERAL MOLECULE

The time-dependent Schrödinger equation for a molecule is,

\[ i\hbar \frac{\partial}{\partial t} \Psi_m = \hat{H}_m \Psi_m. \]  

(2.2)

Here, \( \hat{H}_m = \hat{T}_m + V_m \) is the molecular Hamiltonian operator, \( \hat{T}_m \) the molecular kinetic energy operator, \( V_m \) the molecular potential energy function, \( \Psi_m \) the molecular time-dependent wave function, \( i \) the imaginary unit, \( \hbar = \frac{h}{2\pi} \) the reduced Planck constant, \( h \) Planck’s constant, and \( t \) time. From this molecular time-dependent Schrödinger equation (2.2), assuming that the potential energy function is time-independent and by following the lines of almost all introductory quantum mechanical books such as that of Griffiths \[55\], the molecular time-independent Schrödinger equation arises,

\[ \hat{H}_m \psi_m = E_m \psi_m. \]  

(2.3)

Here, \( \psi_m \) is the time-independent molecular wave function, and \( E_m \) a separation constant, which represents the molecular energy. This is an eigenvalue equation with eigenvalues \( E_m \) and corresponding eigenfunction \( \psi_m \). The general solution of the molecular time-dependent Schrödinger equation is \[55\, p.122]\,

\[ \Psi_m = \sum_n c_n \psi_{m,n} e^{-i \frac{E_m}{\hbar} t}. \]  

(2.4)

Here, \( c_n \) are constants determined by the initial wave function \( \Psi_m (r, t = 0) \), and \( r \) the spatial position coordinates. The properties of a molecule can be determined by considering its molecular wave function \( \psi_m \). Imagine a reference frame through which the center of mass of the molecule can move. The reference frame can also be chosen with its origin \( O \) in the center of mass of the molecule. In the latter, there is no translation of the center of mass, so the motion of molecule consists only of rotation and vibration. These possible choices of reference frames have to be kept in mind when considering the energy of translation, rotation and vibration of molecules in later sections.

Quantization

In order to solve the molecular Schrödinger equation (2.3), or molecular wave equation, the kinetic energy operator \( \hat{T} \) and potential energy function \( V \) have to be considered first. They are deduced from their classical equivalents, namely the kinetic energy \( T \) and the potential energy \( V \). The deduction done through the method of quantization by using the quantization rules \[55\]. This includes taking the classical form of an observable in Hamiltonian form as a function of position \( q \) and momenta \( p \) with respect to a reference frame. Then interpret \( q \) as a multiplicative operator and replace \( p \) by the momentum operator \( \hat{p} = -i\hbar \nabla \), where \( \nabla \) is a differential operator. Classically, the kinetic energy \( T \) of a particle with mass \( m \) is \( T = \frac{p^2}{2m} \). From this, together with the quantization rules, the kinetic energy operator \( \hat{T} \) for a particle with mass \( m \) is,

\[ \hat{T} = -\frac{\hbar^2}{2m} \nabla^2. \]  

(2.5)

The potential energy \( V \) depends on the physical system in which the particle exists. The potential energy \( V = V(r, t) \) is a function of the spatial configuration of the system and, besides that, can also depend on time \( t \). The potential energy \( V \) is associated with the forces that act on the particles. The potential energy \( V \) associated with a force \( F \) is equal to the work \( W \) that has to be exerted on the particle in order to move it against this force \( F \). So the exerted force doing the work \( W \) then has to be equal and oppositely directed to the force \( F \). If the work \( W \) done
by a force is independent of its path, and only depends on the starting-point \( r_1 \) and endpoint \( r_2 \) of the path, then this force is conservative. The work \( W \) done by a conservative force \( F' \) is then \( W = \int_{r_1}^{r_2} F' \cdot dr \). Then, the work \( W \) is equal to the negative of the difference in potential energy, \( W = -\Delta V \). Therefore, a conservative force \( F' \) is the negative derivative of the potential energy \( V \) associated with that force, \( F' = -\nabla V \).

In the considered molecular model the potential energy \( V \) is associated to the electrostatic force \( F_C \). The magnitude of the electrostatic force \( F_C \), or the Coulomb force, between particle \( a \) and \( b \) with electric charge \( q_a \) and \( q_b \) and spatial position \( r_a \) and \( r_b \) is \( F_C = \frac{q_a q_b}{4 \pi \varepsilon_0 |r_a - r_b|^2} \). The potential energy \( V \) stored between these particles is then \( V_C = \frac{q_a q_b}{4 \pi \varepsilon_0 r_{ab}} \). There is no minus sign here because this is the potential energy \( V_C \), which is stored between these particles, and not the work \( W \) that has to be exerted to move the particles against the electrostatic force \( F_C \). The electric potential energy function \( V \) is then given by,

\[
V_C = \frac{q_a q_b}{4 \pi \varepsilon_0 r_{ab}}. \tag{2.6}
\]

Here, \( \varepsilon_0 \) is the vacuum permittivity, and \( r_{ab} = |r_a - r_b| \) is the distance between particles \( a \) and \( b \).

**Coulomb Hamiltonian** In order to solve the molecular wave equation \([2,3]\) the molecular Hamiltonian operator \( \hat{H}_m \) has to be determined. The classical molecular Hamiltonian \( H_m \) can be determined by considering the energy of the nuclei and electrons. Classically, next to kinetic energy \( T \), these particles have potential energy \( V \) as a result of the electrostatic Coulomb interaction. The classical molecular Hamiltonian \( H_m \) containing these terms then is named as the classical Coulomb Hamiltonian. By using the quantization rules, the Coulomb Hamiltonian operator \( \hat{H}_m \) can be determined. The results of some spectroscopic experiments, however, showed that this Coulomb Hamiltonian was not describing all of the physics of a molecule. The discrepancies could only be caused by additional interactions. Among other things, this led to a new degree of freedom for particles called spin. Physicist P. Dirac laid down a theoretical description for it \([57]\), when he introduced the Dirac equation that predicts the interaction of spin with spatial motion, the so-called spin-orbit coupling. Other terms which are not included in the Coulomb Hamiltonian are, among others, the spin-spin coupling, Fermi-contact term and nuclear quadrupole coupling. However, these additional terms have, in general, negligible contribution in comparison to the energies in the Coulomb Hamiltonian. Therefore, for the purpose of this report and in a large part of physics research they are neglected.

Consider a molecule consisting of \( N_n \) nuclei and \( N_e \) electrons, described by coordinates \( r_n \) and \( r_e \), momenta \( p_n \) and \( p_e \), and masses \( m_n \) and \( m_e \). The classical Coulomb Hamiltonian \( H_m \) then consists of the molecular kinetic energy \( T_m \) and the molecular electric potential energy \( V_m \).

The molecular kinetic energy \( T_m \) consists of the nuclear kinetic energy \( T_n \) and the electronic kinetic energy \( T_e \). The molecular electric potential energy \( V_m \) consist of the electric potential energy associated with the Coulomb interaction between the nuclei \( V_{nn} \), between the electrons \( V_{ee} \), and between the nuclei and electrons \( V_{ne} \). The molecular Hamiltonian operator \( \hat{H}_m \) then is written as,

\[
\hat{H}_m = \hat{T}_m + V_m = \hat{T}_n + \hat{T}_e + V_{nn} + V_{ee} + V_{ne}. \tag{2.7}
\]

Then, by using the kinetic energy operator \([2,5]\) and electric potential energy function \([2,6]\) the Hamiltonian operator of the molecule can be determined. The molecular Hamiltonian operator \( \hat{H}_m \), or Coulomb Hamiltonian operator, is,

\[
\hat{H}_m = -\sum_{i=1}^{N_n} \frac{\hbar^2}{2 m_n_i} \nabla^2_i - \sum_{j=1}^{N_e} \frac{\hbar^2}{2 m_e_j} \nabla^2_j + \sum_{i > k}^{} \frac{Z_i Z_k e^2}{4 \pi \varepsilon_0 r_{n_i n_k}} + \sum_{j > l}^{} \frac{e^2}{4 \pi \varepsilon_0 r_{e_j e_l}} - \sum_{i,j}^{} \frac{Z_i e_2}{4 \pi \varepsilon_0 r_{n_i e_j}}. \tag{2.8}
\]

This Coulomb Hamiltonian \([4] \hat{H}_m \), possibly with the additional quantum mechanical coupling terms, is universal for all everyday matter, from metals to plastics, to semiconductors, to biological

\[4\text{It is tiresome to keep reading and writing "operator", so when no confusion is expected to occur, the term is neglected.}\]
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macromolecules and so forth. If the molecular wave equation \( (2.3) \) is solved and the eigenvalues \( E_m \) and eigenfunctions \( \psi_m \) of the molecular Hamiltonian \( \hat{H}_m \) are found then any property of the system could, in principle, be determined. Famous physicist Paul Dirac quoted [58] that "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble". This also applies to finding the exact solution of the molecular wave equation \( (2.3) \), because it is very difficult to solve the Schrödinger equation for this Coulomb Hamiltonian \( \hat{H}_m \) \( (2.8) \). Dirac further quoted [58] "It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation". So approximation methods are needed and it is a focus of quantum chemistry to develop these approximation methods together with their accuracy.

Separation of variables In order to solve a differential equation, such as the molecular wave equation \( (2.3) \), separation of variables is an often used method. The Hamiltonian \( \hat{H} \) is then separated into a sum of terms, which depend on different variables. This causes that the solution of the wave function \( \psi \) can be factorized into parts, which depend on these different variables. In the case of the molecular wave equation \( (2.3) \), the molecular Hamiltonian \( \hat{H}_m = \hat{H}_m(r_n, r_e) \) depends on the nuclei positions \( r_n \) and the electron positions \( r_e \). However, the potential energy term \( V_{nc} = V_{nc}(r_n, r_e) \) depends on both the nuclei positions \( r_n \) and the electrons positions \( r_e \). Therefore, it is not possible to separate these variables in the molecular Hamiltonian \( \hat{H}_m \) and decompose it in a part not depending on \( r_n \) and a part not depending on \( r_e \). As a consequence, the solution of the molecular wave function \( \psi_m \) cannot be factorized in to functions of these variables.

Born-Oppenheimer approximation In order to omit this non-separability of the Coulomb Hamiltonian \( \hat{H}_m \), the Born-Oppenheimer approximation [59] is used. This already indicates that the separation of nuclear and electronic motion is thus an approximation.

Recall the structure of a molecule, in which the electric charge of the protons in the nuclei and the electrons is equal. In general, however, the mass of the nuclei is much greater than the mass of the electrons in the molecule. The physical process governing the interaction between the nuclei and the electrons is the electrostatic force. Due to this electrostatic force, the velocities of the nuclei are much lower than the velocities of the electrons. Hence, on the time scale of electronic motion the nuclei approximately have a fixed position. On the time scale of nuclear motion the cloud of electrons approximately instantaneously follow the motion of the nuclei. The motion of the electrons, therefore, depends on the nuclear positions \( r_n \), which are thus approximately constant. For the first step of the Born-Oppenheimer approximation, it is then assumed that there is only a parametric dependence on the nuclear positions \( r_n \) on the time scale of electronic motion and that they enter the potential term \( V_{nc} = V_{nc}(r_n, r_e) \) as parameters. In addition, on this time scale, the nuclei kinetic energy \( \hat{T}_n \) can thus be neglected. For these reasons this step of the Born-Oppenheimer approximation is often referred to as the "clamped-nuclei" approximation. This allows for the separation of variables in the molecular Hamiltonian \( \hat{H}_m \), which then consist of two terms one not depending \( r_n \) and the other not on \( r_e \). Therefore, the molecular wave equation \( \psi_m \) can be factorized into the nuclear wave function \( \psi_n \), depending on \( r_n \), and the electronic wave function \( \psi_e \), depending on \( r_e \),

\[
\psi_m = \psi_n \psi_e. \tag{2.9}
\]

Through this procedure, from the molecular wave equation \( (2.3) \), the electronic wave equation, or clamped-nuclei equation, emerges,

\[
\left( \hat{T}_c + V_{ee} + V_{nc} \right) \psi_e = \hat{H}_e \psi_e = E_e \psi_e. \tag{2.10}
\]

Here, \( \hat{H}_e \) is the electronic Hamiltonian, which depends only parametrically on \( r_n \), \( E_e \) are the eigenvalues, representing the electronic energy. This electronic wave equation \( (2.10) \) determines
the electron motion in the electrostatic field, which thus depends on the nuclei configuration. The eigenvalues $E_n$ can be determined for a set of nuclear configurations, giving the eigenvalues $E_n = E_n(r_n)$ as a function of the nuclear positions $r_n$. These eigenvalues $E_n$ make up a $f_n$-dimensional potential energy surface $E_{el}$ for each nuclear configuration with $r_n$. These potential energy surfaces are the so-called Born-Oppenheimer surfaces. If the changes made to the nuclear configurations, and therefore to the nuclear positions $r_n$, are infinitesimal this method shows similarities with the adiabatic theorem. Therefore this is method is also called the adiabatic approximation with resulting adiabatic surfaces. An assumption of the Born-Oppenheimer approximation is that there are no electron excitations, through which the surfaces could get coupled. So the electrons are assumed to be in their ground state and the non-adiabatic effects are thus neglected.

In the second step of the Born-Oppenheimer approximation, the electronic part of the molecular Hamiltonian is replaced by these Born-Oppenheimer surfaces $E_{el}$. The potential energy surfaces $E_{el}$ are then the adiabatic contribution to the potential energy of the nuclei. The full internuclear potential energy is then given by $V_{nn} + E_{el}$, and the Hamiltonian depends thus only on the nuclear positions $r_n$. From this procedure the nuclear wave equation arises and is given by,

$$\left(\hat{H}_n + V_{nn} + E_{el}\right) \psi_n = \hat{H}_n \psi_n = E_{nm} \psi_n. \quad (2.11)$$

Here, $\hat{H}_n$ is the nuclear Hamiltonian, $\hat{V}_{nn} + E_{el} = \hat{V}_n$ the effective nuclear potential energy, and $E_{nm} = E_n + E_{el}$ the molecular energy. It is possible to solve this nuclear wave equation on each Born-Oppenheimer surface. The nuclear dynamics are described by the time-dependent Schrödinger equation $\left(2.2\right)$, where the nuclear wave functions $\psi_n$ will evolve on these Born-Oppenheimer surfaces. In Appendix (A) the Born-Oppenheimer approximation is worked out in more mathematical detail.

Separation of nuclear motion The nuclear motion consists, as discussed before, of translation, rotation and vibration. The Eckart conditions, or sometimes referred to as the Eckart-Sayvetz conditions, allow to a large extent the separation of the translational and rotational motion from the vibrational motion of the nuclei. The rotation and vibration cannot fully be separated, but the Eckart conditions minimize the coupling between them. If, for this reason, the interaction between rotation and vibration is neglected, the rotational and vibrational, ro-vibrational, nuclear motion can be simplified. As a result, the nuclear Hamiltonian $\hat{H}_n$ is decomposed into a sum of the translational Hamiltonian $\hat{H}_t$, rotational Hamiltonian $\hat{H}_r$ and vibrational Hamiltonian $\hat{H}_v$. This allows for the assumption that the nuclear wave equation $\psi_n$ can be factorized into the translational wave function $\psi_t$, rotational wave function $\psi_r$ and vibrational wave function $\psi_v$,

$$\psi_n = \psi_t \psi_r \psi_v. \quad (2.12)$$

From the nuclear wave equation $\left(2.11\right)$, by using this factorization of equation $\left(2.12\right)$ and the separation of the different types of motion, emerge the translational wave equation, rotational wave equation, and vibrational wave equation,

$$\hat{H}_t \psi_t = E_t \psi_t, \quad \hat{H}_r \psi_r = E_r \psi_r, \quad \hat{H}_v \psi_v = E_v \psi_v. \quad (2.15)$$

Here, $E_t$ is the translational energy, $E_r$ the rotational energy, and $E_v$ the vibrational energy.

Molecular wave function and molecular energy From the previous discussion it results that the molecular wave function $\psi_m$ is a product of wave functions,

$$\psi_m = \psi_t \psi_r \psi_v. \quad (2.16)$$

5 Remember that the choice of reference frame determines what the translation of the centre of mass of the molecule is. If the origin $O$ of a inertial reference frame coincides with the centre of mass of the molecule there is no translation of the molecule in that frame.
The molecular energy \( E_m \) is then given by,

\[
E_m = E_t + E_r + E_v + E_e.
\]  

(2.17)

The molecular energy \( E_m \) is thus decomposed into a sum of translational, rotational, vibrational and electronic energy. This approximation is frequently much less accurate for polyatomic molecules than it is for diatomic molecules. This comes from the fact that in polyatomic molecules the electronic frequencies are of the same order of magnitude as the vibrational frequencies, which in turn are often of the same order of magnitude as rotational frequencies. Therefore, the interactions of these types of motion can be much stronger for polyatomic molecules than for diatomic molecules.

**Term values** In experiments it is often not the energy which is measured, but the frequency or wave number in respectively the microwave and the infra-red region. In spectroscopy, therefore, energy levels are often converted to so-called term values \( G \). As described for example by Hollas [63, p.106], the term values \( G \) have dimensions of a temporal frequency or of spatial frequency, which have dimensions per unit time \( T^{-1} \) or per unit length \( L^{-1} \) respectively. If the energy is divided by \( h \), the term values have dimension of per unit time \( T^{-1} \). If the energy is divided by \( hc \), the term values have dimension of unit per length \( L^{-1} \). The wave-number \( k \) of a wave is the number of radians per unit length with a dimension of per unit length \( L^{-1} \). The temporal frequency \( \nu \) is the number of wavelengths per unit time with a dimension of per unit time \( T^{-1} \).

The temporal frequency \( \nu \) is given by dividing the speed of light \( c \) by the wavelength \( \lambda \), so \( \nu = \frac{c}{\lambda} \). In spectroscopy the temporal frequencies \( \nu \) tend to be very large, because the wavelengths \( \lambda \) tend to be very small. For convenience \(^6\) the temporal frequency \( \nu \) is divided by the speed of light \( c \), which defines the spectroscopic wavenumber \( \tilde{\nu} \) with dimension of per unit length \( L^{-1} \),

\[
\tilde{\nu} = \frac{\nu}{c}.
\]  

(2.18)

This spectroscopic wavenumber \( \tilde{\nu} \) then represent the number of wavelengths per unit length. In spectroscopy the unit of length is often taken to be the centimeter, which finds its roots in the not widely used CGS system of units. In spectroscopic literature the symbol \( \omega \) is often attributed to the spectroscopic wavenumber if it is given in units of \( \text{cm}^{-1} \), or equivalently a Kayser K. The spectroscopic wave number \( \omega \), in this spectroscopic notation, is,

\[
\omega = \frac{\nu}{c} = \frac{1}{\lambda}.
\]  

(2.19)

This spectroscopic wave-number \( \omega \) thus represents the spatial frequency of a wave and the number of wavelengths per centimeter. The number of oscillations per second, so the actual temporal frequency, is then \( c \) times as great \( \nu_i = \omega c \), where \( c \) is also in CGS units so in centimeters per second, or \( \nu_i = 100\omega i c \) with the speed of light \( c \) in SI units so in meters per second. In this report, the term values \( G \) are defined to have dimensions of spatial frequency so the dimension of per unit length \( L^{-1} \). The term values \( G \) are, therefore, given by,

\[
G = \frac{E}{hc}.
\]  

(2.20)

### 2.1.2 Rotation

The rotation is described while neglecting its interaction with the other types of motion. This means that rotational motion is considered while assuming, for example, that no vibrational motion takes place simultaneously.

\(^6\)One has to wonder how convenient these definitions are in the end, as the physical interpretations become vaguer.
Principal axes  The rotation of a system is about axes which pass through the same spatial point, usually the center of mass. A theorem of mechanics gives that there are three mutually perpendicular directions for which the moment of inertia of the system has a minimum or maximum. Along these directions the principle axes and the principal moments of inertia exist. For molecules with symmetries these principal axes are easy to find, because the symmetry axes are principle axes and symmetry planes are always perpendicular to principal axes. Depending on the relative values of the principal moments of inertia the molecule is categorized into different groups. If, from the three principal moments of inertia, all values are different it is an asymmetric top, if two are equal it is a symmetric top and if all are equal it is a spherical top. A special case of the symmetric top is the linear polyatomic molecule in which a principal moment of inertia is zero and two other are equal. In the gas mixture considered in this report only linear molecules exists. In the following, therefore, the rotation of linear molecules is considered.

Rigid rotator  Depending on whether linear molecules have a symmetry plane perpendicular to the internuclear axis or not they belong to the point groups $D\infty_h$ or $C\infty_v$ respectively. In the Born-Oppenheimer approximation discussed before, it is assumed that all the electrons are in their ground state. For all known linear polyatomic molecules the angular momentum of the electrons in the electronic ground state about the internuclear axis is zero. The rotation of the molecule can be modeled as a so-called rigid rotator. In the rigid rotator model the moment of inertia about the internuclear axis is exactly zero. Furthermore, the finite size of the atoms and non-rigidity of the bond between the nuclei is neglected in this model. Almost all of the atomic mass is located within its nucleus, while the nucleus has a diameter of only an order of magnitude $10^{-12}$ m and the internuclear distance is of order of magnitude $10^{-8}$ m. This, together with the negligible influence of the centrifugal force on the internuclear distance coming from the rotational motion, can make the rigid rotator model a justified choice.

Rotational wave equation  The rotational dynamics of a molecule are governed by the rotational wave equation (2.14). In order to solve this equation the rotational Hamiltonian $\hat{H}_r$ has to be determined. The rotational axis of the rigid rotator passes through the center of mass of the molecule. In classical mechanics the kinetic energy of rotation $T_r$ for a rigid body is,

$$T_r = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}$$  \hspace{1cm} (2.21)

Here, $I$ is the moment of inertia, $\omega$ is the rotational angular velocity, and $L = I \omega$ is the angular momentum. The moment of inertia $I$ is given by,

$$I = \sum_i m_i r_i^2.$$  \hspace{1cm} (2.22)

Here, $r_i$ is the distance of the $i$th nucleus with mass $m_i$ to the axis of rotation. The summation over $i$ in equation (2.22) should, next to the nuclei, also include the electrons. However, the electron mass $m_e$ is very small compared to the nuclear mass $m_i$. Hence, the corresponding atomic masses may be used instead of the nuclear masses, because the error produced in this method is much smaller than the error in measurements of the moments of inertia determined by spectroscopy. The rotational potential energy $V_r$ is zero, because the rotator is rigid. The rotational Hamiltonian operator $\hat{H}_r$ is determined by using the previously discussed quantization rules in section 2.1.1. The rotational Hamiltonian $\hat{H}_r$ for a rigid rotator is,

$$\hat{H}_r = \hat{T}_r + V_r = \frac{\hat{L}^2}{2I}.$$  \hspace{1cm} (2.23)

Substitution of equation (2.23) in equation (2.14) gives the rotational wave equation,

$$\frac{\hat{L}^2}{2I} \psi_r = E_r \psi_r.$$  \hspace{1cm} (2.24)
2.1. DYNAMICS OF A GENERAL MOLECULE

Moment of inertia of a diatomic molecule A diatomic molecule consisting of atoms \(a\) and \(b\) has a moment of inertia about an axis perpendicular to the internuclear axis and through its center of mass. The distances \(r_a\) and \(r_b\) of respectively the atoms \(a\) and \(b\) from the center of mass are given by,

\[
r_a = \frac{m_b}{m_a + m_b} r, \quad (2.25) \quad r_b = \frac{m_a}{m_a + m_b} r. \quad (2.26)
\]

Here, \(r = r_a + r_b\) is the internuclear distance. From equations (2.22), (2.25), and (2.26), the moment of inertia \(I_{\text{diatomic}}\) of a diatomic molecule about this axis is,

\[
I_{\text{diatomic}} = \frac{m_am_b}{m_a + m_b} r^2 = \mu r^2. \quad (2.27)
\]

Here, \(\mu = \frac{m_am_b}{m_a + m_b}\) is the reduced mass. In the consideration of the dynamics of the diatomic molecule it is thus equivalent to describe it by a point particle with mass \(\mu\) at a distance \(r\) from the rotational axis. This single-particle system is the so-called simple rigid rotator.

Rotational eigenvalues and eigenfunctions In order to obtain the rotational eigenfunctions \(\psi_r\) together with the corresponding rotational eigenvalues \(E_t\) the rotational wave equation (2.24) has to be solved [64]. The solutions show that the rotational wave function \(\psi_r\) only exists for certain rotational energies \(E_t\). The rotational energies \(E_t\) are [65],

\[
E_t = \frac{\hbar^2 j(j + 1)}{8\pi^2 I} = \hbar c B (j + 1). \quad (2.28)
\]

Here, \(j = 0, 1, 2, \ldots\) is the rotational quantum number, and \(B = \frac{\hbar}{8\pi^2 \epsilon r}\) the rotational constant. From equations (2.20) and (2.28), the rotational term values \(G_t\) for the rigid rotator are given by,

\[
G_t = B (j + 1). \quad (2.29)
\]

The rotational energies \(E_t\) form a discrete set of levels, which depends quadratically on the rotational quantum number \(j\). The energy of the rigid rotator can only take on these discrete rotational energies. As a result, the angular momentum \(L\) and with it the rotational frequency also have only discrete values. The rotational wave functions \(\psi_r\) are [65],

\[
\psi_r = N_t e^{i m\phi} P_j^{(m)} (\cos (\theta)) = Y_j^m. \quad (2.30)
\]

Here, \(N_t\) is the normalization constant for the rotational wave function, \(m = j, j - 1, j - 2, \ldots, -j\) a quantum number representing the \(z\)-component of the angular momentum, \(P_j^{(m)} (\cos (\theta))\) the associated Legendre function, \(0 < \phi < 2\pi\) the longitude or azimuth, \(0 < \theta < \pi\) the colatitude or polar angle, and \(Y_j^m\) the so-called spherical harmonics or surface harmonics.

For a certain rotational energy \(E_t\), specified by rotational quantum number \(j\), there are then \(2j + 1\) possible values for quantum number \(m\). These are the amount of possibilities that the magnitude of the \(z\)-component of the angular momentum has for a certain total angular momentum. Each of these possibilities corresponds, therefore, to a different eigenfunction with the same rotational energy. The degeneracy \(g_t\) of the rotational energy levels with rotational quantum number \(j\) is,

\[
g_t = 2j + 1. \quad (2.31)
\]

In the solution of the Schrödinger equation for the hydrogen atom these spherical harmonics \(Y_j^m\) also appear. The Hamiltonian of the hydrogen atom is very similar to that of the rigid rotator, the only difference being in the potential energy term. The potential energy term for the hydrogen atom only affects the radial dependence of the eigenfunctions. For the rigid rotator there are no potential energy terms. So the eigenfunctions of the rigid rotator are equal to the hydrogen atom eigenfunctions, when the factors with radial dependence are ignored. Therefore, without performing the whole derivation, the eigenfunctions \(\psi_r\) of the rigid rotator can be concluded to be the spherical harmonics \(Y_j^m\).
Parity of the rotational wave function  By investigation of the rotational wave function $\psi_r$ in equation (2.30) the parity $\Pi$ of the rotational wave function $\psi_r$ depends on the parity of the rotational quantum number $j$. The rotational wave functions $\psi_r$ are even or odd whether the rotational quantum number $j$ is even or odd respectively. Hence, the parity $\Pi [\psi_r]$ of the rotational wave function $\psi_r$ is,

$$\Pi [\psi_r] = \Pi [Y^m_j] = (-1)^j.$$  \hspace{1cm} (2.32)

Rotational state  The rotational state of a molecule is defined by the rotational energy contained in the rotational dofs. The rotational energy $E_r$ consists, according to equation (2.28), of a set of discrete energy levels. Each energy level corresponds to the presence of $j$ rotational energy quanta in the rotational motion. The rotational state containing $j$ rotational quanta is indicated as,

$$[j].$$

2.1.3 Vibration

The vibration is described while neglecting its interaction with the other types of motion. This means that vibrational motion considered while assuming, for example, that no rotational motion takes place simultaneously.

Normal vibrations  The vibration of a molecule is the periodic change of the internuclear distance with respect to an equilibrium position. In order to describe the vibration, the nuclei are modeled as point masses and the internuclear bonds as springs connecting the point masses. The springs act as a model for the internuclear forces, with corresponding potential energy. The potential energy is a function of the relative position of the point masses. If the oscillation amplitudes are assumed to be sufficiently small, strictly speaking infinitesimal, a zeroth order approximation of the potential energy can be made. This results in only considering the quadratic terms in the potential energy. With this assumption the complex vibrational motion can be decomposed into a combination of so-called normal vibrations. The complicated vibrational motion of the molecule can then be described by a superposition of these normal vibrations, with their associated normal vibrational coordinates $\xi$. However, in nature the amplitudes of the nuclear oscillations are small, but certainly not infinitesimal. So for more accurate determinations the higher order terms in the potential energy are considered in section 2.1.4.

The normal vibrations are determined by a characteristic equation such as presented in equations (II.11) and (II.38) of Herzberg [66, p.69, p.74]. The determination of the normal vibrations using this method is, however, long and tedious. By considering the symmetry of a molecule and the symmetry properties of the normal vibrations the determination of these normal modes can be simplified. The minimum number of normal vibrations in which the vibration can be decomposed, is equal to the number of vibrational dofs $f_v$. Therefore, in conclusion, a vibrational system may be expressed in terms of $f_v$ normal coordinates $\xi$, as a superposition of $f_v$ normal vibrations.

Harmonic oscillation  The model for the molecular vibration described in the previous section 2.1.3 when only quadratic terms of the potential energy is considered is the so-called harmonic oscillator. The molecule is then represented by point masses carrying out simple harmonic motion, while having the same oscillation frequency and generally move in phase. In the harmonic oscillator model the point mass with mass $m$ experiences a restoring spring force $F_h$, which is proportional to the displacement $s$ of the point mass and directed towards the equilibrium position. The spring force $F_h$ is given by,

$$F_h = -ks = m\frac{d^2s}{dt^2}.$$  \hspace{1cm} (2.33)

\[7\] The subscript $h$ is deduced from the word "harmonic", as this restoring spring force $F_h$ causes a harmonic oscillation of the point mass.
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Here, \( k \) is the force constant, or spring-constant, and \( s \) the displacement of the point mass with respect to the equilibrium position. The solution of this differential equation (2.33) for the displacement \( s \) is a sinusoidal oscillation, a so-called simple harmonic motion,

\[
s = s_0 \sin (2\pi \nu t + \phi).
\]  

Here, \( s_0 \) is the amplitude of vibration, \( \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \) is the vibrational frequency, \( t \) is time and \( \phi \) is the phase constant. According to section 2.1.1, the spring force \( F_h \) is the negative derivative of its potential energy \( V_h \). The potential energy \( V_h \) of a simple harmonic oscillator is then,

\[
V_h = \frac{1}{2} ks^2 = \frac{1}{2} \pi^2 m\nu^2 s^2.
\]  

**Vibrational wave equation**  
The vibrational dynamics of a molecule are governed by the vibrational wave equation (2.15). In order to solve this equation the vibrational Hamiltonian \( \hat{H}_v \) has to be determined. The vibrational kinetic energy \( \hat{T}_v \) of a harmonic oscillator is given by equation (2.5). The vibrational potential energy \( V_v \) of a harmonic oscillator is given by equation (2.35). Hence, the vibrational Hamiltonian \( \hat{H}_v \) of a system of \( f_v \) harmonic oscillators is,

\[
\hat{H}_v = \hat{T}_v + V_v = \sum_{i=1}^{f_v} \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{i=1}^{f_v} k_i s_i^2.
\]  

Here, \( V_v \) is the potential energy of the nuclei with respect to the equilibrium position where \( V_v = 0 \). As discussed before, the vibrational motion can be decomposed in normal vibrations with corresponding normal coordinates \( \xi \). The vibrational wave equation (2.15) in terms of these normal coordinates \( \xi \) is then given by \[65\],

\[
\sum_{i=1}^{f_v} \left( -\frac{\hbar^2}{2} \nabla^2 + \frac{1}{2} \lambda_i \xi_i^2 \right) \psi_v = E_v \psi_v.
\]  

Here, \( \lambda_i \) are the roots of the characteristic equation which was briefly mentioned in section 2.1.3. By using the method of separation of variables, the vibrational wave function \( \psi_v \) is factorized,

\[
\psi_v = \prod_{i=1}^{f_v} \psi_{v_i}.
\]  

Then, the vibrational wave equation (2.37) can be resolved in a set of \( f_v \) independent equations. These normal vibration equations are,

\[
\left( -\frac{\hbar^2}{2} \nabla^2 + \frac{1}{2} \lambda_i \xi_i^2 \right) \psi_{v_i} = E_{v_i} \psi_{v_i}.
\]  

Here, \( \psi_{v_i} \) is the normal vibration wave function, and \( E_{v_i} \) are the eigenvalues representing the normal vibration energy. This normal vibration equation (2.39) is the wave equation of a harmonic oscillator with mass \( m = 1 \). So in wave mechanics, and equivalently in classical mechanics, the vibration can be described as a superposition of \( f_v \) harmonic oscillations in terms of \( f_v \) normal coordinates \( \xi \). The vibrational energy \( E_v \) is then given by,

\[
E_v = \sum_{i=1}^{f_v} E_{v_i}.
\]  

**Vibrational eigenvalues and eigenfunctions**  
In order to obtain the normal vibration eigenfunctions \( \psi_{v_i} \), together with the corresponding normal vibration eigenvalues \( E_{v_i} \), the normal vibration wave equation (2.39) has to be solved \[65\]. The solutions show that the normal vibration
wave functions $\psi_{v_i}$ only exists for certain vibrational energies $E_{v_i}$. The normal vibration energies $E_{v_i}$ are,

$$E_{v_i} = \hbar \nu_i \left( v_i + \frac{1}{2} \right). \quad (2.41)$$

Here, $\nu_i = \sqrt{\lambda_i/\pi}$ is the oscillation frequency of normal vibration $i$, $v_i = 0, 1, 2, \ldots$ the normal vibration quantum number of normal vibration $i$, and $d_i$ the degeneracy of the vibration with frequency $\nu_i$. The normal vibration term values $G_{v_i}$ for the harmonic oscillator, using equations (2.20) and (2.41), are given by,

$$G_{v_i} = \omega_i \left( v_i + \frac{1}{2} \right). \quad (2.42)$$

The energy of the harmonic oscillator can only take on these normal vibration energies. Note that the lowest possible vibrational state, the vibrational ground state $v_i = 0$, is non-zero and possesses a vibrational energy of $\frac{1}{2} \hbar \nu_i$. This ground state energy of vibration is inherent to the dynamics of the quantum harmonic oscillator and cannot be exchanged or changed.

The normal vibration wave functions $\psi_{v_i}$ are

$$\psi_{v_i} = N_{v_i} H_{v_i} \left( \sqrt{\alpha_i} \xi_i \right) e^{-\alpha_i \xi_i^2}. \quad (2.43)$$

Here, $N_{v_i}$ is the normalization constant, $H_{v_i}$ a Hermite polynomial of degree $v_i$, and $\alpha_i = \frac{2\nu_i \hbar}{\hbar}$. So the vibrational wave function $\psi_v$ is the product of $f_v$ harmonic oscillator functions in a space with $f_v$-dimensional space in terms of $f_v$ normal coordinates $\xi$.

**Parity of normal vibration wave function** By investigation of the normal vibration wave function $\psi_{v_i}$ in equation (2.43) the parity $\Pi$ of the normal vibration wave functions $\psi_{v_i}$ depends on the the parity of the vibrational mode quantum number $v_i$. The normal vibration wave functions $\psi_{v_i}$ are even or odd whether the normal vibrational quantum number $v_i$ is even or odd respectively. Hence, the parity $\Pi[\psi_{v_i}]$ of the normal vibration wave function $\psi_{v_i}$ is,

$$\pi[\psi_{v_i}] = (-1)^{v_i}. \quad (2.44)$$

**Degeneracy** It is possible that the value of a normal vibrational oscillation frequency $\nu_i$ is not unique and that multiple frequencies are the same. Then the molecule is said to have a $d_i$-fold degenerate vibrational mode with oscillation frequency $\nu_i$. The degree of the degeneracy $d_i$ of the vibrational mode is equal to the amount of frequencies with this equivalent value. The vibrational quantum number $v_i$ of the degenerate vibrational mode is given by the sum of the quantum numbers $v_j$ of the involved normal vibrations, so $v_i = \sum_j v_j$. For a given value of the vibrational quantum number $v_i$ of the degenerate vibration, there are multiple combinations for the normal vibration quantum numbers $v_j$. In other words, the quanta in the degenerate vibrational mode can be distributed in multiple ways amongst the normal vibrations. For each possibility there exists a different wave function for the degenerate vibrational mode, all having an equal corresponding energy. The wave function $\psi_{v_i}$ of a $d_i$-fold degenerate vibrational mode is,

$$\psi_{v_i} = N_{v_i} \prod_{j=1}^{d_i} H_{v_j} \left( \sqrt{\alpha_i} \xi_j \right) e^{-\alpha_i \xi_j^2}. \quad (2.45)$$

Note that if the degenerate vibration has a zero-point vibration $v_i = 0$ there is only one unique eigenfunction and no degeneracy exists. The vibrational mode term values $G_{v_i}$ for the vibrational mode with degree of degeneracy $d_i$ are given by,

$$G_{v_i} = \omega_i \left( v_i + \frac{d_i}{2} \right). \quad (2.46)$$
The vibrational mode term values $G_v$ for the $i$ harmonic oscillators with degree of degeneracy $d_i$ are,

$$G_v = \sum_i G_{v_i} = \sum_i \omega_i \left( v_i + \frac{d_i}{2} \right).$$

(2.47)

**Vibrational state** The vibrational state of a molecule is defined by its vibrational energy contained in the vibrational dofs. The vibrational mode energy, and therefore the vibrational energy, consists, according to equation (2.46), of a set of discrete energy levels. Each level corresponds to the presence of $v_i$ vibrational mode energy quanta in the vibrational modes. The vibrational state is written as a sequence of quantum numbers $v_i$. The ordering of the numbers corresponds to the numbering of the vibrational mode. So the first through $i$-th position are associated with the vibrational mode 1 through vibrational mode $i$. The vibrational state containing $v_i$ vibrational mode quanta is indicated as,

$$[v_1, v_2, \ldots, v_i].$$

Usually when denoting the state of a molecule, the translational state and electronic state are not taken in to the notation, and only the rotational state and vibrational state are considered. The state of a molecule is then noted as,

$$[v_1, v_2, \ldots v_i, j].$$

### 2.1.4 Interaction of rotation and vibration and finer details of spectra

Until now, rotation and vibration are treated separately. However, rotation and vibration can occur simultaneously, thereby interacting with each other. The models of the rigid rotator and the harmonic oscillator describe the main characteristics of the infra-red and Raman spectra obtained in experiments. For the description of the finer details of the spectra, more accurate models are needed. In this section the models of the non-rigid rotator and the an-harmonic oscillator are introduced, which describe the rotation and vibration with greater accuracy than their more simplistic counterparts. Finally, to capture the effect of the ro-vibrational interaction the vibrating rotator model is introduced.

**Non rigid rotator** The molecular rotation is previously in section 2.1.2 modeled as a rigid rotator. By doing so, the finite extent of the atoms and the non rigidity of the internuclear bonds is neglected. Neglecting the finite extend of the atom was justified because its mass is almost completely existing within its nucleus. However, the nuclei, though bound, are certainly not bound completely rigid. For one, the molecule is able to vibrate which changes the internuclear distance. Hence, the rotational motion is non rigid and the rotation is modeled as a non rigid rotator. In this non rigid rotator model two point masses are interconnected with a massless spring, where the distance between the point masses is able to vary.

Again, as before, in order to determine the rotational dynamics the rotational wave equation (2.14) has to be solved, for which the rotational Hamiltonian $\hat{H}_r$ of this non rigid rotator has to be determined. The rotational kinetic energy $T_r$ is, as it was in the rigid rotator, given by equation (2.21). However, the rotational potential energy $V_r$ is, in contrast to the rigid rotator model, non zero. The rotational motion of the bound point masses is caused by a centripetal force $F_c$,

$$F_c = \tilde{\omega}^2 \mu r_c = \frac{P^2}{\mu r_c^3}.$$ 

(2.48)

Here, $\tilde{\omega}$ the angular velocity, $\mu$ the reduced mass discussed in section 2.1.2, $r_c$ the internuclear distance, and $P$ the angular momentum. The spring exerts a restoring spring force $F_s$ on the point masses which depends on the displacement $s$ of the point masses from the equilibrium position $r_{eq}$. As a result of the rotational motion, the centripetal force $F_c$ increases causing the internuclear
distance to increase. Note that the restoring spring force $F_s$ is the centripetal force $F_c$ of the rotational motion so they are equal. If the displacement $s$ is small, strictly speaking infinitesimal, only quadratic terms of the potential energy are considered. The potential energy $V_r$ of the non rigid rotator is given by equation (2.35) with the substitution $s = (r_c - r_{eq})$. The rotational Hamiltonian $\hat{H}_r$ is determined using the previously discussed quantization rules in section 2.1.1. The rotational Hamiltonian $\hat{H}_r$ for a non rigid rotator is,

$$\hat{H}_r = \frac{\hat{L}_r^2}{2\mu r_{eq}^2} + \frac{1}{2} k (r_c - r_{eq})^2.$$  

(2.49)

The rotational term values $G_r$ of the non rigid rotator for small displacements are,

$$G_r = \frac{h^2 j(j + 1)}{8\pi^2 \mu r_{eq}^4} - \frac{h^4 j^3}{32\pi^4 \mu^2 r_{eq}^6} k = Bj (j + 1) - D j^2 (j + 1)^2.$$  

(2.50)

Here, $D = \frac{h^4}{32\pi^4 \mu^2 r_{eq}^6}$ is another rotational constant. For an even more accurate description, higher order terms in the rotational potential energy $V_r$ have to be considered. As a result, extra terms in the term values of the non rigid rotator will appear. The rotational term values $G_r$ for the non rigid rotator are then,

$$G_r = Bj (j + 1) - D j^2 (j + 1)^2 + H j^3 (j + 1)^3 + \ldots.$$  

(2.51)

Here, $H$ is yet another rotational constant.

**An-harmonic oscillator** The molecular vibration is previously in section 2.1.3 modeled using harmonic oscillators. By doing so, the finite displacement of the point masses is neglected. The choice was justified because the oscillation amplitudes are small. Remember that also the concept of normal vibrations is based on assumption of infinitesimal displacements. However, the amplitudes of oscillation, although often small, are certainly not infinitesimal. Hence, the vibrational motion is an-harmonic and the vibration is modeled using an-harmonic oscillators. In the an-harmonic oscillator model the point masses are interconnected with a massless spring having a potential energy which includes also, next to quadratic terms, higher order terms.

Again, as before, in order to determine the vibrational dynamics the vibrational wave equation (2.15) has to be solved, for which the vibrational Hamiltonian $\hat{H}_v$ for the an-harmonic oscillator has to be determined. The vibrational kinetic energy $T_v$ is, as it was in the harmonic oscillator, given by equation (2.5). However, the vibrational potential energy $V_v$ is, in contrast to the harmonic oscillator mode, not given by equation (2.35), but contains higher order terms. The potential energy of the an-harmonic oscillator in normal coordinates $\eta$ can have the following from,

$$V_v = \frac{1}{2} \sum_i \lambda_i \eta_i^2 + \sum_{i,j,k} \alpha_{ijk} \eta_i \eta_j \eta_k + \sum_{i,j,k,l} \beta_{ijkl} \eta_i \eta_j \eta_k \eta_l + \ldots.$$  

(2.52)

The rotational vibrational Hamiltonian $\hat{H}_v$ for this an-harmonic oscillator is determined using the previously discussed quantization rules in section 2.1.1. The vibrational wave equation (2.15) cannot be resolved in a set of independent equations, as it did for the harmonic oscillators. The vibrational energy $E_v$ is, therefore, not simply the sum of the vibrational mode energies $E_{v_i}$, but contains cross terms involving multiple vibrational modes. The vibrational term values $G_v$ for $i$ an-harmonic oscillators with possible doubly degenerate vibrations are given by Nielsen 67 to be given by,

$$G_v = \sum_i \omega_i \left( v_i + \frac{d_i}{2} \right) + \sum_i \sum_{k \geq i} x_{ik} \left( v_k + \frac{d_k}{2} \right) + \sum_i \sum_{k \geq i} g_{ik} l_i l_k + \ldots.$$  

(2.53)

Here, the degree of degeneracy $d_i = 1, 2$, $x_{ik}$ and $g_{ik}$ are anharmonicity constants, and $l_i = v_i, v_i - 2, v_i - 4, \ldots$ or 0 are quantum numbers associated with the angular momentum. The third
term in equation (2.53), containing an-harmonic constants $g_{ik}$, are responsible for the appearance of sub-levels, which are caused by the excitation of a degenerate vibrational mode with more than one quantum. Hence, exactly defined degeneracy exists only in the harmonic case, while in the an-harmonic case further splitting of the energy levels will occur. This means that the energy levels of the harmonic oscillator approximation will split into a number of different sub-levels when anharmonicity is taken into account. Note, that if displacements are sufficiently small the vibrational term values $G_v$ of $i$ an-harmonic oscillators of equation (2.53) reduce to the vibrational term values $G_v$ of $i$ harmonic oscillators of equation (2.47).

**Vibrating rotator** The Eckart conditions mentioned previously in section 2.1.1 minimize the coupling between the rotation and vibration, resulting in neglecting the ro-vibrational interaction. However, rotation and vibration can occur simultaneously and thereby influence each other. Hence, the ro-vibrational motion is modeled using a vibrating rotator. The vibrating rotator is the model of a non rigid rotator combined with an an-harmonic oscillator, in which the ro-vibrational interaction is taken into account.

If the ro-vibrational interaction is neglected, the vibrating rotator term values $G_{vr}$ is the sum of the rotational non rigid rotator term values $G_r$ and vibrational an-harmonic oscillator term values $G_v$ from equations (2.51) and (2.53), acquired in treating the motions independently. However, for a more accurate determination the interaction between rotation and vibration has to be considered. In the following, not a full description, but a less rigorous description, is given to introduce the concept of the vibrating rotator. In doing so, generally small deviations will be neglected, which explain the hyperfine structure of the spectrum.

Vibration changes the internuclear distance, which in turn changes the moment of inertia $I$ of the system, which in turn will affect the rotation. This then establishes the ro-vibrational interaction. The rotational constant $B$ depends on the moment of inertia $I$ and therefore also on the internuclear distance $r_{eq}$. The rotational constant $B_v$ in vibrational state $v$ is to a first approximation found by Pauling and Wilson [65] to be given by,

\[ B_v = B - \sum_i \alpha_i \left( v_i + \frac{d_i}{2} \right) . \]  

(2.54)

The vibrational period is usually very small compared to the rotational period. Therefore, according to Hylleraas [68], a mean value for the rational constant $B_v$ can be used for convenience instead,

\[ B_v = \frac{h}{8\pi^2\mu} \left[ \frac{1}{r_{eq}^2} \right] . \]  

(2.55)

Analogue expressions as equation (2.54) can be found for the rotational constants $D$ and $H$. The rotational terms values for a molecule with a degenerate vibration are then given by,

\[ G_r = B_v \left( j(j+1) - \frac{l^2}{2} \right) - D_v \left( j(j+1) - \frac{l^2}{2} \right)^2 + \ldots . \]  

(2.56)

It is possible, and often done in literature, for the terms containing the quantum number $l$ to be taken into the an-harmonic terms for vibration. By doing so, the ro-vibrational term values $G_{rv}$ of a linear molecule as a vibrating rotator are given by,

\[ G_{rv} = \sum_i \omega_i \left( v_i + \frac{d_i}{2} \right) + \sum_{i,k \geq i} x_{ik} \left( v_i + \frac{d_i}{2} \right) \left( v_k + \frac{d_k}{2} \right) \]
\[ + \sum_i \sum_{k \geq i} g_{ik} l_i l_k + \ldots + B_v j(j+1) - D_v j^2 (j+1)^2 + \ldots . \]  

(2.57)

However, as described before, the rotational constant $D$ gives only a small contribution to the energies. Therefore, for the rotational constants smaller than rotational constant $B_v$ the dependence on the vibrational state is often neglected or the terms as a whole are neglected.
Fermi resonance  The possibility exists that the energies of vibrational levels of different vibrational modes are almost equal. If this is the case, then these vibrational levels are in a so-called accidental degeneracy. The an-harmonic potential terms, representing the interaction between vibrations, then result in a perturbation of these vibrational levels. This was first recognized by Fermi [69] for the CO$_2$ molecule by which this phenomenon is also called Fermi resonance. These resonating vibrational levels are not accurately described by the term values $G_v$ of equation (2.53).

As a result of the Fermi resonance the energy levels repel each other, such that the energy separation between the energy levels is greater than expected on the basis of the unperturbed term values $G_r$. At the same time a mixing of the eigenfunctions occurs. The smaller the energy separation between the resonating levels in the zero order approximation is the greater the perturbation is. A mathematical description [66, p.215] shows that magnitude of the perturbation, in addition to the energy separation, depends on the the matrix element $W_{ni}$ of the so-called perturbation function $W$. From this description it can also be concluded that through investigation of the symmetry of the wave functions, only vibrational states of the same species can perturb each other and Fermi resonance occurs. First order perturbation theory gives that the perturbed energies $E$ of vibrational levels in Fermi resonance are [66, p.216] [70, p.17],

$$ E = \bar{E}_{ni} \pm \frac{1}{2} \sqrt{4|W_{ni}|^2 + \delta^2}. \quad (2.58) $$

Here, $\bar{E}_{ni} = \frac{1}{2}(E_{0i} + E_{0n})$ is the mean of the unperturbed energy levels, $E_{0i}$ and $E_{0n}$ the unperturbed energies, and $\delta = E_{0i} - E_{0n}$ the separation of the unperturbed energies.

### 2.2 Population distribution in a laser medium

In this section, a general description for the distribution of energy and populations in a system is presented. Firstly, the distribution of energy in a system using the Boltzmann distribution is considered. This description is essential in the development of the reservoir model in Chapter 3, where the vibrational energy levels in a reservoir are assumed to be in a Boltzmann distribution. Hereafter, the partition function containing the information of the accessible states of the system is considered. The partition function is used in Chapter 3 to determine the populations of energy levels in the laser plasma, especially those of the lasing states.

#### 2.2.1 Boltzmann distribution

Consider an isolated system at thermal equilibrium. The system in some thermodynamic state can exist in $\Omega_{\text{system}}$ micro-states and each configuration, or macro-state, of the system has its own multiplicity $\Omega_S$. Combinatorics provides the combinatorial functions with which the multiplicity $\Omega_S$ of a macro-state can be determined. The multiplicity $\Omega_S$ is equal to the number of ways the configuration of a macro-state can be realized among the subsystems. The multiplicity is then described by a multinomial coefficient [53, A2.10],

$$ \Omega_S = \frac{n!}{\prod_i n_i!}. \quad (2.59) $$

An elaborate description of the exact meaning and the role played by this equation within the framework of statistical physics is presented in Appendix B. This equation can be manipulated to give the Boltzmann distribution. The manipulation of this multiplicity multinomial coefficient and derivation of the Boltzmann distribution is given in Appendix C. The result is that the Boltzmann distribution equation is,

$$ n_i = n \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}. \quad (2.60) $$

This Boltzmann distribution equation (2.60) gives the dependence of the occupation numbers $n_i$ on the energy $E_i$ of the possible states $i$ of the subsystems for the macro-state with greatest
multiplicity $\Omega_{S_{\text{max}}}$ for an isolated system at thermal equilibrium. It will be shown later on in sections 2.2.1 and 2.2.2 that the parameter $\beta = \frac{1}{k_B T}$ is the thermodynamic beta and the sum $Z = \sum e^{-\beta E_i}$ is the partition function. Furthermore, the fraction $\frac{n_i}{n}$ can be interpreted as the probability $P_i$ of a subsystem existing in state $i$ is,

$$P_i = \frac{n_i}{n}. \quad (2.61)$$

Therefore, the Boltzmann distribution equation (2.60) can be rewritten as,

$$P_i = \frac{e^{-\frac{E_i}{k_B T}}}{Z}. \quad (2.62)$$

**Boltzmann factor**  The ratio of the probabilities $P_a$ and $P_b$ or ratio of occupation numbers $n_a$ and $n_b$ states $a$ and $b$ is given by,

$$\frac{n_b}{n_a} = \frac{e^{-\beta E_b}}{e^{-\beta E_a}} = e^{\beta (E_a - E_b)} = e^{\beta \Delta E}. \quad (2.63)$$

Here, $e^{\beta (E_a - E_b)}$ is the Boltzmann factor and it depends on the energy difference $\Delta E = E_a - E_b$ of the considered states.

**Thermodynamic beta $\beta$**  For an isolated system at thermal equilibrium where the accessible energies $E_i$ for the subsystems exist in a non changing way, a single parameter $\beta$, thermodynamic beta, determines the most probable configuration. The thermodynamic beta $\beta$, therefore, relates the subsystems which are in thermal equilibrium with each other. As described by thermodynamics, systems which are in thermal equilibrium with each other have an equal thermodynamic temperature $T$. This suggests a relation between the thermodynamic temperature $T$ and the thermodynamic beta $\beta$. As discussed after equation (C.9) the constants in the method of Lagrange are evaluated at the end. Differentiation of equation (C.11) with respect to $E$ gives,

$$\beta = \frac{d \ln (\Omega_S)}{dE}. \quad (2.64)$$

The Boltzmann entropy equation (B.9) gives,

$$\frac{d \ln (\Omega_{\text{system}})}{dE} = \frac{dS}{k_B}. \quad (2.65)$$

For large enough systems approximation (B.10) holds and substitution of equation (2.65) in (2.64) then gives,

$$\beta = \frac{1}{k_B} \frac{dS}{dE}. \quad (2.66)$$

From thermodynamic the definition of thermodynamic temperature $T$ is given by,

$$\frac{dS}{dE} = \frac{1}{T}. \quad (2.67)$$

Substituting equation (2.67) in (2.66) gives the relation of the thermodynamic beta $\beta$ with thermodynamic temperature $T$,

$$\beta = \frac{1}{k_B T}. \quad (2.68)$$

Apart from the conversion factor $k_B$ the thermodynamic beta $\beta$ is the inverse thermodynamic temperature $T$. For this reason the thermodynamic beta $\beta$ is sometimes also referred to as the coldness.
2.2.2 Partition function

The sum $\sum_i e^{-\beta E_i}$ appearing in the Boltzmann distribution equation (2.60) does not depend on a specific state $i$ and describes statistics of a system at equilibrium. It is therefore named the partition function $Z$. The symbol $Z$ finds its origin from arguably a more illuminating word "Zustandssumme" from the German language. The word "Zustand" means state and "summe" means sum. This shows that the partition function contains the information about the number of accessible states of a subsystem. This becomes apparent when considering the limits $T \to 0$ and $T \to \infty$. The partition function $Z$ is thus given by,

$$Z = \sum_i e^{-\beta E_i}. \quad (2.69)$$

The sum of the probabilities $P_i$, appearing in the Boltzmann distribution equation (2.60), of all the states equals 1, therefore the partition function is sometimes also interpreted as a normalization constant. Multiple possible states $i$ of the subsystems can correspond to the same energy. If $g_i$ states have the same energy this energy level is said to have a $g_i$-fold degeneracy. Therefore, the partition function $Z$ can also be expressed in terms of a sum over the energy levels instead of a sum over all the states,

$$Z = \sum_{\text{states } i} e^{-\beta E_i} = \sum_{\text{levels } i} g_i e^{-\beta E_i}. \quad (2.70)$$

The partition function $Z$ contains all the information for determining the thermodynamic properties. One could argue that the partition function $Z$ in statistical thermodynamics plays a comparable role as that of the wave function in quantum mechanics.

The thermodynamic properties internal energy $E$ and entropy $S$ can be given in terms of the statistical partition function $Z$. In this way the partition function $Z$ provides the connection between statistical physics and thermodynamics. The internal energy $E$ of a system at thermal equilibrium in terms of the partition function $Z$ is given by,

$$E = \sum_i n_i E_i = \frac{n}{Z} \sum_i E_i e^{-\beta E_i} = -\frac{n}{Z} \sum_i \frac{d}{d\beta} e^{-\beta E_i} = -\frac{n}{Z} \left( \frac{dZ}{d\beta} \right)_V = -n \left( \frac{d (\ln (Z))}{d\beta} \right)_V. \quad (2.71)$$

The entropy $S$ of a system at thermal equilibrium in terms of the partition function $Z$ is determined in Appendix D and is given by,

$$S = \frac{E}{T} + n \ k_B \ln (Z). \quad (2.72)$$

Quantum statistics Consider a volume which contains particles. Each particle has a wave function which spreads out into space. If the density of the particles increases these wave functions begin to overlap more with each other. This overlapping causes quantum effects to become more dominant. This overlapping happens in very dense systems such as neutron stars or very cold systems such as liquid helium. Quantum effect such as the Pauli exclusion principle then can come into play. Quantum statistics provide, among many other things, the fairly well-known Fermi-Dirac distribution and Bose-Einstein distribution. Quantum statistics are negligible if the number of available single particle states is much greater than the number of particles [71, p.264 eq.7.17]. It is, however, beyond the scope of this work and unnecessary for the derivation of the reservoir model to discuss quantum statistics here.

Statistics of harmonic oscillators The harmonic oscillator, being a widely used mechanism in physics, is previously used in section 2.1.3 to model the vibrational motion of molecules. In this section the statistical thermodynamics of the harmonic oscillator will be investigated.
In order to do this the partition function has to be determined. Recall that the energy levels of a harmonic oscillator are given by equation (2.41) and the geometric series \( \sum_{k=0}^{\infty} a x^k = \frac{a}{1-x} \) for \( |x| < 1 \). The partition function \( Z_h \) of a harmonic oscillator is,

\[
Z_h = \sum_{v=0}^{\infty} e^{-\beta E_h} = \sum_{v=0}^{\infty} e^{-\beta \hbar \nu (v+\frac{1}{2})} = e^{-\frac{\beta \hbar \nu}{2}} \sum_{v=0}^{\infty} (e^{-\beta \hbar \nu})^v = e^{-\frac{\beta \hbar \nu}{2}} \frac{1}{1-e^{-\beta \hbar \nu}}.
\]

(2.73)

Consider the internal energy \( E_h \) of an isolated system consisting of harmonic oscillator subsystems at thermal equilibrium. The internal energy \( E_h \) is determined in appendix E using equations (2.71) and (2.73) and the relations for hyperbolic functions. As a result the internal energy \( E_h \) of a system of harmonic oscillators is given by,

\[
E_h = n \hbar \nu \left( \frac{1}{2} + \frac{1}{e^{\beta \hbar \nu} - 1} \right) = \frac{n \hbar \nu}{2} \coth \left( \frac{\beta \hbar \nu}{2} \right).
\]

(2.74)

**Molecular partition function**

The molecular energy \( E_m \) can, according to equation (2.17), be decomposed into the translation, rotation, vibration and electronic energy. As discussed in previously this decomposition strictly speaking is only allowed if the modes of motion are independent. In an actual molecule this is, however, not the case, but it is justified as an approximation. The molecular partition function \( Z_m \) for a molecule having possible states \( i \) is, therefore, given by,

\[
Z_m = \sum_{i} e^{-\beta E_m} = \sum_{i} e^{-\beta \sum_{m=1}^{n_m} E_m} = \left( \sum_{i} e^{-\beta E_i} \right)^n = Z_m^n.
\]

(2.75)

Here, \( Z_m \) is the molecular partition function. For a system of \( n \) indistinguishable independent molecules the partition function \( Z \) can be written as,

\[
Z = \frac{Z_m^n}{n!}.
\]

(2.76)

**Translational partition function**
The translational motion consist of three independent spatial motions in the three spatial dimensions. The translational energy can, therefore, be decomposed into three parts which correspond to these independent translational motions,
Substitution of this equation (2.78) in the expression for the translational partition function in equation (2.77), analogously to equations (2.75) and (2.77), gives the translation partition function,

\[ Z_t = \prod_{d=1}^{3} Z_{td}. \]  

(2.79)

The translational energy \( E_{td} \) in one dimension with length \( x_d \) is,

\[ E_{td} = \frac{n_d^2 \hbar^2}{8m x_d^2} = An_d^2 \]  

(2.80)

Here, \( A = \frac{\hbar^2}{8m x_d^2} \). The translational partition function \( Z_{td} \) in one dimension is then given by,

\[ Z_{td} = \sum_{n_d=1}^{\infty} e^{-\beta E_{td}} = \sum_{n_d=1}^{\infty} e^{-\frac{n_d^2 \hbar^2}{8m x_d^2}} = \sum_{n_d=1}^{\infty} e^{-\beta An_d^2}. \]  

(2.81)

If these translational energy levels are very closely spaced the sum in equation (2.81) can be approximated by an integral. For macroscopic dimensions and translation this is usually the case. Furthermore, changing the limits of the integral from \( \int_{n_d=1}^{\infty} \) to \( \int_{n_d=0}^{\infty} \) gives an negligible error, but simplifies the integral to a form which can be solved. This results in,

\[ Z_{td} \approx \int_{n_d=0}^{\infty} e^{-\beta An_d^2} \approx \int_{n_d=0}^{\infty} e^{-\beta An_d^2} = 1 \left( \frac{\pi}{\beta A} \right)^{\frac{1}{2}} = \left( \frac{2\pi m}{\beta \hbar^2} \right)^{\frac{1}{2}} x_d. \]  

(2.82)

Finally, by substitution of this equation (2.82) into equation (2.79) the translational partition function \( Z_t \) is obtained,

\[ Z_t = \prod_{d=1}^{3} \left( \frac{2\pi m}{\beta \hbar^2} \right)^{\frac{1}{2}} x_d = \left( \frac{2\pi m}{\beta \hbar^2} \right)^{\frac{3}{2}} x_1 x_2 x_3 = \left( \frac{2\pi m}{\hbar^2} \right)^{\frac{3}{2}} V = V^* \Lambda. \]  

(2.83)

Here, \( \Lambda = \left( \frac{\beta \hbar^2}{2\pi m} \right)^{\frac{1}{2}} \) is the thermal wavelength of the molecule.

**Rotational partition function** The rotational energy \( E_r \) of a linear rigid rotator is given by equation (2.28) and the degeneracy \( g_r \) of the rotational levels with rotational quantum \( j \) by equation (2.31). The rotational partition function \( Z_r \) of a linear rigid rotator is, therefore, given by,

\[ Z_r = \sum_{j=0}^{\infty} (2j+1) e^{-\beta \hbar c B j(j+1)}. \]  

(2.84)

Again as previously for the translational partition function the sum can be approximated by an integral if many rotational states are occupied and \( k_B T \) is much larger than the separation between neighboring states. This is the so-called high-temperature limit. However, this is not the whole story. A molecule can have some geometric symmetries and rotation of the molecule can lead to indistinguishable states. These indistinguishable states can cause an over-counting of the states and have to be counted as a single state because they are indistinguishable. This leads to a correction of the rotational partition function \( Z_r \) by means of the rotational symmetry number \( \sigma \). This symmetry number \( \sigma \) is equal to the distinct number of ways that a molecule has an indistinguishable configuration by rotation of the molecule. For linear molecules without a center of symmetry \( \sigma = 1 \) and for linear molecules with a center of symmetry \( \sigma = 2 \). In the high-temperature limit the rotational partition function is,

\[ Z_r \approx \frac{1}{\sigma} \int_{j=0}^{\infty} (2j+1) e^{-\beta \hbar c B j(j+1)} = \frac{1}{\sigma \Theta_r} \int_{j=0}^{\infty} T e^{-\Theta_r T} T = \frac{T}{\sigma \Theta_r}. \]  

(2.85)

Here, \( \Theta_r = \frac{\hbar c B}{k_B} \) is the characteristic rotational temperature.
Vibrational partition function The vibrational motion can, as described in section 2.1.3, be decomposed into vibrational modes. The vibrational energy, therefore, can be decomposed into parts which correspond to these vibrational modes as is given in equation (2.40). The vibrational partition function is then given by,

\[
Z_v = \sum_i e^{-\beta E_{v,i}} = \sum_i e^{-\beta \sum_j f_{v,j} E_{v_j,i}} = \prod_j \sum_i e^{-\beta E_{v_j,i}} = \prod_j Z_{v_j},
\] (2.86)

Here, \(Z_{v_j}\) is the vibrational mode partition function and \(E_{v_j,i}\) the energy of vibrational mode \(j\) in state \(i\). The vibrational mode energy is given by equation (2.46). The vibrational mode partition function \(Z_{v_j}\) is then given by,

\[
Z_{v_j} = \sum_{v_j=1}^{\infty} g_{v_j} e^{-\beta E_{v_j}} = \sum_{v_j=1}^{\infty} g_{v_j} e^{-\beta \hbar \nu_j \left(\frac{v_j}{2} + \frac{1}{2}\right)} = e^{-\beta \hbar \nu_j \frac{v_j}{2}} \sum_{v_j=1}^{\infty} g_{v_j} e^{-\beta \hbar \nu_j v_j} = e^{-\beta E_{v_j,gr}} \sum_{v_j=1}^{\infty} g_{v_j} \left(e^{-\beta \hbar \nu_j}\right)^v_j. \] (2.87)

Here, \(E_{v_j,gr} = \frac{\hbar \nu_j d_j}{2}\) is the ground state energy of the vibrational mode, so with \(v_j = 0\) and \(g_{v_j}\) is the degeneracy of vibrational mode \(j\). Note that the sum in equation (2.87) is over the energy levels and not over the states. For this reason the degeneracy \(g_{v_j}\) is incorporated into the equation. If the vibrational mode is not degenerate \(g_{v_j}\) and equation (2.87) becomes,

\[
Z_{v_j} = e^{-\beta E_{v_j,gr}} \sum_{v_j=1}^{\infty} \left(e^{-\beta \hbar \nu_j}\right)^v_j = e^{-\beta E_{v_j,gr}} \frac{1}{1 - e^{-\beta \hbar \nu_j}}. \] (2.88)

The vibrational partition function \(Z_v\) is then given by substitution of equation (2.88) for non-degenerate and equation (2.87) for degenerate and non-degenerate vibrational modes into equation (2.86). Assuming no degenerate vibrational modes for the moment the vibrational partition function is,

\[
Z_v = \prod_j e^{-\beta \hbar \nu_j d_j} = \prod_j e^{-\beta \hbar \nu_j \Theta_{v,j}} = \prod_j \frac{e^{-\Theta_{v,j} d_j}}{1 - e^{-\Theta_{v,j} \hbar \nu_j}} \] (2.89)

Here, \(\Theta_{v,j} = \frac{\hbar \nu_j}{k_B}\) is the characteristic vibrational mode temperature.

Electronic partition function The electronic energies levels can have a degeneracy \(g_{e,i}\). The electronic partition function is then given by,

\[
Z_e = \sum_i g_{e,i} e^{-\beta E_{e,i}}. \] (2.90)

Usually the energy separation between the ground state energy, which can arbitrarily be set to zero, and excited energy states is very high. In that case \(0 = E_{e,1} \ll E_{e,2}, E_{e,3}, \ldots\) and generally only the ground state is accessible for the electrons. This also provides justification for the assumption in the Born-Oppenheimer approximation that all electrons are in the ground state. The electronic partition function \(Z_e\) in this case reduces to,

\[
Z_e \approx g_{e,1}. \] (2.91)

Usually the ground state is not degenerate by which the electronic partition function reduces even more to,

\[
Z_e \approx 1. \] (2.92)
Energies  The energy contained in a certain distribution described by a partition function $Z$ is given by equation (2.71) to be,

$$\langle E \rangle = \frac{E}{n} = -\frac{1}{Z} \left( \frac{\partial Z}{\partial \beta} \right)_V.$$  

The mean translational energy $\langle E_{t, d} \rangle$ in one dimension is,

$$\langle E_{t, d} \rangle = \frac{E_{t, d}}{n} = -\frac{1}{Z_{t, d}} \left( \frac{\partial Z_{t, d}}{\partial \beta} \right)_V = \frac{1}{2} k_B T.$$  

In three dimensions this becomes,

$$\langle E_{t} \rangle = \prod_{d=1}^{3} \langle E_{t, d} \rangle = \frac{3}{2} k_B T.$$  

The mean rotational energy $\langle E_r \rangle$ is given by the rather long expression [53, eq. 17.26]. The mean rotational energy in the high-temperature limit $T \gg \Theta_r$ is,

$$\langle E_r \rangle = k_B T.$$  

The mean vibrational mode energy $\langle E_{v, j} \rangle$ is given by equation (2.97).

$$\langle E_{v, j} \rangle = -\frac{1}{Z_{v, j}} \left( \frac{\partial Z_{v, j}}{\partial \beta} \right)_V = -\frac{1}{e^{-\beta h \nu_j}} e^{-\beta E_{v, j, gr}} \left( 1-e^{-\beta h \nu_j} \right)^{-1} + \left( 1-e^{-\beta h \nu_j} \right)^{-1} \frac{\partial}{\partial \beta} e^{-\beta E_{v, j, gr}}$$

$$= -\frac{h \nu_j e^{-\beta h \nu_j}}{1-e^{-\beta h \nu_j}} + E_{v, j, gr} = \frac{h \nu_j}{e^{\beta h \nu_j} - 1} + \frac{d_j h \nu_j}{2}.$$  

In the vibrational mode energy in the high-temperature limit $T \gg \Theta_r$ or equivalently $\beta h \nu_j \ll 1$ is,

$$Z_{v, j} = \frac{h \nu_j}{e^{\beta h \nu_j} - 1} + E_{v, j, gr} = \frac{h \nu_j}{1 + \beta h \nu_j + \ldots} - 1 + E_{v, j, gr} \approx \frac{1}{\beta} + E_{v, j, gr} = k_B T + \frac{d_j h \nu_j}{2}.$$  

Note that all these high-energy approximations are in agreement with the classical equipartition theorem. This suggests a correct description in the form of statistical physics and its application on molecules.

2.3 Light-matter interaction in lasers

In this section the physical mechanism of light-matter interaction leading to lasing action is described. Firstly, the physical mechanism of lasing action, namely stimulated emission, is described. This leads to a fundamental understanding of the actual physics of one of the most essential parts of the workings of a laser. Hereafter, this theory is used to determine the Einstein coefficients, which are used in Chapter 3 to determine a description of the interaction between certain energy levels of the CO$_2$ molecules and the infra-red radiation present in the system.

2.3.1 Atom-field interaction

Overview  Throughout history this interaction is described in various different ways. The phenomenological analysis of Einstein [72] in terms of the so-called Einstein $A$ coefficient and $B$ coefficients is often used to introduce the physical mechanisms of light-matter interaction, such as absorption and emission. Although this theory, mainly guided by thermodynamic reasoning, gives a good basic understanding of the underlying physics and equation to work with, it does not fully explain the light-matter interaction. An example is spontaneous emission mechanism which
cannot be properly explained by this theory and is merely a postulate resulting from observation. The development of quantum mechanics played a major role in the development of the theory and vice versa. A semi-classical treatment considers the quantized matter and classical electromagnetic fields, described uniquely at every space-time point, in a quantum mechanical framework. This semi-classical approach predicts the existence of so-called Rabi-oscillations using the Rabi-model and a more thorough description of the time evolution of the atomic states in contrast to the Einstein theory. In the weak field limit this theory is essentially equivalent to the Einstein analysis. One of the greatest successes of physics, however, is quantum electrodynamics. It is a relativistic quantum field theory, and the first theory in which quantum mechanics and special relativity are reconciled. Here, spontaneous emission appears as a results of the interaction of matter with the electromagnetic field in the vacuum state. The fully quantum electrodynamic version of the Rabi-model is the so-called the Jaynes-Cummings model. In this section a quantum description is given, which in the weak field limit will give the Einstein coefficients. These Einstein coefficients are eventually used in the description of the energy reservoir model.

**Atom-field system**  Consider a system consisting of an atom and an electromagnetic field. The Hamiltonian of the system is given by equation (F.2), where is the unperturbed Hamiltonian for the system without interaction between the atom and field, and is the interaction Hamiltonian and causes the perturbation of the system. The unperturbed Hamiltonian can be written as a sum of the individual Hamiltonians of the unperturbed atom and field,

\[ \hat{H}_0 = \hat{H}^{(0)}_{\text{atom}} + \hat{H}^{(0)}_{\text{field}}. \]  

(2.99)

Here, is the unperturbed Hamiltonian of the atom and is the unperturbed Hamiltonian of the field. One way to determine the interaction Hamiltonian is to determine the classical expression and using quantization rules to deduce the quantum mechanical equivalent. Classically, the energy of a charge distribution in an electromagnetic field is given by a multi-pole expansion. The moments of the distribution of charges and currents of all orders interact with the gradients of the electric and magnetic fields of the corresponding order. The dimension of the atom is typically a few Angstrom while the wavelength of optical light is around a few hundred nanometers. Therefore, over the extend of the atom the electromagnetic field is nearly uniform in magnitude, however still time varying. Furthermore, the electric terms in the multi-pole expansion are orders of magnitude bigger than the magnetic terms so the dominant term is the electric dipole term. Only letting this term contribute to the interaction Hamiltonian for these reasons is the so-called dipole approximation. In principle all charged particles of the atomic system contribute to the dipole term, but because the protons are bound to the nucleus in the center of the charge distribution their contribution is small and can be neglected. Therefore, only the contribution of the electrons to the dipole moment is considered for the moment. The classical Hamiltonian is \( \hat{H}' = -\hat{\mathcal{E}} \cdot \mu \), where the dipole moment \( \mu = -\varepsilon \sum_{j=1}^{N} r_j \) and \( r_j \) is the position of the \( j \)th electron. The quantum mechanical equivalent is obtained by turning the variables into operators. The interaction Hamiltonian operator is given by,

\[ \hat{H}' = -\hat{\mathcal{E}} \cdot \hat{\mu}. \]  

(2.100)

Here, \( \hat{\mathcal{E}} \) is the electric field operator, and \( \hat{\mu} \) the dipole moment operator.

The unperturbed state of the atom-field system is the product of atom state and field state,

\[ |\psi\rangle = |\psi_{\text{atom}}\rangle |\psi_{\text{field}}\rangle. \]  

(2.101)

This unperturbed state of equation (2.101) is equivalent to the unperturbed wave function of section. The possible atom states are,

\[ |\psi_{\text{atom}}\rangle = |a\rangle, |b\rangle, \ldots. \]  

(2.102)

*The importance of this work of Rabi was rewarded with the Nobel prize for Physics in 1944 as it is the precursor for modern NMR techniques.*
Here, \(|a\rangle, |b\rangle\) are different states of the atomic system. The possible field states \(|\psi_{\text{field}}\rangle\) are,

\[
|\psi_{\text{field}}\rangle = |n_1\rangle |n_2\rangle \cdots |n_s\rangle = \{|n_s\}\). \tag{2.103}
\]

Here, \(|n_s\rangle\) is a single mode photon number state of mode \(s\). The electromagnetic field has a \(s\) number of modes and each mode \(s\) contains a \(n_s\) number of quanta. The quanta in the electromagnetic field are the so-called photons. The time-independent wave equation \((\ref{eq:wave_eq})\) of this unperturbed system is given by substitution of the unperturbed Hamiltonian of equation \((\ref{eq:hamiltonian_0})\) and the system state of equation \((\ref{eq:wave_eq})\) into the wave equation \((\ref{eq:wave_eq})\),

\[
\left(\hat{H}^{(0)}_{\text{atom}} + \hat{H}^{(0)}_{\text{field}}\right) |\psi_{\text{atom}}\rangle |\psi_{\text{field}}\rangle = E |\psi_{\text{atom}}\rangle |\psi_{\text{field}}\rangle. \tag{2.104}
\]

Here, \(E\) is the energy of the unperturbed system. Investigation of this wave equation \((\ref{eq:wave_eq})\) shown that a separate wave equations arise for the atom and field,

\[
\hat{H}^{(0)}_{\text{atom}} |\psi_{\text{atom}}\rangle = E_{\text{atom}} |\psi_{\text{atom}}\rangle, \tag{2.105}
\]

\[
\hat{H}^{(0)}_{\text{field}} |\psi_{\text{field}}\rangle = E_{\text{field}} |\psi_{\text{field}}\rangle. \tag{2.106}
\]

Here, \(E_{\text{atom}}\) are the unperturbed atom energies corresponding to the atom eigenstates \(|\psi_{\text{atom}}\rangle\) and \(E_{\text{field}}\) the unperturbed field energy corresponding to the field eigenstates \(|\psi_{\text{field}}\rangle\). This is not at all surprising, because in the unperturbed case where no interaction is considered the atom and the field can be considered as two separate systems, each for which separately the Schrödinger equation applies. The energies \(E\) corresponding to the unperturbed eigenstates \(|\psi\rangle\) are given by \((\ref{eq:energy})\).

\[
\langle \psi | \hat{H}_0 | \psi \rangle = E = E_{\text{atom}} + E_{\text{field}} = E_{\text{atom}} + \sum_{s=1}^{\infty} \left(n_s + \frac{1}{2}\right) \hbar \omega_s. \tag{2.107}
\]

Note that the field energy is infinite, because the ground state energy is non-zero for all the modes. So even when no photons are present, the electromagnetic field has an energy, which is a property of the quantum harmonic oscillator. The problems caused by this infinite vacuum state energy are tackled by re-normalization theory. Recall, however, that energies can arbitrarily be chosen relative to this ground state energy. In that case the vacuum state energy can be ignored, which effectively means that the \(\frac{1}{2}\) term in equation \((\ref{eq:energy})\) can be dropped.

**Stimulated emission and absorption** The interaction in the system is described by the evolution of the wave function of the system. The system starts out in an initial state and the evolution of the wave function as a result of the perturbation lets the system evolve to some final state. In making the change of the system state actually what happens is that energy quanta are exchanged between the two subsystems leaving them in in a state with a different energy. In the electromagnetic field described in equation \((\ref{eq:wave_eq})\) there are, however, an infinite number of possible final states, because the electromagnetic field has an infinite number of modes \(s\). To omit the infinite amount of transitions only the interaction of two atom states \(|a\rangle\) and \(|b\rangle\) with one single free space field mode with state state \(|n\rangle\) is considered. The corresponding energies from equation \((\ref{eq:energy})\) and \((\ref{eq:energy_2})\) of these states are the atom energies \(E_a\) and \(E_b\) and field energy \((n + \frac{1}{2}) \hbar \omega\) when considering the absolute field energy and field energy \(\hbar n \omega\) when considering the field energy above the vacuum state. The initial state of the system is taken to be,

\[
|\psi_{i}\rangle = |i\rangle = |a\rangle |n\rangle = |a, n\rangle. \tag{2.108}
\]

The system can, as a result of the interaction, evolve to two possible final states \(|f_1\rangle\) and \(|f_2\rangle\),

\[
|\psi_{f_1}\rangle = |f_1\rangle = |b\rangle |n - 1\rangle = |b, n - 1\rangle, \tag{2.109}
\]

\[
|\psi_{f_2}\rangle = |f_2\rangle = |b\rangle |n + 1\rangle = |b, n + 1\rangle. \tag{2.110}
\]
2.3. LIGHT-MATTER INTERACTION IN LASERS

Note that at this point it is not specified whether $|b\rangle$ has a higher or lower energy than $|a\rangle$. The energies above the vacuum field energy corresponding to these states are according to equation (2.107) given by,

$$E_i = E_a + n\hbar\omega,$$  \hspace{1cm} (2.111)

$$E_{f_1} = E_b + (n-1)\hbar\omega,$$  \hspace{1cm} (2.112)

$$E_{f_2} = E_b + (n+1)\hbar\omega.$$  \hspace{1cm} (2.113)

The time-dependent wave function $|\Psi\rangle$, as given by equation (F.7), of the this atom-field system is, therefore, given by,

$$|\Psi\rangle = c_i (t) |i\rangle e^{-\frac{E_{f_1} t}{\hbar}} + c_{f_1} (t) |f_1\rangle e^{-\frac{E_{f_1} t}{\hbar}} + c_{f_2} (t) |f_2\rangle e^{-\frac{E_{f_1} t}{\hbar}}.$$  \hspace{1cm} (2.114)

The system is initially in its initial state $|i\rangle$, which defines the initial conditions to be $c_i (0) = 1$ and $c_{f_1} (0) = c_{f_2} (0) = 0$ so that $|\Psi (0)\rangle = |i\rangle$.

In section F the interaction Hamiltonian is assumed to be small, which in the atom-field system can be the results of a weak driving field from for example a low intensity light source which is applied for a short time. Therefore, the coefficients $c$ remain approximately the same as time evolves and the atomic populations change very little. So the initial conditions $c_n (0) = \delta_{in}$ give the determine that to a good approximation for $t > 0$ the coefficients are $c_n (t) \approx \delta_{in}$, so $c_i(t) \approx c_i(0) = 1$ and $c_{f_1} (t) \approx c_{f_2} (0) = 0$. As the system evolves in time from the initial state $|i\rangle$ the coefficients $c_{f_1}$ and $c_{f_2}$ of the final states will change. To zeroth order the coefficients $c$ do not change as is just shown using the weak field limit. To investigate any perturbation or transition of the system the first order terms of the coefficients $c^{(1)}_k$ of the final states have to be determined from equation (F.10)

$$\dot{c}_{k}^{(1)} = -\frac{i}{\hbar} \sum_n c_n^{(0)} (t) \hat{H}_{kn}' e^{i\omega_{kn}t}.$$  \hspace{1cm} (2.115)

The only term remaining in the sum is that for which $n = i$ because to zeroth order $c_n^{(0)} (t) = \delta_{in}$. This gives,

$$\dot{c}_k^{(1)} = -\frac{i}{\hbar} \hat{H}_{ki}' e^{i\omega_{ki}t}.$$  \hspace{1cm} (2.116)

To get an expression for the coefficient $c_k^{(1)}$ this equation (2.116) is integrated over $t$ to get,

$$c_k^{(1)} = -\frac{i}{\hbar} \int_0^t \hat{H}_{ki}' (t') e^{i\omega_{ki}t'} dt'.$$  \hspace{1cm} (2.117)

This equation (2.117) gives the expression for the coefficients $c_{f_1}^{(1)}$ and $c_{f_2}^{(1)}$ for the final states $|f_1\rangle$ and $|f_2\rangle$. The coefficient $c_f$ of the system in a final state $|f\rangle$, or equivalently the atom being in state $|b\rangle$, is the sum of the coefficients $c_{f_1}$ and $c_{f_2}$. The first order coefficient $c_f^{(1)}$ for the final state $|f\rangle$ is together with equation (2.117) given by,

$$c_f^{(1)} = c_{f_1}^{(1)} + c_{f_2}^{(1)} = -\frac{i}{\hbar} \int_0^t \hat{H}_{f_1,i}' (t') e^{i\omega_{f_1 i}t'} dt' - \frac{i}{\hbar} \int_0^t \hat{H}_{f_2,i}' (t') e^{i\omega_{f_2 i}t'} dt'.$$  \hspace{1cm} (2.118)

To evaluate these integrals the matrix elements $\hat{H}'_{f_1}$ have to be determined. Therefore, the interaction Hamiltonian $\hat{H}'$ from equation (2.100) has to be determined. For a single free space field mode the electromagnetic field operator $\hat{E}$ in the Schrödinger picture is given by (7.7),

$$\hat{E} = ie \left( \frac{\hbar \omega}{2\epsilon_0 V} \right) \frac{i}{2} (\hat{a} - \hat{a}^\dagger).$$  \hspace{1cm} (2.119)
Here, $\omega$ is the radiation frequency, $V$ the volume, $\epsilon_0$ the electric vacuum permittivity, $e$ the elementary charge, $\hat{a}$ is the annihilation ladder operator, and $\hat{a}^\dagger$ the creation ladder operator. Substitution of this electric field operator (2.119) into the interaction Hamiltonian (2.100) gives,

$$\hat{H}' = -\hat{\mu} \cdot \mathcal{E}_0 (\hat{a} - \hat{a}^\dagger). \quad (2.120)$$

Here, $\mathcal{E}_0 = ie \left( \frac{\mu_a}{\sqrt{\pi V}} \right)^{\frac{3}{2}}$ is a system constant. The evaluation of the matrix elements $\hat{H}'_{f,1}$ and $\hat{H}'_{f,2}$ is left to Appendix I and are determined to be,

$$\hat{H}'_{f,1} = -\hat{\mu}_{ba} \cdot \mathcal{E}_0 \sqrt{n}, \quad (2.121) \quad \hat{H}'_{f,2} = \hat{\mu}_{ba} \cdot \mathcal{E}_0 \sqrt{n+1}. \quad (2.122)$$

Here, $\hat{\mu}_{ba} = \langle b | \hat{\mu} | a \rangle$ is the electric dipole operator matrix element between states $|b\rangle$ and $|a\rangle$. The integrals in equation (2.118) can now be evaluated using the expression (2.121) and (2.122) as described in Appendix I. As a result, the first order coefficient $c_f^{(1)}$ of the final state $|f\rangle$ is given by,

$$c_f^{(1)} = \frac{i}{\hbar} \langle a | \hat{\mu} | b \rangle \left( (n+1)^{\frac{1}{2}} \left( \frac{e^{i(\omega+\omega_a)t} - 1}{(\omega+\omega_a)} - n^{\frac{1}{2}} \frac{e^{i(\omega-\omega_a)t} - 1}{(\omega-\omega_a)} \right) \right). \quad (2.123)$$

In this equation (2.123) the first term represents emission, where the system evolves to finale state $|f_1\rangle$, and the second term represents absorption, where the system evolves to final state $|f_2\rangle$. Further investigation of this equation (2.123) shows that if $|b\rangle$ is the excited state then $\omega_{ba} > 0$ is positive. The frequency of the field $\omega$ is always positive and can therefore be near the atom transition frequency $\omega_{ba}$, so $\omega \approx \omega_{ba}$. In that case the second term is much larger than the first term and the first term can be ignored, which essentially is the rotating wave approximation. The remaining equation describes the system evolving from the initial state $|i\rangle$ through absorption to the final state $|f_1\rangle$. If there are no photons present $n = 0$ the coefficient $c_f^{(1)}$ is zero. Physically this means that if there are no photons present in the field, no absorption can take place and the system cannot evolve to state $|f_1\rangle$. If, however, $|a\rangle$ is the excited state $\omega_{ba} < 0$ is negative. Because the frequency $\omega$ of the field is always positive it can be near the negative of the atom transition frequency $\omega_{ba}$, so $\omega \approx -\omega_{ba}$. In that case the first term is much larger than the second term and the second term can be ignored. The remaining equation describes the system evolving from the initial state $|i\rangle$ through emission to the final state $|f_2\rangle$. In this case, however, if there are no photons present $n = 0$ the coefficient $c_f^{(1)}$ is non-zero. This means that if there are no photons present in present in the field, emission can still take place and the system can evolve to state $|f_2\rangle$.

This analysis shows that there are two processes involved with the evolution of the system as a results of the atom-field interaction, namely absorption and emission. A distinction is made for emission between the electromagnetic field containing no photons and when it does contain photons. If the field contains photons the emission is the so-called stimulated emission. If the field contains no photons the emission is the so-called spontaneous emission. The latter is a results of the interaction between the atom and the vacuum state of the electromagnetic field causing the emission of energy as a photon and the decay of the atom to a state which is lower in energy.

### 2.3.2 Einstein coefficients

**Limits** Consider the case where the number of photons in the electromagnetic field is very large $n \gg 1$. Then the approximation $\sqrt{n+1} \approx \sqrt{n}$ can be made and the first order coefficient $C_f^{(1)}$ in equation (2.123) reduces to,

$$c_f^{(1)} = \frac{1}{2\hbar} \langle \mu_{ba} | \mathcal{E}_{0,cl} \rangle \left( \frac{e^{i(\omega+\omega_a)t} - 1}{(\omega+\omega_a)} - \frac{e^{-i(\omega-\omega_a)t} - 1}{(\omega-\omega_a)} \right). \quad (2.124)$$
Here, the identification $E_{0,cl} \leftrightarrow 2iE_0\sqrt{n}$ is made between the classical and quantum mechanical field amplitudes, which is only approximately valid in this case of $n \gg 1$. The semi-classical treatment of light-matter interaction, when the electromagnetic field is given by $E = E_{0,cl} \cos(\omega_f t)$, also results in equation (2.124). Here, an agreement is established between the two approaches as the quantum electrodynamic theory reduces to the semi-classical treatment when the number of photons is large, which thus can be approximated by a classical electromagnetic field. The field frequency $\omega$ is assumed to be near to the atom transition frequency $\omega_{ab}$, $\omega \approx \omega_{ab}$. The second term in equations (2.124) and (2.123) becomes much larger than the first term, so the first term can be ignored making the rotating wave approximation. Then together with Euler’s formula $e^{ix} = \cos(x) + i \sin(x)$ equation (2.124) reduces to,

$$P_{i \rightarrow f}^{(1)} = \frac{(\hat{\mu}_{ba} \cdot E_{0,cl})}{\hbar} \left( e^{i(\omega-\omega_{ab})t} - 1 \right) = \frac{i (\hat{\mu}_{ba} \cdot E_{0,cl})}{\hbar} e^{i\frac{1}{2}(\omega-\omega_{ab})t} \left( e^{\frac{1}{2}(\omega-\omega_{ab})t} - e^{-\frac{1}{2}(\omega-\omega_{ab})t} \right)$$

$$= \frac{i (\hat{\mu}_{ba} \cdot E_{0,cl})}{\hbar} e^{i\frac{1}{2}\Delta \omega t} \sin \left( \frac{1}{2} \Delta \omega t \right).$$

(2.125)

Here, $\Delta \omega = \omega - \omega_{ab}$ is the detuning between the atom transition frequency and the field frequency. The first order probability $P_{i \rightarrow f}^{(1)}$, or transition probability, of the system going from the initial state $|i\rangle$ to a final state $|f\rangle$ is,

$$P_{i \rightarrow f}^{(1)} = c_f^{(1)*} c_f^{(1)} = \left| c_f^{(1)} \right|^2 = \frac{|\hat{\mu}_{ba} \cdot E_{0,cl}|^2}{\hbar^2} \frac{\sin^2 \left( \frac{\Delta \omega t}{2} \right)}{\Delta \omega^2}.$$

(2.126)

The continuum The electromagnetic field in free space will not be perfectly monochromatic and possesses some finite frequency range. The electromagnetic field could also be created by a broad-band source such as a black body lamp. In either case the field possesses a range of frequencies. The energy density $u$ in an electromagnetic wave is $u = \frac{E^2}{2}$ and the energy density by $u = \rho(\omega)d\omega$, where $\rho$ is the spectral energy density in the range $d\omega$. At this point it is assumed that the electric dipole moment is aligned with the electric field polarization, so that the angle $\theta$ between them is therefore zero. The product is then written as $|\hat{\mu}_{ba} \cdot E_{0,cl}|^2 = \mu_{ba}^2 E_{0,cl}^2 \cos(\theta) = \mu_{ba}^2 E_{0,cl}^2$ Equation (2.126) describes the transition probability for a single frequency of the field. The transition probability induced by all the frequencies is obtained by substitution of the previous description of the field and integrating over the whole frequency range. The transition probability for a continuum electromagnetic field is given by,

$$P_{i \rightarrow f}^{(1)} = \frac{2\mu_{ba}^2}{\epsilon_0 \hbar^2} \int_{-\infty}^{\infty} \rho(\omega) \frac{\sin^2 \left( \frac{\Delta \omega t}{2} \right)}{\Delta \omega^2} d\omega.$$

(2.127)

The term $\sin^2 \left( \frac{\Delta \omega t}{2} \right)$ has a maximum at the resonance frequency $\omega_{ab}$ and falls of fast away from it. Therefore, for a single frequency the transition probability $P_{i \rightarrow f}^{(1)}$ is sharply peaked around the resonance value. On the contrary, the spectral density $\rho(\omega)$ varies slowly with the frequency, by which it can be to a good approximation be equated to its resonance value $\rho(\omega_{ab})$ and be taken outside of the integral. Then the integral can be evaluated using $\int \frac{\sin^2(x)}{x^2} dx = \pi$. The transition probability $P_{i \rightarrow f}^{(1)}$ becomes,

$$P_{i \rightarrow f}^{(1)} = \frac{\mu_{ba}^2 \rho(\omega_{ab}) \pi t}{\epsilon_0 \hbar^2}.$$

(2.128)

Planck’s distribution law Up to this point a single atom in an electromagnetic field is considered. Now take a whole collection of identical atoms in an electromagnetic field. Atom state $|a\rangle$ is set as the state with higher energy $E_a > E_b$. Let $N_a$ and $N_b$ represent the number of atoms, or populations, in state $|a\rangle$ and $|b\rangle$ respectively. The atoms each individually interact with the
electromagnetic field through absorption and emission as described above. The emission causes the atom to go from state $|a\rangle$ to state $|b\rangle$ and the absorption it to go from state $|b\rangle$ to state $|a\rangle$. The number of atoms per unit time making the transition from the initial state $|i\rangle$ to a final state $|f\rangle$ is given by the transition probability rate,

$$W_{i \rightarrow f} = \frac{\partial P_{i \rightarrow f}}{\partial t}. \quad (2.129)$$

If the atom start out in atom state $|a\rangle$ then $W_{i \rightarrow f}$ represents the probability that the system will make a transition were the atom is in state $|b\rangle$ per unit time. The evolution of the populations $N_a$ and $N_b$ is described by the continuity equation. The creation/annihilation $S$ consist of terms by which and absorption create or annihilate atoms from the population. The transition probability rate in equation (2.129) holds for a single atom, so for the collection of atoms the total rate is determined by multiplying the rate $W_{i \rightarrow f}$ by the population $N$. The evolution of the populations can then be written as,

$$\frac{\partial N_a}{\partial t} = -N_a W_{a \rightarrow b} + N_b W_{b \rightarrow a}, \quad (2.130) \quad \frac{\partial N_b}{\partial t} = N_a W_{a \rightarrow b} - N_b W_{b \rightarrow a}. \quad (2.131)$$

Here, $W_{a \rightarrow b}$ is the transition probability rate of emission where the system goes from the initial state with atom state $|a\rangle$ to the final state with atom state $|b\rangle$, and $W_{b \rightarrow a}$ is the transition probability rate of absorption where the system goes from the initial state with the atom in state $|a\rangle$ to the final state with atom state $|b\rangle$. The ratio of $\frac{W_{a \rightarrow b}}{W_{b \rightarrow a}}$ is given by the ratio of the first and second term in equation (2.129) to be $\frac{n+1}{n}$. At thermal equilibrium the populations are stationary $\frac{\partial N}{\partial t} = 0$. This together with the Boltzmann distribution equation, the population evolution equations (2.130) or (2.131) give the Planck distribution law [78].

$$n = \frac{1}{e^{\beta \hbar \omega} - 1}. \quad (2.132)$$

Einstein coefficients In section [2.3.2] is assumed that in the description of a single atom in an electromagnetic field the electric dipole is aligned with the polarization of the electric field. However, in a collection of atoms such as for example a gas this is not the case for every single atom. Therefore, averaging over the three polarization directions effectively means that for the collections of atoms the transition probability is multiplied by $\frac{1}{3}$. The first order transition probability rate $W_{i \rightarrow f}^{(1)}$ for the collection of identical atoms is,

$$W_{i \rightarrow f}^{(1)} = \frac{\partial P_{i \rightarrow f}^{(1)}}{\partial t} = \frac{\mu_{ba}^2 \rho (\omega_{ba}) \pi}{3 \epsilon_\| \hbar^2} = B_{ba} \rho_{ab}. \quad (2.133)$$

Here, $B_{ba} = \frac{\mu_{ba}^2 \pi}{3 \epsilon_\| \hbar^2}$ is the Einstein $B$ coefficient, and $\rho_{ab} = \rho (\omega_{ba})$ the spectral energy density at its resonance value $\omega_{ab}$. Einstein in a phenomenological description of light-matter interaction introduced not only the Einstein $B$ coefficients for emission and absorption. He also introduced the Einstein $A$ coefficient separately for spontaneous emission. The equations equivalent to equations (2.130) and (2.131) then are,

$$\frac{\partial N_a}{\partial t} = -N_a (A_{ab} + B_{ba} \rho_{ab}) + N_b B_{ba} \rho_{ab}, \quad (2.134)$$

$$\frac{\partial N_b}{\partial t} = +N_a (A_{ab} + B_{ba} \rho_{ab}) - N_b B_{ba} \rho_{ab}. \quad (2.135)$$

The uniform distribution of polarizations of an isotropic field gives $|\vec{\varepsilon}_{0,cl} \cdot \vec{x}| = |\vec{\varepsilon}_{0,cl} \cdot \vec{y}| = |\vec{\varepsilon}_{0,cl} \cdot \vec{z}| = \frac{1}{\sqrt{3}} |\vec{\varepsilon}_{0,cl}|^2$.  

\[ \text{CHAPTER 2. BACKGROUND THEORY} \]
Here, $A_{ab}$ is the Einstein $A$ coefficient for spontaneous emission for the system going from an initial state with atom state $|a\rangle$ to a final state with atom state $|b\rangle$. Analogous to the derivation of the Planck law in section 2.3.2 at thermal equilibrium and using the Boltzmann distribution gives the relations between the Einstein coefficients $A$ and $B$ \cite{78},

$$A = B \frac{\hbar \omega^3}{\pi \epsilon_0 c^3} = \frac{\mu_{ba}^2 \omega^3}{3 \epsilon_0 \hbar \pi c^3}. \tag{2.136}$$

**Selection rules** By looking at the electric dipole matrix element, or transition dipole moment, it can be noted that this is often equal to zero. This can be seen by considering the state in terms of quantum numbers and considering its wave function. Often by only looking at the parity of this wave function it becomes apparent is the transition dipole moment is zero. It follows that for some values of the quantum number the matrix element becomes zero so the probability of a transition is zero according to that process. These are the selection rules which put restrictions on the possible transitions by considering the value of the quantum numbers. Selection rules for higher order terms can cause that if a transition is forbidden it can be allowed for a higher order interaction such as the magnetic dipole and electric quadrupole.
Reservoir model and CO$_2$-laser amplification

"Reality is wrong. Dreams are for real."

Tupac Shakur

In this chapter the dynamics of a CO$_2$-laser amplification system are described. The theory presented in the previous chapter [2] is applied to the system under consideration having a CO$_2$-N$_2$-He-CO gas mixture and radiation with a wavelength of 10.58 µm and 10.206 µm.

The chapter is divided into five sections. In section 3.1 the structure and dynamics of a CO$_2$ molecule are described. The general concepts described in section 2.1 are applied to the CO$_2$ molecule, as this molecule plays a central role in the dynamics of a CO$_2$-laser plasma. In section 3.2 the general reservoir model is developed and derived from the first principles described in chapter 2. The molecular dynamics described in section 2.1 and the distribution of energy in the system described previously in section 2.2 are used to explain the distribution of species and energy among the defined energy density reservoirs. In section 3.3 the general reservoir model is applied to a CO$_2$-N$_2$-He-CO plasma with a specific chemistry. The energy density rate equations are developed for the system under consideration. These equations contain the terms describing the effect of the energy transfer processes of the chemistry. In section 3.4 the reservoir model for CO$_2$-laser amplification is developed. The general concepts of light-matter interaction described previously in section 2.3 are applied to determine the specific lasing action occurring in the system. The model is a coupling between the reservoir model for a CO$_2$-N$_2$-He-CO gas mixture, a description of the evolution of the radiation, and a rotational relaxation model. In section 3.5 briefly the numerical approach using the PLASIMO code is considered.

3.1 CO$_2$ molecule

In this section the structure and dynamics of a CO$_2$ molecule are described. Firstly, the geometric structure, the ro-vibrational dynamics, and its molecular state are considered. Here, the concepts described in sections 2.1.1, 2.1.2, and 2.1.3 are applied to the CO$_2$ molecule. Hereafter, the energy levels of CO$_2$ are determined using the theory about energy levels, Fermi resonance, wave-numbers, and anharmonicity of the general molecule of section 2.1.

3.1.1 Structure of CO$_2$

The carbon-dioxide molecule, CO$_2$, consists of two oxygen O atoms and a carbon C atom. The configuration of the nuclei of these atoms is such that they form a straight line with the carbon C atom positioned in the middle of the two oxygen O atoms. This makes CO$_2$ a linear polyatomic molecule. The CO$_2$ molecule is centrosymmetric, a property derived from group theory, which is a point group with an inversion center as one of its symmetry elements. Along the internuclear axis there exists a symmetry axis. In addition, there exists a symmetry plane perpendicular to
the internuclear axis through the center of mass. According to section 2.1.1, a CO2 molecule can be modeled as a system of \( N = 3 \) point particles with \( f = 3N = 9 \) spatial dofs. The translation of its center of mass is again, as always in 3-dimensional space, described by \( f_t = 3 \) translational dofs. The rotation is described by \( f_r = 2 \) rotational dofs. The vibration is given by equation (2.22) to be described, therefore, by \( f_v = 4 \) vibrational dofs.

### 3.1.2 Rotation of CO2

The rotation of the CO2 molecule is about an axis perpendicular to the internuclear axis through its center of mass, which is the equilibrium position of the carbon C nucleus. The molecule is modeled as a rigid rotator described in section 2.1.2. The moment of inertia \( I_{CO2} \) of a CO2 molecule about this axis is according to equation (2.22),

\[
I_{CO2} = 2mOr_0^2. \tag{3.1}
\]

Here, \( m_O \) is the mass of an oxygen O nucleus, and \( r_0 \) the distance of the oxygen O nucleus to the axis of rotation. The carbon C nucleus has no moment of inertia about this axis, because it is positioned on this rotational axis.

### 3.1.3 Vibration of CO2

The vibration of a CO2 molecule can, according to sections 3.1.1 and 2.1.3, be described by \( f_v = 4 \) normal vibrations with corresponding normal coordinates \( \xi \). A normal vibration exists which changes the internuclear distances between the C nucleus and the both of the oxygen O nuclei symmetrically with respect to the symmetry plane perpendicular to the symmetry axis. This longitudinal normal vibration with oscillation frequency \( \nu_1 \) and vibrational quantum number \( v_1 \) is the so-called symmetric stretching mode, which in this report is referred to with mode number 1.

Another normal vibration exists which also changes the internuclear distances between the carbon C nucleus and both of the oxygen O nuclei, but without changing the distance between the two oxygen O nuclei, making it asymmetrical with respect to the symmetry plane perpendicular to the symmetry axis. This longitudinal normal vibration with oscillation frequency \( \nu_3 \) vibrational quantum number \( v_3 \) is the so-called asymmetric stretching mode, which in this report is referred to with mode number 3. Finally, there exist two normal vibrations which describe the motion of the C nucleus in the symmetry plan perpendicular to the symmetry axis. These transversal normal vibrations posses oscillation frequencies \( \nu_{2a} \) and \( \nu_{2b} \) and quantum numbers \( v_{2a} \) and \( v_{2b} \). However, the frequencies \( \nu_{2a} \) and \( \nu_{2b} \) are equal which, according to section 2.1.3, results in a degenerate vibration. This twofold degenerate transversal normal vibration with oscillation frequency \( \nu_2 = \nu_{2a} = \nu_{2b} \) and vibrational quantum number \( v_2 = v_{2a} + v_{2b} \) is the so-called bending mode, which in this report is referred to with mode number 2. The degeneracy of a state of this vibrational bending mode depends on the amount of possible distributions that exist for the present energy quanta amongst the two normal vibrations. This is equivalent to the number of combinations in which \( v_2 \) can be written as the sum of two positive integers, that is \( g_{v_2} = v_2 + 1 \).

#### Bending mode wave function of CO2

Let’s consider the wave function of the bending mode for a moment to get some more insight into this degenerate bending mode. Using equation (2.45), the bending mode wave function \( \psi_{v_2} \) can be determined in terms of normal coordinates \( \xi \). Pauling and Wilson [65] found that, because the force field in the \( x-y \) plane is isotropic, a description in terms of normal polar coordinates, later adopted by [79] [80], is more convenient. The bending mode wave function \( \psi_{v_2} \) in normal coordinates \( \xi_a \) and \( \xi_b \) and in normal polar coordinates \( \rho_2 \) and \( \phi_2 \) is given by,

\[
\psi_{v_2} = N_{v_2} H_{v_{2a}} (\sqrt{\alpha_2} \xi_{2a}) H_{v_{2b}} (\sqrt{\alpha_2} \xi_{2b}) e^{-\alpha_2 (\xi_{2a}^2 + \xi_{2b}^2)} = F_{v_2}^{l_2} (\sqrt{\alpha_2} \rho_2) e^{-\alpha_2 \rho_2^2} e^{\pm il_2 \phi_2}. \tag{3.2}
\]

Here, \( F_{v_2}^{l_2} (\sqrt{\alpha_2} \rho_2) \) is polynomial of degree \( v_2 \) in \( \rho_2 \) and \( l_2 = v_2, v_2 - 2, v_2 - 4, ... \) or 0 a quantum number associated with the angular momentum depending on whether \( v_2 \) is odd or even.
3.1.4 Molecular state of CO$_2$

The molecular state of CO$_2$ is noted as outlined in section 2.1.3. The twofold degenerate vibrational bending mode 2 has a quantum number $l$ associated with it. This quantum number $l$ is noted as a superscript of the quantum number $v_2$ of bending mode 2. The molecular state of CO$_2$ is then noted as,

$$[v_1, v_2, v_3, j].$$  \tag{3.3}

3.1.5 Energy levels of CO$_2$

If displacements of the nuclei from their equilibrium position are assumed to be sufficiently small, strictly speaking infinitesimal, and ro-vibrational interaction is neglected, the situation can be approximated in so-called zeroth order. The rotation is then described by the rigid rotator of section 2.1.2 and the vibration by the harmonic oscillator of section 2.1.3. In zeroth order the rotational Hamiltonian $\hat{H}_r$ and the vibrational Hamiltonian $\hat{H}_v$ of CO$_2$ are given by equations (2.23) and (2.36) respectively. The term values $G^r_{v, CO_2}$ for rotation and vibration of CO$_2$ in zeroth order are then the sum of the rotational term values $G^r_{v}$ of equation (2.29) and the vibrational term values $G^v_{v}$ of equation (2.47)\footnote{The superscript (0) indicates the zero order approximation of the concerned variable.},

$$G^r_{v, CO_2} = G^r_{v} + G^v_{v} = \omega_1 \left(v_1 + \frac{1}{2}\right) + \omega_2 \left(v_2 + 1\right) + \omega_3 \left(v_3 + \frac{1}{2}\right) + B j (j + 1).$$ \tag{3.4}

Here, the rotational constant $B = \frac{\hbar}{16\pi^2\epsilon m_O r_O^2}$. In zeroth order the unperturbed wave function \(\psi^{(0)}_{rv, CO_2}\) of rotation and vibration of CO$_2$, according to equations (2.12), (2.30), (2.38), (2.45), and (3.2), in normal coordinates $\xi_i$ is given by,

$$\psi^{(0)}_{rv, CO_2} = \psi_{r}\psi_{v_1}\psi_{v_2}\psi_{v_3} = N_{rv, CO_2}Y^m_j H_{v_1} \left(\sqrt{\alpha_1}\xi_1\right) e^{-\alpha_1\xi_1^2} \times
$$

$$\times H_{v_2} \left(\sqrt{\alpha_2}\xi_2a\right) H_{v_2} \left(\sqrt{\alpha_2}\xi_2b\right) e^{-\frac{\alpha_2}{2}(\xi_2a^2 + \xi_2b^2)} \times
$$

$$\times H_{v_3} \left(\sqrt{\alpha_3}\xi_3\right) e^{-\frac{\alpha_3}{2}\xi_3^2}.$$ \tag{3.5}

Here, $N_{rv, CO_2}$ is a normalization constant. For a more accurate description of the dynamics of CO$_2$, such as discussed in section 2.1.3, involved higher order terms the ro-vibrational interaction. In that case, the ro-vibrational Hamiltonian $\hat{H}_{rv}$ in general, is not separable, as in the case of the vibrating rotator from section 2.1.4. However, if this ro-vibrational interaction is sufficiently small it can be treated as a perturbation. The ro-vibrational Hamiltonian $\hat{H}_{rv}$ can then be written as $\hat{H}_{rv} = \hat{H}_r + \hat{H}_v + \hat{H}_{rv}$. Dimensionless variables $\zeta_i$ can be introduced to make computations and equations less complex, as used in Dennison [79], Statz [80], and Witteman [70, p.11]. The dimensionless variables $\zeta_i$ in terms of the normal coordinates $\xi_i$ are,

$$\zeta_1 = 2\pi \left(\frac{\omega_1 m_O c}{\hbar}\right)^{1/2} \xi_1,$$ \tag{3.6}

$$\zeta_2 = 2\pi \left(\frac{\omega_2 m c}{\hbar}\right)^{1/2} \xi_2a,$$ \tag{3.7}

$$\zeta_3 = 2\pi \left(\frac{\omega_3 m c}{\hbar}\right)^{1/2} \xi_2b,$$ \tag{3.8}

$$\zeta_4 = 2\pi \left(\frac{\omega_4 m c}{\hbar}\right)^{1/2} \xi_3.$$ \tag{3.9}

Here, $m_O$ is the mass of an oxygen O atom, and $\mu = \frac{2m_O m_C}{(2m_O + m_C)}$ is the reduced mass defined in equation (2.27). The ro-vibrational Hamiltonian $\hat{H}_{rv, CO_2}$ in terms of the dimensionless variables $\zeta_i$ is given by,

$$\hat{H}_{rv, CO_2} = \frac{\hbar^2}{2I} + \frac{2m^2c}{\hbar} (\omega_1 p^2_{\zeta_1} + \omega_2 (p^2_{\zeta_2a} + p^2_{\zeta_2b}) + \omega_3 p^2_{\zeta_3}) + \frac{1}{2} \hbar c \left(\omega_1 \zeta_1^2 + \omega_2 \zeta_2^2 + \omega_3 \zeta_3^2\right) +
$$

$$\hbar c \left(a_1 \zeta_1^2 + a_2 \zeta_1 \zeta_2^2 + a_3 \zeta_1 \zeta_3^2 + a_4 \zeta_1^4 + a_5 \zeta_2^4 + a_6 \zeta_3^4 + a_7 \zeta_1^2 \zeta_2^2 + a_8 \zeta_1 \zeta_2^2 \zeta_3^2 + a_9 \zeta_2^2 \zeta_3^2\right).$$ \tag{3.10}
Here, $p$ are the canonical conjugate momenta of the dimensionless variables $\zeta, \Xi = (\zeta^2 + \zeta_3^2)^{\frac{1}{2}}$ a distance, and symbols $a_i$ through $a_9$ the an-harmonic potential coefficients\(^2\). In equation (3.10), the first term represents the kinetic energy of rotation, the second term the kinetic energy of vibration, the third term the harmonic potential energy, and the fourth and fifth term the anharmonic potential energy. The rotational term values $G_r$ are given in section 2.1.4, where, as described before, the term involving $D_c$ is, in general, very small and can therefore be chosen to be neglected. The rotational term values $G_{r, CO_2}$, given by equation (2.56), for CO$_2$ are,

$$
G_r = B_v (j (j + 1) - l^2) = \left( B + \sum_i a_i \left( v_i + \frac{d_i}{2} \right) \right) (j (j + 1) - l^2)
$$

$$
= B \left( 1 + \chi_1 \left( v_1 + \frac{1}{2} \right) + \chi_2 (v_2 + 1) + \chi_3 (v_3 + \frac{1}{2}) \right) (j (j + 1) - l^2). \tag{3.11}
$$

Here, $\chi$ are the an-harmonic term coefficients. Expression for these anharmonicity coefficients $\chi$ are found by Dennison\(^7\) to be given by\(^3\)

$$
\chi_1 = \frac{3h}{4\pi^2 c I_{eq} \omega_1} + \frac{3a_1 h^\frac{1}{2}}{\pi (c I_{eq} \omega_1^3)^{\frac{1}{2}}}, \tag{3.12}
$$

$$
\chi_2 = \frac{h (\omega_2^3 + 3\omega_2^2)}{8\pi^2 c I_{eq} \omega_2 (\omega_2^2 - \omega_3^2)} + \frac{a_2 h^\frac{1}{2}}{\pi (c I_{eq} \omega_1^3)^{\frac{1}{2}}}, \tag{3.13}
$$

$$
\chi_3 = \frac{h (\omega_3^3 + 3\omega_3^2)}{4\pi^2 c I_{eq} \omega_3 (\omega_3^2 - \omega_2^2)} + \frac{a_3 h^\frac{1}{2}}{\pi (c I_{eq} \omega_1^3)^{\frac{1}{2}}}. \tag{3.14}
$$

Here, $I_{eq}$ is the equilibrium moment of inertia. The vibrational Hamiltonian $\hat{H}_v$ can be obtained from the ro-vibrational Hamiltonian $\hat{H}_r$ in equation (3.10) by ignoring the first term representing the kinetic energy of rotation. Then, this is the Hamiltonian of four non-linear coupled harmonic oscillators, where two oscillator have the same frequency. The vibrational term values $G_v$ are determined from equation (2.53), while similar equations are given by Dennison\(^7\) and Herzberg\(^6\) p.211]. The vibrational term values $G_v$ for CO$_2$ are,

$$
G_v = \omega_1 (v_1 + \frac{1}{2}) + \omega_2 (v_2 + 1) + \omega_3 (v_3 + \frac{1}{2}) + x_{11} (v_1 + \frac{1}{2})^2 + x_{22} (v_2 + 1)^2 + + g_l (l^2 - 1)
$$

$$
+ x_{33} (v_3 + \frac{1}{2})^2 + x_{12} (v_1 + \frac{1}{2}) (v_2 + 1) + x_{13} (v_1 + \frac{1}{2}) (v_3 + \frac{1}{2}) + x_{23} (v_2 + 1) (v_3 + \frac{1}{2}). \tag{3.15}
$$

The anharmonicity coefficients $x$ and $g$ in terms of the potential coefficients $a_i$ are found by

---

\(^2\) Note that the choice of symbols for these an-harmonic potential coefficients in the literature, such as in the works of Dennison\(^7\), Statz\(^8\), and Wittenman\(^9\), can cause some confusion. There, the symbols are chosen to be the letters $a$ through $i$, which is very inconvenient with regard to, for example, the simultaneous use of $c$ for the speed of light, $h$ for Planck’s constant, and $i$ for the imaginary unit. This, therefore, requires unnecessary carefulness of the reader.

\(^3\) In Dennison\(^7\) the coefficients $\chi$ are denoted with symbols $\alpha$. 
3.1. CO$_2$ MOLECULE

Dennison [79], to be given by,

\[
x_{11} = \frac{3a_4}{2} - \frac{15a_1^2}{4\omega_1}, \tag{3.16}
\]

\[
x_{22} = \frac{3a_5}{2} - \frac{a_2^2}{2\omega_1} - \frac{a_2^2}{8(2\omega_2 + \omega_1)} + \frac{a_2^2}{8(2\omega_2 - \omega_1)}, \tag{3.17}
\]

\[
x_{33} = \frac{3a_6}{2} - \frac{a_3^2}{2\omega_1} - \frac{a_3^2}{8(2\omega_3 + \omega_1)} + \frac{a_3^2}{8(2\omega_3 - \omega_1)}, \tag{3.18}
\]

\[
x_{12} = a_7 - \frac{3a_1a_2}{\omega_1} - \frac{a_2^3}{2(2\omega_2 + \omega_1)} - \frac{a_2^3}{2(2\omega_2 - \omega_1)}, \tag{3.19}
\]

\[
x_{13} = a_8 - \frac{3a_1a_3}{\omega_1} - \frac{a_3^3}{2(2\omega_3 + \omega_1)} - \frac{a_3^3}{2(2\omega_3 - \omega_1)}, \tag{3.20}
\]

\[
x_{23} = a_9 - \frac{a_2a_3}{\omega_1} h + \frac{\left(\omega_2 - \omega_3\right)}{8\pi I_{eq}c} \tag{3.21}
\]

Note that in equation (3.19) for $g_{II}$ the last term is a contribution of the rotational term values $G_r$ of equation (2.56), where terms containing quantum number $l$ are taken into the an-harmonic terms for vibration, as discussed briefly in section 2.1.4.

The vibrational term values $G_v$ of equation (3.15) do not take in to account the possibility of resonating frequencies. In the case of CO$_2$ the frequencies $v_1$ and $v_2$ resonate, so that $v_1 \approx 2v_2$. Therefore, according to equation (2.19), it follows that $\omega_1 \approx \omega_2$. By investigation of equations (3.17), (3.19), and (3.20) of anharmonicity coefficients $x_{22}$, $g_{II}$, and $x_{12}$ respectively, the terms $(2\omega_2 - \omega_1)^{-1}$ can then blow up. Hence, the perturbation method breaks down here and only the term values of the non-resonating vibrational states are described by equation (3.15). The term values of the vibrational states in Fermi resonance, however, are not well described by equation (3.15) and an alternative expression is needed. A solution is provided by Adel and Dennison [82], later a more straightforward procedure is given by Dennison [79]. A similar procedure for Fermi resonance is previously discussed in section 2.1.4 and will be applied to CO$_2$ in the next section 3.1.6.

### 3.1.6 Fermi resonance of CO$_2$

As described before in section 2.1.4 if two vibrational levels each belonging to different vibrational modes have nearly the same energy Fermi resonance occurs. In the CO$_2$ molecule the frequency $v_1$ of vibrational mode 1 is almost equal to twice the frequency $v_2$ of vibrational mode 2, so $v_1 \approx 2v_2$. As a result, for example, the vibrational state with one quantum in symmetric stretching mode 1 and zero in the other modes $[1,0^0,0]$ is close in energy value to the vibrational state with two quanta in the bending modes 2 and zero in the other modes $[0,2^1,0]$. Here, the quantum number $l$ can, according to section 2.1.4, for $v_2 = 2$ take on the values 0 or 2. The vibrational state $[0,2^1,0]$ thus consists of two vibrational sub-states corresponding to the two different values of quantum number $l$. These vibrational sub-states $[0,0^0,0]$ and $[0,2^2,0]$ have species $\Sigma^+_2$ and $\Delta_2$, respectively and vibrational state $[1,0^0,0]$, has species $\Sigma^+_2$. As mentioned in section 2.1.4 only vibrational states of the same species can be in Fermi resonance. Therefore only vibrational states $[1,0^0,0]$ and $[0,2^2,0]$ are in Fermi resonance. This relatively strong perturbation causes a strong mixing of the vibrational state eigenfunctions $\psi_{[1,0^0,0]}$ and $\psi_{[0,2^2,0]}$. This results in two vibrational states which are a mixture of the unperturbed vibrational states in which neither of the states can be indicated by one of the unperturbed states. Hence the perturbed states are indicated by $[I]$ and $[II]$. Here, the vibrational state $[I]$ is state with the higher energy and vibrational state $[II]$ the one with lower energy. In the literature, often the vibrational state $[I]$ is seen as the upward
shifted unperturbed vibrational state \([1,0^0,0]\) and \([H]\) as the downward shifted vibrational state \([0,2^0,0]\). The perturbations among states with higher vibrational levels of CO\(_2\) are considered by Adel and Dennison [82]. The perturbed energies \(E\) for the vibrational states in Fermi resonance are given by equation (2.58). The matrix element \(W\) for the anharmonic potential coefficients, which is in my opinion more conveniently chosen as \(\omega\) for the vibrational terms in equation (2.58), is given by,

\[
W_{[1,0,0],[0,2^0,0]} = -\frac{\hbar^2 a_2}{8\sqrt{2\pi^3 c^3 \omega_1^3 \omega_2}}.
\]  

(3.23)

3.1.7 Coefficients and wave-numbers of CO\(_2\)

In this section the potential coefficients \(\omega\) and \(a\), the anharmonicity coefficients \(\chi\), the matrix element \(W_{ni}\), energy difference \(\delta\), and calculated as well as experimentally observed spectroscopic wave-numbers are considered.

Potential coefficients of CO\(_2\) As discussed in section 2.1.3 the vibrational ground state possesses a non-exchangeable energy. Therefore, the energy of a vibrational state can be chosen as the absolute energy or the energy above the ground state. To go from the latter to the former one needs to know the absolute energy or the energy above the ground state. These potential coefficients \(G\) for a particular vibrational state the coefficients \(\{\omega\}\), \(\{x\}\), and \(\{g\}\) have to be known.

The spectroscopic wave-number \(\omega\) can, as described previously in section 2.1.1, be used to indicate an amount of energy \(\hbar\) such as the energy difference between two vibrational states. In the unperturbed case the vibrational term values \(G_{v}^{(0)}\) are given by the vibrational terms in equation (3.4), where only the potential coefficients \(\omega_1\), \(\omega_2\), and \(\omega_3\) need to be known. The three possible unperturbed states which have one quantum in a vibrational mode are \([1,0^0,0]\), \([0,1^1,0]\), and \([0,0^0,1]\). By investigation of equation (3.4) it can be noted that the spectroscopic wave-numbers \(\omega\) corresponding to the energy differences between the ground state \([0,0^0,0]\) and these three unperturbed states are equal to the potential coefficients \(\omega_1\), \(\omega_2\), and \(\omega_3\) respectively. In other words, these potential coefficients \(\omega_1\), \(\omega_2\), and \(\omega_3\) are equal to the spectroscopic wave-numbers \(\omega\) of the energy above the ground state of these states. These potential coefficients \(\{\omega\}\), or spectroscopic wave-numbers \(\{\omega^{(0)}\}\) for these three states in the unperturbed case, are given by Dennison [79, Table II] to be \(\omega_1 = 1351.2\text{ cm}^{-1}\), \(\omega_2 = 672.2\text{ cm}^{-1}\), and \(\omega_3 = 2396.4\text{ cm}^{-1}\). These values are also presented in the first column of Table 3.1 and Table 3.3.

Now consider the perturbed case without rotation. Then, the ro-vibrational Hamiltonian \(H_{rv,CO_2}\) in equation (3.10), when the first term coming from rotation is ignored, reduces to a vibrational Hamiltonian describing the vibration of the CO\(_2\) molecule. Statz [80] uses the following method to obtain the vibrational state energies and vibrational wave functions. A linear combination of the unperturbed vibrational wave function, such as those in equation (3.5), together with the vibrational part of the ro-vibrational Hamiltonian is inserted into the Schrödinger equation. The result is multiplied by the complex conjugate of the unperturbed wave functions and integrated over the normal coordinates \(\xi\). By doing so, a set of linear and homogeneous equations for the coefficients of the linear combination of wave functions is obtained. The linear equations only have a solution when the determinant of the coefficients vanishes. From this condition the energy of the wave functions can be determined. These energies in turn make in possible to solve the linear equations and obtain the wave functions. Using this method, Statz obtained solutions for different sets of potential coefficients \(\{a\}\). The results obtained for these calculated

\[\text{In the work of Dennison [79] the matrix element } W_{[1,0,0],[0,2^0,0]} \text{ is indicated as } -\frac{1}{b}. \text{ Note that } b \text{ is one of the anharmonic potential coefficients, which is in my opinion more conveniently chosen as } a_2 \text{ in this report.}\]

\[\text{Here, the curly brackets } \{\}\text{ indicate that it concerns a set. So, for example, } \{\omega\} = \{\omega_1, \omega_2, \omega_3\}.\]

\[\text{This can be imagined as the spatial frequency in units of } \text{cm}^{-1} \text{ of an electromagnetic wave or photon having that amount of energy.}\]
3.1. \textit{CO}_2 \text{ MOLECULE}

Table 3.1: Potential coefficients of CO\textsubscript{2}.

<table>
<thead>
<tr>
<th>$\omega_1$</th>
<th>$\omega_2$</th>
<th>$\omega_3$</th>
<th>$a_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1351.2 *</td>
<td>672.2 *</td>
<td>2396.4 *</td>
<td>−30</td>
</tr>
<tr>
<td>$a_2$</td>
<td>$a_3$</td>
<td>$a_4$</td>
<td>$a_5$</td>
</tr>
<tr>
<td>71.3</td>
<td>−250</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$a_6$</td>
<td>$a_7$</td>
<td>$a_8$</td>
<td>$a_9$</td>
</tr>
<tr>
<td>6.4</td>
<td>1.9</td>
<td>8.9</td>
<td>−25.7</td>
</tr>
</tbody>
</table>

* The value of these potential coefficients are equal to the value of spectroscopic wave-numbers $\omega$ of the second column of Table 3.3 and to the harmonic term value coefficients in the first row of Table 3.2.

Table 3.2: Term value coefficients of CO\textsubscript{2}.

<table>
<thead>
<tr>
<th>$\omega_1$</th>
<th>$\omega_2$</th>
<th>$\omega_3$</th>
<th>$x_{11}$</th>
<th>$x_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1351.2 *</td>
<td>672.2 *</td>
<td>2396.4 *</td>
<td>−0.3</td>
<td>5.7</td>
</tr>
<tr>
<td>$x_{22}$</td>
<td>$x_{33}$</td>
<td>$g_{22}$</td>
<td>$x_{23}$</td>
<td></td>
</tr>
<tr>
<td>−1.3</td>
<td>−12.5</td>
<td>1.7</td>
<td>−11.0</td>
<td>16.7</td>
</tr>
<tr>
<td>$\delta$</td>
<td>$W_{[1,0,0][0,2^0,0]}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>−50.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The value of these harmonic term value coefficients are equal to the value of potential coefficients in the first row of Table 3.1 and to the spectroscopic wave-number $\omega$ in the second column of Table 3.3.

energies with respect to the ground state energy for several vibrational states are presented in terms of spectroscopic wave-numbers $\omega$ by Statz [80 Table I]. By investigation of these results, the set of potential coefficients $\{a\}$, which was previously determined by Dennison [79 Table II], has the best agreement with experimental results. Although the agreement is good, it is not as good as expected. Therefore, Statz draws the conclusion that the set of chosen potential coefficients $\{a\}$ are not quite correct, as the above mentioned method is seen as superior to other attempted perturbation methods by Statz. This potential coefficients $\{a\}$ together with the potential coefficients $\{\omega\}$ are given by Dennison [79 Table II] and Statz [80 Table I, set 4], and are presented here in Table 3.1.

Furthermore, the vibrational wave functions $\psi_v$ for some vibrational states, using this set of potential coefficients $\{a\}$, are determined by Statz [80 Table II] and later adopted by Witteman [70] p.14, Table 2.1.

\textbf{Anharmonicity coefficients of CO\textsubscript{2}} In order to determine the vibrational term values for CO\textsubscript{2} from equation (3.15), the term value coefficients have to be known, which include the potential coefficients $\{\omega\}$ and anharmonicity coefficients $\{x\}$ and $\{g\}$. In principle, these anharmonicity coefficients can be determined from equations (3.16)-(3.22) by using the potential coefficients from Table 3.1. Values for these anharmonicity coefficients are given by Dennison [79 p.187] and Herzberg [66 p.276, III,54] and are presented here in Table 3.2.

As previously discussed in sections 3.1.3 and 3.1.6 in order to determine the energy of the vibrational states of CO\textsubscript{2}, next to the term value coefficients $\{a\}$, $\{x\}$ and $\{g\}$, the values of $W_{ni}$ and $\delta$ are needed to account for the Fermi resonance of certain vibrational levels. The matrix element $W_{[1,0,0][0,2^0,0]}$ given in equation (3.23) is strictly speaking only valid for the Fermi resonance between the vibrational states $[1,0,0]$ and $[0,2^0,0]$. However, for other resonating vibrational states the value of the matrix element $W_{ni}$ differs from $W_{[1,0,0][0,2^0,0]}$ only by a constant. This allows for the use of the value of the matrix element $W_{[1,0,0][0,2^0,0]}$ for all other Fermi resonant pairs. The matrix element $W_{[1,0,0][0,2^0,0]}$ and energy difference $\delta$ are given by Dennison [79] and Herzberg [66 p.218, p.276] and are presented here in the bottom row of Table 3.2. In fact, Dennison actually determined the set of potential coefficients $\{a\}$ from Table 3.1 by using the term value

7 Note that in Dennison [79] not the matrix element is given but a value for $b^2 = 5081$. From footnote 4 it becomes apparent that indeed $W_{[1,0,0][0,2^0,0]} = −\sqrt{1} = −50.4$. 


Table 3.3: Spectroscopic wave-numbers for vibrational states with respect to the vibrational ground state in CO$_2$.

<table>
<thead>
<tr>
<th>States</th>
<th>Unperturbed $\omega^{(0)}$ (cm$^{-1}$)</th>
<th>Calculated $\omega^{(calc)}$ (cm$^{-1}$)</th>
<th>Observed $\omega^{(obs)}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[II]</td>
<td>1351.2</td>
<td>1388.1</td>
<td>1388.4</td>
</tr>
<tr>
<td>[II]</td>
<td>1344.4*</td>
<td>1285.8</td>
<td>1285.5</td>
</tr>
<tr>
<td>[0, 1$^1$, 0]</td>
<td>672.2</td>
<td>667.3</td>
<td>667.3</td>
</tr>
<tr>
<td>[0, 0$^0$, 1]</td>
<td>2396.4</td>
<td>2349.4</td>
<td>2349.3</td>
</tr>
</tbody>
</table>

* This value is twice the value of $\omega_2^{(0)} = 672.2$ cm$^{-1}$, because in the unperturbed case the states [II] and [0, 2, 0] are the same state.

coefficients from Table 3.2, which were deduced from the most accurately known measured energies in experiments.

Wave-numbers of CO$_2$ With the values for all the term value coefficients from Table 3.2, the vibrational term values $G_v$ of the vibrational states of CO$_2$ can be determined. From these vibrational term values $G_v$, the spectroscopic wave-numbers $\omega$ that corresponds to the energy difference between two vibrational states can be calculated. For various different combinations of vibrational states these calculated spectroscopic wave-numbers $\{\omega^{(calc)}\}$ are presented by Dennison [79] Table I and Herzberg [66] p.274, Table 56. The calculated spectroscopic wave-numbers $\{\omega^{(calc)}\}$ corresponding to the energy difference of the vibrational states [I], [II], [0, 1$^1$, 0], and [0, 0$^0$, 1] with the ground state [0, 0$^0$, 0] are adopted in the third column Table 3.3.

These calculated spectroscopic wave-numbers $\{\omega^{(calc)}\}$ of these perturbed vibrational states can be compared to the wave-numbers $\{\omega^{(0)}\}$ of the unperturbed vibrational states. In doing so, it becomes apparent that the an-harmonic potential terms in equation (3.10) express themselves by shifting the energy levels of CO$_2$. Furthermore, it can be noted that the spectroscopic wave-number $\omega^{(calc)}_{[0,0^0,0]-[0,0^0,0]} = 1388.1$ cm$^{-1}$ is indeed higher than expected on the basis of the unperturbed case where it is $\omega^{(0)}_{[0,0^0,0]-[0,0^0,0]} = \omega_1 = 1351.2$ cm$^{-1}$. Also, the spectroscopic wave-number $\omega^{(calc)}_{[0,2^0,0]-[0,0^0,0]} = 1285.8$ cm$^{-1}$ is lower than expected on the basis of the unperturbed case where it is $\omega^{(0)}_{[0,2^0,0]-[0,0^0,0]} = 2 \times \omega_2 = 1344.4$ cm$^{-1}$, or even in the perturbed case without including the correction for the Fermi resonance where it is $\omega^{(0)}_{[0,2^0,0]-[0,0^0,0]} = 2 \times \omega_2^{(calc)} = 1334.6$ cm$^{-1}$. This shows that the energy separation between the considered states is thus indeed larger than when Fermi resonance is not included.

These spectroscopic wave-numbers $\omega$ can also be determined experimentally [8]. Experiments with a low resolution in the spectra of CO$_2$ show the presence of relatively strong bands at 667.3 cm$^{-1}$, 2349.3 cm$^{-1}$, and 1340 cm$^{-1}$. Experiments with a higher resolution show that the band at 1340 cm$^{-1}$ actually consists of two bands at 1285.5 cm$^{-1}$ and 1388.4 cm$^{-1}$ with an intensity ratio of 10:59 [84, 85]. The observed spectroscopic wave-numbers $\omega^{(obs)}$ for various different bands are given by Dennison [79] Table I and Herzberg [66] p.274, Table 56. The observed spectroscopic wave-numbers $\omega^{(obs)}$ corresponding to the energy difference of, again, the vibrational states [I], [II], [0, 1$^1$, 0], and [0, 0$^0$, 1] with the ground state [0, 0$^0$, 0], are adopted in Table 3.3. By comparing the calculated spectroscopic wave-numbers $\{\omega^{(calc)}\}$ with the observed spectroscopic wave-numbers $\{\omega^{(obs)}\}$, it can be concluded that there is a very good agreement between them for CO$_2$. This suggest that the previous analysis and models are a correct interpretation of the CO$_2$ molecule.

[8] How this is done exactly depends on the type of experiment and is not part of the discussion here. What can be said is that the energy difference between states can be emitted as or absorbed through electromagnetic waves, with a corresponding spectroscopic wave-number $\omega$. These wave-number are the so-called "bands" in the spectra.
3.2 Reservoir model

In this section the reservoir model is derived and developed in a general form. Firstly, a description for the species densities is given, which is used to formulate a description for the energy densities. Hereafter, this description is extended using a stoichiometric energy matrix. Next, the concept of energy transfer processes between energy density reservoirs are explained and the ro-translational reservoir is defined. Finally, an expression for the vibrational temperature is determined, which are used in the model to determine the populations in the system.

3.2.1 Species densities

The continuity equation described the temporal and spatial evolution of a quantity. Its differential form is presented in Appendix K. For the particle spatial number density $n$, or just particle density, the continuity equation (K.7) is,

$$\frac{dn}{dt} = -\nabla \cdot \Phi + R.$$  \hspace{1cm} (3.24)

Here, $\Phi$ is the particle density flux, $R$ the particle density source rate. In a zero dimensional model of the gas, a so-called global model, the divergence of the flux $\nabla \cdot \Phi = 0$. In zero dimensions the continuity equation (3.24) reduces to,

$$\frac{dn}{dt} = R.$$  \hspace{1cm} (3.25)

The gas can consist of different types $t$ of molecules. Each molecular type $t$ has a particle type density $n_t$ and a source $R_t$ for which the following conditions hold,

$$n = \sum_t n_t, \hspace{1cm} R = \sum_t R_t.$$  \hspace{1cm} (3.26, 3.27)

Substitution of equation (3.26) and (3.27) in equation (3.25) gives,

$$\sum_t \frac{dn_t}{dt} = \sum_t R_t.$$  \hspace{1cm} (3.28)

This equation (3.28) suggests a continuity equation for each molecular type $t$,

$$\frac{dn_t}{dt} = R_t.$$  \hspace{1cm} (3.29)

A particular type of molecule can occupy different states. The state is defined by the energy distribution within the molecule and is a so-called species $s$. Each species $s$ has a particle species density $n_s$ and a source $R_s$ for which the following conditions hold,

$$n_t = \sum_s n_s, \hspace{1cm} R_t = \sum_s R_s.$$  \hspace{1cm} (3.30, 3.31)

Substitution of equation (3.30) and (3.31) in equation (3.29) gives,

$$\sum_s \frac{dn_s}{dt} = \sum_s R_s.$$  \hspace{1cm} (3.32)

This equation (3.32) suggests a continuity equation for each species $s$,

$$\frac{dn_s}{dt} = R_s.$$  \hspace{1cm} (3.33)
The set of species density equations (3.33) for each species $s$ can be used to describe the evolution of the state of the gas. The set of species density equations can be written compactly in matrix form resulting in the species density matrix equation,

$$\dot{n}_s = R_s$$ \hspace{1cm} (3.34)

with,

$$\dot{n}_s = \begin{bmatrix} \frac{dn_1}{dt} \\ \vdots \\ \frac{dn_s}{dt} \end{bmatrix}, \quad R_s = \begin{bmatrix} R_1 \\ \vdots \\ R_s \end{bmatrix}$$ \hspace{1cm} (3.35)

3.2.2 From species densities to energy densities

A typical particle or molecule occupies one of many possible states depending on the amount of energy it possesses. Therefore, in a gas, which can consist of various types of particles, the number of species can be very large. The particles interact with each other through collisions giving rise to chemical reactions. These reactions describe the redistribution of energy quanta among the colliding particles as a result of their collision. The particles belonging to a certain species can, as a result of this chemical reaction, change to particles belonging to other species. Therefore, these chemical reactions cause changes in the species densities $n_s$. As a consequence the species sources $R_s$ are dependent on multiple species densities $n_s$. These large amount of possible reactions, typically, give rise to a set of species density differential equations (3.33), which is large, complex and coupled. The set is large because of the large number of species $s$ and the large number of possible interactions. The set is coupled because the sources of the species density equations can depend on multiple species density. The set is complex in a way that setting up the equations by taking a particular chemistry is not trivial. These are some disadvantages of using this set of equations to describe the state of a gas or laser plasma.

An alternative description is provided by a so-called reservoir model, being a smaller less complex coupled set of reservoir energy density equations. Each reaction in the whole chemistry of a system has its own probability of occurrence and therefore its own rate of occurrence. Some chemical reactions are very likely to occur an therefore have a relatively high rate in comparison to unlikely chemical reactions which therefore have relatively low rate of occurrence. Often in physics the concept of time scales is one of the first things which taken into account when making a model to make some justified simplifications. The chemistry which only has a significant influence on time scales much larger than the time scale of interest can be ignored simply because it does not have a contribution for the model at hand. For the chemistry on shorter time scales the reactions have occurred so many times that the chemistry reaches an equilibrium state. Often these chemical reactions having a high and low rate are called slow and fast reactions. Note that this has nothing to do with the time the collisional process itself takes, but only with the rate of occurrence within a certain time scale. Results of experiments show that the types of chemical reactions which are considered to be fast are reactions involving only translation, only rotation, only translation and rotation, and only a single specific vibrational mode. The energy levels of these degrees of freedom, therefore, are in thermal equilibrium and have a Boltzmann distribution.

3.2.3 Energy densities

The reservoir energy density equations are derived from the species density equations. In this way, the reservoir model is derived in a general framework from the comforts of the often used species density description.

The total energy of a particle is given by equation (2.17) and is distributed among its dofs. This distribution of energy in the particle defines its state $a$, therefore the species $s$. The species
3.2. RESERVOIR MODEL

Energy $E_s$ consists of the species dof energies $E_{s,i}$ contained in the different dofs $i$ of the particle,

$$E_s = \sum_i E_{s,i}. \quad (3.37)$$

Multiplying the species continuity equation (3.33) with the species energy of equation (3.37) gives,

$$E_s \frac{dn_s}{dt} = \sum_i E_{s,i} \frac{dn_s}{dt} = \frac{d}{dt}(\sum_i E_{s,i,n_s}) = \sum_i \frac{dU_{s,i,tot}}{dt} = E_s R_s = \sum_i E_{s,i} R_s = \sum_i P_{s,i}. \quad (3.38)$$

Here, $U_{s,i,tot}$ is the total energy density of degree of freedom $i$ of all the particles of species $s$, and $P_{s,i}$ is the power density source of energy density $U_{s,i,tot}$ of degree of freedom $i$ of species $s$. This equation (3.38) suggests a differential equation for each total energy density $U_{s,i,tot}$ of dof $i$ of species $s$,

$$\frac{dU_{s,i,tot}}{dt} = P_{s,i}. \quad (3.39)$$

This creates an equation set with a differential equation for each total energy density of dof $i$ of species $s$. Note that this set is at this point even bigger than the large complex coupled set of species density equations, because for every species now not one equation exists but an equation for every dof of that species. Now, however, the equations for all species $s$ for a dof $i$ are summed, giving,

$$\sum_s \frac{dU_{s,i,tot}}{dt} = \frac{d}{dt}(\sum_s U_{s,i,tot}) = \frac{dU_i}{dt} = \sum_s P_{s,i} = P_{i,tot} = P_i. \quad (3.40)$$

Here, $U_{i,tot} = U_i$ is the total energy density of dof $i$ of all species or reservoir energy density, and $P_{i,tot} = P_i$ the power density source of energy density of dof $i$ of all species. This gives an equation set with a differential equation for each reservoir energy density $U_i$ given by,

$$\frac{dU_i}{dt} = P_i. \quad (3.41)$$

The equation set for the reservoir energy densities $U_i$ in matrix form is,

$$\dot{\mathbf{U}} = \mathbf{P}. \quad (3.42)$$

Here, $\dot{\mathbf{U}}$ is the reservoir energy density rate matrix, and $\mathbf{P}$ is the power density source matrix. The energy density rate vector $\dot{\mathbf{U}}$ is,

$$\dot{\mathbf{U}} = \begin{bmatrix} \frac{dU_0}{dt} \\ \vdots \\ \frac{dU_i}{dt} \end{bmatrix}. \quad (3.43)$$

The power density source matrix $\mathbf{P}$ is,

$$\mathbf{P} = \begin{bmatrix} P_0 \\ \vdots \\ P_i \end{bmatrix}. \quad (3.44)$$

The power density sources $P_i$ result from chemical reactions, which change the energy densities $U_i$ of the reservoirs. This set of reservoir energy density equations is much smaller than the set of species density equations because the number of energy density reservoirs is much smaller than
the number of species. The power density sources result from the reactions in the chemistry which cause energy transfer between the energy density reservoirs making the set less complex. This leads to the reservoir model being a relatively less complex, small, and coupled set of energy density reservoir equations in contrast to the relatively large, complex, and coupled set of species density equations.

The reactions which previously are assumed to be fast are exactly those which do not change the reservoir energy density. These fast reaction redistributes the energy only within a reservoir. As a result, within an energy density reservoirs thermal equilibrium prevails. The energy levels of the dof associated with a reservoir are in thermal equilibrium and, therefore, have a Boltzmann distribution, which is described in section 2.2.1. This Boltzmann distribution of an energy density reservoir is characterized by a temperature defined in equation (2.67) or thermodynamic $\beta$ defined in equation (2.68). Therefore, each energy density reservoir has an associated reservoir temperature $T_i$.

By changing from the species density model to the reservoir model the set of equations has become smaller and less complex. Together with the assumption that the energy levels have a known Boltzmann distribution show some of the advantages of the reservoir model over the species density model.

### 3.2.4 Stoichiometry

In order to set up the energy density equations the power density source matrix $P$ has to be determined. The power density source matrix $P$ is, among other processes, determined by the chemical reactions and their effect on the energy density of the reservoirs. A stoichiometric energy density matrix $\Gamma$ is introduced and used to set up the power source matrix $P$. The power density source matrix $P$ is given by,

$$P = \Gamma R.$$  \hspace{1cm} (3.45)

Here, $R$ is the reaction rate matrix, and $\Gamma$ the stoichiometric energy density matrix. The reaction rate matrix $R$ contains the rate of all chemical reactions,

$$R = \begin{bmatrix} R_1 \\ \vdots \\ R_{N_r} \end{bmatrix}.$$  \hspace{1cm} (3.46)

Here, $N_r$ is the number of reactions. The stoichiometric energy density matrix $\Gamma$ contains the energy density changes on all energy density reservoirs of all chemical reactions,

$$\Gamma = \begin{bmatrix} U_1^{R_1} & \cdots & U_1^{R_{N_r}} \\ \vdots & \ddots & \vdots \\ U_i^{R_1} & \cdots & U_i^{R_{N_r}} \end{bmatrix}.$$  \hspace{1cm} (3.47)

Here, $U_i^{R_{N_r}}$ is the energy density change on energy density reservoir $i$ of chemical reaction $R$. In this stoichiometric energy density matrix $\Gamma$ the number of columns is equal to the number of reaction rate matrix $R$ contains the rate of all chemical reactions, and the number of rows is equal to the number of reservoirs. Substitution of

---

5 Here, the power source matrix $P$ results from the chemical reactions. However, other physical processes leading to changes in the energy densities of reservoirs, such as the interaction with radiation, are also a part of this power density source vector $P$. 

equation (3.46) and (3.47) in to equation (3.45) gives,

\[
\begin{align*}
P &= \begin{bmatrix}
U^{R_1}_0 & \ldots & U^{R_{N_r}}_0 \\
\vdots & \ddots & \vdots \\
U^{R_1}_i & \ldots & U^{R_{N_r}}_i \\
\end{bmatrix}
\begin{bmatrix}
R_1^0 \\
\vdots \\
R_{N_r}^0 \\
\end{bmatrix} = \begin{bmatrix}
U^{R_1}_0 R_1 + \ldots + U^{R_{N_r}}_0 R_{N_r} \\
\vdots \\
U^{R_1}_i R_1 + \ldots + U^{R_{N_r}}_i R_{N_r} \\
\end{bmatrix} = \\
\begin{bmatrix}
\sum_{k=0}^{N_r} P^{R_k}_0 \\
\vdots \\
\sum_{k=0}^{N_r} P^{R_k}_{N_r} \\
\end{bmatrix}.
\end{align*}
\]

(3.48)

Here, \(P^{R_k}_i\) is the power density source of chemical reaction \(k\) on energy density reservoir \(i\).

Setting up the energy density equation set of the reservoir model requires the chemical reaction rates, which are used in the reaction rate matrix \(R\) in equation (3.46). In addition, the stoichiometric energy density matrix \(\Gamma\) of equation (3.47) has to be set up using which requires the energy density changes of the reservoir for all chemical reactions. The power density source matrix \(P\) is then calculated using equation (3.48). This power density source vector in turn can be substituted into equation (3.42) to obtain the energy density equations.

### 3.2.5 Ro-translational reservoir

The energy density reservoirs of translation and rotation do not only have an internal thermal equilibrium, but are also in thermal equilibrium with each other as assumed in section 3.2.2. The translational energy density reservoir has an associated translational temperature and also the rotational energy density reservoir has an associated rotational temperature. The reservoirs being in thermal equilibrium with each other means that this translational temperature and rotational temperature are equal. For this reasons these reservoirs can be taken as one single energy density reservoir containing the energy density of translation and rotation of all particles of all types. This energy density reservoir is characterized by a single temperature for the Boltzmann distribution as explained in section 2.2.1 of both the translational energy levels and rotational energy levels. To the ro-translational energy density reservoir the number 0 is assigned.

In the previous section 3.2.4 the stoichiometric matrix consists of elements, which represent the energy change of a reservoir due to a chemical reaction. The chemical reactions are in essence a redistribution of the energy in the collisions of particles with each other for which energy conservation holds. Using the energy density analogue of Kirchhoff’s circuit law, the energy changes of the reservoirs due to chemical reactions can be related to each other. The energy decrease in reservoirs causes an energy increase in other reservoirs in such a way that energy is conserved. This energy exchange can be considered as the flow of energy between the reservoirs. This flow of energy density to different reservoirs is related using Kirchhoff’s law,

\[
\sum U_i^{R_{N_r}} = 0.
\]

(3.49)

The power density source matrix \(P\) consists of elements which represent the power density change of a reservoir due to a chemical reaction and can be also be related using Kirchhoff’s law,

\[
\sum P_i^{R_{N_r}} = 0.
\]

(3.50)

### 3.2.6 Vibrational temperature

Within an energy density reservoir the energy levels are in thermal equilibrium with each other and have a Boltzmann distribution, with a corresponding reservoir temperature \(T_i\). Applying equation (2.74) for the energy of a collection of harmonic oscillators in thermal equilibrium having a Boltzmann distribution to the vibrational mode reservoir gives the vibrational mode reservoir energy density,

\[
U_{v_x} = n_{v_x} h \nu_x \left( \frac{1}{2} + \frac{1}{e^{\beta_x h \nu_x} - 1} \right).
\]

(3.51)
Here, $n_{t\nu_x}$ is the spatial density. This reservoir energy $U_{\nu_x}$ associated with a vibrational mode consists of two parts, the ground state energy density $U_{\nu_x=0}$ and the internal energy density $U_{\text{int}}$. In the limit that the temperature $T_x$, which is related to the thermodynamic $\beta_x$ in equation (2.68), goes to zero all the harmonic oscillators are in their ground state and the ground state energy density is,

$$\lim_{T \to 0} U_v = \frac{1}{2} n_{t\nu_x} h\nu_x = U_{\nu_x=0}$$  \hspace{1cm} (3.52)

This energy cannot be exchanged and is an inherent motion of the harmonic oscillator. The internal energy density $U_{\text{int}}$ is the energy that can be exchanged and, therefore, can be associated with a vibrational temperature $T_x$. The internal energy density $U_{\text{int}}$ is,

$$U_{\text{int}} = \frac{n_{t\nu_x} h\nu_x}{e^{\beta_x h\nu_x} - 1}. \hspace{1cm} (3.53)$$

This expression (3.53) for the internal energy is used to define an effective vibrational temperature $T_x$. The vibrational temperature $T_x$ associated with the internal energy density is given by,

$$U_{\text{int}} = \frac{n_{t\nu_x} h\nu_x}{e^{\beta_x h\nu_x} - 1} \rightarrow e^{\beta_x h\nu_x} = \frac{n_{t\nu_x} h\nu_x}{U_{\text{int}}} + 1 \rightarrow \beta_x h\nu_x = \ln \left( \frac{n_{t\nu_x} h\nu_x}{U_{\text{int}}} + 1 \right)$$

$$\rightarrow \beta_x = \frac{\ln \left( \frac{n_{t\nu_x} h\nu_x}{U_{\text{int}}} + 1 \right)}{h\nu_x} \rightarrow \frac{1}{k_B T} = \frac{\ln \left( \frac{n_{t\nu_x} h\nu_x}{U_{\text{int}}} + 1 \right)}{h\nu_x}$$

$$\rightarrow T_x = \frac{h\nu_x}{k_B \ln \left( \frac{n_{t\nu_x} h\nu_x}{U_{\text{int}}} + 1 \right)}. \hspace{1cm} (3.54)$$

This expression for the vibrational temperature is associated with the exchangeable energy only. The vibrational temperature can also be defined to be associated with the total energy, which includes not only the internal energy density $U_{\text{int}}$, but also the ground state energy density $U_{\nu_x=0}$. The vibrational temperature $T_x$ associated with the total energy density is given by,

$$\frac{n_{t\nu_x} h\nu_x}{2} + \frac{n_{t\nu_x} h\nu_x}{e^{\beta_x h\nu_x} - 1} = U_{0(0)} + U_{\text{int}} = U_i \rightarrow \frac{n_{t\nu_x} h\nu_x}{e^{\beta_x h\nu_x} - 1} = U_i - \frac{n_{t\nu_x} h\nu_x}{2} = U_{\text{int}}$$

$$\rightarrow T_x = \frac{h\nu_x}{k_B \ln \left( \frac{n_{t\nu_x} h\nu_x}{U_{\text{int}}} + 1 \right)} \rightarrow T_x = \frac{h\nu_x}{k_B \ln \left( \frac{n_{t\nu_x} h\nu_x}{U_{\text{int}} - U_{0(0)}} + 1 \right)} \hspace{1cm} (3.55)$$

Having a total energy density of a collection of harmonic oscillators comprised of a non-exchangeable ground state energy density $U_{\nu_x=0}$ and an exchangeable internal energy density $U_{\text{int}}$ one can choose when talking about the energy in a vibrational dof between the total energy and the exchangeable internal energy density $U_{\text{int}}$. Carefulness is required in dealing with these definitions and it is important to clearly state which definition is used. In this thesis the vibrational temperature of equation (3.54) is used, which is based on the exchangeable internal energy $U_{\text{int}}$ alone. The vibrational mode reservoir temperatures $T_i$ are, therefore, using equation (3.54), given by,

$$T_i = \frac{h\nu_x}{k_B \ln \left( k_i \frac{n_{t\nu_x} h\nu_x}{B_i} + 1 \right)}. \hspace{1cm} (3.56)$$

Here, $k_i$ is the degeneracy of the vibrational mode.

### 3.2.7 Populations

All particles are in some particular state and, therefore, belong to a particular species. The number of particles occupying a certain state is the occupation number. The occupation numbers
Figure 3.1: Energy levels of a particle consisting of a stack of translational energy levels between the rotational level and a stack of rotational levels between the vibrational levels.

...are related using a particular form of the Boltzmann distribution equation (2.60) to the energy of the states. A state described the distribution of the total energy of the particle amongst its dofs. The spacing between the energy levels depends on the particular dof. As described in section 2.2.2, the energy spacing between the translational energy levels is very small, so small even that they can be assumed to be almost continuous leading to the approximation of the sum in equation (2.61) to an integral in equation (2.82) for the translational partition function. Furthermore, the spacing between the rotational energy levels is much smaller than the spacing between the vibrational energy levels, leading again to the transition to an integral in equation (2.85) for the rotational partition function. The electronic energy levels are even more widely spaced than the vibrational levels. In considering the rotational and vibrational energy of a particle, the spacing between the energy levels of the particle for the most part corresponds to that of the rotational levels. Many energy levels of the particle exist between subsequent vibrational energy levels of the particle caused by the many much smaller possible rotational energy levels. In this way, each vibrational energy level can be imagined to have a stack of rotational energy levels. In turn, each rotational level can be imagined to have a stack of translational energy levels, as illustrated in Figure 3.1. Together the energy levels of the dofs comprise the total energy level or state of the particle.

3.3 Reservoir model for a CO$_2$-N$_2$-He-CO gas mixture

In this section the general reservoir model, previously derived in section 3.2, is applied to a CO$_2$-N$_2$-He-CO gas mixture with a specific chemistry. Firstly, the specific chemistry is introduced, containing the considered collisional processes in which energy can be transferred between the energy reservoirs. Using this chemistry the energy density reservoir equations are developed, containing the contribution of all considered energy transfers. Hereafter, general expression for specific energy transfer processes such as VT, VV, and VVV-transitions and the VV-transition between symmetric and bending mode of CO$_2$ are determined. These are used to rewrite the previously developed energy density reservoir equations. Next, the terms for different energy density reservoirs arising from a single collisional process are related to each other. Next, additional expressions describing the gas flow and the electron excitation are presented. Explicit expressions for the reservoir temperatures are determined using the general expression developed in section 3.2.6. Finally, all the expressions and relations are used to construct the reservoir model equations.

3.3.1 Chemistry

To determine the energy density equations (3.42) describing the gas mixture the power source matrix $P$ of equations (3.45) and (3.48) has to be determined. This power source matrix depends on the chemistry and only the chemical reactions which change the energy density of the reservoirs...
have a contribution to the power source matrix $P$. The stoichiometric matrix $\Gamma$ is then used to determine what the effect of a chemical reaction is on the energy density reservoirs.

The complete chemistry of a gas consists all the possible chemical reactions that occur. For the reservoir model not the complete chemistry has to be taken into account. As discussed in section 3.2.2 some part of chemistry is considered to be fast. This chemistry is responsible for the energy transfer within the energy density reservoirs and not between them. For these reasons that part of the chemistry does not contribute to the power source matrix $P$. For the chemical reactions which do contribute to the energy transfer between the energy density reservoirs some assumptions can be made. Reactions involving more than two particles, more than two dofs, and the change of more than one quantum, are ignored. In reactions involving more than one vibrational mode the change of energy in the vibrational modes is of opposite sign. In reactions involving more vibrational modes the change of one vibrational mode is in one molecule and the change of the other vibrational mode is in the other molecule. There are, however, some exceptions to these assumptions and these chemical reactions are stated explicitly below. In Table 3.4 the chemical reactions assumed to occur in the CO$_2$-N$_2$-He-CO gas mixture are listed.

Table 3.4: Reaction equations of the chemistry used for the CO$_2$-N$_2$-He-CO gas mixture.

<table>
<thead>
<tr>
<th>Reaction equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$-CO$_2$ collisions</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + \text{CO}_2[v_1, v_2, v_3] \rightarrow \text{CO}_2[v_1 \pm 1, v_2, v_3] + \text{CO}_2[v_1, v_2, v_3]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + \text{CO}_2[v_1, v_2, v_3] \rightarrow \text{CO}_2[v_1 \pm 1, v_2, v_3] + \text{CO}_2[v_1, v_2 \mp 1, v_3]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + \text{CO}_2[v_1, v_2, v_3] \rightarrow \text{CO}_2[v_1 \pm 1, v_2, v_3] + \text{CO}_2[v_1, v_2, v_3 \mp 1]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + \text{CO}_2[v_1, v_2, v_3] \rightarrow \text{CO}_2[v_1, v_2 \pm 1, v_3] + \text{CO}_2[v_1, v_2, v_3]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + \text{CO}_2[v_1, v_2, v_3] \rightarrow \text{CO}_2[v_1, v_2 \pm 1, v_3] + \text{CO}_2[v_1, v_2, v_3]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + \text{CO}_2[v_1, v_2, v_3] \rightarrow \text{CO}_2[v_1 \mp 1, v_2 \pm 1, v_3] + \text{CO}_2[v_1, v_2, v_3]$</td>
</tr>
<tr>
<td>CO$_2$-N$_2$ collisions</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + N_2[v_4] \rightarrow \text{CO}_2[v_1 \pm 1, v_2, v_3] + N_2[v_4]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + N_2[v_4] \rightarrow \text{CO}_2[v_1 \pm 1, v_2, v_3] + N_2[v_4 \mp 1]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + N_2[v_4] \rightarrow \text{CO}_2[v_1, v_2 \pm 1, v_3] + N_2[v_4]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + N_2[v_4] \rightarrow \text{CO}_2[v_1, v_2, v_3 \mp 1] + N_2[v_4]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + N_2[v_4] \rightarrow \text{CO}_2[v_1, v_2, v_3 \pm 1] + N_2[v_4]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + N_2[v_4] \rightarrow \text{CO}_2[v_1, v_2, v_3 \pm 1] + N_2[v_4 \mp 1]$</td>
</tr>
<tr>
<td>CO$_2$-He collisions</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + N_2[v_4] \rightarrow \text{CO}_2[v_1 \pm 1, v_2 \pm 1, v_3] + N_2[v_4]$</td>
</tr>
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<td>$\text{CO}_2[v_1, v_2, v_3] + N_2[v_4] \rightarrow \text{CO}_2[v_1 \pm 1, v_2 \pm 1, v_3] + N_2[v_4 \mp 1]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + N_2[v_4] \rightarrow \text{CO}_2[v_1 \pm 1, v_2 \pm 1, v_3 \mp 1] + N_2[v_4 \mp 1]$</td>
</tr>
<tr>
<td>$\text{CO}_2[v_1, v_2, v_3] + N_2[v_4] \rightarrow \text{CO}_2[v_1 \pm 1, v_2 \pm 2, v_3] + N_2[v_4]$</td>
</tr>
</tbody>
</table>

Continued on next page
### 3.3. RESERVOIR MODEL FOR A CO$_2$-N$_2$-HE-CO GAS MIXTURE

**Reaction equation**

<table>
<thead>
<tr>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$[v$_1$, v$_2$, v$_3$] + He $\rightarrow$ CO$_2$[v$_1$ ± 1, v$_2$, v$_3$] + He</td>
</tr>
<tr>
<td>CO$_2$[v$_1$, v$_2$, v$_3$] + He $\rightarrow$ CO$_2$[v$_1$, v$_2$ ± 1, v$_3$] + He</td>
</tr>
<tr>
<td>CO$_2$[v$_1$, v$_2$, v$_3$] + He $\rightarrow$ CO$_2$[v$_1$, v$_2$, v$_3$ ± 1] + He</td>
</tr>
<tr>
<td>CO$_2$[v$_1$, v$_2$, v$_3$] + He $\rightarrow$ CO$_2$[v$_1$ ± 1, v$_2$ ± 1, v$_3$ ± 1] + He</td>
</tr>
<tr>
<td>CO$_2$[v$_1$, v$_2$, v$_3$] + He $\rightarrow$ CO$_2$[v$_1$, v$_2$, v$_3$ ± 2] + He</td>
</tr>
</tbody>
</table>

**CO$_2$-CO collisions**

<table>
<thead>
<tr>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$[v$_1$, v$_2$, v$_3$] + CO[v$_5$] $\rightarrow$ CO$_2$[v$_1$ ± 1, v$_2$, v$_3$] + CO[v$_5$]</td>
</tr>
<tr>
<td>CO$_2$[v$_1$, v$_2$, v$_3$] + CO[v$_5$] $\rightarrow$ CO$_2$[v$_1$ ± 1, v$_2$, v$_3$] + CO[v$_5$ ± 1]</td>
</tr>
<tr>
<td>CO$_2$[v$_1$, v$_2$, v$_3$] + CO[v$_5$] $\rightarrow$ CO$_2$[v$_1$, v$_2$ ± 1, v$_3$] + CO[v$_5$]</td>
</tr>
<tr>
<td>CO$_2$[v$_1$, v$_2$, v$_3$] + CO[v$_5$] $\rightarrow$ CO$_2$[v$_1$, v$_2$, v$_3$ ± 1] + CO[v$_5$]</td>
</tr>
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<td>CO$_2$[v$_1$, v$_2$, v$_3$] + CO[v$_5$] $\rightarrow$ CO$_2$[v$_1$, v$_2$, v$_3$ ± 1] + CO[v$_5$ ± 1]</td>
</tr>
<tr>
<td>CO$_2$[v$_1$, v$_2$, v$_3$] + CO[v$_5$] $\rightarrow$ CO$_2$[v$_1$, v$_2$, v$_3$ ± 2] + CO[v$_5$]</td>
</tr>
</tbody>
</table>

**N$_2$-N$_2$ collisions**

<table>
<thead>
<tr>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$[v$_4$] + N$_2$[v$_4$] $\rightarrow$ N$_2$[v$_4$ ± 1] + N$_2$[v$_4$]</td>
</tr>
</tbody>
</table>

**N$_2$-He collisions**

<table>
<thead>
<tr>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$[v$_4$] + He $\rightarrow$ N$_2$[v$_4$ ± 1] + He</td>
</tr>
</tbody>
</table>

**N$_2$-CO collisions**

<table>
<thead>
<tr>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$[v$_4$] + CO[v$_5$] $\rightarrow$ N$_2$[v$_4$ ± 1] + CO[v$_5$]</td>
</tr>
<tr>
<td>N$_2$[v$_4$] + CO[v$_5$] $\rightarrow$ N$_2$[v$_4$ ± 1] + CO[v$_5$ ± 1]</td>
</tr>
<tr>
<td>N$_2$[v$_4$] + CO[v$_5$] $\rightarrow$ N$_2$[v$_4$] + CO[v$_5$ ± 1]</td>
</tr>
</tbody>
</table>

**He-CO collisions**

<table>
<thead>
<tr>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>He + CO[v$_5$] $\rightarrow$ He + CO[v$_5$ ± 1]</td>
</tr>
</tbody>
</table>

**CO-CO collisions**

<table>
<thead>
<tr>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO[v$_5$] + CO[v$_5$] $\rightarrow$ CO[v$_5$ ± 1] + CO[v$_5$]</td>
</tr>
</tbody>
</table>
3.3.2 Energy density reservoir equations

The different types of molecules in the CO$_2$-N$_2$-He-CO gas mixture each have different translational, rotational and vibrational dofs. The ro-translational energy density reservoir consists of the translational energy and rotational energy of all particles of all types. Distinct vibrational modes exist in the CO$_2$, N$_2$ and CO molecules, where CO$_2$ has three vibrational modes, while N$_2$ and CO each have one vibrational mode. For these five unique vibrational modes there are five corresponding energy density reservoirs. In total there are thus six energy density reservoirs in the reservoir model for this particular gas mixture. Together these energy densities contain all the energy possessed by the particles in the system. The energy density content together with their associated number label for the reservoirs is listed next.

- Reservoir 0 contains the translational energy and rotational energy of all particles of all types.

- Reservoir 1 contains the energy density of the symmetric stretching mode of all CO$_2$ molecules.

- Reservoir 2 contains the energy density of the bending mode of all CO$_2$ molecules.

- Reservoir 3 contains the energy density of the asymmetric stretching mode of all CO$_2$ molecules.

- Reservoir 4 contains the energy density of the vibrational mode of all N$_2$ molecules.

- Reservoir 5 contains the energy density of the vibrational mode of all CO molecules.

In the following the energy density equations with the chemistry from section 3.3.1 are set up. The power density source terms $P$ have superscripts indicating the types of particles which are involved in the chemical reaction described by the term. Their subscripts indicate the change in the number of energy quanta of the energy reservoirs as a result of the described chemical reaction. The power source acts on the reservoir associated with the first subscript of the power source term. For a clear overview the power sources terms are sorted such that terms which involve equal energy density reservoirs and equal energy changes are presented on the same equation line. This sorting is especially helpful when in section 3.3.3 section 3.3.4 section 3.3.5 and section 3.3.6 expressions are developed for the power source terms which involve equal energy density reservoirs and equal
3.3. RESERVOIR MODEL FOR A CO$_2$-N$_2$-He-CO GAS MIXTURE

energy changes. The energy density reservoir equations for the CO$_2$-N$_2$-He-CO reservoir model,

\[
\frac{dU_0}{dt} = + p^{CO_2-CO}_1 + p^{CO_2-N_2}_1 + p^{CO_2-He}_1 + p^{CO_2-CO}_1
\]

\[
+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
\]

\[
+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
\]

\[
+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
\]

\[
+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
\]

\[
+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
\]

\[
+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
\]

\[
\frac{dU_1}{dt} = - p^{CO_2-CO}_1 - p^{CO_2-N_2}_1 - p^{CO_2-He}_1 - p^{CO_2-CO}_1
\]

\[
+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
\]

\[
+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
\]

\[
+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
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+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
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\]

\[
+ p^{CO_2-CO}_v + p^{CO_2-N_2}_v + p^{CO_2-He}_v + p^{CO_2-CO}_v
\]
3.3.3 VT-transitions

General VT-transitions

Energy transfer between vibrational dofs and translational dofs is often referred to as VT-transitions. A general expression is determined to describe the power source terms involving an energy density reservoir \( U_x \) corresponding to a vibrational mode \( v_x \) with \( x = 1, 2, 3, 4, 5 \) and the ro-translational reservoir, where the energy changes by one energy quantum. The power \( R_{v_x \pm 1}^{t_{v_x \pm 1}} \) is given by,

\[
P_{v_x \pm 1}^{t_{v_x \pm 1}} = U_{v_x \pm 1}^{t_{v_x \pm 1}} R_{v_x \pm 1}^{t_{v_x \pm 1}}.
\]

Here, \( U_{v_x \pm 1}^{t_{v_x \pm 1}} \) is the energy change caused by the reactions between molecule types \( t_{v_x} \) and \( t \), which involve only the change of \( v_x \) of one quantum, and \( R_{v_x \pm 1}^{t_{v_x \pm 1}} \) is the rate caused by the reactions.
between molecule types \( t_{xz} \) and \( t \), which involve only the change of \( v_x \) of one quantum. The vibration is modeled as a harmonic oscillator, as described in section \( 2.1.3 \), and the energy change in vibrational mode \( x \) is according to equation \( (2.41) \), therefore, given by,

\[
U^{t_{xz}}_{v_x \pm 1} = \pm \hbar \nu_x. \tag{3.64}
\]

The energy change in the ro-translational reservoir is then given by the same term with opposite sign,

\[
U^{t_{xz}}_{v_x \pm 1} = \mp \hbar \nu_x. \tag{3.65}
\]

The rate is given by,

\[
R^{t_{xz}}_{v_x \pm 1} = \sum_{[v_x],[j]} n_{t_{v_x}} n_{t_{j}} k^{t_{v_x}}_{v_x \pm 1}. \tag{3.66}
\]

Here, \([v_x] \) is the energy level of \( v_x \), \( n_{t_{v_x}} \) is the spatial number density of molecules of type \( t_{v_x} \) having energy level \([v_x] \) of \( v_x \), \( [j] \) is the energy level or the state of the molecules of type \( t \), and \( k^{t_{v_x}}_{v_x \pm 1} \) is the rate coefficient caused by the reactions between molecule types \( t_{v_x} \) and \( t \), which involve only the change of \( v_x \) of one quantum. For these spatial number densities the following conditions hold \( \sum_{[v_x]} n_{t_{v_x}} = n_{t_{v_x}} \) and \( \sum_{[j]} n_{t_{j}} = n_{t} \). Substitution of equation \( (3.64) \) and equation \( (3.66) \) into equation \( (3.63) \) gives,

\[
P^{t_{v_x}}_{v_x \pm 1} = \pm \hbar \nu_x \sum_{[v_x],[j]} n_{t_{v_x}} n_{t_{j}} (k^{t_{v_x}}_{v_x \pm 1}) = \pm \hbar \nu_x n_{t_{v_x}} n_{t_{j}} k^{t_{v_x}}_{v_x \pm 1}. \tag{3.67}
\]

Writing out the terms for the plus-minus signs in the subscripts of the rate coefficient gives,

\[
P^{t_{v_x}}_{v_x \pm 1} = \sum_{[v_x],[j]} \pm \hbar \nu_x n_{t_{v_x}} n_{t_{j}} (k^{t_{v_x}}_{v_x \pm 1} - k^{t_{v_x}}_{v_x \pm 1}). \tag{3.68}
\]

The rate coefficient \( k^{t_{v_x}}_{v_x \pm 1} \), which corresponds to reactions involving different levels \( v_x \) of vibrational mode \( v_x \) and increasing it by one energy quantum, is related to the rate coefficient \( k^{t_{v_x}}_{v_x=0=v_x=1} \) of the reaction involving the change of level \( v_x = 0 \rightarrow v_x = 1 \) according to,

\[
k^{t_{v_x}}_{v_x = 0 = v_x = 1} = (v_x + 1) k^{t_{v_x}}_{v_x = 0 = v_x = 1}. \tag{3.69}
\]

The rate coefficient \( k^{t_{v_x}}_{v_x-1} \), which corresponds to reaction involving different levels \( v_x \) of vibrational mode \( v_x \) and decreasing it by one energy quantum, is related to the rate coefficient \( k^{t_{v_x}}_{v_x=1=v_x=0} \) of the reaction involving the change of level \( v_x = 1 \rightarrow v_x = 0 \) according to,

\[
k^{t_{v_x}}_{v_x = 1 = v_x = 0} = v_x k^{t_{v_x}}_{v_x = 1 = v_x = 0}. \tag{3.70}
\]

Substitution of equations \( (3.69) \) and \( (3.70) \) into equation \( (3.68) \) gives,

\[
P^{t_{v_x}}_{v_x \pm 1} = \sum_{[v_x],[j]} \pm \hbar \nu_x n_{t_{v_x}} n_{t_{j}} ((v_x + 1) k^{t_{v_x}}_{v_x = 0 = v_x = 1} - v_x k^{t_{v_x}}_{v_x = 1 = v_x = 0}). \tag{3.71}
\]

Writing out the terms and sorting the summations gives,

\[
P^{t_{v_x}}_{v_x \pm 1} = k^{t_{v_x}}_{v_x=0 \rightarrow v_x=1} \left( \sum_{[v_x]} n_{t_{v_x}} v_x h \nu_x \sum_{[j]} n_{t_{j}} + h \nu_x \sum_{[v_x]} n_{t_{v_x}} \sum_{[j]} n_{t_{j}} \right) - k^{t_{v_x}}_{v_x=1 \rightarrow v_x=0} \left( \sum_{[v_x]} n_{t_{v_x}} v_x h \nu_x \sum_{[j]} n_{t_{j}} \right). \tag{3.72}
\]

The summations in this equation \( (3.72) \) are given by,
Here, \( n_{t_{v_x}} \) is the spatial number density of molecule of type \( t_{v_x} \), \( n_t \) the spatial number density of molecules of type \( t \), and \( U_t \) the energy above ground state of vibrational mode \( x \) of all molecules with all levels \([v_x]\). Substitution of these summations into equation (3.72) gives,

\[
p_{t_{v_x} \rightarrow t_{v_x}} = k_{t_{v_x} = 0 
rightarrow v_x} (U_x n_t + h\nu_x n_{t_{v_x}} n_t) - k_{t_{v_x} = 1 
rightarrow v_x} (U_x n_t).
\]

The rate coefficients \( k_{t_{v_x} = 0 
rightarrow v_x} \) and \( k_{t_{v_x} = 1 
rightarrow v_x} \) are related to each other by,

\[
k_{t_{v_x} = 0 
rightarrow v_x} = k_{t_{v_x} = 1 
rightarrow v_x} (e^{-\beta \nu_x} - 1) + n_{t_{v_x}} h\nu_x e^{-\beta \nu_x}.
\]

Substitution of this relation (3.77) into equation (3.76) gives,

\[
p_{t_{v_x} \rightarrow t_{v_x}} = n_t \left( k_{t_{v_x} = 0 
rightarrow v_x} (U_x + h\nu_x n_{t_{v_x}}) - k_{t_{v_x} = 1 
rightarrow v_x} (U_x + h\nu_x n_{t_{v_x}}) - U_x \right)
\]

At equilibrium the energy density above ground state of a collection of identical harmonic oscillators is given by,

\[
U_x^q (T_0) = n_{t_{v_x}} h\nu_x (e^{\beta \nu_x} - 1)^{-1} \rightarrow n_{t_{v_x}} h\nu_x = U_x^q (T_0) (e^{\beta \nu_x} - 1).
\]

Substitution of equation (3.79) into equation (3.78) gives,

\[
p_{t_{v_x} \rightarrow t_{v_x}} = n_t k_{t_{v_x} = 0 
rightarrow v_x} (U_x + h\nu_x n_{t_{v_x}}) - k_{t_{v_x} = 1 
rightarrow v_x} (U_x + h\nu_x n_{t_{v_x}}) - U_x
\]

Note that this power source term \( P_{t_{v_x} \rightarrow t_{v_x}} \) is for the reaction between molecules of type \( t_{v_x} \) with type \( t \). Every type \( t \) molecule has a translational energy mode so the reaction can occur with all types \( t \) of molecules present in the system. Therefore the power source terms for the reactions of molecules of type \( t_{v_x} \) with type \( t \) are summed over all types \( t \) to give the source \( P_{t_{v_x} \pm 1} \) that contains all sources that change \( v_x \) given by,

\[
P_{t_{v_x} \pm 1} = \sum_t (U_x - U_x^q (T_0)) n_t k_{t_{v_x} = 0 
rightarrow v_x} (e^{-\beta \nu_x} - 1).
\]

This can be rewritten to give a more compact mathematical description for the power source term,

\[
P_{t_{v_x} \pm 1} = \frac{U_x - U_x^q (T_0)}{\tau_x (T_0)}.
\]

Here \( \tau_x \) is the relaxation time defined as,

\[
\tau_x (T_0)^{-1} = (e^{-\beta \nu_x} - 1) \sum_t n_t k_{t_{v_x} = 0 
rightarrow v_x}.
\]
3.3. RESERVOIR MODEL FOR A CO$_2$-N$_2$-HE-CO GAS MIXTURE

For an approximation independent of the ro-translational temperature $T_0$ the relaxation time $\tau_{x0}(T_0)$ is given by [20, p.51 eq.2.79] [30],

$$\tau_{x0}(T_0)^{-1} \approx \sum t_n k_{v_x=1 \rightarrow v_x=0}.$$

(3.84)

This general expression for VT-transitions can be applied to the VT-transitions of the considered chemistry. In this way, the explicit expressions for the VT-transitions substitute the power density source terms in the energy density reservoir equations. The VT-relaxation times appearing in the explicit terms of the energy density reservoir equations are presented next.

VT-relaxation $\tau_{10}$

The relaxation time $\tau_{10}(T_0)$ is given by,

$$\tau_{10}(T_0)^{-1} = \left( e^{-\frac{\hbar v_{10}}{kT_0}} - 1 \right) \left( n_{\text{CO}_2} k_{v_1=1 \rightarrow v_2=0} + n_{\text{N}_2} k_{v_1=1 \rightarrow v_2=0} + n_{\text{CO}} k_{v_1=1 \rightarrow v_2=0} \right) \left( n_{\text{He}} k_{v_1=1 \rightarrow v_2=0} + n_{\text{CO}} k_{v_1=1 \rightarrow v_2=0} \right)$$

(3.85)

For an approximation which is independent of the ro-translational temperature $T_0$ Manes and Seguin [36], and Smith [20, p.51 eq.2.79] give that the relaxation time $\tau_{10}(T_0)$ is given by,

$$\tau_{10}(T_0)^{-1} \approx \sum t_n k_{v_1=1 \rightarrow v_2=0} = n_{\text{CO}_2} k_{v_1=1 \rightarrow v_2=0} + n_{\text{N}_2} k_{v_1=1 \rightarrow v_2=0} + n_{\text{CO}} k_{v_1=1 \rightarrow v_2=0} + n_{\text{He}} k_{v_1=1 \rightarrow v_2=0} + n_{\text{CO}} k_{v_1=1 \rightarrow v_2=0}.$$  

(3.86)

According to Smith [20, p.49 ch2.7.2],

$$\tau_{10}(T_0) = 4.5 \tau_{20}(T_0).$$

(3.87)

VT-relaxation $\tau_{20}$

The relaxation time $\tau_{20}(T_0)$ is given by,

$$\tau_{20}(T_0)^{-1} = \left( e^{-\frac{\hbar v_{20}}{kT_0}} - 1 \right) \left( n_{\text{CO}_2} k_{v_1=1 \rightarrow v_2=0} + n_{\text{N}_2} k_{v_1=1 \rightarrow v_2=0} + n_{\text{CO}} k_{v_1=1 \rightarrow v_2=0} + n_{\text{He}} k_{v_1=1 \rightarrow v_2=0} + n_{\text{CO}} k_{v_1=1 \rightarrow v_2=0} \right).$$

(3.88)

The rate coefficients $k_{v_1=1 \rightarrow v_2=0}$ and $k_{v_1=1 \rightarrow v_2=0}$ are given by Smith [20] to be,

$$k_{v_1=1 \rightarrow v_2=0} = 4.6 \cdot 10^{-10} e^{-77T_0^{-\frac{1}{2}}}.$$  

(3.89)

$$k_{v_1=1 \rightarrow v_2=0} = 6.82 \cdot 10^{-8} e^{-77T_0^{-\frac{1}{2}}}.$$  

(3.90)

The rate coefficients $k_{v_1=1 \rightarrow v_2=0}$ and $k_{v_1=1 \rightarrow v_2=0}$ are given by Taylor [36] to be,

$$k_{v_1=1 \rightarrow v_2=0} = 9.6 \cdot 10^{-11} e^{-77T_0^{-\frac{1}{2}}}.$$  

(3.91)

$$k_{v_1=1 \rightarrow v_2=0} = 8.1 \cdot 10^{-11} e^{-45T_0^{-\frac{1}{2}}}.$$  

(3.92)

For an approximation which is independent of the ro-translational temperature $T_0$ Manes and Seguin [36], and Smith [20, p.51 eq.2.79] give that the relaxation time $\tau_{20}(T_0)$ is given by,

$$\tau_{20}(T_0)^{-1} \approx \sum t_n k_{v_1=1 \rightarrow v_2=0} = n_{\text{CO}_2} k_{v_1=1 \rightarrow v_2=0} + n_{\text{N}_2} k_{v_1=1 \rightarrow v_2=0} + n_{\text{CO}} k_{v_1=1 \rightarrow v_2=0} + n_{\text{He}} k_{v_1=1 \rightarrow v_2=0} + n_{\text{CO}} k_{v_1=1 \rightarrow v_2=0}.$$  

(3.93)
VT-relaxation $\tau_{30}$

The relaxation time $\tau_{30}$ ($T_0$) is given by,

$$\tau_{30} (T_0)^{-1} = \left( e^{-\frac{h\nu_{CO}}{kT}} - 1 \right) (n_{CO}k_{CO^{-}CO}^{\text{N}_2-\text{CO}_2} + n_{N_2}k_{N_2-\text{CO}}^{\text{He}-\text{CO}} + n_{He}k_{\text{He}-\text{CO}}^{\text{N}_2-\text{He}} + n_{CO}k_{\text{CO}^{-}CO}^{\text{N}_2-\text{CO}_2})^0 (3.94)$$

According to Witteman [14] the process corresponding to this relaxation time is negligibly slow compared to the $\tau_{3}$ transitions.

VT-relaxation $\tau_{40}$

The relaxation time $\tau_{40}$ ($T_0$) is given by,

$$\tau_{40} (T_0)^{-1} = \left( e^{-\frac{h\nu_{CO}}{kT}} - 1 \right) (n_{CO}k_{CO^{-}CO}^{\text{N}_2-\text{CO}_2} + n_{N_2}k_{N_2-\text{CO}}^{\text{He}-\text{CO}} + n_{He}k_{\text{He}-\text{CO}}^{\text{N}_2-\text{He}} + n_{CO}k_{\text{CO}^{-}CO}^{\text{N}_2-\text{CO}_2})^0 (3.95)$$

VT-relaxation $\tau_{50}$

The relaxation time $\tau_{50}$ ($T_0$) is given by,

$$\tau_{50} (T_0)^{-1} = \left( e^{-\frac{h\nu_{CO}}{kT}} - 1 \right) (n_{CO}k_{CO^{-}CO}^{\text{N}_2-\text{CO}_2} + n_{N_2}k_{N_2-\text{CO}}^{\text{He}-\text{CO}} + n_{He}k_{\text{He}-\text{CO}}^{\text{N}_2-\text{He}} + n_{CO}k_{\text{CO}^{-}CO}^{\text{N}_2-\text{CO}_2})^0 (3.96)$$

### 3.3.4 VV-transitions

**General VV-transitions**

Energy transfer between vibrational dofs is referred to as VV-transitions. In this section a general expression is determined to describe the power source terms involving a energy density reservoir $U_x$ corresponding to a vibrational mode $v_x$ and an energy density reservoir $U_y$ corresponding to a vibrational mode $v_y$ with $x, y = 1, 2, 3, 4, 5,$ where the energy changes by one energy quantum.

The power source term $P_{v_x \pm 1, v_y \mp 1}$ describing a reaction which involves the change of two vibrational modes $v_x$ and $v_y$ each by one quantum and of opposite sign between molecules each containing one of the vibrational modes can be written as,

$$P_{v_x \pm 1, v_y \mp 1} = \sum_{m} P_{v_x \pm 1, v_y \mp 1}^{t_{v_x} - t_{v_y}}$$

(3.97)

Here, $v_x$ the vibrational mode $x$, $v_y$ the vibrational mode $y$, $P_{v_x \pm 1, v_y \mp 1}$ the power caused by reactions which involve only a change of two vibrational modes $v_x$ and $v_y$ each by one quantum and of opposite sign, $m$ the possible type of molecules with which the molecule of type $t_{v_x}$ can react to involve both $v_x$ and $v_y$. The power $P_{v_x \pm 1, v_y \mp 1}$ is given by,

$$P_{v_x \pm 1, v_y \mp 1}^{t_{v_x} - t_{v_y}} = U_{v_x \pm 1, v_y \mp 1}^{t_{v_x} - t_{v_y}} R_{v_x \pm 1, v_y \mp 1}^{t_{v_x} - t_{v_y}}$$

(3.98)

Here, $U_{v_x \pm 1, v_y \mp 1}^{t_{v_x} - t_{v_y}}$ is the energy change caused by the reaction between molecules of type $t_{v_x}$ and $t_{v_y}$, which involve the change of one quantum of $v_x$ and a change of opposite sign of one quantum of $v_y$, and $R_{v_x \pm 1, v_y \mp 1}^{t_{v_x} - t_{v_y}}$ is the rate caused by the reaction between molecules of type $t_{v_x}$ and $t_{v_y}$, which involve the change of one quantum of $v_x$ and a change of opposite sign of one quantum of $v_y$. Substitution of this equation (3.98) into equation (3.97) gives,

$$P_{v_x \pm 1, v_y \mp 1} = U_{v_x \pm 1, v_y \mp 1}^{t_{v_x} - t_{v_y}} R_{v_x \pm 1, v_y \mp 1}^{t_{v_x} - t_{v_y}}$$

(3.99)
The summations in this equation (3.107) are given by,

\[ P_{v_x \pm 1, v_y \mp 1} = \pm h\nu_x. \]  

(3.100)

The rate \( R_{v_x \pm 1, v_y \mp 1} \) is given by,

\[
R_{v_x \pm 1, v_y \mp 1} = \sum_{[v_x],[v_y]} n_{[v_x]} n_{[v_y]} k_{[v_x] \pm 1,[v_y] \mp 1}^{v_x - v_y}. \tag{3.101}
\]

Here, \( k_{[v_x] \pm 1,[v_y] \mp 1}^{v_x - v_y} \) is the rate coefficient caused by the reactions between molecule types \( t_{v_x} \) and \( t_{v_y} \), which involve only the change of \( v_x \) of one quantum and a change of opposite sign of one quantum of \( v_y \). Substitution of equation (3.100) and equation (3.101) into equation (3.99) gives,

\[
P_{v_x \pm 1, v_y \mp 1} = \pm h\nu_x \sum_{[v_x],[v_y]} n_{[v_x]} n_{[v_y]} k_{[v_x] \pm 1,[v_y] \mp 1}^{v_x - v_y} = \sum_{[v_x],[v_y]} \pm h\nu_x n_{[v_x]} n_{[v_y]} k_{[v_x] \pm 1,[v_y] \mp 1}^{v_x - v_y}. \tag{3.102}
\]

Writing out the terms for the plus-minus signs in the subscripts of the rate coefficients gives,

\[
P_{v_x \pm 1, v_y \mp 1} = \sum_{[v_x],[v_y]} h\nu_x n_{[v_x]} n_{[v_y]} \left( k_{[v_x] \pm 1,[v_y] \mp 1}^{v_x - v_y} - k_{[v_x] \mp 1,[v_y] \pm 1}^{v_x - v_y} \right). \tag{3.103}
\]

The rate coefficient \( k_{[v_x] \pm 1,[v_y] \mp 1}^{v_x - v_y} \) and \( k_{[v_x] \mp 1,[v_y] \pm 1}^{v_x - v_y} \) are related to respectively the rate coefficients \( k_{[v_x] = 0,[v_y] = 0}^{v_x \rightarrow v_y} \) and \( k_{[v_x] = 0,[v_y] = 0}^{v_y \rightarrow v_x} \) according to

\[
k_{[v_x] = 0,[v_y] = 0}^{v_x \rightarrow v_y} = (v_x + 1) v_y k_{[v_x] = 0,[v_y] = 1}^{v_x \rightarrow v_y} = (v_x - 1) v_y k_{[v_x] = 1,[v_y] = 0}^{v_x \rightarrow v_y}.
\]  

(3.104)

\[
k_{[v_x] = 0,[v_y] = 0}^{v_y \rightarrow v_x} = v_x (v_y + 1) k_{[v_x] = 1,[v_y] = 0}^{v_y \rightarrow v_x} = v_x (v_y - 1) k_{[v_x] = 0,[v_y] = 1}^{v_y \rightarrow v_x}.
\]  

(3.105)

Substitution of these relations (3.104) and (3.105) into equation (3.103) gives,

\[
P_{v_x \pm 1, v_y \mp 1} = \sum_{[v_x],[v_y]} h\nu_x n_{[v_x]} n_{[v_y]} \left( (v_x + 1) v_y k_{[v_x] = 0,[v_y] = 1}^{v_x \rightarrow v_y} - v_x (v_y + 1) k_{[v_x] = 1,[v_y] = 0}^{v_x \rightarrow v_y} \right). \tag{3.106}
\]

Writing out the terms and sorting the summations gives,

\[
P_{v_x \pm 1, v_y \mp 1} = k_{[v_x] = 0,[v_y] = 1}^{v_x \rightarrow v_y} = \sum_{[v_x]} n_{[v_x]} v_x h\nu_x + \sum_{[v_y]} n_{[v_y]} v_y h\nu_x + v_x u_x = k_{[v_x] = 0,[v_y] = 0}^{v_x \rightarrow v_y} = \sum_{[v_x]} n_{[v_x]} v_x h\nu_x + \sum_{[v_y]} n_{[v_y]} v_y h\nu_x + v_x u_x \tag{3.107}
\]

The summations in this equation (3.107) are given by,

\[
\sum_{[v_x]} n_{[v_x]} = n_{v_x}, \tag{3.108}
\sum_{[v_y]} n_{[v_y]} = n_{v_y}, \tag{3.109}
\sum_{[v_x]} n_{[v_x]} v_x h\nu_x = U_x, \tag{3.110}
\]

\[
\sum_{[v_y]} n_{[v_y]} v_y h\nu_y = U_y \rightarrow \sum_{[v_y]} n_{[v_y]} v_y = \frac{U_y}{h\nu_y}. \tag{3.111}
\]
Substitution of these summations \((3.108)-(3.111)\) into equation \((3.107)\) gives,

\[
P_{v_x \pm 1, v_y \mp 1} = k_{v_x = 0, v_y = 1 \to v_x = 1, v_y = 0} \left( \frac{U_y}{\hbar v_y} U_x + \frac{U_y}{\hbar v_y} n_{t_{v_x}} \right)
- k_{v_x = 1, v_y = 0 \to v_x = 0, v_y = 1} \left( \frac{U_y}{\hbar v_y} U_x + n_{t_{v_x}} U_x \right)
= k_{v_x = 0, v_y = 1 \to v_x = 1, v_y = 0} \left( \frac{U_y}{\hbar v_y} + 1 \right)
- k_{v_x = 1, v_y = 0 \to v_x = 0, v_y = 1} n_{t_{v_x}} U_x \left( \frac{U_y}{\hbar v_y} + 1 \right).
\]

The rate coefficients \(k_{v_x = 0, v_y = 1 \to v_x = 1, v_y = 0} \) and \(k_{v_x = 1, v_y = 0 \to v_x = 0, v_y = 1} \) are related to each other by

\[
k_{v_x = 0, v_y = 1 \to v_x = 1, v_y = 0} = k_{v_x = 1, v_y = 0 \to v_x = 0, v_y = 1} e^{-\beta \hbar (v_x - v_y)}. \tag{3.113}
\]

Substitution of this relation \((3.113)\) into equation \((3.112)\) gives,

\[
P_{v_x \pm 1, v_y \mp 1} = k_{v_x = 1, v_y = 0 \to v_x = 0, v_y = 1} \left( \frac{U_x}{n_{t_{v_x}} \hbar v_x} + 1 \right) \frac{\nu_x n_{t_{v_x}} U_y}{\nu_y}
- k_{v_x = 0, v_y = 1 \to v_x = 1, v_y = 0} \left( \frac{U_y}{n_{t_{v_x}} \hbar v_x} + 1 \right) \frac{\nu_x n_{t_{v_x}} U_y}{\nu_y}
= k_{v_x = 1, v_y = 0 \to v_x = 0, v_y = 1} \left( \frac{U_x}{n_{t_{v_x}} \hbar v_x} + 1 \right) \frac{\nu_x n_{t_{v_x}} U_y}{\nu_y}
- k_{v_x = 0, v_y = 1 \to v_x = 1, v_y = 0} \left( \frac{U_x}{n_{t_{v_x}} \hbar v_x} + 1 \right) \frac{\nu_x n_{t_{v_x}} U_y}{\nu_y}
= k_{v_x = 1, v_y = 0 \to v_x = 0, v_y = 1} \left( \frac{U_x}{n_{t_{v_x}} \hbar v_x} + 1 \right) \frac{\nu_x n_{t_{v_x}} U_y}{\nu_y}
- k_{v_x = 0, v_y = 1 \to v_x = 1, v_y = 0} \left( \frac{U_x}{n_{t_{v_x}} \hbar v_x} + 1 \right) \frac{\nu_x n_{t_{v_x}} U_y}{\nu_y}
= k_{v_x = 1, v_y = 0 \to v_x = 0, v_y = 1} \left( \frac{U_x}{n_{t_{v_x}} \hbar v_x} + 1 \right) \frac{\nu_x n_{t_{v_x}} U_y}{\nu_y}
- k_{v_x = 0, v_y = 1 \to v_x = 1, v_y = 0} \left( \frac{U_x}{n_{t_{v_x}} \hbar v_x} + 1 \right) \frac{\nu_x n_{t_{v_x}} U_y}{\nu_y}
= k_{v_x = 1, v_y = 0 \to v_x = 0, v_y = 1} \left( \frac{U_x}{n_{t_{v_x}} \hbar v_x} + 1 \right) \frac{\nu_x n_{t_{v_x}} U_y}{\nu_y}
- k_{v_x = 0, v_y = 1 \to v_x = 1, v_y = 0} \left( \frac{U_x}{n_{t_{v_x}} \hbar v_x} + 1 \right) \frac{\nu_x n_{t_{v_x}} U_y}{\nu_y}
\]

The equilibrium energy densities \(U_{x}^{eq}(T_0)\) and \(U_{y}^{eq}(T_0)\) above ground state is of a collection of identical harmonic oscillators is given by,

\[
U_{x}^{eq}(T_0) = n_{t_{v_x}} \hbar v_x \left( e^{\beta \hbar v_x} - 1 \right)^{-1} \to n_{t_{v_x}} \hbar v_x = U_{x}^{eq}(T_0) \left( e^{\beta \hbar v_x} - 1 \right), \tag{3.115}
\]

\[
U_{y}^{eq}(T_0) = n_{t_{v_y}} \hbar v_y \left( e^{\beta \hbar v_y} - 1 \right)^{-1} \to n_{t_{v_y}} \hbar v_y = U_{y}^{eq}(T_0) \left( e^{\beta \hbar v_y} - 1 \right), \tag{3.116}
\]
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Substitution of these expressions (3.115) and (3.116) for the equilibrium energy densities gives,

\[
P_{v_x+1,v_y+1} = k_{v_x,v_y} U_{v_x,v_y} \left( U_y + U_{v_x} \frac{U_y}{U_{v_x}} + 1 \right)
\]

\[
= k_{v_x,v_y} U_{v_x,v_y} \left( U_y + U_{v_x} \frac{U_y}{U_{v_x}} + 1 \right) \int 0_{v_x} + U_{v_x} \frac{U_y}{U_{v_x}} \frac{1 - e^{-\beta h(v_x-v_y)}}{1 - e^{-\beta h(v_x-v_y)}}
\]

\[
= k_{v_x,v_y} U_{v_x,v_y} \left( U_y + U_{v_x} \frac{U_y}{U_{v_x}} + 1 \right) \int 0_{v_x} + U_{v_x} \frac{U_y}{U_{v_x}} \frac{1 - e^{-\beta h(v_x-v_y)}}{1 - e^{-\beta h(v_x-v_y)}}
\]

\[
= k_{v_x,v_y} U_{v_x,v_y} \left( U_y + U_{v_x} \frac{U_y}{U_{v_x}} + 1 \right) \int 0_{v_x} + U_{v_x} \frac{U_y}{U_{v_x}} \frac{1 - e^{-\beta h(v_x-v_y)}}{1 - e^{-\beta h(v_x-v_y)}}
\]

\[
= k_{v_x,v_y} U_{v_x,v_y} \left( U_y + U_{v_x} \frac{U_y}{U_{v_x}} + 1 \right) \int 0_{v_x} + U_{v_x} \frac{U_y}{U_{v_x}} \frac{1 - e^{-\beta h(v_x-v_y)}}{1 - e^{-\beta h(v_x-v_y)}}
\]

This can be rewritten in a more compact mathematical description for the power source term
The relaxation time $\tau_{VV}$ defined as,

$$P_{v_x \pm 1, v_y \mp 1} = - \frac{U_x - U_{eq}^x (T_0, T_y)}{\tau_{xy} (T_0, T_y)}.$$  \hspace{1cm} (3.118)

The relaxation time $\tau_{xy}^{-1} (T_0, T_y)$ defined as,

$$\tau_{xy}^{-1} (T_0, T_y) = k_{v_x - 1, v_y}^{1} = \frac{1}{n_{v_x = 1, v_y = 0}} \frac{1}{\tau_{xy} (T_0, T_y)} e^{\beta_x h \nu_x} \left( e^{\beta_x h \nu_x} - 1 \right)^{-1} \left( e^{\beta_y h \nu_y} - \beta_y h (\nu_y - \nu_x) - 1 \right). \hspace{1cm} (3.119)$$

The equilibrium energy density $U_{eq}^x (T_0, T_y)$ is given by,

$$U_{eq}^x (T_0, T_y) = n_{v_x} h \nu_x \left( e^{\beta_x h \nu_x} - \beta_x h (\nu_x - \nu_y) - 1 \right)^{-1}. \hspace{1cm} (3.120)$$

This general expression for VV-transitions can be applied to the VV-transitions of the considered chemistry. In this way, the explicit expressions for the VV-transitions substitute the power density source terms in the energy density reservoir equations. The VV-relaxation times appearing in the explicit terms of the energy density reservoir equations are presented next.

**VV-relaxation $\tau_{21}$**

The relaxation time $\tau_{21} (T_0, T_1)$ is given by,

$$\tau_{21} (T_0, T_1)^{-1} = k_{v_2 = 0, v_1 = 1}^{CO_2 - CO_2} \frac{1}{n_{v_2 = 0, v_1 = 1}} \frac{1}{R_{CO_2} \nu_2} \nu_1 \left( e^{\beta_1 h \nu_1} - 1 \right)^{-1} \left( e^{\beta_1 h \nu_1} - \beta_1 h (\nu_1 - \nu_2) - 1 \right). \hspace{1cm} (3.121)$$

**VV-relaxation $\tau_{31}$**

The relaxation time $\tau_{31} (T_0, T_1)$ is given by,

$$\tau_{31} (T_0, T_1)^{-1} = k_{v_3 = 0, v_1 = 1}^{CO_2 - CO_2} \frac{1}{n_{v_3 = 0, v_1 = 1}} \frac{1}{R_{CO_2} \nu_3} \nu_1 \left( e^{\beta_1 h \nu_1} - 1 \right)^{-1} \left( e^{\beta_1 h \nu_1} - \beta_1 h (\nu_1 - \nu_3) - 1 \right). \hspace{1cm} (3.122)$$

**VV-relaxation $\tau_{41}$**

The relaxation time $\tau_{41} (T_0, T_1)$ is given by,

$$\tau_{41} (T_0, T_1)^{-1} = k_{v_4 = 0, v_1 = 1}^{N_2 - CO_2} \frac{1}{n_{v_4 = 0, v_1 = 1}} \frac{1}{R_{CO_2} \nu_4} \nu_1 \left( e^{\beta_1 h \nu_1} - 1 \right)^{-1} \left( e^{\beta_1 h \nu_1} - \beta_1 h (\nu_1 - \nu_4) - 1 \right). \hspace{1cm} (3.123)$$

**VV-relaxation $\tau_{51}$**

The relaxation time $\tau_{51} (T_0, T_1)$ is given by,

$$\tau_{51} (T_0, T_1)^{-1} = k_{v_5 = 0, v_1 = 1}^{CO - CO_2} \frac{1}{n_{v_5 = 0, v_1 = 1}} \frac{1}{R_{CO_2} \nu_5} \nu_1 \left( e^{\beta_1 h \nu_1} - 1 \right)^{-1} \left( e^{\beta_1 h \nu_1} - \beta_1 h (\nu_1 - \nu_5) - 1 \right). \hspace{1cm} (3.124)$$
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**VV-relaxation \( \tau_{32} \)**

The relaxation time \( \tau_{32} (T_0, T_2) \) is given by,

\[
\tau_{32} (T_0, T_2)^{-1} = k_{v_3=1,v_2=0 \rightarrow v_3=0,v_2=1} CO₂ e^{\delta_{h} (\nu_2 - \nu_3)} (e^{\beta_2 h \nu_2} - 1)^{-1} (e^{\beta_2 h \nu_2 - \beta_0 h (\nu_2 - \nu_3)} - 1) \tag{3.125}
\]

**VV-relaxation \( \tau_{42} \)**

The relaxation time \( \tau_{42} (T_0, T_2) \) is given by,

\[
\tau_{42} (T_0, T_2)^{-1} = k_{v_4=1,v_2=0 \rightarrow v_4=0,v_2=1} CO₂ e^{\delta_{h} (\nu_2 - \nu_4)} (e^{\beta_2 h \nu_2} - 1)^{-1} (e^{\beta_2 h \nu_2 - \beta_0 h (\nu_2 - \nu_4)} - 1) \tag{3.126}
\]

**VV-relaxation \( \tau_{52} \)**

The relaxation time \( \tau_{52} (T_0, T_2) \) is given by,

\[
\tau_{52} (T_0, T_2)^{-1} = k_{v_3=1,v_2=0 \rightarrow v_3=0,v_2=1} CO₂ e^{\delta_{h} (\nu_2 - \nu_5)} (e^{\beta_2 h \nu_2} - 1)^{-1} (e^{\beta_2 h \nu_2 - \beta_0 h (\nu_2 - \nu_5)} - 1) \tag{3.127}
\]

**VV-relaxation \( \tau_{43} \)**

The relaxation time \( \tau_{43} (T_0, T_3) \) is given by,

\[
\tau_{43} (T_0, T_3)^{-1} = k_{v_3=1,v_4=0 \rightarrow v_3=0,v_4=1} N₂ CO₂ e^{\delta_{h} (\nu_3 - \nu_4)} (e^{\beta_3 h \nu_3} - 1)^{-1}
\]

\[
\left( e^{\beta_3 h \nu_3 - \beta_0 h (\nu_3 - \nu_4)} - 1 \right). \tag{3.128}
\]

The rate coefficient \( k_{v_4=1,v_2=0 \rightarrow v_4=0,v_2=1} N₂ CO₂ \) is given by Davies \[87\] to be the largest of two expressions for the rate coefficients which are given by,

\[
k_{v_4=1,v_2=0 \rightarrow v_4=0,v_2=1} N₂ CO₂ = 1.71 \cdot 10^{-6} e^{-175.37 T_0^{-0.4}} \tag{3.129}
\]

\[
k_{v_4=1,v_2=0 \rightarrow v_4=0,v_2=1} N₂ CO₂ = 6.07 \cdot 10^{-14} e^{15.37 T_0^{-0.4}} \tag{3.130}
\]

The values of the vibrational frequencies of vibrational modes 3 and 4 are very close to each other \( \nu_3 \approx \nu_4 \). In that case the relaxation time \( \tau_{43} (T_0, T_3) \) of equation \( \ref{3.128} \) is,

\[
\tau_{43} (T_0, T_3)^{-1} \approx k_{v_4=1,v_2=0 \rightarrow v_4=0,v_2=1} N₂ CO₂ (e^{\beta_3 h \nu_3 - 1})^{-1} (e^{\delta_{h} \nu_3} - 1) \tag{3.131}
\]

**VV-relaxation \( \tau_{53} \)**

The relaxation time \( \tau_{53} (T_0, T_3) \) is given by,

\[
\tau_{53} (T_0, T_3)^{-1} = k_{v_4=1,v_2=0 \rightarrow v_4=0,v_2=1} CO₂ e^{\delta_{h} (\nu_3 - \nu_5)} (e^{\beta_3 h \nu_3} - 1)^{-1} (e^{\delta_{h} \nu_3} - 1) \tag{3.132}
\]

The rate coefficient \( k_{v_5=1,v_3=0 \rightarrow v_5=0,v_3=1} CO₂ \) is given by Gordietz \[35\] to be,

\[
k_{v_5=1,v_3=0 \rightarrow v_5=0,v_3=1} CO₂ = 1.56 \cdot 10^{-11} e^{-30.17 T_0^{-0.4}} \tag{3.133}
\]
VV-relaxation \( \tau_{54} \)

The relaxation time \( \tau_{54} (T_0, T_4) \) is given by,

\[
\tau_{54} (T_0, T_4)^{-1} = k_{\nu_5=1, \nu_4=0} = v_n = 0, \nu_4 = 1 \text{N}_2 \ e^{\beta h \nu_4} \left( e^{\beta h \nu_4} - 1 \right)^{-1} \left( e^{\beta h \nu_4 - \beta h (\nu_4 - \nu_5)} - 1 \right). \quad (3.134)
\]

The rate coefficient \( k_{\nu_5=1, \nu_4=0} = v_n = 0, \nu_4 = 1 \text{N}_2 \) is given by Davies [27] to be the largest of two expressions for the rate coefficients given by,

\[
k_{\nu_5=1, \nu_4=0} = v_n = 0, \nu_4 = 1 \text{N}_2 = 1.78 \cdot 10^{-6} \ e^{-210T_0^{-1/2}}, \quad (3.135)
\]

\[
k_{\nu_5=1, \nu_4=0} = v_n = 0, \nu_4 = 1 \text{N}_2 = 6.98 \cdot 10^{-13} \ e^{-25.6T_0^{-1/4}}. \quad (3.136)
\]

3.3.5 VVV-transitions

Explicit expression for the power source terms \( p_{CO_2}^{-1} \) involving the simultaneous change of one quantum in three vibrational modes are presented here. Furthermore, explicit expression for the VVV-relaxation times appearing in the reservoir equations (3.179–3.184) are presented.

VV-relaxation \( \tau_3 \)

The power sources \( p_{CO_2}^{-1} \) can be summarized as,

\[
\sum_t \ p_{\nu_3+1, \nu_1+1, \nu_2+1} = - \frac{U^3_{\text{eq}}(T_0, T_1, T_2)}{\tau_3(T_0, T_1, T_2)}. \quad (3.137)
\]

The equilibrium energy density \( U^3_{\text{eq}}(T_0, T_1, T_2) \) is given by,

\[
U^3_{\text{eq}}(T_0, T_1, T_2) = n_{CO_2} \left( e^{\beta h \nu_1 + \beta h \nu_2 + \beta h (\nu_3 - \nu_2 - \nu_1)} - 1 \right)^{-1}. \quad (3.138)
\]

The relaxation time \( \tau_3 (T_0, T_1, T_2) \) is given by,

\[
\tau_3 (T_0, T_1, T_2)^{-1} = e^{\beta h (\nu_1 + \nu_2 - \nu_3)} \left( e^{\beta h \nu_2} - 1 \right)^{-1} \left( e^{\beta h \nu_2 - 1} \right)^{-1} \left( e^{\beta h \nu_1 + \beta h \nu_2 + \beta h (\nu_3 - \nu_2 - \nu_1)} - 1 \right)^{-1} \sum_t \ n_t k_{CO_2}^{-1} \quad (3.139)
\]

Writing out the summation gives the relaxation time in explicit form,

\[
\tau_3 (T_0, T_1, T_2)^{-1} = e^{\beta h (\nu_1 + \nu_2 - \nu_3)} \left( e^{\beta h \nu_2} - 1 \right)^{-1} \left( e^{\beta h \nu_1 + \beta h \nu_2 + \beta h (\nu_3 - \nu_2 - \nu_1)} - 1 \right) \quad (3.140)
\]

The rate coefficients \( k \) are given by Fischer and Smith [20] to be,

\[
k_{\nu_1=0, \nu_2=0, v_3=1, v_1=1, v_2=1, v_3=0} = 9.6 \cdot 10^{23} T_0^{-5.89} F(T_0), \quad (3.141)
\]

\[
k_{\nu_1=0, \nu_2=0, v_3=1, v_1=1, v_2=1, v_3=0} = 6.87 \cdot 10^{23} T_0^{-5.89} F(T_0), \quad (3.142)
\]
The power source equation (3.140) is used. The rate coefficients of equations (3.141)-(3.144) are then substituted in equation (3.146) to give \( \tau \). Here, \( F(T_0) \) is a function given by,

\[
F(T_0) = e^{-4.223T_0^{-1} - 672.77T_0^{-\frac{3}{2}} + 2683T_0^{-\frac{5}{2}}}. \tag{3.145}
\]

To determine \( \tau_3(T_0, T_1, T_2) \) Manes and Seguin [36] used the rate coefficients with \( T_1 = T_2 = T_0 \) so for a relaxation time \( \tau_3(T_0, T_0, T_0) \) using this, the relaxation time \( \tau_3(T_0, T_0, T_0) \) is given by,

\[
\tau_3(T_0, T_0, T_0)^{-1} = n_{CO_2}k^CO_2_{v_1=0,v_2=0,v_3=1}\rightarrow v_1=1,v_2=1,v_3=0 + n_{N_2}k^CO_2_{v_1=0,v_2=0,v_3=1}\rightarrow v_1=1,v_2=1,v_3=0 + n_{N_2}k^CO_2_{v_1=0,v_2=0,v_3=1}\rightarrow v_1=1,v_2=1,v_3=0 + n_{CO_2}k^CO_2_{v_1=0,v_2=0,v_3=1}\rightarrow v_1=1,v_2=1,v_3=0. \tag{3.146}
\]

The rate coefficients of equations (3.141)-(3.144) are then substituted in equation (3.146) to give the relaxation time \( \tau_3(T_0, T_0, T_0) \). This is then used to calculate \( A_3 \) which is given by,

\[
e^{\beta_h(\nu_1 + \nu_2 - \nu_3)} \sum_t n_t k^{CO_2}_{v_1=0,v_2=0,v_3=1}\rightarrow v_1=1,v_2=1,v_3=0 = n_{CO_2}A_3. \tag{3.147}
\]

The reservoir model accounts for the evolution of \( T_0 \) so in this model the temperature dependent equation (3.140) is used.

**VVV-relaxation \( \tau_4 \)**

The power source \( p^{CO_2-N_2}_{v_4=\pm 1,v_1=\pm 1,v_2=\pm 1} \) is given by,

\[
p^{CO_2-N_2}_{v_4=\pm 1,v_1=\pm 1,v_2=\pm 1} = \frac{U_4 - U_4^{eq}(T_0, T_1, T_2)}{\tau_4(T_0, T_1, T_2)}. \tag{3.148}
\]

The equilibrium energy density \( U_4^{eq}(T_0, T_1, T_2) \) is given by,

\[
U_4^{eq}(T_0, T_1, T_2) = n_{N_2}h\nu_4 \left( e^\beta_1h\nu_1 + \beta_2h\nu_2 + \beta_3h(\nu_4 - \nu_2 - \nu_1) - 1 \right)^{-1}. \tag{3.149}
\]

The relaxation time \( \tau_4(T_0, T_1, T_2) \) in explicit form is,

\[
\tau_4(T_0, T_1, T_2)^{-1} = n_{N_2}k^{CO_2-N_2}_{v_1=0,v_2=0,v_3=1}\rightarrow v_1=1,v_2=1,v_4=0 \left( e^{\beta_2h\nu_2} - 1 \right)^{-1} \left( e^{\beta_1h\nu_1} - 1 \right)^{-1} \left( e^{\beta_3h(\nu_4 - \nu_2 - \nu_1)} - 1 \right). \tag{3.150}
\]

**VVV-relaxation \( \tau_5 \)**

The power source \( p^{CO_2-CO}_{v_5=\pm 1,v_1=\pm 1,v_2=\pm 1} \) is given by,

\[
p^{CO_2-CO}_{v_5=\pm 1,v_1=\pm 1,v_2=\pm 1} = \frac{U_5 - U_5^{eq}(T_0, T_1, T_2)}{\tau_5(T_0, T_1, T_2)}. \tag{3.151}
\]

The equilibrium energy density \( U_5^{eq}(T_0, T_1, T_2) \) is given by,

\[
U_5^{eq}(T_0, T_1, T_2) = n_{CO}h\nu_5 \left( e^\beta_1h\nu_1 + \beta_2h\nu_2 + \beta_3h(\nu_5 - \nu_2 - \nu_1) - 1 \right)^{-1}. \tag{3.152}
\]

The relaxation time \( \tau_5(T_0, T_1, T_2) \) in explicit form is,

\[
\tau_5(T_0, T_1, T_2)^{-1} = n_{CO}k^{CO_2-CO}_{v_1=0,v_2=0,v_3=1}\rightarrow v_1=1,v_2=1,v_5=0 \left( e^{\beta_2h\nu_2} - 1 \right)^{-1} \left( e^{\beta_1h\nu_1} - 1 \right)^{-1} \left( e^{\beta_3h(\nu_5 - \nu_2 - \nu_1)} - 1 \right). \tag{3.153}
\]
The rate coefficient $k_{\text{CO}_2\text{-CO}}^{\text{CO}_2\text{-CO}}$ is given by Smith \[20\] to be,

$$k_{\text{CO}_2\text{-CO}}^{\text{CO}_2\text{-CO}} = 5.96 \cdot 10^{-22} T_0^{-5.86} F(T_0).$$  \hspace{1cm} (3.154)

Here, $F(T_0)$ is a function given by,

$$F(T_0) = e^{-42237 T_0^{-1} - 672 T_0^{-\frac{3}{2}} + 26837 T_0^{-\frac{5}{2}}}. \hspace{1cm} (3.155)$$

### 3.3.6 VV transition between symmetric and bending mode of CO$_2$

The symmetric vibrational mode and the bending mode are in Fermi degeneracy $\nu_1 \approx 2\nu_2$ as previously discussed in section \[2.1.4\]. Due to this resonance transitions between these two vibrational modes becomes more probable, as the energy exchange with the ro-translational reservoir is negligibly small. The power source term $P_{v_1+1,v_2\pm 2}$ involving the change of one quantum of the energy density reservoir corresponding to the symmetric vibrational mode of CO$_2$ and a change of opposite sign of two quanta of the energy density reservoir corresponding to the bending mode of CO$_2$ can be written as,

$$P_{v_1+1,v_2\pm 2} = \sum_{t} P_{v_1+1,v_2\pm 2}. \hspace{1cm} (3.156)$$

The equilibrium energy densities $U_1^{eq}(T_2)$ and $U_2^{eq}(T_2)$ are given by,

$$U_1^{eq}(T_2) = 2U_2^{eq}(T_2) \left(e^{\beta_2 h \nu_2} + 1\right)^{-1}, \hspace{1cm} (3.157)$$

$$U_2^{eq}(T_2) = n_{\text{CO}_2} h \nu_2 \left(e^{\beta_2 h \nu_2} - 1\right)^{-1}. \hspace{1cm} (3.158)$$

The power sources $P_{v_1+1,v_2\pm 2}$ can be written in a mathematical compact form, which is determined in Smith \[20\] p.36 ch.2.5], as \[20\] p.38 eq.2.37,

$$P_{v_1+1,v_2\pm 2} = \frac{U_1 - U_2^{eq}(T_2)}{\tau_1^{12}(T_2)}. \hspace{1cm} (3.159)$$

Here, $\tau_1^{12}(T_2)$ is the relaxation time defined as \[20\] p.38 eq.2.38,

$$\tau_1^{12}(T_2)^{-1} = 2 \left(1 + e^{-\beta_2 h \nu_2}\right) \left(1 - e^{-\beta_2 h \nu_2}\right)^{-1} \sum_{t} n_t k_{v_1=0,v_2=2\rightarrow v_1=1,v_2=0}. \hspace{1cm} (3.160)$$

The relaxation time $\tau_1^{12}(T_2)$ in explicit form is,

$$\tau_1^{12}(T_2)^{-1} = 2 \left(1 + e^{-\beta_2 h \nu_2}\right) \left(1 - e^{-\beta_2 h \nu_2}\right)^{-1} \left(n_{\text{CO}_2} k_{\text{CO}_2\text{-CO}}^{\text{CO}_2\text{-CO}} + n_{\text{CO}_2} k_{\text{CO}_2\text{-N}_2}^{\text{CO}_2\text{-N}_2} + n_{\text{CO}_2} k_{\text{CO}_2\text{-He}}^{\text{CO}_2\text{-He}} + n_{\text{CO}_2} k_{\text{CO}_2\text{-CO}}^{\text{CO}_2\text{-CO}}\right). \hspace{1cm} (3.161)$$

The rate coefficients $k$ are given by Stark \[52\] and Smith \[20\] to be,

$$k_{v_1=0,v_2=2\rightarrow v_1=1,v_2=0}^{\text{CO}_2\text{-CO}} = 8.65 \cdot 10^{-15} T_0^{\frac{5}{2}}, \hspace{1cm} (3.162)$$

$$k_{v_1=0,v_2=2\rightarrow v_1=1,v_2=0}^{\text{CO}_2\text{-N}_2} = 3.68 \cdot 10^{-16} T_0^{\frac{5}{2}}, \hspace{1cm} (3.163)$$

$$k_{v_1=0,v_2=2\rightarrow v_1=1,v_2=0}^{\text{CO}_2\text{-He}} = 4.23 \cdot 10^{-17} T_0^{\frac{5}{2}}, \hspace{1cm} (3.164)$$

$$k_{v_1=0,v_2=2\rightarrow v_1=1,v_2=0}^{\text{CO}_2\text{-CO}} = 3.68 \cdot 10^{-16} T_0^{\frac{5}{2}}. \hspace{1cm} (3.165)$$
3.3. RESERVOIR MODEL FOR A CO$_2$-N$_2$-HE-CO GAS MIXTURE

3.3.7 Coupling of VV-transition power sources

In this section a relation between the power source terms of equal VV-transitions but on different energy reservoirs is determined. The power source $P_{v_x \mp 1, v_y \pm 1}$ can be written as,

$$P_{v_x \mp 1, v_y \pm 1} = \mp \hbar \nu_x R_{v_x \mp 1, v_y \pm 1} = - \hbar \nu_x R_{v_x - 1, v_y + 1} + \hbar \nu_x R_{v_x + 1, v_y - 1}$$

$$= \hbar \nu_x (R_{v_x + 1, v_y - 1} - R_{v_x - 1, v_y + 1}) = \frac{\hbar \nu_x}{\hbar \nu_y} (R_{v_x + 1, v_y - 1} - R_{v_x - 1, v_y + 1})$$

$$= \frac{\hbar \nu_x}{\hbar \nu_y} (R_{v_x + 1, v_y - 1} - R_{v_x - 1, v_y + 1})$$

$$= - \frac{\hbar \nu_x}{\hbar \nu_y} R_{v_x + 1, v_y - 1} + \hbar \nu_y R_{v_x - 1, v_y + 1}$$

$$= - \frac{\hbar \nu_x}{\hbar \nu_y} R_{v_x - 1, v_y + 1} + \hbar \nu_y R_{v_x + 1, v_y - 1}$$

$$= - \frac{\hbar \nu_x}{\hbar \nu_y} P_{v_x \mp 1, v_y \pm 1}. \quad (3.169)$$

The relation between the power sources $P_{v_x \pm 1, v_y \mp 1}$ and $P_{v_y \mp 1, v_x \pm 1}$ using equations (3.167) and (3.168) is given by,

$$P_{v_x \pm 1, v_y \mp 1} = \pm \hbar \nu_x R_{v_x \pm 1, v_y \mp 1} = - \hbar \nu_x R_{v_x - 1, v_y + 1} - \hbar \nu_x R_{v_x + 1, v_y - 1}$$

$$= \hbar \nu_x (R_{v_x + 1, v_y - 1} - R_{v_x - 1, v_y + 1}) = \frac{\hbar \nu_x}{\hbar \nu_y} (R_{v_x + 1, v_y - 1} - R_{v_x - 1, v_y + 1})$$

$$= \frac{\hbar \nu_x}{\hbar \nu_y} (R_{v_x + 1, v_y - 1} - R_{v_x - 1, v_y + 1})$$

$$= - \frac{\hbar \nu_x}{\hbar \nu_y} R_{v_x + 1, v_y - 1} + \hbar \nu_y R_{v_x - 1, v_y + 1}$$

$$= - \frac{\hbar \nu_x}{\hbar \nu_y} R_{v_x - 1, v_y + 1} + \hbar \nu_y R_{v_x + 1, v_y - 1}$$

$$= - \frac{\hbar \nu_x}{\hbar \nu_y} P_{v_x \mp 1, v_y \pm 1}. \quad (3.169)$$

Substituting the general expression for the VV-transition power sources, given in section 3.3.4 by equation 3.118 in equation 3.169 gives,

$$- \frac{U_x - U_{eq}^x (T_0, T_y)}{\tau_{xy} (T_0, T_y)} = \frac{\hbar \nu_x}{\hbar \nu_y} \frac{U_y - U_{eq}^y (T_0, T_x)}{\tau_{yx} (T_0, T_x)}$$

$$\rightarrow - \frac{U_y - U_{eq}^y (T_0, T_x)}{\tau_{yx} (T_0, T_x)} = \frac{\hbar \nu_y}{\hbar \nu_x} \frac{U_x - U_{eq}^x (T_0, T_y)}{\tau_{xy} (T_0, T_y)}. \quad (3.170)$$

The relations 3.166, 3.169, and 3.170 developed above can be used to simplify the VV-transition power source terms in the energy density equations 3.57-3.62.

3.3.8 Gas flow

Gas is constantly flowing in and out of the system, which influences the energy density in the reservoirs. This process can be described by a power source term which is given by,

$$P_{x,d} = - \frac{U_x - U_{eq}^x}{\tau_d} \quad (3.171)$$

Here, $\tau_d$ is the average gas residence time. These power source terms are added to the energy density equations 3.57-3.62 in order to account for this effect.
3.3.9 Electron excitation

In order to create a state of the gas mixture in which it can accommodate amplification of infrared CO\textsubscript{2}-laser radiation. A constant input power $P_{in}$ is delivered to the gas mixture through electron excitation. High-energy electrons are put into the system, which upon collision with the constituents of the gas mixture will excite or ionize the molecules, thereby feeding their higher energy level populations and create a plasma. To each energy density reservoir a fraction $\chi_x$ of this total input power is provided. The power source term describing this electron excitation process for a reservoir is given by,

$$P_{x,e} = \chi_x P_{in}. \quad (3.172)$$

3.3.10 Reservoir temperatures

The definition of the vibrational mode reservoir temperatures $T_i$ in equation (3.56) is used to obtain explicit expression for the six reservoir temperatures associated with the energy density reservoirs. The ro-translational reservoir temperature $T_0$ is defined as,

$$T_0 = T_{in} e^{\frac{n_{\text{mix}}}{R_{\text{mix}} p_{\text{in}} C_{p,mix}}} U_0. \quad (3.173)$$

Here, $T_{in}$ in the input initial gas temperature, $R_{\text{mix}} X$, $p_{\text{in}} X$ input gas pressure, and $C_{p,mix} X$. The remaining five reservoirs are all associated with a vibrational mode. Therefore, equation (3.56) can be used to obtain the expressions for the remaining five reservoir temperatures. The five reservoir temperatures for the five vibrational mode energy density reservoirs are given by,

$$T_1 = \frac{h \nu_1}{k_B \ln \left( \frac{n_{\text{CO}_2} h \nu_1}{U_1} + 1 \right)}, \quad (3.174)$$

$$T_2 = \frac{h \nu_2}{k_B \ln \left( \frac{2 n_{\text{CO}_2} h \nu_2}{U_2} + 1 \right)}, \quad (3.175)$$

$$T_3 = \frac{h \nu_3}{k_B \ln \left( \frac{n_{\text{CO}_2} h \nu_3}{U_3} + 1 \right)}, \quad (3.176)$$

$$T_4 = \frac{h \nu_4}{k_B \ln \left( \frac{n_{\text{N}_2} h \nu_4}{U_4} + 1 \right)}, \quad (3.177)$$

$$T_5 = \frac{h \nu_5}{k_B \ln \left( \frac{n_{\text{CO}} h \nu_5}{U_5} + 1 \right)}. \quad (3.178)$$

3.3.11 Reservoir model equations

The expressions and relations in equations (3.82), (3.118), (3.137), (3.148), (3.151), (3.159), and (3.170) for the power source terms developed in the previous sections are used to rewrite the energy density equations (3.57)-(3.62) resulting in the reservoir model equations. Furthermore, the power sources $P_{x,d}$ and $P_{x,e}$ for the gas flow and the electron excitation input power are added to these equations.

In section 3.3.2 the energy density equations (3.57)-(3.62) are sorted such that terms which involve equal energy density reservoirs and equal energy changes are written on the same line. The reason for this sorting now becomes clear, as the expressions for the power source terms developed in the previous section describe exactly the power source terms written on a single line in a single mathematically more compact term. By substituting these expressions all the resulting reservoir equations have thus one term per line if the sorting is kept up. The reservoir model equations are being presented in with the same sorting as the energy density equations to get a clear overview of the substitution that are made and to see the relation between both sets of equations.
reservoir model equations for a CO₂-N₂-He-CO gas mixture are given by,

\[
\frac{dU_0}{dt} = - \frac{U_0 - U_0^{eq}}{\tau_d} + \frac{U_1 - U_1^{eq}(T_0)}{\tau_{10}(T_0)} + \frac{U_2 - U_2^{eq}(T_0)}{\tau_{20}(T_0)} + \frac{U_3 - U_3^{eq}(T_0)}{\tau_{30}(T_0)} + \frac{U_4 - U_4^{eq}(T_0)}{\tau_{40}(T_0)} + \frac{U_5 - U_5^{eq}(T_0)}{\tau_{50}(T_0)} + \frac{(1 - \frac{h\nu_1}{h\nu_2})}{\tau_{21}(T_0, T_1)} U_2 - U_2^{eq}(T_0, T_1) + \frac{(1 - \frac{h\nu_1}{h\nu_3})}{\tau_{32}(T_0, T_2)} U_3 - U_3^{eq}(T_0, T_2) + \frac{(1 - \frac{h\nu_1}{h\nu_4})}{\tau_{31}(T_0, T_1)} U_4 - U_4^{eq}(T_0, T_3) + \frac{(1 - \frac{h\nu_1}{h\nu_5})}{\tau_{43}(T_0, T_3)} U_4 - U_4^{eq}(T_0, T_3) + \frac{(1 - \frac{h\nu_2}{h\nu_3})}{\tau_{42}(T_0, T_2)} U_4 - U_4^{eq}(T_0, T_2) + \frac{(1 - \frac{h\nu_2}{h\nu_4})}{\tau_{41}(T_0, T_1)} U_4 - U_4^{eq}(T_0, T_1) + \frac{(1 - \frac{h\nu_2}{h\nu_5})}{\tau_{54}(T_0, T_4)} U_5 - U_5^{eq}(T_0, T_4) + \frac{(1 - \frac{h\nu_3}{h\nu_5})}{\tau_{53}(T_0, T_3)} U_5 - U_5^{eq}(T_0, T_3) + \frac{(1 - \frac{h\nu_2}{h\nu_5})}{\tau_{52}(T_0, T_2)} U_5 - U_5^{eq}(T_0, T_2) + \frac{(1 - \frac{h\nu_3}{h\nu_5})}{\tau_{51}(T_0, T_1)} U_5 - U_5^{eq}(T_0, T_1) + \frac{(1 - \frac{h\nu_4}{h\nu_5})}{\tau_3(T_0, T_1, T_2)} U_4 - U_4^{eq}(T_0, T_1, T_2) + \frac{(1 - \frac{h\nu_4}{h\nu_5})}{\tau_4(T_0, T_1, T_2)} U_4 - U_4^{eq}(T_0, T_1, T_2) + \frac{(1 - \frac{h\nu_5}{h\nu_5})}{\tau_5(T_0, T_1, T_2)} U_5 - U_5^{eq}(T_0, T_1, T_2) + \chi_{tr} P_{in} - \frac{U_0 - U_0^{eq}}{\tau_d},
\]
\[
\frac{dU_1}{dt} = -\frac{U_1 - U_1^{eq}(T_0)}{\tau_{10}(T_0)} \\
+ \frac{h\nu_1 U_2 - U_2^{eq}(T_0,T_1)}{\tau_{21}(T_0,T_1)} \\
+ \frac{h\nu_2 U_3 - U_3^{eq}(T_0,T_1)}{\tau_{31}(T_0,T_1)} \\
+ \frac{h\nu_3 U_4 - U_4^{eq}(T_0,T_1)}{\tau_{41}(T_0,T_1)} \\
+ \frac{h\nu_4 U_5 - U_5^{eq}(T_0,T_1)}{\tau_{51}(T_0,T_1)} \\
+ \frac{h\nu_5 U_6 - U_6^{eq}(T_0,T_1)}{\tau_{61}(T_0,T_1)} \\
+ \frac{U_1 - U_1^{eq}(T_2)}{\tau_{12}^{eq}(T_2)} \\
+ \chi_1 P_m \\
- \frac{U_1 - U_1^{eq}}{\tau_d},
\]

\[
\frac{dU_2}{dt} = -\frac{U_2 - U_2^{eq}(T_0)}{\tau_{20}(T_0)} \\
+ \frac{U_2 - U_2^{eq}(T_0,T_1)}{\tau_{21}(T_0,T_1)} \\
+ \frac{h\nu_1 U_3 - U_3^{eq}(T_0,T_2)}{\tau_{32}(T_0,T_2)} \\
+ \frac{h\nu_2 U_4 - U_4^{eq}(T_0,T_2)}{\tau_{42}(T_0,T_2)} \\
+ \frac{h\nu_3 U_5 - U_5^{eq}(T_0,T_2)}{\tau_{52}(T_0,T_2)} \\
+ \frac{h\nu_4 U_6 - U_6^{eq}(T_0,T_2)}{\tau_{62}(T_0,T_2)} \\
+ \frac{U_2 - U_2^{eq}(T_2)}{\tau_{12}^{eq}(T_2)} \\
+ \chi_2 P_m \\
- \frac{U_2 - U_2^{eq}}{\tau_d},
\]
3.3. RESERVOIR MODEL FOR A CO$_2$-N$_2$-HE-CO GAS MIXTURE

\[
\frac{dU_3}{dt} = - \frac{U_3 - U_3^{\text{eq}}(T_0)}{\tau_{30}(T_0)} - \frac{U_3 - U_3^{\text{eq}}(T_0, T_2)}{\tau_{32}(T_0, T_2)} - \frac{U_3 - U_3^{\text{eq}}(T_0, T_1)}{\tau_{31}(T_0, T_1)} + \frac{h\nu_3 U_4 - U_4^{\text{eq}}(T_0, T_3)}{\tau_{43}(T_0, T_3)} + \frac{h\nu_5 U_5 - U_5^{\text{eq}}(T_0, T_3)}{\tau_{53}(T_0, T_3)} - \frac{U_3 - U_3^{\text{eq}}(T_0, T_1, T_2)}{\tau_{3}(T_0, T_1, T_2)} + \chi_3 P_{\text{in}} - \frac{U_3 - U_3^{\text{eq}}}{\tau_3},
\]

\[
\frac{dU_4}{dt} = - \frac{U_4 - U_4^{\text{eq}}(T_0)}{\tau_{40}(T_0)} - \frac{U_4 - U_4^{\text{eq}}(T_0, T_1)}{\tau_{41}(T_0, T_1)} - \frac{U_4 - U_4^{\text{eq}}(T_0, T_2)}{\tau_{42}(T_0, T_2)} - \frac{U_4 - U_4^{\text{eq}}(T_0, T_3)}{\tau_{43}(T_0, T_3)} + \frac{h\nu_4 U_5 - U_5^{\text{eq}}(T_0, T_4)}{\tau_{54}(T_0, T_4)} - \frac{U_4 - U_4^{\text{eq}}(T_0, T_1, T_2)}{\tau_4(T_0, T_1, T_2)} + \chi_4 P_{\text{in}} - \frac{U_4 - U_4^{\text{eq}}}{\tau_4},
\]

\[
\frac{dU_5}{dt} = - \frac{U_5 - U_5^{\text{eq}}(T_0)}{\tau_{50}(T_0)} - \frac{U_5 - U_5^{\text{eq}}(T_0, T_1)}{\tau_{51}(T_0, T_1)} - \frac{U_5 - U_5^{\text{eq}}(T_0, T_2)}{\tau_{52}(T_0, T_2)} - \frac{U_5 - U_5^{\text{eq}}(T_0, T_3)}{\tau_{53}(T_0, T_3)} - \frac{U_5 - U_5^{\text{eq}}(T_0, T_4)}{\tau_{54}(T_0, T_4)} - \frac{U_5 - U_5^{\text{eq}}(T_0, T_1, T_2)}{\tau_5(T_0, T_1, T_2)} + \chi_5 P_{\text{in}} - \frac{U_5 - U_5^{\text{eq}}}{\tau_5}.
\]

The relaxation times $\tau$ appearing in the reservoir model equations together with possible approx-
3.4 Reservoir model for CO₂-laser amplification

In this section the reservoir model for CO₂-laser amplification is developed. The reservoir model, developed in section 3.3, is combined with a description for the evolution of radiation through the system and a description to account for rotational relaxation. Firstly, a description for the evolution of the radiation through the system is developed. Here, the light-matter interactions, described in section 2.3, are applied to the specific lasing transitions using the Einstein coefficients of section 2.3.2. Here, next to forward also backward propagation is accounted for. Hereafter, the expressions to determine the populations in the system are developed using the partition functions of section 2.2.2. A model for rotational relaxation is developed and the effect of the rotational relaxation and of the light-matter interactions on the populations are described. Finally, the full reservoir model for CO₂-laser amplification describing the evolution of the laser plasma and the radiation is presented.

3.4.1 Evolution of the electromagnetic field

Amplification of radiation  An electromagnetic field consists of photons, which have an energy that corresponds to the wavelength of the electromagnetic waves. The number of photons corresponds to the intensity of the electromagnetic field. The total number of photons $N_{ph}$ in a volume $V$ is given by,

$$N_{ph} = \int_V n_{ph} dV.$$  \hfill (3.185)

Here, $n_{ph}$ is the photon spatial density. For the photon spatial density $n_{ph}$ the continuity equation is,

$$\frac{dn_{ph}}{dt} = -c \nabla \cdot \Phi_{ph} + S_{ph} = -c \frac{dn_{ph}}{dx} + S_{ph}. \hfill (3.186)$$

Here, $\Phi_{ph}$ is the photon density flux, and $S_{ph}$ the photon density source rate. The photon spatial density $n_{ph}$ consists of photons in different states and, therefore, with different energies corresponding to wavelength $\lambda$. The photon spatial density $n_{ph}$ and the photon density source rate $S_{ph}$ is given by,

$$n_{ph} = \sum_{\lambda} n_{\lambda}, \hfill (3.187)$$

$$S_{ph} = \sum_{\lambda} S_{\lambda}. \hfill (3.188)$$

Here, $n_{\lambda}$ is the photon spatial density of photons with wavelength $\lambda$, and $S_{\lambda}$ is the photon spatial density source rate for photons with wavelength $\lambda$. Substitution of equations (3.187) and (3.188) into equation (3.186) gives,

$$\sum_{\lambda} \frac{dn_{\lambda}}{dt} = -c \sum_{\lambda} \frac{dn_{\lambda}}{dx} + \sum_{\lambda} S_{\lambda}. \hfill (3.189)$$

This equation (3.189) implies a continuity equation for each photon spatial density $n_{\lambda}$ for wavelength $\lambda$,

$$\frac{dn_{\lambda}}{dt} + c \frac{dn_{\lambda}}{dx} = S_{\lambda}. \hfill (3.190)$$
3.4. RESERVOIR MODEL FOR CO$_2$-LASER AMPLIFICATION

Sources The sources $S$ are a result from the light-matter interaction previously discussed in section 2.3. The number of photons per volume per time added to the electromagnetic field due to stimulated emission is equal to the number of stimulated emissions per volume per time. The number of photons per volume per time lost from the electromagnetic field due to stimulated absorption is equal to the number of stimulated absorptions per volume per time. The first order transition probability for the collection of CO$_2$ atoms is given by equation (2.133). The stimulated emission time rate $W_{st}$ and the stimulated absorption time rate $W_{ab}$ are given by,

$$W_{st} = B_{st} \rho_{\lambda}, \quad (3.191)$$
$$W_{ab} = B_{ab} \rho_{\lambda}. \quad (3.192)$$

The stimulated emission source $S_{st}^{\lambda}$ is the number of stimulated emissions per volume per time and the stimulated absorption source $S_{ab}^{\lambda}$ is the number of stimulated absorptions per volume per time. Using equations (3.191) and (3.192) they are equivalent to the terms in equations (2.130) and (2.131) and given by,

$$S_{st}^{\lambda} = W_{st} n_{up} = B_{st}^{\lambda} \rho_{\lambda} n_{up}, \quad (3.193)$$
$$S_{ab}^{\lambda} = W_{ab} n_{lo} = B_{ab}^{\lambda} \rho_{\lambda} n_{lo}. \quad (3.194)$$

Here, $\rho_{\lambda}$ is the spectral energy density at is resonance value $\lambda$, $n_{up}$ the spatial number density of the upper lasing state, and $n_{lo}$ the spatial number density of the lower lasing state. The source $S_{\lambda}$ for the electromagnetic field is given by an equation similar to equations (2.134) and (2.135),

$$S_{\lambda} = S_{st}^{\lambda} - S_{ab}^{\lambda} = B_{st}^{\lambda} \rho_{\lambda} n_{up} - B_{ab}^{\lambda} \rho_{\lambda} n_{lo}. \quad (3.195)$$

Here, $\rho_{\lambda}$ is the spectral energy density is for its resonance value. In practice the Einstein $B$ coefficient depends on the spectral line shape $g(\lambda)$,

$$B_{\lambda} = B g(\lambda). \quad (3.196)$$

The relation between the Einstein coefficients $B_{st}^{\lambda}$ and $B_{ab}^{\lambda}$ depends on the degeneracies $\theta_{up}$ and $\theta_{lo}$ of respectively the upper and lower lasing levels,

$$B_{st}^{\lambda} \theta_{up} = B_{ab}^{\lambda} \theta_{lo}. \quad (3.197)$$

Substitution of equations (3.196) and (3.197) into equation (3.195) gives,

$$S_{\lambda} = B_{st}^{\lambda} \rho_{\lambda} n_{up} - B_{ab}^{\lambda} \rho_{\lambda} n_{lo} = B_{st}^{\lambda} \rho_{\lambda} \left( n_{up} - \frac{\theta_{up}}{\theta_{lo}} n_{lo} \right) = B_{st}^{\lambda} g(\lambda) \rho_{\lambda} \left( n_{up} - \frac{\theta_{up}}{\theta_{lo}} n_{lo} \right). \quad (3.198)$$

An expression for the Einstein $B$ coefficient can be given by rewriting equation (2.136),

$$B = \frac{A \pi^2 c^3}{h \nu^3} = \frac{A \pi^2 c^3}{h (2\pi \nu)^3} = \frac{A c^3}{8 \pi h \nu^3}. \quad (3.199)$$

The Einstein $A$ coefficient can be written as,

$$A = \frac{1}{\tau_{sp}}. \quad (3.200)$$

Here, $\tau_{sp}$ is the spontaneous emission time constant. Substitution of equation (3.199) and (3.200) for the Einstein coefficient into equation (3.198) gives,

$$S_{\lambda} = \frac{A c^3}{8 \pi h \nu^3} g(\lambda) \rho_{\lambda} \left( n_{up} - \frac{\theta_{up}}{\theta_{lo}} n_{lo} \right) = \frac{g(\lambda) \rho_{\lambda} c^3}{8 \pi h \tau_{sp} \nu^3} \left( n_{up} - \frac{\theta_{up}}{\theta_{lo}} n_{lo} \right). \quad (3.201)$$
The population inversion density $\delta$ between the upper and lower lasing state is defined as,

$$\delta = n_{up} - \frac{\theta_{up}}{\theta_{lo}} n_{lo}.$$  \hspace{1cm} (3.202)

The absorption cross section $\sigma$ is defined as,

$$\sigma (\lambda) = \frac{\lambda^2 g (\lambda)}{8\pi \tau_{sp}}.$$  \hspace{1cm} (3.203)

The spectral energy density $\rho_\lambda$ is related to the number of photons $n_\lambda$ and the intensity $I_\lambda$ \footnote{Here intensity $I$ is defined of having units of energy density per spatial area. The quantity associated with these units is strictly speaking the energy flux density, while the intensity is the energy density per spatial area per steradian per wavelength. However, as is often the case with this quantity intensity in literature we will use the quantity intensity here as stated.}

$$\rho_\lambda = n_\lambda h\nu = \frac{I_\lambda}{c}.$$  \hspace{1cm} (3.204)

Substitution of equation (3.202), (3.203) and (3.204) into equation (3.201) gives,

$$S_\lambda = \frac{g (\lambda) \rho_\lambda c^3}{8\pi h\tau_{sp} \nu^3} \delta = \frac{\lambda^2 g (\lambda) \rho_\lambda c^3}{8\pi \tau_{sp} h\nu} \delta = \sigma (\lambda) c \frac{\rho_\lambda}{h\nu} \delta = \sigma (\lambda) \delta cn_\lambda = G (\lambda) cn_\lambda.$$  \hspace{1cm} (3.205)

Here, $G (\lambda) = \sigma (\lambda) \delta$ is the gain coefficient.

**Energy sources** The light-matter interaction is responsible for the source $S_\lambda$ for radiation. In this interaction energy is exchanged between the electromagnetic field and the matter, leading to a change in their states as explained in section 2.3.1. Due to energy conservation the amount of energy density change of the electromagnetic field is of equal amount and of opposite sign as that of energy density of the matter. The source $S_\lambda$ of equation (3.205) describes the number of stimulated emissions and stimulated absorptions per unit time. The state of the matter is described by the reservoir model though energy density rate equations. As discussed previously the reservoir energy densities $E_i$ change due to the source powers densities $P_i$. The source power density $P_\lambda^{(i)}$ on reservoir $i$ resulting from the interaction with wavelength $\lambda$ is given by,

$$P_\lambda^{(i)} = E_\lambda^{(i)} S_\lambda.$$  \hspace{1cm} (3.206)

Here, $E_\lambda^{(i)}$ is the energy resulting from the interaction with wavelength $\lambda$ on reservoir $i$. The source $S_\lambda$ in terms of the intensity $I$ is given by substitution of equation (3.204) into equation (3.205),

$$S_\lambda = \frac{1}{h\nu} G (\lambda) I_\lambda.$$  \hspace{1cm} (3.207)

The energy $E_\lambda^{(i)}$ is the energy difference in reservoir $i$ between before and after the interaction. The interaction itself consists of a change of ro-vibrational state of a CO$_2$ molecule. The lasing states of the 10$P20$ and 10$R26$ transitions consist of an upper and lower state of the CO$_2$ molecule. The energy difference $\Delta E_\lambda$ between these states is given by,

$$\Delta E_\lambda = E_{up} - E_{lo} = (E_{r,up} + E_{v,up}) - (E_{r,lo} + E_{v,lo}) = E_{r,up} + E_{v,up} - E_{r,lo} - E_{v,lo}$$
$$= E_{r,up} - E_{r,lo} + E_{v,up} - E_{v,lo} = \Delta E_r + \Delta E_v.$$  \hspace{1cm} (3.208)

Using equation (2.28) for the rotational energy, the difference in rotational energy $\Delta E_r$ is,

$$\Delta E_r = E_{r,up} - E_{r,lo} = h\nu B j_{up} (j_{up} + 1) - h\nu B j_{lo} (j_{lo} + 1) =$$
$$h\nu B (j_{up} (j_{up} + 1) - j_{lo} (j_{lo} + 1)) = R_{up} - R_{lo}.$$  \hspace{1cm} (3.209)
3.4. RESERVOIR MODEL FOR CO\textsubscript{2}-LASER AMPLIFICATION

Using equation (2.41), the difference in vibrational energy is written as,

\[ \Delta E_v = E_{v, \text{up}} - E_{v, \text{lo}} = h\nu \left( v_{\text{up}} + \frac{1}{2} \right) - h\nu \left( v_{\text{lo}} + \frac{1}{2} \right) = h\nu \left( v_{\text{up}} - v_{\text{lo}} \right). \]  

From these equations the source power terms \( P_{\lambda}^{(i)} \) for the energy density reservoirs can be determined to be,

\[ P_{a}^{(0)} = E_{a}^{(0)} S_{a} = - \left( R_{\text{up}, a} - R_{\text{lo}, a} \right) \frac{1}{h\nu_{a}} G_{a} I_{a}, \]  

\[ P_{b}^{(0)} = E_{b}^{(0)} S_{b} = - \left( R_{\text{up}, b} - R_{\text{lo}, b} \right) \frac{1}{h\nu_{b}} G_{b} I_{b}, \]  

\[ P_{a}^{(1)} = E_{a}^{(1)} S_{a} = + \frac{h\nu_{a}}{h\nu_{a}} G_{a} I_{a}, \]  

\[ P_{b}^{(1)} = E_{b}^{(1)} S_{b} = + \frac{h\nu_{b}}{h\nu_{b}} G_{b} I_{b}, \]  

\[ P_{a}^{(3)} = E_{a}^{(3)} S_{a} = - \frac{h\nu_{a}}{h\nu_{a}} G_{a} I_{a}, \]  

\[ P_{b}^{(3)} = E_{b}^{(3)} S_{b} = - \frac{h\nu_{b}}{h\nu_{b}} G_{b} I_{b}. \]  

**Evolution of radiation**

Expression (3.207) for the sources \( S_{\lambda} \) in combination with equation (3.204) can be substituted into the continuity equation (3.190) for the photon spatial density to give,

\[ \frac{dn_{\lambda}}{dt} + c \frac{dn_{\lambda}}{dx} = G_{\lambda} c n_{\lambda}. \]  

The equations for the evolution of the radiation developed in the previous sections can be applied to the lasing states of the 10\textit{P}20 and 10\textit{R}26 transitions. The evolution of the radiation for the two wavelengths \( \lambda_{a} \) and \( \lambda_{b} \) in terms of intensity \( I \), using equations (3.204 and (3.217), is then given by,

\[ \frac{dI_{a}}{dt} + c \frac{dI_{a}}{dx} = G_{a} c I_{a}, \]  

\[ \frac{dI_{b}}{dt} + c \frac{dI_{b}}{dx} = G_{b} c I_{b}. \]  

**Backward propagation**

In the 1D model radiation can propagate in two directions, in the forward direction along an increasing value of \( x \), and backward direction of decreasing \( x \) along the \( x \)-axis. The radiation of a single wavelength is described in equation (3.217) by a continuity equation. However, this single wavelength radiation can propagate in both the forward and backward direction. The radiation of a single wavelength is, therefore, described by two continuity equations, one for the forward and the other for the backward propagation. The evolution of forward and backward radiation of two wavelengths \( \lambda_{a} \) and \( \lambda_{b} \) in terms of the intensity \( I \) is given by,

\[ \frac{dI_{a}^{\text{wd}}}{dt} + c \frac{dI_{a}^{\text{wd}}}{dx} = G_{a} c I_{a}^{\text{wd}}, \]  

\[ \frac{dI_{b}^{\text{wd}}}{dt} + c \frac{dI_{b}^{\text{wd}}}{dx} = G_{b} c I_{b}^{\text{wd}}. \]  

\[ \frac{dI_{a}^{\text{bd}}}{dt} + c \frac{dI_{a}^{\text{bd}}}{dx} = G_{a} c I_{a}^{\text{bd}}, \]  

\[ \frac{dI_{b}^{\text{bd}}}{dt} + c \frac{dI_{b}^{\text{bd}}}{dx} = G_{b} c I_{b}^{\text{bd}}. \]  

The small-signal gain coefficients \( G_{a} \) and \( G_{b} \) are given by,
\[ G_a = \sigma_a \delta_a, \quad G_b = \sigma_b \delta_b. \]  

The absorption cross sections \( \sigma_a \) and \( \sigma_b \) are given by,

\[
\sigma_a = \sigma(\lambda_a) = \frac{\lambda_a^2 g(\lambda_a)}{8\pi \tau_{sp,a}}, \quad \sigma_b = \sigma(\lambda_b) = \frac{\lambda_b^2 g(\lambda_b)}{8\pi \tau_{sp,b}}.
\]

The spectral line shapes \( g(\lambda_a) \) and \( g(\lambda_b) \) for monochromatic waves are given by,

\[
g(\lambda_a) = \frac{2}{\pi \Delta \nu_a}, \quad g(\lambda_b) = \frac{2}{\pi \Delta \nu_b}.
\]

The population inversions \( \delta_a \) and \( \delta_b \) between the upper and lower lasing states are given by,

\[
\delta_a = n_{up,a} - \frac{\theta_{up,a}}{\theta_{lo,a}} n_{lo,a}, \quad \delta_b = n_{up,b} - \frac{\theta_{up,b}}{\theta_{lo,b}} n_{lo,b}.
\]

### 3.4.2 Population inversion and rotational relaxation

The chemical reactions involving only rotation are assumed to be so fast that their effect on the dynamics of the system is negligible. The rotational energy levels are assumed to be in thermal equilibrium with each other and have, therefore, a Boltzmann distribution. In CO\(_2\)-laser amplification the electromagnetic pulses propagating through the system can have a duration in the order of nanoseconds. In a typical CO\(_2\)-laser mixtures at 1 atm the rotational energy levels are coupled via interactions with a time constant of \(0.15-2\) ns \[49\] \[50\]. For a pulse in the order of 1 ns the assumption that the rotational energy levels are thermalized seems justified. In that case, the radiation can evolve and amplify using the total rotational population of the lasing levels. However, research on short-pulse energy extraction in CO\(_2\)-laser amplifiers shows that not all rotational energy is available for amplification \[48\]. A rotational relaxation model shows that not all rotational energy can be used for amplification \[51\]. Here, a model to account for this rotational relaxation effect is presented.

**Equilibrium population** The occupation numbers of rotational levels at thermal equilibrium in a Boltzmann distribution are given by equation \(2.60\). The spatial number density of particles in a state \(s\) at thermal equilibrium is equivalent to equation \(2.61\),

\[
n_s = n_t \prod_a P_a.
\]

Here, \(n_t\) is the total number of particles of type \(t\), and \(P_a\) is the probability of particles having substate \(a\) of \(s\). The spatial number density of CO\(_2\) molecules in a ro-vibrational state \([v_1, v_2, v_3, j]\) at thermal equilibrium of the rotational and vibrational energy levels is given by equation \(3.232\) to be,

\[
n_{eq}[v_1, v_2, v_3, j] = n_{CO_2} P_{v_1} P_{v_2} P_{v_3} P_j = n_{eq}[v_1, v_2, v_3] P_j.
\]

Here, \(n_{eq}[v_1, v_2, v_3, j]\) is the spatial number density of CO\(_2\) molecules in a state \([v_1, v_2, v_3, j]\) at partial thermal equilibrium of the rotational and vibrational energy levels, or equilibrium spatial number
density $n_{\text{eq}}^{\text{CO}_2}$ the spatial number density of CO$_2$ molecules, $P_v$ the probability of a CO$_2$ molecule having energy level $v_i$ of vibrational mode $i$, $P_j$ the probability of a CO$_2$ molecule having energy level $j$ of rotation, and $n_{\text{eq}}^{[v_1,v_2,v_3]}$ the spatial number density of CO$_2$ molecules in the state $[v_1,v_2,v_3]$ at thermal equilibrium of the vibrational energy levels. Using equations (2.61), (2.62) and (2.70), the probability $P_v$ is given by,

$$P_v = \frac{g_v e^{-\beta_j E_{v_i}}}{\sum_{v_i} g_v e^{-\beta_j E_{v_i}}} = \frac{g_v e^{-\beta_j E_{v_i}}}{Z_v}.$$  \hspace{1cm} (3.234)

The probability $P_j$ is given by,

$$P_j = \frac{\theta_j e^{-\beta_j E_j}}{\sum_j \theta_j e^{-\beta_j E_j}} = \frac{\theta_j e^{-\beta_j E_j}}{Z_j}.$$ \hspace{1cm} (3.235)

The vibrational partition functions $Z_{v_1}$, $Z_{v_2}$, and $Z_{v_3}$ can be determined using equation (2.87) for the vibrational partition functions $Z_v$, and equation (2.88) for the non-degenerate vibrational modes partition functions. The partition function $Z_{v_i}$ of symmetric vibrational mode 1 with degeneracy $g_{v_1} = 1$ is,

$$Z_{v_1} = \sum_{v_1=0}^{\infty} g_{v_1} e^{-\beta_j h\nu_i (v_1 + \frac{1}{2})} = e^{-\frac{1}{2} \beta_j h\nu_i} \sum_{v_1=0}^{\infty} (e^{-\beta_j h\nu_i})^{v_1} = e^{-\frac{1}{2} \beta_j h\nu_i} \left( \frac{1}{1 - e^{-\beta_j h\nu_i}} \right).$$  \hspace{1cm} (3.236)

The partition function $Z_{v_2}$ of vibrational bending mode 2 with degeneracy $g_{v_2} = v_2 + 1$ is,

$$Z_{v_2} = \sum_{v_2=0}^{\infty} g_{v_2} e^{-\beta_j h\nu_2 (v_2 + 1)} = e^{-\beta_j h\nu_2} \sum_{v_2=0}^{\infty} (v_2 + 1) (e^{-\beta_j h\nu_2})^{v_2} = e^{-\beta_j h\nu_2} \left( \frac{1}{1 - e^{-\beta_j h\nu_2}} \right)^2.$$  \hspace{1cm} (3.237)

The partition function $Z_{v_3}$ of asymmetric vibrational mode 3 with degeneracy $g_{v_3} = 1$ is,

$$Z_{v_3} = \sum_{v_3=0}^{\infty} g_{v_3} e^{-\beta_j h\nu_3 (v_3 + \frac{1}{2})} = e^{-\frac{1}{2} \beta_j h\nu_3} \sum_{v_3=0}^{\infty} (e^{-\beta_j h\nu_3})^{v_3} = e^{-\frac{1}{2} \beta_j h\nu_3} \left( \frac{1}{1 - e^{-\beta_j h\nu_3}} \right).$$  \hspace{1cm} (3.238)

The rotational partition function $Z_j$ with degeneracy $\theta_j = 2j + 1$ is determined using equation (2.84) and (2.85) for the rotational partition function $Z_r$ to be,

$$Z_j = \frac{1}{\sigma} \sum_j \theta_j e^{-\beta_j h\nu B(j+1)} \approx \frac{1}{\sigma} \int_{j=0}^{\infty} (2j+1) e^{-\beta_j h\nu B(j+1)} \, dj = \frac{1}{\sigma} \beta_j h\nu B.$$  \hspace{1cm} (3.239)

Substitution of equations (3.234), (3.235), (3.236), (3.237), (3.238), and (3.239) into equation (4.233) gives for the equilibrium spatial number density $n_{\text{eq}}^{[v_1,v_2,v_3,j]}$ of CO$_2$ molecules in a ro-vibrational state $[v_1,v_2,v_3,j]$,

$$n_{\text{eq}}^{[v_1,v_2,v_3,j]} = n_{\text{CO}_2} \frac{g_{v_1} g_{v_2} g_{v_3} \theta_j e^{-\beta_j h\nu_1 v_1} e^{-\beta_j h\nu_2 v_2} e^{-\beta_j h\nu_3 v_3} e^{-\beta_j h\nu B(j+1)}}{(1-e^{-\beta_j h\nu_1}) (1-e^{-\beta_j h\nu_2}) (1-e^{-\beta_j h\nu_3}) (1-e^{-\beta_j h\nu B})} \frac{1}{2\beta_j h\nu B}$$

$$= n_{\text{CO}_2} (v_2 + 1)(2j+1) e^{-\beta_j h\nu_1 v_1} e^{-\beta_j h\nu_2 v_2} e^{-\beta_j h\nu_3 v_3} e^{-\beta_j h\nu B(j+1)}$$

$$\left(1 - e^{-\beta_j h\nu_1} \right) \left(1 - e^{-\beta_j h\nu_2} \right) \left(1 - e^{-\beta_j h\nu_3} \right) \frac{1}{2\beta_j h\nu B}$$

$$= n_{\text{CO}_2} (v_2 + 1) e^{-\beta_j h\nu_1 v_1} e^{-\beta_j h\nu_2 v_2} e^{-\beta_j h\nu_3 v_3} \sigma P_j$$

$$= n_{\text{eq}}^{[v_1,v_2,v_3,j]} P_j.$$ \hspace{1cm} (3.240)

Here, the functions $p_v$ and $P_j$ are given by,

$$p_v = \left(1 - e^{-\beta_j h\nu_1} \right) \left(1 - e^{-\beta_j h\nu_2} \right) \left(1 - e^{-\beta_j h\nu_3} \right),$$ \hspace{1cm} (3.241)

$$P_j = 2\beta_j h\nu B(2j+1) e^{-\beta_j h\nu B(j+1)},$$ \hspace{1cm} (3.242)

\footnote{This is at partial thermal equilibrium of the rotational and vibrational energy levels, and must not be confused with the total thermal equilibrium of the system.}
Rotational relaxation effect. For rotational levels which do not have a Boltzmann distribution, the probability $P_j$ of a CO$_2$ molecule having rotational energy level $j$ is not given by equation (3.235) as this is only valid at thermal equilibrium of the rotational energy levels. The rotational relaxation time $\tau_r$ is defined as,

$$\tau_r^{-1} = \sum_j k_j.$$  

(3.243)

Here, $k_j$ are the rate coefficients of the collisions involving only rotational levels. The change of spatial number density $n_{[v_1,v_2,v_3,j]}$ of CO$_2$ molecules in state $[v_1,v_2,v_3,j]$, using equations (3.243) and (3.233), is given by,

$$\frac{\partial n_{[v_1,v_2,v_3,j]}}{\partial t} = \frac{n_{[v_1,v_2,v_3,j]}^{eq} - n_{[v_1,v_2,v_3,j]}}{\tau_r} = \frac{P_j n_{[v_1,v_2,v_3]}^{eq} - n_{[v_1,v_2,v_3,j]}}{\tau_r}.$$  

(3.244)

The lasing occurs between two states, which are the lasing levels. The upper and lower lasing level have respectively a higher and lower energy relative to each other and have spatial number densities $n_{up}$ and $n_{lo}$. Applying equation (3.244) to these lasing levels gives the rotational relaxation effect on both spatial number densities,

$$\frac{\partial n_{up}}{\partial t} = \frac{n_{up}^{eq} - n_{up}}{\tau_{r,up}},$$  

(3.245)

$$\frac{\partial n_{lo}}{\partial t} = \frac{n_{lo}^{eq} - n_{lo}}{\tau_{r,lo}}.$$  

(3.246)

Here, $\tau_{r,up}$ is the rotational relaxation time of the upper lasing level, and $\tau_{r,lo}$ the rotational relaxation time of the lower lasing level. It is assumed that these rotational relaxation times are equal $\tau_{r,up} = \tau_{r,lo} = \tau_r$. Equation (3.246) can be rewritten using $1 = \frac{\theta_{up} n_{up}}{n_{up}^{eq}} \frac{\theta_{lo} n_{lo}}{n_{lo}^{eq}}$ to give,

$$\frac{\partial}{\partial t} \left( \frac{\theta_{up} n_{lo}}{n_{lo}^{eq}} \right) = \frac{\theta_{up} n_{lo}^{eq} - n_{lo}}{\tau_r}.$$  

(3.247)

Subtraction of this equation (3.247) from equation (3.245) for the upper lasing level gives,

$$\frac{\partial n_{up}}{\partial t} - \frac{\partial}{\partial t} \left( \frac{\theta_{up} n_{lo}}{n_{lo}^{eq}} \right) = \frac{n_{up}^{eq} - \theta_{up} n_{lo}^{eq}}{\tau_r} - \frac{\theta_{up} n_{lo}^{eq} - n_{lo}}{\tau_r} = \left( \frac{n_{up}^{eq} - \theta_{up} n_{lo}^{eq}}{\tau_r} \right) - \left( \frac{n_{up} - \theta_{up} n_{lo}}{\tau_r} \right).$$  

(3.248)

The population inversion $\Delta$ between the upper and lower lasing state at thermal equilibrium of the rotational and vibrational states, or equilibrium population inversion is defined as,

$$\Delta = n_{up}^{eq} - \frac{\theta_{up} n_{lo}^{eq}}{\theta_{lo}}.$$  

(3.249)

Using equation (3.202) for the population inversion density $\delta$ between the lasing levels and equation (3.249) for the equilibrium population inversion density $\Delta$, to obtain an expression for the effect of rotational relaxation,

$$\frac{\partial \delta}{\partial t} = - \frac{\delta - \Delta}{\tau_r}.$$  

(3.250)

If the rotational energy levels are in thermal equilibrium then the lasing level populations $n_{up}$ and $n_{lo}$ are equal to the equilibrium lasing level population $n_{up}^{eq}$ and $n_{lo}^{eq}$. Similarly, the population inversion $\delta$ is then equal to the equilibrium population inversion $\Delta$.

\[ \text{This is at partial thermal equilibrium of the rotational and vibrational energy levels, and must not be confused with total thermal equilibrium of the system.} \]
Population inversion of light-matter interactions  The populations of the lasing levels also change due to the light-matter interactions according to equations (2.134) and (2.135) or analogously to equation (3.205). The rate of change of spatial number density of the upper \( n_{up} \) and lower \( n_{low} \) lasing levels are,

\[
\frac{\partial n_{up}}{\partial t} = -\frac{\sigma I \delta}{h \nu}, \quad (3.251) \quad \frac{\partial n_{lo}}{\partial t} = \frac{\sigma I \delta}{h \nu}. \quad (3.252)
\]

Equation (3.252) can be rewritten using \( 1 = \frac{\theta_{up}}{\theta_{lo}} \theta_{lo} \theta_{up} \) to give,

\[
\frac{\partial}{\partial t} \left( \frac{\theta_{up} \theta_{lo} n_{lo}}{\theta_{lo}} \right) = \frac{\sigma I \delta}{h \nu}. \quad (3.253)
\]

Subtraction of this equation (3.253) from equation (3.251) for the upper lasing level gives,

\[
\frac{\partial n_{up}}{\partial t} - \frac{\partial}{\partial t} \left( \frac{\theta_{up} \theta_{lo} n_{lo}}{\theta_{lo}} \right) = -\frac{\sigma I \delta}{h \nu} - \delta - \Delta \tau_r. \quad (3.254)
\]

Using the definition (3.202) for the population inversion density \( \delta \) the expression for the effect of the light-matter interactions on the population inversion density is given by,

\[
\frac{\partial \delta}{\partial t} = -\left( 1 + \frac{\theta_{up}}{\theta_{lo}} \right) \frac{\sigma I \delta}{h \nu}. \quad (3.255)
\]

Population inversion equation  The population inversion \( \delta \) is affected by both rotational relaxation and the light-matter interactions as described above. Combining the expression (3.250) and (3.255) accounting for these physical processes gives an expression for the population inversion density \( \delta \),

\[
\frac{\partial \delta}{\partial t} = -\left( 1 + \frac{\theta_{up}}{\theta_{lo}} \right) \frac{\sigma I \delta}{h \nu} - \frac{\delta - \Delta}{\tau_r}. \quad (3.256)
\]

Rotational relaxation for CO\(_2\) laser amplification  The model for rotational relaxation developed in the previous sections can be applied to the lasing states of the 10\(P\)20 and 10\(R\)26 transitions in the CO\(_2\)-laser amplification system with a CO\(_2\)-N\(_2\)-He-CO gas mixture. The evolutions of the population inversions \( \delta_a \) and \( \delta_b \) are given by equation (3.256) to be,

\[
\frac{\partial \delta_a}{\partial t} = -\left( 1 + \frac{\theta_{up, a}}{\theta_{lo, a}} \right) \frac{\sigma_a I_a \delta_a}{h \nu_a} - \frac{\delta_a - \Delta_a}{\tau_r}, \quad (3.257)
\]

\[
\frac{\partial \delta_b}{\partial t} = -\left( 1 + \frac{\theta_{up, b}}{\theta_{lo, b}} \right) \frac{\sigma_a I_a \delta_b}{h \nu_b} - \frac{\delta_b - \Delta_b}{\tau_r}. \quad (3.258)
\]

The population inversions \( \delta_a \) and \( \delta_b \) are again defined by equations (3.230) and (3.231). The equilibrium population inversions \( \Delta_a \) and \( \Delta_b \) are given by equation (3.249) to be,

\[
\Delta_a = n_{eq, up, a} - \frac{\theta_{lo, a}}{\theta_{up, a}} n_{eq, lo, a}, \quad (3.259) \quad \Delta_b = n_{eq, up, b} - \frac{\theta_{lo, b}}{\theta_{up, b}} n_{eq, lo, b}. \quad (3.260)
\]

The rotational degeneracy \( \theta = 2j + 1 \) of the lasing levels are given by,

\[
\theta_{up, a} = \theta(j = 19) = 2(19) + 1 = 39, \quad (3.261)
\]
The equilibrium populations of the lasing levels are given by equation (3.240) to be,
\[ \theta_{\text{lo},a} = \theta(j = 20) = 2(20) + 1 = 41, \]  
\[ \theta_{\text{up},b} = \theta(j = 27) = 2(27) + 1 = 55, \]  
\[ \theta_{\text{lo},b} = \theta(j = 26) = 2(26) + 1 = 53. \]  

The equilibrium populations of the lasing levels are given by equation (3.240) to be,
\[ n_{\text{up},a}^{eq} = n_{[0,0,1,19]}^{eq} = n_{\text{CO}_2} e^{-\beta_3 h \nu_3} p_v p_r (j = 19), \]  
\[ n_{\text{lo},a}^{eq} = n_{[1,0,0,20]}^{eq} = n_{\text{CO}_2} e^{-\beta_1 h \nu_1} p_v p_r (j = 20), \]  
\[ n_{\text{up},b}^{eq} = n_{[0,0,1,27]}^{eq} = n_{\text{CO}_2} e^{-\beta_3 h \nu_3} p_v p_r (j = 27), \]  
\[ n_{\text{lo},b}^{eq} = n_{[1,0,0,26]}^{eq} = n_{\text{CO}_2} e^{-\beta_1 h \nu_1} p_v p_r (j = 26). \]  

### 3.4.3 Summary of the reservoir model for CO2-laser amplification

**The equations** In sections 3.3 and 3.4, descriptions are developed for the evolution of the gas mixture, radiation, and rotational relaxation. The equations describing the evolution of the radiation through the system are given in section 3.4.1 by equations (3.220)–(3.223). To solve these intensity equations, the small-signal gain coefficients \( G_a \) and \( G_b \) have to be known and are given by equations (3.224) and (3.225). The small-signal gain coefficients \( G_a \) and \( G_b \) depend respectively on the absorption cross sections \( \sigma_a \) and \( \sigma_b \) given by equations (3.226) and (3.227), which in turn depend on the spectral line shapes \( g(\lambda_a) \) and \( g(\lambda_b) \) given in equations (3.228) and (3.229) for monochromatic waves. Furthermore, the small-signal gain coefficients \( G_a \) and \( G_b \) depend respectively on the population inversions \( \delta_a \) and \( \delta_b \) defined in equations (3.230) and (3.231). These population inversions depend on the populations of the lasing levels. Due to the lasing and the effect of rotational relaxation these population inversions evolve in time. The time evolution of these population inversions \( \delta_a \) and \( \delta_b \) is given by equations (3.257) and (3.258). To solve these population inversion equations the equilibrium population inversions \( \Delta_a \) and \( \Delta_b \) have to be known and are given by equations (3.259), (3.260), (3.257), and (3.258). The equilibrium population inversions \( \Delta_a \) and \( \Delta_b \) depend on the rotational degeneracies \( \theta_{\text{up},a} \), \( \theta_{\text{lo},a} \), \( \theta_{\text{up},b} \), and \( \theta_{\text{lo},b} \) given by equations (3.261)–(3.264). Furthermore, the equilibrium population inversions \( \Delta_a \) and \( \Delta_b \) depend on the equilibrium populations \( n_{\text{up},a}^{eq} \), \( n_{\text{lo},a}^{eq} \), \( n_{\text{up},b}^{eq} \), and \( n_{\text{lo},b}^{eq} \) given in equations (3.265)–(3.268). The equilibrium populations in turn depend on the functions \( p_v \) and \( p_r \) which are given by respectively equations (3.241) and (3.242). These populations depend directly and indirectly through the functions \( p_r \) and \( p_v \) on the the thermodynamic betas \( \beta \) which in turn depend on the reservoir temperatures \( T_0 \), \( T_1 \), \( T_2 \), \( T_3 \), \( T_4 \), \( T_5 \) given by equations (3.173)–(3.175). These reservoir temperatures depend on the reservoir energy densities \( U_0 \), \( U_1 \), \( U_2 \), \( U_3 \), \( U_4 \), \( U_5 \). Due to the collisions, the interaction with the electromagnetic radiation, input power through electron excitation, and gas flow, these reservoir energy densities evolve in time. Considering the chemistry given in Table 3.4, the gas flow, and the input power through electron excitation, the energy density equations for the CO2-N2-He-CO gas mixture are given by equations (3.179)–(3.184). To account for the change of reservoir energies due to the interaction of the gas mixture with the electromagnetic field the addition of the source powers of equations (3.211)–(3.216) is needed. The full reservoir equations are given by,
\[ \frac{dU_0}{dt} = \frac{U_1 - U_{13}^{eq}(T_0)}{\tau_{10}(T_0)} + \frac{U_2 - U_{23}^{eq}(T_0)}{\tau_{20}(T_0)} + \frac{U_3 - U_{31}^{eq}(T_0)}{\tau_{30}(T_0)} + \frac{U_4 - U_{41}^{eq}(T_0)}{\tau_{40}(T_0)} + \frac{U_5 - U_{51}^{eq}(T_0)}{\tau_{50}(T_0)} + \left(1 - \frac{h\nu_1}{h\nu_2}\right) \frac{U_2 - U_{13}^{eq}(T_0, T_1)}{\tau_{11}(T_0, T_1)} + \left(1 - \frac{h\nu_2}{h\nu_3}\right) \frac{U_3 - U_{23}^{eq}(T_0, T_2)}{\tau_{22}(T_0, T_2)} + \left(1 - \frac{h\nu_3}{h\nu_4}\right) \frac{U_4 - U_{31}^{eq}(T_0, T_3)}{\tau_{33}(T_0, T_3)} + \left(1 - \frac{h\nu_4}{h\nu_5}\right) \frac{U_5 - U_{41}^{eq}(T_0, T_4)}{\tau_{44}(T_0, T_4)} + \left(1 - \frac{h\nu_5}{h\nu_6}\right) \frac{U_6 - U_{51}^{eq}(T_0, T_5)}{\tau_{55}(T_0, T_5)} + \left(1 - \frac{h\nu_6}{h\nu_7}\right) \frac{U_7 - U_{61}^{eq}(T_0, T_6)}{\tau_{66}(T_0, T_6)} + \left(1 - \frac{h\nu_7}{h\nu_8}\right) \frac{U_8 - U_{71}^{eq}(T_0, T_7)}{\tau_{77}(T_0, T_7)} + \left(1 - \frac{h\nu_8}{h\nu_9}\right) \frac{U_9 - U_{81}^{eq}(T_0, T_8)}{\tau_{88}(T_0, T_8)} + \cdots + \chi_{\text{tr}}P_{\text{in}} - \frac{U_0 - U_{01}^{eq}}{\tau_1} - (R_{\text{up,a}} - R_{\text{lo,a}}) \frac{1}{h\nu_0}G_4I_a - (R_{\text{up,b}} - R_{\text{lo,b}}) \frac{1}{h\nu_0}G_5I_b. \]

\[ \frac{dU_1}{dt} = -\frac{U_1 - U_{13}^{eq}(T_0)}{\tau_{10}(T_0)} + \frac{h\nu_1 U_2 - U_{23}^{eq}(T_0, T_1)}{\tau_{21}(T_0, T_1)} + \frac{h\nu_2 U_3 - U_{31}^{eq}(T_0, T_2)}{\tau_{32}(T_0, T_2)} + \frac{h\nu_3 U_4 - U_{41}^{eq}(T_0, T_3)}{\tau_{43}(T_0, T_3)} + \frac{h\nu_4 U_5 - U_{51}^{eq}(T_0, T_4)}{\tau_{54}(T_0, T_4)} + \frac{h\nu_5 U_6 - U_{61}^{eq}(T_0, T_5)}{\tau_{65}(T_0, T_5)} + \frac{h\nu_6 U_7 - U_{71}^{eq}(T_0, T_6)}{\tau_{76}(T_0, T_6)} + \frac{h\nu_7 U_8 - U_{81}^{eq}(T_0, T_7)}{\tau_{87}(T_0, T_7)} + \frac{h\nu_8 U_9 - U_{91}^{eq}(T_0, T_8)}{\tau_{98}(T_0, T_8)} + \frac{1}{\nu_{\text{in}}}G_4I_a - \frac{1}{\nu_{\text{out}}}G_5I_b. \]

\[ \frac{dU_2}{dt} = -\frac{U_2 - U_{23}^{eq}(T_0)}{\tau_{20}(T_0)} + \frac{h\nu_2 U_3 - U_{31}^{eq}(T_0, T_2)}{\tau_{32}(T_0, T_2)} + \frac{h\nu_3 U_4 - U_{41}^{eq}(T_0, T_3)}{\tau_{43}(T_0, T_3)} + \frac{h\nu_4 U_5 - U_{51}^{eq}(T_0, T_4)}{\tau_{54}(T_0, T_4)} + \frac{h\nu_5 U_6 - U_{61}^{eq}(T_0, T_5)}{\tau_{65}(T_0, T_5)} + \frac{h\nu_6 U_7 - U_{71}^{eq}(T_0, T_6)}{\tau_{76}(T_0, T_6)} + \frac{h\nu_7 U_8 - U_{81}^{eq}(T_0, T_7)}{\tau_{87}(T_0, T_7)} + \frac{h\nu_8 U_9 - U_{91}^{eq}(T_0, T_8)}{\tau_{98}(T_0, T_8)} + \frac{1}{\nu_{\text{in}}}G_4I_a - \frac{1}{\nu_{\text{out}}}G_5I_b. \]

\[ \frac{dU_3}{dt} = -\frac{U_3 - U_{33}^{eq}(T_0)}{\tau_{30}(T_0)} + \frac{h\nu_3 U_4 - U_{41}^{eq}(T_0, T_3)}{\tau_{43}(T_0, T_3)} + \frac{h\nu_4 U_5 - U_{51}^{eq}(T_0, T_4)}{\tau_{54}(T_0, T_4)} + \frac{h\nu_5 U_6 - U_{61}^{eq}(T_0, T_5)}{\tau_{65}(T_0, T_5)} + \frac{h\nu_6 U_7 - U_{71}^{eq}(T_0, T_6)}{\tau_{76}(T_0, T_6)} + \frac{h\nu_7 U_8 - U_{81}^{eq}(T_0, T_7)}{\tau_{87}(T_0, T_7)} + \frac{h\nu_8 U_9 - U_{91}^{eq}(T_0, T_8)}{\tau_{98}(T_0, T_8)} + \frac{1}{\nu_{\text{in}}}G_4I_a - \frac{1}{\nu_{\text{out}}}G_5I_b. \]

\[ \frac{dU_4}{dt} = -\frac{U_4 - U_{44}^{eq}(T_0)}{\tau_{40}(T_0)} + \frac{h\nu_4 U_5 - U_{51}^{eq}(T_0, T_4)}{\tau_{54}(T_0, T_4)} + \frac{h\nu_5 U_6 - U_{61}^{eq}(T_0, T_5)}{\tau_{65}(T_0, T_5)} + \frac{h\nu_6 U_7 - U_{71}^{eq}(T_0, T_6)}{\tau_{76}(T_0, T_6)} + \frac{h\nu_7 U_8 - U_{81}^{eq}(T_0, T_7)}{\tau_{87}(T_0, T_7)} + \frac{h\nu_8 U_9 - U_{91}^{eq}(T_0, T_8)}{\tau_{98}(T_0, T_8)} + \frac{1}{\nu_{\text{in}}}G_4I_a - \frac{1}{\nu_{\text{out}}}G_5I_b. \]

\[ \frac{dU_5}{dt} = -\frac{U_5 - U_{55}^{eq}(T_0)}{\tau_{50}(T_0)} + \frac{h\nu_5 U_6 - U_{61}^{eq}(T_0, T_5)}{\tau_{65}(T_0, T_5)} + \frac{h\nu_6 U_7 - U_{71}^{eq}(T_0, T_6)}{\tau_{76}(T_0, T_6)} + \frac{h\nu_7 U_8 - U_{81}^{eq}(T_0, T_7)}{\tau_{87}(T_0, T_7)} + \frac{h\nu_8 U_9 - U_{91}^{eq}(T_0, T_8)}{\tau_{98}(T_0, T_8)} + \frac{1}{\nu_{\text{in}}}G_4I_a - \frac{1}{\nu_{\text{out}}}G_5I_b. \]
Figure 3.2: The 1D space with a vertex-centered grid. The variables are evaluated at the nodal point $P$ at the center of a cell. The fluxes $\Gamma_w$ and $\Gamma_e$ are evaluated at the cell boundaries at respectively the west and east side of the cells.

The explicit expressions for the relaxation times $\tau$ are given in sections 3.3.3-3.3.6.

**Calculation flow path**  In order to solve the equations of the model a particular sequence of calculations, a calculation flow path, has to be performed. First all parameters and constants are specified, which leaves only the variables to be unknown. The starting point are the initial conditions for the energy densities $U_i$ with $i = 0, 1, 2, 3, 4, 5$ in the reservoir energy density equations (3.269)-(3.274). The energy densities $U_i$ are used to calculate the reservoir temperatures $T_i$ of equations (3.173)-(3.178). The reservoir temperatures $T_i$ are used to calculate multiple variables. In the reservoir model itself, describing the laser plasma, they are used to calculate the equilibrium energy densities $U^{eq}$ and the relaxation times $\tau$ appearing in the reservoir energy density equations (3.269)-(3.274). In the absence of radiation, these reservoir energy density equations are used to calculate the reservoir energy densities $U_i$ at the next time step. In the presence of radiation the reservoir temperatures $T_i$ are used to calculate the equilibrium populations $n^{eq}$ of the lasing levels of equations (3.265)-(3.268). The equilibrium populations $n^{eq}$ of the lasing levels are used to calculate the equilibrium population inversions $\Delta$ of equations (3.259) and (3.260). The equilibrium population inversions $\Delta$ together with initial conditions are used to calculate the populations inversions $\delta$ of equations (3.257) and (3.258). The populations inversions $\delta$ are used to calculate the small-signal gain coefficients $G$ of equations (3.224) and (3.225). The small-signal gain coefficients $G$ together with initial conditions are used to calculate the intensities $I$ of equations (3.220)-(3.223) at the next time step. The intensities $I$, together with the small-signal gain coefficients $G$, are used to calculate the additional power density source terms $P_\lambda$ of equations (3.211)-(3.216) appearing in the reservoir energy density equations as a result of the interaction of the radiation. These power density source terms $P_\lambda$ are used to calculate the reservoir energy densities $U_i$ of the reservoir energy density equations (3.269)-(3.274) at the next time step. This completes the calculation loop, which can be repeated to calculate the reservoir energy densities $U_i$ and radiation intensity $I$ at subsequent time steps, thereby calculating their evolution in time.

### 3.5 Numerical approach using PLASIMO

In this section the numerical approach using the PLASIMO code is considered. The radiation transport module of PLASIMO is used to analyze the evolution of radiation in a one-dimensional space using an implicit time-stepping method. The 1D space of the amplifier system has a vertex-centered grid with a nodal point $P$ at the center of the cells. The intensity equations (3.220)-(3.223) are discretized on this grid such that the variables are evaluated at the nodal point $P$ of a cell and the fluxes $\Gamma_w$ and $\Gamma_e$ at the respectively the west and east boundary of a cell. For the discretization in space, when a control volume is used, the equations are solved in integral form rather than in differential form. The control volume method requires the perpendicular components of the fluxes to be discretized on the control volume boundary surface. A (semi)-implicit time-stepping method is used for the linearization of the equations for radiation, population inversions, and energy sources. The evolution of radiation through a laser plasma is investigated in the next Chapter 4 using the numerical implementation in PLASIMO of the reservoir model for CO$_2$-laser amplification.
Results: CO$_2$-laser amplification

Susskind: "I probably need an eraser."
Audience: "There are four over there."
Susskind: "No, no, no, no, no, you are not understanding me."
Audience: "A person to erase."
Susskind: "Yes."

Leonard Susskind

In this chapter the evolution of infra-red CO$_2$-laser pulses through a CO$_2$-N$_2$-He gas mixture is investigated using a numerical implementation in PLASIMO of the reservoir model for CO$_2$-laser amplification developed in the previous chapter [3]. The simulation results of various different cases are presented showing the capabilities of the model and its verification.

The chapter is divided into eight sections. In section [4.1] the system under consideration is set up by defining the initial conditions and specifying the parameters for simulations with PLASIMO. In section [4.2] the creation of the laser plasma is considered to determine typical values of the variables and the desired steady state for amplification. In section [4.3] numerical convergence of the simulation results for its spatial and temporal resolution is determined to assure that the resolved physics is independent of the resolutions. In section [4.4] the evolution of a single forward pulse put into the system at different times during the creation of the laser plasma is investigated to determine its amplification behavior under different conditions. In section [4.5] the effect of rotational relaxation on the amplification of a forward pulse is determined. In section [4.6] the evolution of a single long pulse is compared to a that of a forward pulse train consisting of shorter pulses. In section [4.7] the evolution of backward pulses is investigated together with their effect on the amplification of forward pulses. In section [4.8] the CO$_2$-laser amplification system is simulated as close as possible to a realistic operational situation. Here, the output radiation is investigated for the evolution of a forward pulse train accompanied by a backward pulse train.

4.1 Setting up the system

The parameters for the simulations with PLASIMO of the system under consideration used in the equations of the reservoir model for CO$_2$-laser amplification are specified in Table [4.1]. The parameters are the pressure $p$, the initial temperature $T_{in}$, the average gas residence time $\tau_{res}$, the input power $P_{in}$, the rotational relaxation time $\tau_R$, fraction $\chi_{tr}$ of input power to the ro-translational reservoir, fraction $\chi_x$ with $x = 1, 2, 3, 4$ of input power to the vibrational mode reservoirs, the fraction $f_\alpha$ of particles of type $\alpha$, and the length $L$ of the system.

The initial conditions for the differential equations of the reservoir energy densities $U_i$ are such that the reservoir temperatures $T_i$ given by equations (3.173), (3.178), are all equal to an input initial gas temperature $T_{in}$ at time $t = 0$ s. The initial condition for the ro-translational energy density $U_0$ is determined by substitution of $T_0(t = 0) = T_{in}$ in equation (3.173) for the
Table 4.1: Parameters values used in the PLASIMO simulations of the amplification setup.

<table>
<thead>
<tr>
<th>Plasma parameters</th>
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</thead>
<tbody>
<tr>
<td>$p$</td>
</tr>
<tr>
<td>$T_{in}$</td>
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<tr>
<td>$\tau_{res}$</td>
</tr>
<tr>
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<tr>
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</tr>
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<td>$\chi_4$</td>
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<table>
<thead>
<tr>
<th>Gas mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{CO_2}$</td>
</tr>
<tr>
<td>$f_{N_2}$</td>
</tr>
<tr>
<td>$f_{He}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amplifier medium</th>
</tr>
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<tbody>
<tr>
<td>$L$</td>
</tr>
</tbody>
</table>
4.1. SETTING UP THE SYSTEM

ro-translational temperature $T_0$ giving,

$$T_0 (t = 0) = T_{in} = T_{in} e^{-\frac{h \nu_{max}}{k_B T_{in}}} U_0 (t = 0) \rightarrow U_0 (t = 0) = 0. \quad (4.1)$$

The initial conditions for the reservoir energy densities $U_x$ with $x = 1, 2, 3, 4, 5$ are determined by substitution of $T_x (t = 0) = T_{in}$ in equation (3.56) for the vibrational temperatures $T_x$ giving,

$$U_x (t = 0) = k_x n_{in}, h\nu_x \left( e^{\frac{h\nu_x}{k_B T_{in}}} - 1 \right)^{-1} = k_x U_x^{eq} (T_x = T_{in}). \quad (4.2)$$

The vibrational mode degeneracies are $k_1 = k_3 = k_4 = k_5 = 1$ and $k_2 = 2$ for the vibrational modes in the system. In conclusion, using equations [4.1] and [4.2] the initial conditions are determined using the ideal gas law,

$$N_\alpha = \frac{f_\alpha p}{RT_{in}}. \quad (4.4)$$

Here, $f_\alpha$ is the fraction of molecules of type $\alpha$, $p$ the pressure, and $R$ the gas constant. The initial conditions for the equations (3.257) and (3.258) for the populations inversions $\delta$ are given by the fact that the system initially is in thermal equilibrium, where the population inversions $\delta$ are equal to the equilibrium populations inversions $\Delta$,

$$\delta_\alpha (t = 0) = \Delta_\alpha (t = 0), \quad (4.5)$$

$$\delta_\alpha (t = 0) = \Delta_\alpha (t = 0). \quad (4.6)$$

The initial conditions for the equations (3.220)-(3.223) for the intensity $I$ are given by,

$$I_\alpha^{fwd} (x, t = 0) = 0, \quad (4.7)$$

$$I_\alpha^{bwd} (x, t = 0) = 0. \quad (4.8)$$

$$I_\beta^{fwd} (x, t = 0) = 0, \quad (4.9)$$

$$I_\beta^{bwd} (x, t = 0) = 0. \quad (4.10)$$

Next to initial conditions the equations (3.220), (3.223) for the intensity $I$ require boundary conditions. The boundary conditions are given by the input intensity at the left and right boundary,

$$I_\alpha^{fwd} (x = 0, t) = I_{\alpha, in}^{fwd} (t), \quad (4.11)$$

$$I_\alpha^{bwd} (x = L, t) = I_{\alpha, in}^{bwd} (t), \quad (4.12)$$

$$I_\beta^{fwd} (x = 0, t) = I_{\beta, in}^{fwd} (t), \quad (4.13)$$

$$I_\beta^{bwd} (x = L, t) = I_{\beta, in}^{bwd} (t). \quad (4.14)$$

1 If the process with relaxation time $\tau_{in}$ is not included in the chemistry and $U_{\alpha, in}^{eq} (T_0)$ is not specified the equilibrium value is chosen to be $U_{\alpha, in}^{eq} (T_0 = T_{in}, T_1 = T_{in}, T_2 = T_{in})$, which gives an equivalent expression.
CHAPTER 4. RESULTS: CO$_2$-LASER AMPLIFICATION

Table 4.2: The performed simulations together with their characteristic parameters.

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<th>Label</th>
<th>$N_{cp}$</th>
<th>$N_{fp}$</th>
<th>$t_p$ [μs]</th>
<th>$t_{in}$ [ms]</th>
<th>$t_d$ [ns]</th>
<th>$N_{bp}$</th>
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The numerical approach of section 3.5 is used to perform the simulations. The performed simulations together with their characteristic parameters such as the number of spatial calculation points $N_{cp}$, number of forward pulses $N_{fp}$, number of backward pulses $N_{bp}$, duration of the pulses $\tau_p$, time of initial input of radiation $t_{in}$, delay of initial forward input relative to backward input $t_d$, delay between subsequent pulses in a pulse train $\tau_{td}$, the rotational relaxation time $\tau_R$, and the minimum time step $\Delta t_{min}$ of the simulations are listed in Table 4.2.

4.2 Creating the laser plasma

In this section first the creation of the laser plasma in the system is investigated before any radiation is put into the system to be amplified. This is done to determine the typical values of the variables under the given conditions and to establish the desired state for amplification.

Initially, at $t = 0$, the gas mixture is in a state of thermal equilibrium described by the initial conditions equations (4.3). All reservoir temperatures $T_i$ of the gas mixture are at that moment equal to $T_i = 360$ K as presented in Figure 4.1a, which is in agreement with the initial conditions (4.3). In thermal equilibrium, the populations of energy levels are distributed according to a Boltzmann distribution. Levels with a lower energy have higher populations than those with higher energy, which will not facilitate conditions for amplification of radiation.
4.2. CREATING THE LASER PLASMA

Figure 4.1: Reservoir temperatures $T_i$ as a function of time $t$. Figure 4.1a shows that initially all $T_i$ are equal to $T_{in} = 360$ K. In Figure 4.1b their long-term behavior shows that the system reaches a steady state together with their characteristic values under these conditions.

This is confirmed by Figure 4.2a showing that, initially, the upper lasing level population density $n_{up}$ is $3.81 \times 10^{17}$ m$^{-3}$ which is smaller than the lower lasing level population density $n_{lo}$ of $1.75 \times 10^{19}$ m$^{-3}$. The radiation intensity $I$ and the gain factor $G$ are related in equation (3.218). The small-signal gain $G$, defined in equation (3.224), indicates the magnitude with which amplification occurs and depends on the population inversion $\delta$. According to these equations a positive small-signal gain amplifies the input intensity and a negative small-signal gain reduces it. The population inversion $\delta$, defined by the upper and lower lasing level population densities $n_{up}$ and $n_{lo}$ in equation (3.230), initially is negative as shown in Figure 4.2a. This results in a negative small-signal gain $G$ leading to a negative amplification of radiation, or in other words absorption of radiation. This confirms that the system starts from thermal equilibrium, which is not suited for the amplification of radiation. In Figure 4.3 the reservoir energy densities $U_i$ as a function of time $t$ are presented. The reservoir energy densities $U_0$, $U_1$, $U_2$, $U_3$, and $U_4$, initially, have values of respectively $0$ J m$^{-3}$, $8.47$ J m$^{-3}$, $155$ J m$^{-3}$, $0.3$ J m$^{-3}$, and $2$ J m$^{-3}$ as can be seen in Figure 4.3a. The goal of creating the steady state plasma is to acquire a state of the laser plasma which can accommodate amplification of input radiation. A constant input power $P_{in}$ is delivered to the gas mixture through electron excitation. High-energy electrons are put into the system, which upon collision with the constituents of the gas mixture will excite or ionize the molecules, thereby populating their higher energy levels and create a laser plasma. This leads to a changing state of the laser plasma together with changing reservoir temperatures $T_i$, populations $n_i$, and reservoir energies $E_i$. The laser plasma will reach a steady state, because the input power fractions $\chi$ of the inflowing gas mixture and input power $P_{in}$ are constant in time. This steady state is created to fulfill the main goal of the amplification system, which is the amplification of infra-red CO$_2$-laser pulses.

In order to determine the long-term behavior of the amplification system the evolution is simulated for 0.03 s. Figure 4.1b shows that the reservoir temperatures $T_i$ evolve towards a constant value, meaning that the system reaches the steady state. The reservoir temperatures $T_0$, $T_1$, $T_2$, $T_3$ eventually reach values of respectively $429$ K, $438$ K, $437$ K, and $1743$ K. It can be concluded that already 5 ms after starting from thermal equilibrium the steady state is reached and the plasma is created.

The population inversion $\delta$, initially, is negative and switches sign after approximately 10 µs, corresponding to the time at which the upper population density $n_{up}$ becomes larger than the lower populations density $n_{lo}$. In the steady state the lasing levels reach a constant population of $n_{up} = 3.93 \times 10^{20}$ m$^{-3}$ and $n_{lo} = 2.86 \times 10^{19}$ m$^{-3}$ as shown in Figure 4.2a.
CHAPTER 4. RESULTS: CO$_2$-LASERAMPLIFICATION

Figure 4.2: The upper lower lasing level populations $n_{\text{up}}$ and $n_{\text{lo}}$, and the population inversion \( \delta \) as a function of time \( t \). Figure 4.2a shows that initially $n_{\text{lo}}$ is larger than $n_{\text{up}}$, resulting in a negative \( \delta \). After 10 \( \mu \text{s} \), $n_{\text{up}}$ becomes larger than $n_{\text{up}}$, resulting in a positive \( \delta \). Figure 4.2b shows their evolution towards their constant values in the steady state.

Figure 4.3: Reservoir energy densities $U_i$ as a function of time $t$. Figure 4.3a shows that initially at thermal equilibrium all $U_i$ have values specified by the initial conditions (4.3). In Figure 4.3b they reach their steady state values, where $U_0$ and $U_4$ show the most dramatic increase.
4.3. CONVERGENCE

In the process of creating the plasma next to changing reservoir temperatures $T_i$, also the corresponding reservoir energy densities $U_i$ change as shown in Figure 4.3. The reservoir energy densities $U_1$, $U_2$, and $U_3$ respectively increase to values of $19 \text{ J m}^{-3}$, $219 \text{ J m}^{-3}$, and $517 \text{ J m}^{-3}$. Energy densities $U_0$ and $U_4$ show a more dramatic increase up to a few thousand Joule per cubic meter. The cause of this dramatic increase can be explained as follows. The relaxation time $\tau_{40}$ is relatively large, therefore the corresponding energy transfer process from the vibrational mode of $N_2$ to the asymmetric mode of CO$_2$ is slow. In addition, in the reservoir model only one energy transfer process with relaxation time $\tau_{43}$ is able to decrease the reservoir energy density $U_4$. On the contrary, as the fraction $\chi_4$ is large the electron excitation of the vibrational mode of $N_2$ occurs with a relatively large portion of the input power $P_\text{in}$. As a result of these processes, energy density $U_4$ increases at a fast rate. Because the fraction $f_{N_2}$ of $N_2$ molecules is 0.77 there are a large number of $N_2$ molecules in the system resulting in the large value for $U_4$ of $3606 \text{ J m}^{-3}$. All energies except $U_0$ increase directly as a result of electron excitation. The energy transfer processes transferring energy from these reservoirs to the ro-translational reservoir become more dominant as other energy densities increase. Therefore, the energy density $U_0$ of the ro-translational energy reservoir, initially, increases relatively slow compared to the other energy densities, and eventually reaches the large value of $6361 \text{ J m}^{-3}$.

The steady state has a positive population inversion and, therefore, a positive small-signal gain $G$ of $12.8 \text{ m}^{-1}$ as shown in Figure 4.4. The conditions of the steady state allows for input radiation to amplify as it propagates through the laser plasma. In the following, therefore, radiation is put into the system after $t_s = 5 \text{ ms}$, unless indicated otherwise.

4.3 Convergence

In this section the numerical convergence of the simulation results for its spatial and temporal resolution is determined to assure that the resolved physics is independent of the resolution. The reason that this analysis is important is because higher spatial and temporal resolutions increase the computational costs, but a resolution which is too low leads to simulation results dominated by numerical effects and do not represent the physics very well.

In the simulations a single forward pulse is send into the system through which it evolves and eventually exits as output radiation. A higher spatial resolution is acquired by increasing the number of spatial nodal points $N_{\text{sp}}$ in the 1D space. A higher temporal resolution is achieved by decreasing the minimum time step $\Delta t_{\text{min}}$. In each case, the initial time step is chosen to be equal
to the minimum time step. The number of spatial nodal points $N_{\text{cp}}$ is varied between 1000, 10000, and 100000. The minimum time step $\Delta t_{\text{min}}$ is varied between $\Delta t_0 = 1 \cdot 10^{-11}$ s, $\Delta t_a = 1 \cdot 10^{-12}$ s, $\Delta t_b = 1 \cdot 10^{-13}$ s, $\Delta t_c = 1 \cdot 10^{-14}$ s, and $\Delta t_d = 1 \cdot 10^{-15}$ s, where these specific minimum time steps have been given the labels 0, a, b, c, and d respectively. The output radiation for a varying temporal resolution and $N_{\text{cp}} = 10000$ is presented in Figure 4.5. This figure shows that an increase of the temporal resolution results in numerical results for the output radiation which differs considerably. For too large minimum time steps specific details of the output radiation are not captured. For example, for the case with $\Delta t_0$ the peak intensity at the head of the pulse is not resolved at all. These results also apply to the cases with 1000 and 100000 nodal points. In order to do a convergence analysis an indicator of convergence has to be chosen. The maximum intensity $I_{\text{max}}$ of the output radiation differs dramatically between the different simulations. The maximum output radiation intensity $I_{\text{max}}$ is, therefore, used as an indicator of convergence.

The relative difference $\epsilon$, or relative error, of $I_{\text{max}}$ between simulations with different spatial and temporal resolutions indicates the magnitude of the effect of the numerical resolution on the simulation results. In order to show convergence, this error $\epsilon$ has to decrease for increasing resolutions. This can, in principle, be continued to the point that an increase of the resolution does not affect the simulation results anymore. In that case, the simulations have converged and the numerical results accurately represent the physics. The relative error $\epsilon(Q)_{XY}$ of a quantity $Q$ between simulations X and Y is,

$$\epsilon(Q)_{XY} = \frac{Q_X - Q_Y}{Q_X}. \quad (4.15)$$

Here, $Q_X$ is the value of the quantity in simulation X and $Q_Y$ is the value of the quantity in simulation Y. For this convergence analysis the relative error $\epsilon(\max I_{\Delta t_X \Delta t_Y})$ of the maximum intensity $I_{\text{max}}$ between simulations with temporal resolutions $t_X$ and $t_Y$ is used. The relative errors $\epsilon(\max I_{\Delta t_X \Delta t_Y})$ between simulations with different temporal resolutions for all three cases of spatial resolution are presented in Figure 4.6. For all three cases of spatial resolution the
4.3. CONVERGENCE

The relative error \( \epsilon(I_{\text{max}})_{\Delta t_X \Delta t_Y} \) between simulations with increasing temporal resolution becomes increasingly smaller. This is with the exception of the relative errors between simulations with time steps \( 1 \cdot 10^{-11} \) s, \( 1 \cdot 10^{-12} \) s, and \( 1 \cdot 10^{-13} \) s for both 10000 and 100000 nodal points. For these specific cases the error increases which is a result that can be attributed to the choice of \( I_{\text{max}} \) as an indicator of convergence. As the temporal resolution increases specific details, such as peak intensity values, of the output pulse shape are being resolved. This can lead to the increase of the error of the quantity \( I_{\text{max}} \) between simulations with increasing resolutions. However, further increase of the resolution results eventually in a decrease of the error and converging results.

The relative errors \( \epsilon(I_{\text{max}})_{N_{cp,X} N_{cp,Y}} \) of the maximum intensity \( I_{\text{max}} \) between the simulations with different spatial resolutions for all cases of temporal resolution are presented in Figure 4.7. For all temporal resolutions the relative error \( \epsilon(I_{\text{max}})_{N_{cp,X} N_{cp,Y}} \) between simulations with increasing spatial resolution becomes smaller. The previous convergence analysis shows that the simulation results are converging by increasing the spatial and temporal resolution. In the following sections, for the performed simulations a spatial resolution of \( N_{cp} = 100000 \) nodal points and a temporal resolution with a minimum time step of \( \Delta t_{\text{min}} = \Delta t_c = 1 \cdot 10^{-14} \) s is used.

For this 1D setup the CFL condition is,

\[
C = \frac{c \Delta t}{\Delta x} \leq C_{\text{max}}.
\]

Here, \( C \) is the Courant number, \( c \) is the magnitude of the velocity, being the speed of light, \( \Delta t \) the time step, and \( \Delta x \) the length interval. For a spatial resolution of 100000 nodal points the interval length, or grid cell size, is \( \frac{0.1 \text{ m}}{100000} = 1 \cdot 10^{-6} \) m. The time in which radiation with the speed of light \( c = 3 \cdot 10^8 \text{ m s}^{-1} \) traverses a single cell is \( \frac{\Delta x}{c} = \frac{1 \cdot 10^{-6} \text{ m}}{3 \cdot 10^8 \text{ m s}^{-1}} = 3.3 \cdot 10^{-13} \) s. This is the time step for a Courant number of 1 and smaller Courant numbers require a smaller time step. A time step larger than this leads to radiation skipping grid cells, because the time that it takes for radiation to traverse a cell is shorter. This suggests that a time step of \( 1 \cdot 10^{-14} \) s is necessary to ensure that the evolution of radiation is resolved without it skipping a grid cell. This is in agreement with the

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Figure 4.6: Relative error \( \epsilon(I_{\text{max}})_{\Delta t_X \Delta t_Y} \) of \( I_{\text{max}} \) between simulations with \( \Delta t_X \) and \( \Delta t_Y \) for the three cases of spatial calculation points \( N_{cp} \). For all \( N_{cp} \) the error becomes smaller for higher temporal resolutions.

---

\[
\epsilon_a, \epsilon_b, \epsilon_c, \epsilon_d
\]
4.4 Forward pulse

After establishing the conditions of the desired steady state in the previous section 4.2, in this section the evolution of a forward input pulse is investigated. This is done by comparing the evolution of radiation input pulses, which enter the system at different times during the creation of the laser plasma.

Four cases are considered in which the forward pulse is put into the system after 0 s, 20 µs, 100 µs, and 5 ms after the input power is started to be delivered. Specifically these four moments in time are chosen to show the effect on the evolution of radiation of a thermal equilibrium state, the sign of population inversion or small-signal gain, and the desired steady state.

The forward input pulse has an intensity amplitude $I_{in}$ of $7.50312 \cdot 10^9$ W m$^{-2}$ and a duration of 1 ns, as shown in Figure 4.8 by the black line. This intensity and duration of the forward input pulses applies to all cases in this chapter unless indicated otherwise. For the four cases considered in this section the only difference is the time $t_{in}$ at which the first radiation enters the system. The pulse propagates through the 1D space over a distance $L$ of 0.1 m from the left boundary towards the right boundary with the speed of light $c$. An arbitrary part of the pulse is in the system for $\frac{L}{c} = \frac{0.1 \text{ m}}{3.0 \cdot 10^8 \text{ m s}^{-1}} = 3.33 \cdot 10^{-10}$ s = 0.3 ns after which it exits the system.

**Pulse at $t_{in} = 0$ s**

The first case considers a forward input pulse put into the system at $t = 0$ s coinciding with the time at which input power $P_{in}$ is started to be provided. During the relatively short timespan that the pulse propagates through the system, the gas mixture is in a state which is still very close to thermal equilibrium. The population inversion $\delta$ and small-signal gain $G$ are negative, because

![Figure 4.7: Relative error $\epsilon(I_{max})N_{cp,X}N_{cp,Y}$ of $I_{max}$ between simulations with $N_{cp,X}$ and $N_{cp,Y}$ for all cases of minimum time step $\Delta t_{min}$. For all $\Delta t_{min}$ the error becomes smaller for higher spatial resolutions.](image)

previous convergence analysis which resulted in the choice for a similar minimal time step.
the upper lasing level has a smaller population than the lower lasing level as shown in Figures 4.2 and 4.4.

The probability that a photon of the forward pulse encounters a CO$_2$ molecule in the lower lasing level is higher than one in the upper lasing level. Therefore, through the process of stimulated emission, on average the CO$_2$ molecules will absorb more photons than emit photons. As a result, the pulse is partially absorbed by the gas mixture instead of amplified as shown by the red line in Figure 4.8. The intensity of the output pulse is slightly lowered with a maximum value of $7.40 \times 10^9$ W m$^{-2}$, thereby showing this absorption. The effect that the absorption of radiation has on the creation of the laser plasma is negligibly small. In principle the absorption of the pulse will slightly speed up the process as absorption makes the CO$_2$ molecule evolve from the lower lasing state to the upper lasing state.

While the input pulse has the prescribed intensity of a rectangular pulse, the output radiation shows slight rounding of the edges. As the number of spatial nodal points increases this numerical effect will decrease and the output pulse becomes more rectangular with increasingly steeper slopes.

**Pulses at $t = 20 \mu$s and $t = 100 \mu$s**

A forward input pulse put into the system after 20 $\mu$s encounters a population inversion which is positive as shown in Figure 4.2. This leads to a slight amplification of the input pulse obtaining a maximum intensity of $7.72 \times 10^9$ W m$^{-2}$ as indicated by the green line in Figure 4.8.

At an even later time $t = 100 \mu$s the population inversion and small-signal gain have increased even more according to Figures 4.2 and 4.4. This results in an even higher amplification of the pulse with a maximum intensity of $1.24 \times 10^{10}$ W m$^{-2}$ as indicated by the blue line in Figure 4.8.

**Pulse at $t = 5$ ms**

For the last case an input pulse enters the system if the steady state is reached after $t_s$. During the propagation of the pulse it encounters a laser plasma with a much larger population inversion.
and small-signal gain than at earlier times according to Figures 4.2 and 4.4. This pulse, therefore, has the largest amplification as indicated by the pink line in Figure 4.8, with a maximum intensity of $2.63 \times 10^{10}$ W m$^{-2}$.

The amplification of the pulses in these considered cases has an effect on the small-signal gain $G$, which drops dramatically during the time in which the pulse is present in the system. For the cases with an input pulse after 20 µs and 100 µs this dramatic drop in the small-signal gain $G$ is indicated by respectively the red and the green line in Figure 4.9. After the pulse exits the system the small-signal gain recovers and continues to increase in approximately the same way as if no pulse has entered the system at all as indicated by the blue line in Figure 4.9.

## 4.5 Rotational relaxation

After establishing the amplification behavior of a forward pulse in the previous section 4.4, the effect of rotational relaxation on the evolution of a pulse is considered in this section. The rotational relaxation model described in section 3.4.2 takes into account the rotational relaxation time $\tau_R$ it takes for the rotational energy levels to rearrange into a Boltzmann distribution after a disturbance. If rotational relaxation is not taken into account, as is the case in the previous sections, it is assumed that the rearranging occurs so fast that a Boltzmann distribution is maintained at all times for the rotational energy levels.

Two cases are compared in which the evolution of a single forward pulse is considered with and without rotational relaxation corresponding to rotational relaxation times of respectively $\tau_R = 0.2$ ns and $\tau_R = 0$ s. The output radiation for a single forward input pulse with and without rotational relaxation is presented in Figure 4.10. Clearly the output radiation is affected by taking rotational relaxation into account. Without rotational relaxation the output pulse has a maximum intensity of $2.63 \times 10^{10}$ W m$^{-2}$, while with rotational relaxation it is $2.01 \times 10^{10}$ W m$^{-2}$. Both pulses show a
4.5. ROTATIONAL RELAXATION

decrease in intensity from their heads to tails. The head of the pulse exits the system first and is amplified the most, while the tail of the pulse exits the system after the head and is amplified less. The relative intensity decrease in the tail of the pulse depends on the consideration of rotational relaxation or not. With rotational relaxation the end of the pulse tail has an intensity of $8.70 \cdot 10^9$ W m$^{-2}$, which is 43 percent of its maximum intensity at the head of the pulse. Without rotational relaxation the tail of the pulse has an intensity of $1.03 \cdot 10^{10}$ W m$^{-2}$, which is 39 percent of the maximum intensity. This shows that the decrease of intensity is larger if rotational relaxation is taken into account. In fact, over the whole length of the pulse the amplification is smaller if rotational relaxation is accounted for.

The intensity decrease is a consequence of a decreasing population inversion as the pulse is propagating through the laser plasma. The head of the pulse encounters a laser plasma in steady state and is amplified accordingly. This amplification leads to a decrease of the upper lasing level population and an increase of the lower lasing level population, because CO$_2$ molecules transition from the upper to the lower lasing level due to stimulated emission. The pulse tail reaches the positions of the pulse head at later times when the head already interacted with the laser plasma. The tail of the pulse, therefore, encounters a laser plasma which has a lower small-signal gain resulting in a smaller amplification.

The lasing level populations and the population inversions for both without and with rotational relaxation are presented in Figure 4.11. Before a pulse passes the upper and lower lasing level populations for both with and without rotational relaxation are respectively $3.93 \cdot 10^{20}$ m$^{-3}$ and $2.86 \cdot 10^{19}$ m$^{-3}$, and the population inversion between the lasing levels is $3.66 \cdot 10^{20}$ m$^{-3}$, which is in agreement with equation (3.259).

Without rotational relaxation the upper lasing level population $n_{\text{up}} = n_{\text{equ}}$ drops during the passage of the pulse towards $2.42 \cdot 10^{20}$ m$^{-3}$, while the lower lasing level population $n_{\text{lo}} = n_{\text{equ}}$ increases to $2.01 \cdot 10^{20}$ m$^{-3}$. As a result, the population inversion $\delta = \Delta$ drops during the passage of the pulse towards $5.13 \cdot 10^{19}$ m$^{-3}$. This leads to the particular shape of the output pulse having a gradual decrease of intensity from its head to the end of its tail.
CHAPTER 4. RESULTS: CO$_2$-LASER AMPLIFICATION

Figure 4.11: The equilibrium upper and lower lasing level populations $n_{\text{eq}}^{\text{up}}$ and $n_{\text{eq}}^{\text{lo}}$, the equilibrium population inversion $\Delta$, and the population inversion $\delta$ as a function of time $t$ for relaxation times $\tau_R = 0$ s and $\tau_R = 0.2$ ns. For $\tau_R = 0$ s, $n_{\text{eq}}^{\text{up}} = n_{\text{up}}$, $n_{\text{eq}}^{\text{lo}} = n_{\text{lo}}$, and $\Delta = \delta$, while for $\tau_R = 0$ s this is not the case. The effect of rotational relaxation becomes apparent in the difference between $\delta$ and $\Delta$ during the passage of the pulse.

Without rotational relaxation the populations $n_{\text{eq}}^{\text{up}} = n_{\text{up}}$, $n_{\text{eq}}^{\text{lo}} = n_{\text{lo}}$, and $\Delta = \delta$, while for a finite relaxation time this is not the case, except when the rotational energy levels reach a thermal equilibrium with each other. With rotational relaxation the equilibrium upper lasing level population $n_{\text{eq}}^{\text{up}}$ drops less drastically to $3.66 \cdot 10^{20}$ m$^{-3}$ during the passage of the pulse, which is higher than the upper lasing level population without rotational relaxation. The equilibrium lower lasing level population $n_{\text{eq}}^{\text{lo}}$ increases to $6.33 \cdot 10^{19}$ m$^{-3}$, which is lower than lower lasing level population without rotational relaxation. During the passage of the pulse the equilibrium population inversion $\Delta \neq \delta$ drops towards $3.06 \cdot 10^{20}$ m$^{-3}$, which is higher than without rotational relaxation. The population inversion $\delta$ drops rapidly after the pulse arrives towards $4.27 \cdot 10^{19}$ m$^{-3}$. For the remainder of the length of the pulse it drops relatively slow towards $4.10 \cdot 10^{19}$ m$^{-3}$. After the pulse passes the rotational energy levels restore towards a Boltzmann distribution, resulting in a relatively fast increase of the population inversion $\delta$ towards the equilibrium population inversion $\Delta$.

The effect of rotational relaxation clearly shows up here in the difference between $\delta$ and $\Delta$ during the passage of the pulse. The fast drop of the population inversion $\delta$ results from the amplification of the pulse, thereby depleting the upper lasing level population $n_{\text{up}}$ and feeding the lower lasing level population $n_{\text{lo}}$. It takes a finite amount of time, characterized by the rotational relaxation time $\tau_R$, for the rotational energy levels to rearrange into a Boltzmann distribution. As a result, the population inversion $\delta$ drops fast, because the rotational energy levels are not instantaneously redistributed into populations corresponding to that of a Boltzmann distribution. After the fast drop the population inversion $\delta$ shows a relatively slow decrease, because the rotational relaxation constraints the amplification process. The fast drop of population inversion leads to a large pulse amplification resulting in the high peak intensity at the head of the pulse. Hereafter, the relatively slow population inversion decrease leads to a smaller amplification of the tail of the pulse. After the pulse has passed the rotational energy levels relax towards a Boltzmann distribution, thereby increasing the population inversion $\delta$ again towards $\Delta$.

This analysis shows the effect of rotational relaxation on the amplification of the pulse and the particular shape of the pulse. With rotational relaxation the amplification is smaller, because the
4.6 Long forward pulse and pulse train

In this section the amplification of a long 10 ns single forward pulse and multiple 1 ns forward pulses, or a pulse train is considered.

The output radiation of the 10 ns pulse, shown in Figure 4.12 by the red line, has a similar overall shape as the 1 ns pulse considered in the previous section. In this Figure 4.12 also the output radiation of the 1 ns pulse is indicated by the green line and the 10 ns input pulse by the black line. The 10 ns pulse gets amplified to a maximum intensity of $2.01 \cdot 10^{10}$ W m$^{-2}$ which is identical to the 1 ns pulse. This is expected because the first nanosecond of the long pulse amplifies as if it were a 1 ns pulse. After reaching the maximum intensity the intensity of the long pulse decreases to an intensity of $7.85 \cdot 10^9$ W m$^{-2}$ after which the pulse ends after 10 ns.

For the second case a sequence of identical forward input pulses, or a pulse train, is being send into the system. The delay between the pulses is 2 ns resulting in a 1 ns duration between the tail of a pulse and the head of the next pulse as shown in Figure 4.13 by the black line. The first pulse of the pulse train evolves in exactly the same way as the single forward pulse from the previous section and the first nanosecond of the long pulse, where the pulse has a maximum value of $2.01 \cdot 10^{10}$ W m$^{-2}$ at its head and decreases in intensity towards $8.70 \cdot 10^9$ W m$^{-2}$ at its tail. Subsequent output pulses of the pulse train have a similar shape, however, with a lower maximum and overall intensity. The second pulse, for example, has a maximum at its head of $1.72 \cdot 10^{10}$ W m$^{-2}$ and intensity of $8.5 \cdot 10^9$ W m$^{-2}$ at its tail. The decrease of maximum intensity relative to the previous pulse is 14, 12, 10, and 8 percent for respectively the second, third, fourth, and fifth pulse. This smaller amplification of the subsequent pulses is caused by the same reason as the decreasing intensity in the tail of the first output pulse. The depletion of the upper lasing level
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Figure 4.13: Intensity $I$ as a function of time $t - t_s$. For the pulse train with $I_{in}$ the output pulses, except for the first, have higher amplification than the 10 ns pulse, because between the pulses the laser plasma has time to recover. Furthermore, the subsequent pulses of the pulse train have a similar shape, however, with a lower maximum and overall intensity.

by stimulated emission as the first pulse reaches every position prior to the second pulse.

During the evolution of the whole pulse train the electron excitation with input power $P_{in}$ continues feeding the gas mixture with energy and feeding the upper lasing level to increase the population inversion towards its value of the steady state. In the time between the end of a pulse and the start of the next pulse, no radiation passes. The population inversion partially recovers as a result of the electron excitation. It is for this reason the intensity of the tail of a pulse is lower than the intensity of the head of the next pulse. This is nicely illustrated when the output pulse train is compared to the output of the 10 ns pulse in Figure 4.13. During the long pulse the gas mixture does not have the time to recover, resulting in a lower intensity of the pulse compared to the subsequent pulses of the pulse train.

The magnitude of the amplification of the pulses in a pulse train depends of the duration of the delay between the pulses as during this time the gas mixture recovers. In Figure 4.14 the output radiation of two distinct pulse trains, having delays between the heads of the pulses of $2 \cdot 10^{-7}$ s and $2 \cdot 10^{-6}$ s. For both of these two cases the first pulse is amplified equal to the first pulse of the pulse train with a delay of 2 ns. The second pulse has a maximum intensity of $1.84 \cdot 10^{10}$ W m$^{-2}$ and $1.90 \cdot 10^{10}$ W m$^{-2}$ for the pulse trains with a delay of respectively $2 \cdot 10^{-7}$ s and $2 \cdot 10^{-6}$ s. The maximum intensity of the second pulse is, therefore, 86, 92, and 95 percent of the first pulse for the three cases with a delay between the pulses of respectively 2 ns, $2 \cdot 10^{-7}$ s and $2 \cdot 10^{-6}$ s. As the delay becomes larger the reduction of amplification is decreases for subsequent pulses.

For a delay of 5 ms the gas mixture is expected to recover back to the steady state, as it took this amount of time to reach the steady state from thermal equilibrium. A single pulse, however, does not deplete the population inversion that much as for it to return to the population inversion at thermal equilibrium, which makes the time that the gas mixture needs to recover shorter than 5 ms. For the gas mixture to recover to the steady state after the first pulse and to amplify the second pulse with a similar magnitude as the first the delay between the pulses has to be a least 2.8 ms.
4.7. BACKWARD PULSE

Figure 4.14: Intensity $I$ as a function of time $t - t_s$. Figure 4.14a shows the output pulse train for $\tau_{td} = 0.2$ ms. Figure 4.14b shows the output pulse train for $\tau_{td} = 2$ ms. For an increasing $\tau_{td}$ the laser plasma has more time to recover and the amplification decrease of subsequent pulses becomes smaller.

The relative decrease of amplification drops as more pulses pass through the system. For the case with a delay of $2 \cdot 10^{-7}$ s after the 4th and 5th pulse have a maximum intensity of respectively $1.61 \cdot 10^{10}$ W m$^{-2}$ and $1.52 \cdot 10^{10}$ W m$^{-2}$. This comes down to a decrease of 5 percent and output pulses after these pulses have a decrease of less than 5 percent of the previous pulse. For the case with a delay of $2 \cdot 10^{-6}$ s this decrease of 5 percent is already the case after the 2nd pulse. Depending on many factors such as the input power $P_{in}$, delay between pulses, and intensity of input pulse, this decrease of the reduction of amplification changes.

4.7 Backward pulse

Up until now radiation propagating in the forward direction, from left to right, is considered as the desired output radiation is chosen to exit the system at the right boundary. Radiation going through the entire amplification system and exiting the system can outside of the system reflect back into it. This undesired effect can cause input radiation at the right boundary propagating from right to left. This backward radiation can interact with the gas mixture and influence the conditions for amplification of forward pulses. In this section these backward pulses are investigated.

First a backward pulse identical to a forward pulse except for its direction of propagation is put into the system. The resulting output radiation of the backward and forward pulse shows that they are identical, meaning that both initially identical pulses are amplified equally. From this it can be concluded that the symmetry in the system is respected by the model and simulations as the symmetry of the system demands that the evolution of a backward and forward pulse are identical except for their direction of propagation.

In the remainder of this section the effect of a backward pulse on the evolution of a forward pulse is investigated. Here, it is assumed that 10 percent of the forward pulse is reflected back into the system as a backward pulse. The forward and backward pulse are put into the system at the same time and travel, obviously, with the same speed towards each other and encounter each other at the center as shown in Figure 4.15. Before both pulses encounter each other both pulses propagate through the system as if no other radiation is present in the system, because neither pulse has affected the gas mixture at the position of the other pulse.

After the pulses pass each other both pulses encounter a gas mixture that is already affected by the other pulse, which will affect their amplification. The amplification of the backward pulse
CHAPTER 4. RESULTS: CO\textsubscript{2}-LASER AMPLIFICATION

Figure 4.15: Snapshot of the PLASIMO interface showing the intensity $I$ as a function of position $x$ for the forward and backward pulse at a specific time. At the left the forward pulse (blue) is propagating to the right, while on the right the backward pulse (green) is propagating to the left.

has caused a depletion of the upper lasing level and a decrease of the small-signal gain of the gas mixture at the positions where it has passed. This results in a smaller amplification of the forward pulse compared to the case without a backward pulse which is shown in Figure 4.16. In the presence of the backward pulse the maximum intensity at the head of the forward output pulse is $1.76 \cdot 10^{10} \text{ W m}^{-2}$, which is smaller than the $2.01 \cdot 10^{10} \text{ W m}^{-2}$ peak intensity without the presence of a backward pulse. This is thus a decrease of 12 percent of the maximum intensity in the presence of the backward pulse for this particular case. Furthermore, over the full length of the pulse the amplification is less in the case where a backward pulse is present in the system. This can be seen in Figure 4.16 where the red line lies above the black line over the length of the pulse. The backward pulse in this case is amplified to a maximum value of $1.55 \cdot 10^{9} \text{ W m}^{-2}$ shown later in Figure 4.17.

The backward pulse will, in practice, enter the system a finite time after the forward pulse has left the system as output radiation. The time that it will take for a forward pulse to be reflected back into the system as a backward pulse depends on geometrical parameters, such as the path taken by the pulse outside of the system. The backward pulse will then affect the amplification of a subsequent forward pulse depending on their relative delay.

Three cases are considered, where the forward pulse has a delay of $-1 \text{ ns}$, $1 \text{ ns}$, and $2 \text{ ns}$ with respect to a backward pulse. The first two cases show the effect on the amplification of the forward pulse, while the backward and forward pulse are in the system simultaneously and, therefore, encounter each other in the system. In the third case the backward pulse has evolved completely through the system and already completely exited before the forward pulse enters the system. The output radiation for these three cases as well as the case of simultaneous entry into the system is shown in Figure 4.17.

In the case with a delay of $-1 \text{ ns}$ the forward pulse gets amplified to a maximum intensity of $2.06 \cdot 10^{10} \text{ W m}^{-2}$. Comparing this results to the case with no delay shows that the amplification here is larger because the backward pulse has not depopulated the upper lasing level as much. This becomes apparent in the amplification of the backward pulse which reaches a maximum value of only $1.11 \cdot 10^{9} \text{ W m}^{-2}$.

In the case with a delay of $1 \text{ ns}$ the opposite occurs and the pulse gets amplified only to a
4.7. BACKWARD PULSE

Figure 4.16: Intensity $I$ as a function of time $t - t_s$ for $N_{bp} = 1$ and $N_{bp} = 0$. In the presence of a backward pulse the pulse amplification is smaller.

Figure 4.17: Intensity $I$ as a function of time $t - t_{ref}$ of forward and backward output pulses for four cases of different $\tau_d$. The reference time $t_{ref}$ is sum of $t_s$ and $\tau_d$ for both the forward and backward pulses such that all input radiation starts at $t - t_{ref} = 0$. 
maximum intensity of $1.30 \cdot 10^{10}$ W m$^{-2}$. This is lower than in the case with no delay because now the backward pulse partially depopulates the upper lasing level in a larger part of the system. This results in a smaller amplification for the forward pulse. The backward pulse in this case is amplified to a maximum value of $2.58 \cdot 10^{9}$ W m$^{-2}$.

In the case with a delay of 2 ns the backward pulse has evolved through the entire system and exited it before the forward pulse enters the system to be amplified. At the positions in the system where the backward pulse has passed the medium starts to recover. Next to this, during the time between the backward pulse leaving and the forward pulse entering the system the medium recovers even further. Hereafter, the forward pulse is evolving through the system and for this specific case amplifies to a pulse with a maximum intensity of $1.90 \cdot 10^{10}$ W m$^{-2}$. This maximum intensity is higher than for the case with a delay of 1 s and also even higher than that with no delay. This occurs because the backward pulse has partially drained the lasing level population but the laser plasma, however, has enough time to recover for this larger amplification. The backward pulse amplification is equivalent to the case without a forward pulse, because in both cases no forward pulse is present in the system at the time that the backward pulse is amplified. The backward pulse, then, reaches a maximum value of $2.58 \cdot 10^{9}$ W m$^{-2}$ which is equal to the case with a delay of 1 s, because in that case the head of the backward pulse is amplified while no forward pulse is present. After the forward pulse enters the system the backward pulses show differences.

4.8 Forward and backward pulse train

In the previous sections specific cases are considered to verify the numerical implementation of the model and show its capabilities. In this section the CO$_2$-laser amplification system is represented as close as possible to a realistic operational situation. Here, the output radiation of a forward pulse train accompanied by a backward pulse train is investigated.

First a forward and backward pulse train enter the system simultaneously. The forward output radiation in presented in Figure 4.18. The first output pulse is equal to the output pulse of a single forward pulse in the presence of a backward pulse discussed in section 4.7 with a maximum intensity of $1.76 \cdot 10^{10}$ W m$^{-2}$. Furthermore, the subsequent pulses in the pulse train have an
increasingly smaller maximum intensity, which is expected according to the discussion of section 4.6 and is due to the depopulation of the upper lasing levels by previous pulses. All the pulses show a decrease in the intensity starting from their heads having a peak maximum intensity and a smaller amplification towards their tails. This results in the typical shape of the output pulse as a result of rotational relaxation discussed in section 4.5.

The second pulse has a maximum intensity of $1.54 \times 10^{10}$ W m$^{-2}$, which is considerably lower than the first pulse. The third, fourth, and fifth pulses have a maximum intensity of respectively $1.37 \times 10^{10}$ W m$^{-2}$, $1.25 \times 10^{10}$ W m$^{-2}$, and $1.16 \times 10^{10}$ W m$^{-2}$. The decrease of the maximum intensity relative the previous pulse for this pulse train is 13, 11, 9, and 8 percent of respectively the second, third, fourth, and fifth pulse. This shows that the decrease in intensity becomes increasingly smaller as more pulses pass through the system, as was the case for the pulse train without the presence of backward pulses. As discussed in section 4.6, this decrease in maximum intensity of consecutive pulses can be decreased by increasing the delay between the pulses.

Now, the backward pulse train enters with a delay of 1 ns to represent some finite time the radiation needs to reflect and enter the system again. The forward output and backward output radiation is presented in Figure 4.18. It is clear that here the output pulses after the first pulse have a smaller amplification than in the case of simultaneous entry. This result can be contributed to the fact that here the laser plasma has less time to recover because a backward pulse is being amplified closer in time to the entry of the forward pulses. The second pulse has a maximum intensity of $1.31 \times 10^{10}$ W m$^{-2}$, which is considerably lower than the second pulse in the case of simultaneous entry. The third, fourth, and fifth pulses have a maximum intensity of respectively $1.19 \times 10^{10}$ W m$^{-2}$, $1.10 \times 10^{10}$ W m$^{-2}$, and $1.03 \times 10^{10}$ W m$^{-2}$. The decrease of the maximum intensity relative the previous pulse for this pulse train is 36, 9, 8, and 6 percent of respectively the second, third, fourth, and fifth pulse.

These final cases show a more realistic situation of a plasma cell in the amplification system. The output radiation depends heavily on the delay between pulses, molecular fractions of the gas mixture, spatial length of the system, input power, input intensity, and rotational relaxation time. These parameters can be changed in order to obtain desired specifications.
Summary, discussion, and outlook

"All science is either physics or stamp collecting."

Ernest Rutherford

5.1 Summary

In many technological applications, such as the process of extreme ultraviolet lithography, high-intensity CO$_2$-laser pulses are used. Some technological applications require such high-intensity laser radiation that this cannot be produced by a single CO$_2$-laser. The CO$_2$-laser radiation has to be amplified in order to meet these demands. The output radiation of a CO$_2$-laser is led into an amplification system, possibly consisting of multiple amplifiers in series, amplifying the CO$_2$-laser radiation to the desired intensity. The physical principles of such an CO$_2$-laser amplifier and a CO$_2$-laser are very similar such that a model can be applied to a single plasma cell of both of these amplification systems.

The objective is to learn about the dynamics of a CO$_2$-laser amplification system in order to be able to make predictions about its characteristics and performance. The research on the model used to describe the amplification system involves its theoretical derivation and development, going hand in hand with the investigation and verification of the results of its numerical implementation in PLASIMO.

A thorough description of laser plasmas involves various fields of physics, such as molecular dynamics, thermodynamics, statistical physics, quantum mechanics, quantum optics, and electrodynamics. A fundamental and in-depth treatment of laser plasmas and laser physics combines the theory of these fields of physics. The essential parts of these fields necessary for the development and derivation of the reservoir model for CO$_2$-laser amplification are described in Chapter 2. The molecular dynamics of a general molecule are considered, which can be applied to the constituents of the gas mixture in an amplification system. Furthermore, the distribution of energy in a system is described for its application on the laser plasma populations. Finally, the fundamental mechanism of lasing action through light-matter interaction is treated. This theory of Chapter 2 is then applied Chapter 3 to a CO$_2$-laser amplification system in order to describe its dynamics. The molecular dynamics are applied to the CO$_2$ molecule, as this molecule plays a central role in the dynamics of a CO$_2$-laser plasma. Furthermore, a theoretical derivation of the model is given from the first principles described in Chapter 2. The system contains a pre-mixture of CO$_2$:N$_2$:He-CO through which infra-red radiation with a wavelength of 10.58 µm and 10.206 µm, corresponding to the the 10P20 and 10R26 transitions of CO$_2$ molecules, is propagating. The developed general model is then applied to the system under consideration leading to the reservoir model for CO$_2$-laser amplification. The numerical implementation of the model in PLASIMO is used in Chapter 4 to investigate the evolution of radiation pulses through the system under consideration. Various cases are presented showing the behavior of the system together with the capabilities of the model.
5.2 Discussion

It takes 5 ms for the CO\textsubscript{2}-N\textsubscript{2}-He-CO gas mixture, which is initially in thermal equilibrium, to reach a steady state laser plasma under the given specific conditions and input power.

The numerical convergence of the simulation results is established to assure that the resolved physics is independent of the resolutions. From this convergence analysis it can be concluded that for a system length of 0.1 m with 100000 spatial calculation points, leading to a grid cell size of $\Delta x = 1 \, \mu m$, and a temporal resolution with a time step of $1 \cdot 10^{-14} \, s$ are viable choices for the resolution for the performed simulations.

A forward pulse which is put into the system when the gas mixture is still in a thermal equilibrium will be partially absorbed instead of amplified. Under the given conditions the small-signal gain becomes positive at 10 $\mu$s and grows larger towards its maximum value in the steady state. Forward pulses send into the system after 10 $\mu$s are amplified depending on the time of entry. This also shows that the magnitude of amplification depends on magnitude of the small-signal gain and, therefore, on the population inversion. In the steady state the input radiation is amplified to the greatest extend to a maximum intensity of 3.5 times that of the input pulse.

A rotational relaxation time 0.2 ns is chosen, which is typical for gas mixtures under atmospheric pressure [51]. Taking into account rotational relaxation reduces the amplification of the pulse to a maximum intensity which is 2.68 times that of the input pulse. Furthermore, the intensity decrease over the length of the pulse starting from the maximum intensity at the head of the pulse shows a much steeper drop if rotational relaxation is taking into account. This results in an overall different output pulse shape having a high peak intensity at the head and an overall lower amplification of the pulse.

In comparing the output pulse for a relatively long pulse and a pulse train it is shown that the consecutive pulses in a pulse train are subject to a decrease in amplification. This is caused by the same effect responsible for the intensity decrease over the length of a pulse, which is the depletion of the upper lasing level and population inversion. During the time in between the pulses of a pulse train the population inversion of the laser plasma recovers as a result of the constant input power. The reduction of the amplification depends on the delay between the pulses of the pulse train. For larger pulse train delays the amplification reduction decreases. For a delay of 2.8 $\mu$s the subsequent pulses are amplified with a similar magnitude as the first pulse, because the laser plasma needs this amount of time to recover from the particular input pulses under these conditions. In addition, the relative decrease of amplification drops as more pulses pass through the system.

In a more realistic operation situation a forward and backward pulses continuously enter the system. The output radiation shows the characteristics discovered in the previous cases. In the presence of backward pulses the amplification of forward pulses is smaller, as a result of the depletion of the population inversion of the laser plasma. In addition, the subsequent output pulses
have increasingly smaller maximum intensity. Furthermore, all the pulses have the typical pulse shape with a large peak intensity at their heads and a smaller amplification towards their tails as a result of the rotational relaxation. The output radiation depends heavily on the parameters such as the delay between pulses, molecular fractions of the gas mixture, spatial length of the system, input power, input intensity, and rotational relaxation time, which can be changed accordingly in order to obtain desired output pulses.

5.3 Outlook

This thesis sets a solid basis for future research on the reservoir model for CO$_2$-laser amplification. There are many possibilities for future research within this field. The model can be validated using its numerical implementation against analytical results such as those for pulse propagation in laser amplifiers by Frantz and Nodvik [45] and rotational relaxation by Schappert [51]. Furthermore, energy conservation in the system can be determined which should prevail in a self-consistent model. In the present model the physical phenomenon of spontaneous emission is ignored. Spontaneous emission, however, inevitably occurs in any lasing system. This spontaneous emitted radiation can be amplified leading to the undesired effect of amplified spontaneous emission (ASE) [83] [89] [90] [91] [92] [93] [94] [95] [96] [97] [98] [99] described by Linford’s formula [100] [101] [102]. The model can be extended to account for the ASE to be able to show to which extend this could damage the lasing system or have other undesired effects. In Appendix E the first steps undertaken to incorporate this phenomena in the forms of notes are added. Another possibility is the comparison to experimental results of the time evolution of the vibrational temperatures in a CO$_2$ glow discharge measured in infrared absorption spectroscopy by Klarennaar [103].
**Appendices**

A Born-Oppenheimer approximation

Here, the Born-Oppenheimer approximation is considered in more mathematical detail. Starting from the molecular wave equation,

\[
\hat{H}_m(\psi_m) = E_m \psi_m, \quad (A.1)
\]

in the end the nuclear wave equation is acquired,

\[
\hat{H}_n(\psi_n) = E_m \psi_n. \quad (A.2)
\]

Here, parentheses "()" are used to indicate on which part the operator acts. The molecular Hamiltonian \( \hat{H}_m \) is given by the Coulomb Hamiltonian,

\[
\hat{H}_m = -\sum_{i=1}^{N_n} \frac{\hbar^2}{2m_n} \nabla_i^2 - \sum_{j=1}^{N_e} \frac{\hbar^2}{2m_e} \nabla_j^2 + \sum_{i>j} Z_i Z_k \frac{e^2}{4\pi\varepsilon_0 r_{ni}r_{nj}} + \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0 r_{ni}r_{ej}}. \quad (A.3)
\]

The molecular wave equation is factorized into the nuclear wave function \( \psi_n \) and the electronic wave function \( \psi_e \),

\[
\psi_m = \psi_n \psi_e. \quad (A.4)
\]

The molecular wave equation \( (A.1) \) then becomes,

\[
-\sum_{i=1}^{N_n} \frac{\hbar^2}{2m_n} \nabla_i^2 (\psi_n \psi_e) - \sum_{j=1}^{N_e} \frac{\hbar^2}{2m_e} \nabla_j^2 (\psi_n \psi_e) + V_m \psi_n \psi_e = E_m \psi_n \psi_e. \quad (A.5)
\]

Applying the product rule to equation \( (A.5) \) results in,

\[
-\sum_{i=1}^{N_n} \frac{\hbar^2}{2m_n} (\nabla_i^2 (\psi_n) \psi_e + \psi_n \nabla_i^2 (\psi_e) + 2\nabla_i (\psi_n) \cdot \nabla_i (\psi_e))
-\sum_{j=1}^{N_e} \frac{\hbar^2}{2m_e} (\nabla_j^2 (\psi_n) \psi_e + \psi_n \nabla_j^2 (\psi_e) + 2\nabla_j (\psi_n) \cdot \nabla_j (\psi_e)) + V_m \psi_n \psi_e = E_m \psi_n \psi_e \quad (A.6)
\]

Now, if the variation of the electronic wave function \( \psi_e \) with the internuclear distance is sufficiently slow, the first \( \nabla (\psi_e) \) and second derivatives \( \nabla^2 (\psi_e) \) can be neglected. This is a consequence of the difference in mass, so that the nuclear wave function is more spatially localized than the electron wave function. Equation \( (A.6) \) can then be approximated by,

\[
-\sum_{i=1}^{N_n} \frac{\hbar^2}{2m_n} (\psi_n \nabla_i^2 (\psi_e)) + V_m \psi_n \psi_e = E_m \psi_n \psi_e. \quad (A.7)
\]

This can be written more compact as,

\[
\hat{T}_n (\psi_n) \psi_e + \psi_n \hat{T}_e (\psi_e) + V_m \psi_n \psi_e = E_m \psi_n \psi_e. \quad (A.8)
\]
Equation (A.8) is divided by $\psi_n\psi_e$,
\[
\frac{1}{\psi_n\psi_e} \left( \hat{T}_n (\psi_n) \psi_e + \psi_n \hat{T}_e (\psi_e) + V_m \psi_n \psi_e \right) = \frac{1}{\psi_n\psi_e} (E_m \psi_n \psi_e),
\]
this results in,
\[
\frac{\hat{T}_n (\psi_n)}{\psi_n} + \frac{\hat{T}_e (\psi_e)}{\psi_e} + V_m = E_m. \tag{A.9}
\]
By making the substitution $V_m = V_{nn} + V_{ee} + V_{ne}$ and rearranging terms,
\[
\left( \hat{T}_n + \hat{V}_{nn} \right) \frac{(\psi_n)}{\psi_n} + \left( \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne} \right) \frac{(\psi_e)}{\psi_e} = E_m. \tag{A.10}
\]
This equation (A.11) can also be written as,
\[
\hat{H}_n (\psi_n) + \hat{H}_e (\psi_e) = E_m. \tag{A.11}
\]
Note that the Hamiltonian $\hat{H}_e$ depends only parametrically on the nuclear positions $r_n$. Therefore, separation of variables gives,
\[
\hat{H}_e (\psi_e) = E_e - \hat{H}_n (\psi_n) = E_e, \tag{A.12}
\]
or written differently,
\[
\hat{H}_e (\psi_e) = E_e \psi_e. \tag{A.13}
\]
Here, $E_e$ is a separation constant and the eigenvalues of this equation, which represents the electron energies. This electronic wave equation (A.14) can be solved for a set of nuclear configurations $\{r_n\}$ giving the eigenvalues $E_e$ as a function of the nuclear positions. This gives rise to the potential energy surfaces, the so-called Born-Oppenheimer surfaces. Then, the electronic part of the molecular Hamiltonian can be substituted by these potential energy surfaces. This can be seen as a adiabatic contribution to the potential energy of the nuclei. This procedure gives the nuclear wave equation,
\[
\left( \hat{T}_n + \hat{V}_{nn} + E_{el} \right) (\psi_n) = \hat{H}_n (\psi_n) = E_m \psi_n. \tag{A.15}
\]

B Boltzmann distribution in statistical physics

Thermodynamics and statistical physics  Thermodynamics is the theory of internal dynamics of many-body systems, such as solids, liquids, and gases. Therefore, thermodynamics is a widely applicable theory. These macroscopic many-body systems are comprised of a very large numbers of elements, such as the number of molecules in a gas mixture or photons in an electromagnetic field. These numbers are so large that describing the dynamics of all the individual element is not a desired description. Thermodynamics describe the state of the system using a number of quantities, which is much smaller than the number of degrees of freedom of the system. These macroscopic properties do not depend on the dynamics of the individual elements, but depend on the average dynamics of all the elements. These thermodynamic quantities thus depend on the statistical behavior of the elements of the system. Statistical physics is the theory that considers the statistics of systems consisting of a large numbers of elements. Again these elements can be many things, such as particles, spins, and bits. The branch of statistical mechanics which is concerned with thermodynamics is called statistical thermodynamics. Statistical thermodynamics thus produces a connection between the macroscopic thermodynamic properties and the microscopic behavior of a system.
Systems, subsystems and ensembles  The concept of a system can be very abstract. A system is a group of elements, or subsystems, forming a unified whole. A system can thus represent many things, such as a single molecule, a vessel containing a gas or even the universe as a whole. In physics a system is often specified as a spacial volume with boundaries were matter and other forms of energy exist inside. The system can be subject to some constraints which define the type of system. In an open system, energy and matter can cross the boundaries. In a closed system, energy can cross the boundary but matter cannot. In an isolated system neither energy nor matter can cross the boundary. Another example is a system were the elements are imaginary identical subsystems, which can represent, for example, a physical system. This imaginary collection of subsystem is referred to as an ensemble. In statistical physics there are three statistical ensemble which are often described in literature and worth mentioning here, namely the canonical ensemble, micro-canonical ensemble, and the grand canonical ensemble. In the canonical ensemble the subsystems are closed and in thermal contact with each other. Therefore, the volume $V$, the number of elements $N$ of the subsystems, and the temperature $T$ of all subsystems are equal, thereby also referred to as the $NVT$-ensemble. In the micro-canonical ensemble the subsystems are isolated. Therefore, the volume $V$, the number of elements $N$ of the subsystems, and the energy $E$ of all subsystems are equal, thereby also referred to as the $NVE$-ensemble. In the grand canonical ensemble the subsystems are open and in thermal contact with each other. Therefore, the volume $V$, temperature $T$, and the chemical potential $\mu$ of all subsystems are equal, thereby also referred to as the $\mu VT$-ensemble.

Micro-states and macro-states  Imagine a system consisting of $n$ subsystems, existing in a certain state. Multiple subsystems, incidentally, can be identical and in the following it assumed that all the subsystems are identical. Each individual subsystem also is in a certain state and all the states of the subsystems together make up the state of the system. The number $n_i$ of subsystem in state $i$ is the occupation number of state $i$. The number of subsystems $n$ in terms of these occupation numbers $n_i$ is,

$$n = \sum_i n_i.$$  \hfill (B.1)

Here, the sum $\sum_i$ is over all the potentially accessible states of the subsystems, which can be infinite. Each individual subsystem possesses a certain energy and all the energies of the subsystems together make up the energy of the system. The energy $E$ of the system is,

$$E = \sum_n E_n = \sum_i n_i E_i.$$  \hfill (B.2)

Here, $E_n$ is the energy of subsystem $n$ and $E_i$ is the energy of the subsystems in state $i$. The concept of the 'state' at this point is not very clear. Therefore, in the following the concept of a state is elaborated. The concept of a state can be defined in a formal way by stating that the state of a system is a description of the information contained in the system. All the physical things happening to all the elements, or for that matter subsystems, in a system have some amount of information associated with them. The micro-state of a system is a description of all the information contained in a system. It specifies the states of every subsystem. As an illustration of the concept of a micro-state consider a volume filled with particles. In classical mechanics the micro-state specifies the position and momentum, hence the energy, of all the particles. In quantum mechanics the micro-state specifies the complete set of quantum numbers of every particle. A description can also contain less than all information contained in the system. The configuration of a system is the set of occupation numbers of all states and is noted as $\{n_i\}$ \footnote{The accolades {} indicate that it concerns a set. The configuration $\{n_i\}$ is thus the set $[n_1, n_2, \cdots]$.}. The configuration does not contain the information about a specific subsystem, but only about the distribution of subsystems among their possible states. The thermodynamic state of a system is given by thermodynamic properties of the system, such as the number $n$ of subsystems, the energy
E, the temperature \( T \), the entropy \( S \) and the volume \( V \) of the system. The thermodynamic state contains no information about specific subsystems or about their distribution, but only about averages of states of subsystems. In literature both of these descriptions are sometimes confusingly referred to as the macro-state of the system. This confusion especially arises when concepts such as multiplicity, statistical entropy and the second law of thermodynamics are discussed. To avoid confusion in this work the macro-state of the system is the configuration \( \{ n_i \} \) of the system. The thermodynamic state of the system is sometimes just referred to as the state of the system. By investigation of the information contained in the previous descriptions it becomes apparent that the micro-state specifies the macro-state, vice versa this does not hold. Another conclusion is that it is possible that different micro-states realize the same macro-state. The number of micro-states that correspond to the same macro-state \( S \) is called the multiplicity \( \Omega_S \) of the macro-state \( S \). Hence, the total number of micro-states, or multiplicity of the system, \( \Omega_{\text{system}} \) of a system in some state is,

\[
\Omega_{\text{system}} = \sum_S \Omega_S. \tag{B.3}
\]

Here, the sum \( \sum_S \) is over all possible macro-states, or configurations, of the system in a certain state. Again, as in the case of the possible accessible states of the subsystems \( i \), the possible number of macro-states can be infinite. The multiplicity \( \Omega_{\text{system}} \) is thus the number of accessible micro-states of the system in some thermodynamic state.

**Fundamental postulate of statistical physics**  A system can be subject to constraints, by which the number of accessible states in which it can exist is limited. The fundamental postulate of statistical mechanics is the principle of equal a priori probability and gives that,

*for an isolated system at thermal equilibrium all accessible microstates are equally probable.*

This postulate can also be slightly altered to form a fundamental definition of thermal equilibrium. This definition gives that *an isolated system for which all accessible micro-states are equally probable is at thermal equilibrium*. According to this postulate the probability \( P_s \) of an isolated system at thermal equilibrium existing in a micro-state is given by,

\[
P_s = \frac{1}{\Omega_{\text{system}}}. \tag{B.4}
\]

In other words, the probability of the isolated system at thermal equilibrium being in a certain micro-state is the inverse of the number of accessible micro-states or multiplicity of the system \( \Omega_{\text{system}} \), because all micro-states are equally probable. Of course the probabilities \( P_s \) for all micro-states should sum to 1, because the system exists in one of the accessible micro-states \( s \), so \( \sum_s P_s = 1 \). The probability \( P_S \) of an isolated system at thermal equilibrium existing in a macro-state is then given by,

\[
P_S = \Omega_S P_s = \frac{\Omega_S}{\Omega_{\text{system}}}. \tag{B.5}
\]

Again the condition \( \sum_S P_S = 1 \) holds as can be checked with equation (B.3).

**Entropy**  In thermodynamics the thermodynamic entropy is defined only by its defining equation,

\[
dS = \frac{dQ}{T}. \tag{B.6}
\]

Here, \( dS \) is the change in entropy, \( dQ \) the added reversible energy, and \( T \) is the thermodynamic temperature. This definition of entropy is deduced from the Clausius theorem derived by Rudolf Clausius in 1855. This thermodynamic description of entropy, however, is not very satisfying,
because this does not provide deep insight in the true meaning of entropy. With the development of the fundamentals of statistical physics in the late part of the 19th century, thermodynamics became understood in a more fundamental way. The foundations for statistical physics can for a significant part be contributed to the work of Josiah Willard Gibbs. His book ‘Elementary principles in statistical mechanics ’ published in 1902 formed the first formal statistical physics description of a general system [104]. The foundations from this book are for the most part still used today in modern statistical physics. In this book Gibbs determines a quantity called the average index of probabilities as 
\[ \eta_{av} = \int P \ln (P) \, dq_1 \ldots dq_n. \]
Using thermodynamics Gibbs identifies the average index of probabilities \( \eta_{av} \) with its sign reversed being proportional to the entropy, so \( S \propto -\eta_{av} \). Gibbs states [104, p.44] "But in the thermodynamic equation the entropy is a quantity which is only defined by the equation itself, and incompletely defined in that the equation only determines its differential, and the constant of integration is arbitrary. On the other hand, the \( \eta \) in the statistical equation has been completely defined as the average value in a canonical ensemble of systems of the logarithm of the coefficient of probability phase. ". The Gibbs entropy can then be written as,
\[ S = -k_B \sum_s P_s \ln (P_s). \] (B.7)
Here, \( k_B \) the Boltzmann constant. Note that the Gibbs entropy also holds for non-equilibrium systems by which the probability \( P_s \) of the system being in micro-state \( s \) does not have to be given by equation (B.4) Gibbs described the statistical mechanics in a classical mechanical framework. These concepts, however, were so general that they are able to be described in the framework of quantum mechanics. In quantum statistical mechanics the von Neumann entropy was described by John von Neumann in 1927 as,
\[ S = -\Tr[\rho \ln (\rho)]. \] (B.8)
Here, \( \Tr \) is the trace and \( \rho \) the density matrix. The von Neumann entropy is thus the quantum mechanical extension of the Gibbs entropy. In quantum mechanics the density matrix \( \rho \) is in general non-diagonal. However, in the classical limit it is diagonal and the elements on the diagonal are the probabilities \( P_s \). Then, the von Neumann entropy equation (B.8) reduces to the Gibbs entropy equation (B.7). The Gibbs entropy equation (B.7) holds for a system in equilibrium as well as in non-equilibrium. For a system at thermal equilibrium the fundamental postulate of statistical physics gives that all accessible micro-states are equally probable. By substitution of equation (B.4) into the Gibbs entropy equation (B.7) the Boltzmann entropy equation arises,
\[ S = k_B \ln (\Omega_{\text{system}}). \] (B.9)
This equation [B.9] was derived by Ludwig Boltzmann around 1875. Therefore this derivation of Boltzmann was historically prior to the work of Gibbs. The Boltzmann entropy is a special case of the more general Gibbs entropy, which also holds for non-equilibrium systems with non-equiprobable micro-states. The Boltzmann entropy can be interpreted as a measure of the number \( \Omega_{\text{system}} \) of accessible macro-state of the isolated system at thermal equilibrium.

The discussion of entropy in modern times cannot be complete without mentioning the information entropy or Shannon entropy. This description of entropy is obtained from the work of Claude Shannon around 1948 on information theory [105]. Information theory is arguably so fundamental in physics that it gives even deeper insight into physics and therefore entropy. Shannon showed that a function for a quantity which satisfies certain conditions had a unique mathematical form. These conditions are that the function is continuous, monotonically increasing with the number of subsystems \( n \) and is extensive. This obtained function has exactly the same form as the classical limit of the von Neumann entropy, or equivalently the Gibbs entropy. For this reason von Neumann suggested to Shannon that he should name the quantity 'entropy', as is described in the famous physics book "Maxwell’s Demon: Entropy, Information, and Computing" [106].

\footnote{The Boltzmann equation in a slightly different notation \( S = k \log W \) is engraved in the tombstone of Boltzmann.}
information theory the Shannon entropy is understood as the lack of information or the uncertainty. A good source to fully understand information entropy is the work of Shannon [105], but this is beyond the scope of this section.

**Second law of thermodynamics** Consider now again an isolated system consisting of \( n \) subsystems. This system has possible macro-states and micro-states in which it can exist, for which the probabilities are \( P_S \) and \( P_s \). According to equation (B.5) the probability of the macro-state depends on the multiplicity of that macro-state. Suppose that the system initially exists in a macro-state not having the greatest probability \( P_S \). Incidentally, this is thus also the macro-state not having the greatest multiplicity. After sufficient time the system will be in thermal equilibrium with itself, meaning that the energy had the necessary time to travel around and distribute itself. Then as a consequence of the fundamental postulate of statistical mechanics the macro-state with the greatest multiplicity will be the most probable one for the system to exist in. The multiplicity \( \Omega_{\text{system}} \) is the number of accessible micro-states for the system. Therefore, this number depends on the time scale of evolution of the system to make micro-states accessible. In physical systems the number of subsystems \( n \) is in general very large. As a result, the multiplicity of the most probable macro-state is so overwhelmingly large that other probabilities can easily be neglected. This will becomes clearer later on when examining the multiplicity as function of the number of subsystems \( n \). There we will see that the sharpness of the multiplicity function increases rapidly with increasing the number of subsystems \( n \), to the point where the probability for the system existing in another the most probable macro-state is negligible. So for large systems,

\[
\Omega_{\text{system}} \approx \Omega_{S_{\text{max}}} = \Omega. \tag{B.10}
\]

Here, \( \Omega \) is the multiplicity of the most probable macro-state. This approximation (B.10) is often not properly discussed in textbooks, but holds a very important subtle piece of information in understanding the concept of entropy and the second law of thermodynamics which will be presented right now. Remember that the Boltzmann entropy (B.9) for an isolated system in thermal equilibrium is proportional to the multiplicity \( \Omega_{\text{system}} \) of the system. Using approximation (B.10) the Boltzmann entropy is proportional to the multiplicity \( \Omega \) of the most probable macro-state. So the system initially having an entropy proportional the multiplicity \( \Omega \) of its at that time most probable macro-state. The system will evolve in time to a more probable macro-state, having a higher multiplicity, which in turn causes the entropy to increase. This is essentially the second law of thermodynamics. Note that this is not actually a fundamental law, it is just a statement about probabilities. The second law of thermodynamics can then be rephrased as,

> **The entropy of an isolated system almost always increases.**

This way it becomes clear that there is a probability that the entropy can decrease, but this probability is just utterly small.

### C Derivation of the Boltzmann distribution

The multiplicity is described by the multinomial coefficient in equation (2.59) [53, A2.10],

\[
\Omega_S = \frac{n!}{\prod_i n_i!}. \tag{C.1}
\]

For several reasons the natural logarithm of the multiplicity is an interesting quantity to consider. For one, the multiplicities in physical systems tend to be very large numbers [74, p.61], which are hard to work with. The logarithm of a very large number is an ordinary large number which is much easier to work with. Another reason is that the natural logarithm of the multiplicity \( \Omega_S \) using the approximation (B.10) is proportional to the entropy according to the Boltzmann entropy
The natural logarithm of the multiplicity can be written as,
\[
\ln (\Omega_S) = \ln \left( \frac{n!}{\prod_i n_i!} \right) = \ln (n!) - \ln \left( \prod_i n_i! \right) = \ln (n!) - \sum_i \ln (n_i!).
\] (C.2)

These combinatorial functions involve factorials and the factorials of large numbers can be evaluated using Stirling’s approximation. For \( n \gg 1 \) the Stirling’s approximation is given by ref [schoeder p62 eq 2.14] to be,
\[
n! \approx n^n e^{-n} \sqrt{2\pi n}.
\] (C.3)

If \( n \) is a large number the term \( \sqrt{2\pi n} \) is negligible because it is a large number and \( n^n e^{-n} \) is a very large number. The approximation can thus be approximated as \( n! \approx n^n e^{-n} \). In considering the natural logarithm of \( n! \) this approximation is in general sufficient. Hence,
\[
\ln (n!) \approx n \ln (n) - n.
\] (C.4)

By applying equation (C.4) on equation (C.2),
\[
\ln (\Omega_S) \approx (n \cdot \ln (n) - n) - \sum_i (n_i \cdot \ln (n_i) - n_i) = n \cdot \ln (n) - n - \sum_i n_i \cdot \ln (n_i) + \sum_i n_i
\]
\[
= n \cdot \ln (n) - n - \sum_i n_i \cdot \ln (n_i) + n = n \cdot \ln (n) - \sum_i n_i \cdot \ln (n_i).
\] (C.5)

As described by equation (B.5) the most probable macro-state for an isolated system in thermal equilibrium is the one with the largest multiplicity \( \Omega_{S_{\text{max}}} \).

For large systems this probability is overwhelmingly larger than all the other probabilities of the system existing in other accessible macro-states. Therefore, deviation of the system from the most probable macro-state is highly improbable, and the system can be assumed to be in the most probable macro-state. To determine the configuration of the most probable macro-state the maximum value of the multiplicity with respect to the occupation numbers \( n_i \) has to be determined. The maximum of the multiplicity \( \Omega_{S_{\text{max}}} \), or equivalently the maximum for \( \ln (\Omega_S) \), is obtained using the variational principle. Whether, maximum of \( \Omega_S \) or \( \ln (\Omega_S) \) is considered the results for the most probable configuration will be the same. If the occupation numbers \( n_i \) change to \( n_i + dn_i \), then \( \ln (\Omega_S) \) changes to \( \ln (\Omega_S) + d (\ln (\Omega_S)) \). Hence, the change in the natural logarithm of the multiplicity is given by,
\[
d (\ln (\Omega_S)) = \sum_i \left( \frac{\partial \ln (\Omega_S)}{\partial n_i} \right) dn_i.
\] (C.6)

This equation (C.6) states that the change in \( \ln (\Omega_S) \) is the sum of contributions made by changes of the occupation numbers \( n_i \). The variation of the occupation numbers \( n_i \) is subject to two constraints, because for an isolated system the total energy \( E \) and number of subsystems \( n \) are constant. These constraints are given by,
\[
\sum_i E_i dn_i = 0, \quad \sum_i dn_i = 0.
\] (C.7) (C.8)

Therefore, not all occupation numbers \( n_i \) are independent. The constraints are taken into account by the method of undetermined multipliers, developed by Lagrange. ref This method results in multiplying the constraints with constants and adding these terms to the variation equation (C.6). This results in,
\[
d (\ln (\Omega_S)) = \sum_i \left( \frac{\partial \ln (\Omega_S)}{\partial n_i} \right) dn_i + \alpha \sum_i dn_i - \beta \sum_i E_i dn_i
\]
\[
= \sum_i \left( \left( \frac{\partial \ln (\Omega_S)}{\partial n_i} \right) + \alpha - \beta E_i \right) dn_i.
\] (C.9)
Here, $\alpha$ and $\beta$ are constants. The variables $dn_i$ in equation (C.9) are then treated as being independent and the constants $\alpha$ and $\beta$ can be evaluated at the end. To determine the maximum multiplicity $\Omega_{S_{\text{max}}}$ for equation (C.9) the following condition holds,

$$d (\ln (\Omega_S)) = 0.$$  \hfill (C.10)

Remember again that what is done here is that the values for the occupation numbers $n_i$ are determined for which the natural logarithm of the multiplicity $\ln (\Omega_S)$ is at a maximum. In order for equation (C.9) to satisfy equation (C.10) it follows that for each state $i$ of the subsystems it is required that,

$$\frac{\partial \ln (\Omega_S)}{\partial n_i} + \alpha - \beta E_i = 0.$$  \hfill (C.11)

This equation (C.11) is rewritten using equations (C.5) (B.1) and some calculus. First consider the first term of equation (C.11). By substitution of equation (C.5) this gives,

$$\frac{\partial \ln (\Omega_S)}{\partial n_i} = \frac{\partial \ln (n \ln (n))}{\partial n_i} - \sum_j \frac{\partial \ln (n_j \ln (n_j))}{\partial n_i}.$$  \hfill (C.12)

The first term of equation (C.12) gives,

$$\frac{\partial \ln (n \ln (n))}{\partial n_i} = \frac{\partial n}{\partial n_i} \ln (n) + n \left( \frac{\partial \ln (n)}{\partial n_i} \right) = (1) \ln (n) + \frac{n}{n} \left( \frac{\partial n}{\partial n_i} \right) = \ln (n) + \frac{\partial n}{\partial n_i} = \ln (n) + 1.$$  \hfill (C.13)

The second term of equation (C.12) gives,

$$\sum_j \frac{\partial \ln (n_j \ln (n_j))}{\partial n_i} = \sum_j \left( \frac{\partial n_j}{\partial n_i} \ln (n_j) + n_j \frac{\partial \ln (n_j)}{\partial n_i} \right) = \sum_j \frac{\partial n_j}{\partial n_i} \left( \ln (n_j) + 1 \right) = \sum_j \delta_{ij} \left( \ln (n_j) + 1 \right) = \ln (n_j) + 1.$$  \hfill (C.14)

Substitution of equations (C.13) and (C.14) in equation (C.12) gives,

$$\frac{\partial \ln (\Omega_S)}{\partial n_i} = \ln (n) + 1 - \ln (n_j) - 1 = -\ln \left( \frac{n_j}{n} \right).$$  \hfill (C.15)

Substitution of this equation (C.15) in equation (C.11) gives,

$$-\ln \left( \frac{n_j}{n} \right) + \alpha - \beta E_i = 0 \rightarrow n_i = ne^{\alpha-\beta E_i}.$$  \hfill (C.16)

Summing this equation (C.16) over $i$ gives,

$$\sum_i n_i = \sum_i ne^{\alpha-\beta E_i} = n = ne^\alpha \sum_i e^{-\beta E_i} \rightarrow 1 = e^\alpha \sum_i e^{-\beta E_i} \rightarrow e^\alpha = \frac{1}{\sum_i e^{-\beta E_i}}.$$  \hfill (C.17)

Substitution of equation (C.17) into equation (C.16) gives the Boltzmann distribution equation,

$$\frac{n_i}{n} = e^{\alpha-\beta E_i} = e^\alpha e^{-\beta E_i} = \frac{1}{\sum_i e^{-\beta E_i}} e^{-\beta E_i} \rightarrow n_i = n e^{-\beta E_i}.$$  \hfill (C.18)
D Derivation of entropy in terms of partition function

In this section the entropy $S$ in terms of the partition function $Z$ is determined from the Boltzmann entropy equation (B.9),

$$ S = k_B \ln (\Omega_{\text{system}}). $$  \hspace{1cm} (D.1)

Ultimately this results in the expression for the entropy $S$ in terms of the partition function $Z$,

$$ S = \frac{E}{T} + n k_B \ln (Z). $$  \hspace{1cm} (D.2)

Substitution of equation (C.5) in equation (D.1) gives,

$$ S = k_B \ln (\Omega_S) \approx k_B \left( n \ln (n) - \sum_i n_i \ln (n_i) \right) = k_B \sum_i (n_i \ln (n_i) - n_i \ln (n_i)) $$

$$ = -k_B \sum_i n_i \ln (n_i - n_i) = -k_B \sum_i n_i \ln \left( \frac{n_i}{n} \right) = -k_B \sum_i \frac{n_i}{n} \ln \left( \frac{n}{n_i} \right) $$

$$ = -n k_B \sum_i P_i \ln (P_i). $$  \hspace{1cm} (D.3)

Substitution of equation (2.62) in equation (D.3) gives,

$$ S = -n k_B \sum_i P_i \left( -\beta E_i - \ln (Z) \right) = -n k_B \left( -\beta \sum_i P_i E_i - \ln (Z) \sum_i P_i \right) $$

$$ = k_B \beta \sum_i n_i E_i + n k_B \ln (Z) \sum_i P_i = k_B \beta \sum_i n_i E_i + n k_B \ln (Z) (1) $$

$$ = k_B \beta E + n k_B \ln (Z) = \frac{E}{T} + n k_B \ln (Z). $$  \hspace{1cm} (D.4)

E Derivation of internal energy of a harmonic oscillator

In this section the internal energy $E_h$ of a system of $n$ harmonic oscillators is determined from equation (2.71),

$$ E_h = -\frac{\partial \ln (Z_h)}{\partial \beta} = -\frac{1}{Z_h} \frac{\partial Z_h}{\partial \beta}. $$  \hspace{1cm} (E.1)

The partition function $Z_h$ for a system of a harmonic oscillator is given by equation (2.73). In this equation two equivalent expressions are given for the partition function $Z_h$. Ultimately these lead to two equivalent expressions for the internal energy $E_h$,

$$ E_h = n h \nu \left( \frac{1}{2} + \frac{1}{e^{\beta h \nu} - 1} \right) = \frac{n h \nu}{2} \coth \left( \frac{\beta h \nu}{2} \right). $$  \hspace{1cm} (E.2)
CHAPTER 5. SUMMARY, DISCUSSION, AND OUTLOOK

Substitution of the first expression for partition function $Z_h$ of equation (2.73) in equation (E.1) gives,

$$E_h = -\frac{1}{Z_h} \frac{\partial Z_h}{\partial \beta} = -\left( e^{\frac{\beta \nu}{2}} - e^{-\frac{\beta \nu}{2}} \right) \left( e^{-\frac{\beta \nu}{2}} \frac{\partial}{\partial \beta} \left( \frac{1}{1 - e^{-\frac{\beta \nu}{2}}} \right) + \frac{1}{1 - e^{-\frac{\beta \nu}{2}}} \frac{\partial}{\partial \beta} \left( e^{\frac{\beta \nu}{2}} \right) \right)$$

$$= -\left( e^{\frac{\beta \nu}{2}} - e^{-\frac{\beta \nu}{2}} \right) \left( e^{\frac{\beta \nu}{2}} - \frac{\hbar \nu e^{\frac{\beta \nu}{2}}}{(1 - e^{-\frac{\beta \nu}{2}})} + \frac{1}{1 - e^{-\frac{\beta \nu}{2}}} \right)$$

$$= \frac{\hbar \nu e^{\frac{\beta \nu}{2}}}{(1 - e^{-\frac{\beta \nu}{2}})^2} + \frac{\hbar \nu e^{-2\beta \nu}}{(1 - e^{-\frac{\beta \nu}{2}})^2} = \frac{\hbar \nu e^{-\beta \nu}}{2(1 - e^{-\frac{\beta \nu}{2}})}$$

$$= \hbar \nu \left( \frac{1}{2} + \frac{1}{e^{\beta \nu} - 1} \right). \quad (E.3)$$

Substitution of the second expression for the partition function $Z_h$ of equation (2.73) in equation (E.1) gives,

$$E_h = -\frac{1}{Z_h} \frac{\partial Z_h}{\partial \beta} = -\frac{1}{2} \sinh \left( \frac{\beta \nu}{2} \right) \frac{\partial}{\partial \beta} \left( \frac{2}{\sinh \left( \frac{\beta \nu}{2} \right)} \right) = -\sinh \left( \frac{\beta \nu}{2} \right) \frac{\partial}{\partial \beta} \left( \sinh^{-1} \left( \frac{\beta \nu}{2} \right) \right). \quad (E.3)$$

Now change the variables to $A = \sinh \left( \frac{\beta \nu}{2} \right) = \sinh (B)$, and $B = \frac{\beta \nu}{2}$ and substitute these into equation (E.4).

$$E_h = -A \frac{\partial A^{-1}}{\partial A} \frac{\partial A}{\partial B} \frac{\partial B}{\partial \beta} = -A \left( -A^{-2} \right) (\cos (B)) \left( \frac{\nu}{2} \right) = \frac{\hbar \nu \cosh (B)}{2A}. \quad (E.5)$$

Now put the expressions for the changing of variables back into this equation (E.5),

$$E_h = \frac{\hbar \nu \cosh \left( \frac{\beta \nu}{2} \right)}{2 \sinh \left( \frac{\beta \nu}{2} \right)} = \frac{\hbar \nu}{2} \coth \left( \frac{\beta \nu}{2} \right). \quad (E.6)$$

### F Time-dependent perturbation theory

Consider a system \[73\] in which the potential energy function is time-dependent $V = V(r,t)$. This potential energy function $V$ can represent, as will be shown in section 2.3.1, the interaction between for example an atom and an electromagnetic field. The time-dependent Schrödinger equation is given by,

$$i \hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi. \quad (F.1)$$

Here, $\Psi = \Psi(r,t)$ is the time-dependent wave function of the system, and $\hat{H} = \hat{H}(r,t)$ the Hamiltonian operator of the system. If the potential energy function $V$ depends on positions $r$ as well as on time $t$, the time-dependent Schrödinger equation cannot be solved by the method of separation of variables. However, as will be shown, if the time-dependent part $\hat{H}' = \hat{H}'(t)$ is of the Hamiltonian $\hat{H}$ is small compared to the time-independent part $\hat{H}_0 = \hat{H}_0(r)$, the time-dependent part $\hat{H}'$ can be treated as a perturbation. The perturbation induces a transition between the stationary states of the unperturbed system. The Hamiltonian $\hat{H}$ of the system is written as,

$$\hat{H}(r,t) = \hat{H}_0(r) + \hat{H}'(t). \quad (F.2)$$
The time-independent part of the Hamiltonian \( \hat{H} \) is the unperturbed Hamiltonian \( \hat{H}_0 \), so without any interactions.

Before turning to the perturbation, first the unperturbed system is considered. The Schrödinger equation for the unperturbed system is,

\[
i\hbar \frac{\partial \Psi \sp{0}}{\partial t} = \hat{H}_0 \Psi \sp{0}.
\] (F.3)

Here, \( \Psi \sp{0} = \Psi \sp{0} (r, t) \) is the unperturbed time-dependent wave function of the unperturbed system. The unperturbed Hamiltonian \( \hat{H}_0 \) is a function only of the positions \( r \) so this equation can be evaluated with the method of separation of variables described in Appendix G. As a result the time-independent wave equation emerges,

\[
\hat{H}_0 \psi \sp{0} \sp{n} = E \sp{n} \sp{0} \psi \sp{0} \sp{n}.
\] (F.4)

Here, \( \psi \sp{0} \sp{n} \) is the time-independent unperturbed wave function with corresponding energies \( E \sp{n} \sp{0} \). These separable solutions are stationary states, in a sense that all probabilities and expectation values are time-independent, and are given by,

\[
\Psi \sp{0} \sp{n} (r, t) = \psi \sp{0} \sp{n} (r) e^{-iE \sp{n} \sp{0} t / \hbar}.
\] (F.5)

The general time-dependent unperturbed wave function \( \Psi \sp{0} \) is a linear combination of these stationary states \( \Psi \sp{0} \sp{n} \),

\[
\Psi \sp{0} = \sum \sp{n} c \sp{n} \Psi \sp{0} \sp{n} = \sum \sp{n} c \sp{n} \psi \sp{0} \sp{n} e^{-iE \sp{n} \sp{0} t / \hbar}.
\] (F.6)

This analysis is for the unperturbed system and not for the system with Hamiltonian \( \hat{H} \) which depends on time \( t \). Note, however, that the unperturbed stationary states \( \Psi \sp{0} \sp{n} \) or unperturbed time-independent wave function \( \psi \sp{0} \sp{n} \) still constitute a complete set. This set, therefore, spans the Hilbert space and can also for the perturbed system serve as a basis. Hence, the time-dependent perturbed wave function \( \Psi \) can still be expressed as the linear combination from equation (F.6), but with time dependent coefficients \( c \sp{n} = c \sp{n} (t) \),

\[
\Psi (r, t) = \sum \sp{n} c \sp{n} (t) \Psi \sp{0} \sp{n} (r, t) = \sum \sp{n} c \sp{n} (t) \psi \sp{0} \sp{n} e^{-iE \sp{n} \sp{0} t / \hbar}.
\] (F.7)

This expansion for the wave function \( \Psi \) and the Hamiltonian \( \hat{H} \) in equation (F.2) are substituted into the Schrödinger equation (F.1). Further the eigenvalue equation (F.4) is used to eliminate some terms and the whole equation is multiplied from the left with \( \psi \sp{k} \sp{0} \) or to be more precise the equation is projected onto \( \ket{\psi \sp{k} } \). From now on the Dirac bracket notation will be used so the whole equation will be multiplied from the left with \( \langle \psi \sp{k} | \) and from the right with \( \ket{\psi \sp{k} } \).

Now, using the orthogonality of the wave functions \( \langle \psi \sp{k} | \psi \sp{n} \rangle = \delta \sp{k} \sp{n} \) a set of coupled differential equations for the coefficients \( c \sp{k} (t) \) is obtained. This procedure is described in Appendix H and results in,

\[
\dot{c} \sp{k} = -i \hbar \sum \sp{n} c \sp{n} \hat{H} \sp{0} \sp{k} \sp{n} e^{i\omega \sp{n} \sp{k} t}.
\] (F.8)

Here, \( \dot{c} \sp{k} = \dfrac{\partial c \sp{k} }{\partial t} \) is the time derivative of the coefficient \( c \sp{k} \), \( \hat{H} \sp{0} \sp{k} \sp{n} = \langle \psi \sp{k} \sp{0} | \hat{H} \sp{0} | \psi \sp{n} \sp{0} \rangle \) is the matrix element with entries \( k \) and \( n \) of the perturbation Hamiltonian \( \hat{H} \sp{0} \), and \( \omega \sp{n} \sp{k} = \frac{E \sp{k} - E \sp{n} \sp{0} }{\hbar} \) the frequency. Up to this point no approximations are made and everything is exact. The perturbation is now assumed to be small compared to the unperturbed part. The perturbation is written as \( \lambda \hat{H} \) where \( \lambda \) is some small number which can later on be set to 1. The coefficient \( c \sp{k} \) is expanded as,

\[
c \sp{k} = c \sp{k} \sp{0} + \lambda c \sp{1} \sp{k} + \lambda^2 c \sp{2} \sp{k} + \cdots = \sum \lambda^j c \sp{j} \sp{k}.
\] (F.9)
Here, the superscripts within parentheses \((j)\) indicates the order of the approximation. This expansion (F.9) can be substituted into the differential equation (F.8) to get,

\[
\dot{c}_k^{(j)} = -\frac{i}{\hbar} \sum_n c_n^{(j-1)} \hat{H}_{kn} e^{i\omega_{kn}t}.
\] (F.10)

This equation (F.10) shows that the \(j\)th order of the approximation can be determined using the \((j-1)\)th order of the approximation. The probability for the system being in state \(k\) at a time \(t\) is then given by,

\[
P_k(t) = \left| c_k^{(0)}(t) + c_k^{(1)}(t) + c_k^{(2)}(t) + \ldots \right|^2 = \left| \sum_j c_k^{(j)}(t) \right|^2.
\] (F.11)

Essentially, the assumption that the perturbation is small is a statement about the system being in an initial state at some moment in time and because the perturbation is weak the probability of the system being in that same state at another moment in time is large. At this point it is, therefore, convenient to introduce a specific system \([77]\) to which this theory is then applied. This system can make a transition from an initial state to some final states.

**G Separation of variables of the time-dependent Schrödinger equation**

In this appendix the time-dependent Schrödinger equation (F.3),

\[
i\hbar \frac{\partial \Psi^{(0)}}{\partial t} = \hat{H}_0 \Psi^{(0)},
\] (G.1)

is evaluated using the method of separation of variables. Ultimately the time-independent Schrödinger equation (F.4) emerges,

\[
\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}.
\] (G.2)

together with the time-dependent part,

\[
\phi(t) = e^{-\frac{iEt}{\hbar}}.
\] (G.3)

The solution for the time-dependent wave function is taken to have the form \( \Psi(r, t) = \psi(r) \phi(t) \)

Substitution of this expression in equation (G.1) gives

\[
i\hbar \frac{\partial (\psi(r) \phi(t))}{\partial t} = \hat{H}_0(r) \psi(r) \phi(t) \rightarrow i\hbar \frac{1}{\phi(t)} \frac{\partial \phi(t)}{\partial t} = \hat{H}_0(r) \psi(r) \psi(r).
\] (G.4)

The left and right side are dependent on different variables which implies that they are equal to a separation constant \(E\) giving,

\[
i\hbar \frac{1}{\phi(t)} \frac{\partial \phi(t)}{\partial t} = E, \quad \hat{H}_0(r) \psi(r) \psi(r) = E.
\] (G.5) (G.6)

The time-dependent equation (G.5) has the rather simple solution,

\[
\frac{\partial \phi(t)}{\partial t} = -\frac{iE}{\hbar} \phi(t) \rightarrow \phi(t) = e^{-\frac{iEt}{\hbar}}.
\] (G.7)

\[3\] The superscript \((0)\) is omitted for a short moment and put back in later to make the equations more easy to read and it should be obvious that the unperturbed case is considered.
The time-independent part is the time-independent wave equation,

\[ \hat{H}_0(r) \psi(r) = E \psi(r). \] (G.8)

This equation (G.8) has separable solutions with wave function \( \psi_n \) and corresponding separation constants \( E_n \). So for each \( n \) the time-independent wave equation with wave function \( \psi_n \) and corresponding energy \( E_n \) holds giving,

\[ \hat{H}_0(r) \psi_n^{(0)}(r) = E_n^{(0)} \psi_n^{(0)}(r). \] (G.9)

**H Derivation of the set of expansion coefficient differential equations**

In this appendix the set differential equations for the expansion coefficients \( c \) is determined from the Schrödinger equation (F.1)

\[ i \hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi. \] (H.1)

Ultimately this results in the set of coupled expansion coefficient differential equations (F.8),

\[ \dot{c}_k = -\frac{i}{\hbar} \sum_n c_n \hat{H}_n \exp(i \omega_n t). \] (H.2)

The expansion (F.7) for the time-dependent wave function \( \Psi \) and the Hamiltonian \( \hat{H} \) of equation (F.2) are substituted into the Schrödinger equation (F.1) and Dirac bracket notation is used to give,

\[ i \hbar \frac{\partial}{\partial t} \sum_n c_n(t) |\psi_n\rangle e^{-i E_n t} = \left( \hat{H}_0(r) + \hat{H}'(t) \right) \sum_n c_n(t) |\psi_n\rangle e^{-i E_n t} \] (H.3)

Rearranging terms gives,

\[ i \hbar \frac{\partial}{\partial t} \sum_n c_n(t) |\psi_n\rangle e^{-i E_n t} = \sum_n c_n(t) \hat{H}_0 |\psi_n\rangle e^{-i E_n t} + \sum_n c_n(t) \hat{H}'(t) |\psi_n\rangle e^{-i E_n t} \] (H.4)

Substitution of equation (F.4)

\[ i \hbar \frac{\partial}{\partial t} \sum_n c_n(t) |\psi_n\rangle e^{-i E_n t} = \sum_n c_n(t) E_n^{(0)} |\psi_n\rangle e^{-i E_n t} + \sum_n c_n(t) \hat{H}'(t) |\psi_n\rangle e^{-i E_n t} \] (H.5)

Using the product rule for derivatives gives,

\[ i \hbar \sum_n \left( \frac{\partial c_n(t)}{\partial t} |\psi_n\rangle e^{-i E_n t} + c_n(t) \left( |\psi_n\rangle \frac{\partial}{\partial t} e^{-i E_n t} \right) \right) = \sum_n c_n(t) E_n |\psi_n\rangle e^{-i E_n t} + \sum_n c_n(t) \hat{H}'(t) |\psi_n\rangle e^{-i E_n t} \] (H.6)

Evaluation of the derivative \( \frac{\partial}{\partial t} \) and changing to the notation \( \frac{\partial c_n(t)}{\partial t} = \dot{c}_n(t) = \dot{c}_n \) gives,

\[ i \hbar \sum_n \left( \dot{c}_n |\psi_n\rangle e^{-i E_n t} + c_n |\psi_n\rangle \left( -\frac{i E_n}{\hbar} \right) e^{-i E_n t} \right) = \sum_n c_n E_n |\psi_n\rangle e^{-i E_n t} + \sum_n c_n \hat{H}'(t) |\psi_n\rangle e^{-i E_n t} \] (H.7)

\[ i \hbar \sum_n \dot{c}_n |\psi_n\rangle e^{-i E_n t} + \sum_n c_n |\psi_n\rangle (E_n) e^{-i E_n t} = \sum_n c_n E_n |\psi_n\rangle e^{-i E_n t} + \sum_n c_n \hat{H}'(t) |\psi_n\rangle e^{-i E_n t} \] (H.8)
Recognizing that the second term on the left-hand side and the first term on the right-hand side cancel each other gives,
\[
\hat{c}_k \frac{\hat{c}_k}{\hbar} \sum_n c_n \hat{H}_n e^{-\frac{iE_n t}{\hbar}} = \sum_n c_n \hat{H}_n e^{-\frac{iE_n t}{\hbar}}
\]  
(H.9)

Multiplication from the left with \(\langle \psi_k | \rho \langle \psi_k | \psi_n \rangle e^{-\frac{iE_n t}{\hbar}} = \sum_n c_n \langle \psi_k | \hat{H}_n | \psi_n \rangle e^{-\frac{iE_n t}{\hbar}}
\]  
(H.10)

Taking orthogonality,
\[
\langle \psi_n | \psi_k \rangle = \delta_{nk},
\]  
(H.11)

Rearranging terms gives,
\[
\hat{c}_k \frac{\hat{c}_k}{\hbar} = \sum_n c_n \hat{H}_n e^{-\frac{iE_n t}{\hbar}}
\]  
(H.12)

Rearranging terms gives,
\[
\hat{c}_k = \frac{i}{\hbar} \sum_n c_n \hat{H}_n e^{-\frac{iE_n t}{\hbar}} e^{\frac{iE_n t}{\hbar}} = \frac{i}{\hbar} \sum_n c_n \hat{H}_n e^{i(E_n - E_0)n} = \frac{i}{\hbar} \sum_n c_n \hat{H}_n e^{i\omega_{kn} t}
\]  
(H.13)

Here, \(\omega_{kn} = \frac{(E_k - E_n)}{\hbar}\) is the frequency.

I Evaluation of the matrix elements \(H'_{f_1 i}\) and \(H'_{f_2 i}\)

In this appendix the matrix elements \(H'_{f_1 i}\) and \(H'_{f_2 i}\) are evaluated from the interaction Hamiltonian \(\hat{H}'\) of the atom-field system of equation (2.120),
\[
\hat{H}' = -\hat{\mu} \cdot E_0 \left(\hat{a} - \hat{a}^+\right).
\]  
(I.1)

Ultimately, this results in the expressions (2.121) and (2.122) for the matrix elements \(H'_{f_1 i}\) and \(H'_{f_2 i}\),
\[
H'_{f_1 i} = -\hat{\mu}_a \cdot E_0 \sqrt{n}, \quad (I.2) \quad H'_{f_2 i} = \hat{\mu}_a \cdot E_0 \sqrt{n + 1}. \quad (I.3)
\]

Substitution of equation (I.1) into the expression for matrix element \(H'_{f_1 i}\) gives,
\[
H'_{f_1 i} = \langle f_1 | \hat{H}' | i \rangle = \langle b, n - 1 | H' | a, n \rangle = \langle b, n - 1 | \left( -\hat{\mu} \cdot E_0 \left(\hat{a} - \hat{a}^+\right) \right) | a, n \rangle = \langle b | \langle n - 1 | \left( -\hat{\mu} \cdot E_0 \left(\hat{a} - \hat{a}^+\right) \right) | a \rangle | n \rangle. \quad (I.4)
\]

Rearranging terms gives,
\[
H'_{f_1 i} = -\langle b | \hat{\mu} \cdot E_0 | a \rangle \langle n - 1 | \left(\hat{a} - \hat{a}^+\right) | n \rangle = -\langle b | \hat{\mu} | a \rangle E_0 \langle n - 1 | \left(\hat{a} - \hat{a}^+\right) | n \rangle = -\hat{\mu}_a \cdot E_0 \langle n - 1 | \left(\hat{a} - \hat{a}^+\right) | n \rangle = -\hat{\mu}_a \cdot E_0 \left(\langle n - 1 | \hat{a} | n \rangle - \langle n - 1 | \hat{a}^+ | n \rangle \right). \quad (I.5)
\]

Here, \(\hat{\mu}_a = \langle b | \hat{\mu} | a \rangle\) is the electric dipole moment matrix element between states \(|b\rangle\) and \(|a\rangle\).

Usage of the rules for the creation and annihilation ladder operators gives,
\[
H'_{f_1 i} = -\hat{\mu}_a \cdot E_0 \left(\sqrt{n} \langle n - 1 | n - 1 \rangle - \sqrt{n + 1} \langle n - 1 | n + 1 \rangle \right) = -\hat{\mu}_a \cdot E_0 \left(\sqrt{n}(1) - \sqrt{n + 1}(0)\right) = -\hat{\mu}_a \cdot E_0 \sqrt{n}. \quad (I.6)
\]
J. Determining the first order coefficient $c_f^{(1)}$

In this appendix the first order coefficient $c_f^{(1)}$ is determined from evaluating the integrals in equation (2.118),

$$c_f^{(1)} = \frac{i}{\hbar} \int_0^t \hat{H} f_1(t') e^{i\mu t'} dt' - i \frac{\hat{H} f_1(t') e^{i\omega_{f_2} t'}}{\sqrt{n} + 1}.$$  \hfill (J.1)

Ultimately this results in an expression (2.123) for the first order coefficient for the atom-field system,

$$c_f^{(1)} = \frac{i}{\hbar} \left( \mu_a \cdot E_0 \right) \left( (n + 1) \frac{1}{\sqrt{n} + 1} + n \frac{1}{\omega - \omega_0} \right).$$  \hfill (J.2)

Substitution of the matrix elements $H_{f_1}$ and $H_{f_2}$ from equations (9.121) and (9.122) gives,

$$c_f^{(1)} = -\frac{i}{\hbar} \int_0^t (-\mu_a \cdot E_0 \sqrt{n}) e^{i\omega_{f_1} t'} dt' - i \frac{\int_0^t (\mu_a \cdot E_0 \sqrt{n + 1}) e^{i\omega_{f_2} t'} dt'}{\sqrt{n} + 1}.$$  \hfill (J.3)

Rearranging terms gives,

$$c_f^{(1)} = -\frac{i}{\hbar} \left( \mu_a \cdot E_0 \right) \left( \sqrt{n} + 1 \int_0^t e^{i\omega_{f_1} t'} dt' + i \sqrt{n} \int_0^t e^{i\omega_{f_1} t'} dt' \right).$$  \hfill (J.4)

Evaluating the remaining integrals gives,

$$c_f^{(1)} = -\frac{i}{\hbar} \left( \mu_a \cdot E_0 \right) \left( \sqrt{n} + 1 \left[ \frac{1}{\omega_{f_2}} e^{i\omega_{f_2} t'} \right]_0^t - i \sqrt{n} \left[ \frac{1}{\omega_{f_1}} e^{i\omega_{f_1} t'} \right]_0^t \right)$$

$$= -\frac{i}{\hbar} \left( \mu_a \cdot E_0 \right) \left( \sqrt{n} + 1 \left( e^{i\omega_{f_2} t'} - 1 \right) - i \sqrt{n} \left( e^{i\omega_{f_1} t'} - 1 \right) \omega_{f_1} \right)$$

$$= \frac{1}{\hbar} \left( \mu_a \cdot E_0 \right) \left( \sqrt{n} + 1 \left( e^{i\omega_{f_2} t'} - 1 \right) - i \sqrt{n} \left( e^{i\omega_{f_1} t'} - 1 \right) e^{i\omega_{f_1} t'} \right).$$  \hfill (J.5)

Using the energies in equations (2.111), (2.112) and (2.113) the frequencies $\omega_{f_1}$ and $\omega_{f_2}$ are written as,

$$\omega_{f_1} = \frac{E_f - E_i}{\hbar} = (E_b + (n - 1) \hbar \omega) - (E_a + n \hbar \omega) = \frac{E_b + n \hbar \omega - h \omega - E_a - n \hbar \omega}{\hbar}$$

$$= \frac{E_b - E_a - h \omega}{\hbar} = \frac{E_b - E_a}{\hbar} - \omega = \omega_{ba} - \omega.$$  \hfill (J.6)
\begin{align*}
\omega_{f_{2i}} &= \frac{E_{f_{2}} - E_{i}}{\hbar} = \frac{(E_{b} + (n + 1)\hbar\omega) - (E_{a} + n\hbar\omega)}{\hbar} = \frac{E_{b} + n\hbar\omega + \hbar\omega - E_{a} - n\hbar\omega}{\hbar} \\
&= \frac{E_{b} - E_{a} + \hbar\omega}{\hbar} = \frac{E_{b} - E_{a}}{\hbar} + \omega = \omega_{ba} + \omega. \tag{J.7}
\end{align*}

Here, \(\omega_{ba} = \frac{E_{b} - E_{a}}{\hbar}\). Substitution of these equations (J.6) and (J.7) in equation (J.5) gives,

\begin{align*}
\epsilon_{f^{(1)}} &= -\frac{1}{\hbar} (\hat{\mu}_{ba} \cdot E_{0}) \left( \sqrt{n + 1} e^{i(\omega_{ba} + \omega)t} - 1 - \sqrt{n} e^{i(\omega_{ba} - \omega)t} - 1 \right). \tag{J.8}
\end{align*}

\begin{align*}
\epsilon_{f^{(2)}} &= -\frac{1}{\hbar} (\hat{\mu}_{ba} \cdot E_{0}) \left( \sqrt{n + 1} e^{i(\omega_{ba} + \omega)t} - 1 + \sqrt{n} e^{-i(\omega_{ba} - \omega)t} - 1 \right). \tag{J.9}
\end{align*}

\begin{align*}
\epsilon_{f^{(3)}} &= -\frac{1}{\hbar} (\hat{\mu}_{ba} \cdot E_{0}) \left( \sqrt{n + 1} e^{i(\omega_{ba} + \omega)t} + \sqrt{n} e^{-i(\omega_{ba} - \omega)t} - 1 \right). \tag{J.10}
\end{align*}

### K Continuity equation

Consider a quantity \(q\) in a volume \(V\), with a flux \(j\) of the quantity \(q\) through the contour surface \(S\) of the volume \(V\). The creation and annihilation, or creannihilation, \(\Sigma\) of \(q\) occurs within volume \(V\). The continuity equation in integral form is then given by

\[
\frac{dq}{dt} = -\iint_{S} j \cdot dS + \Sigma. \tag{K.1}
\]

The continuity equation can also be written in differential form where it describes the quantity \(q\) at a point. The divergence theorem is,

\[
\iiint_{V} (\nabla \cdot F) \, dV = \iint_{S} (F \cdot n) \, dS. \tag{K.2}
\]

Applying this to the continuity equation (K.1) in integral form gives,

\[
\frac{dq}{dt} = -\iiint_{V} (\nabla \cdot j) \, dV + \Sigma. \tag{K.3}
\]

The integral expressions for the quantity \(q\) and the creannihilation \(\Sigma\) are given by,

\[
\frac{dq}{dt} = \frac{d}{dt} \iiint_{V} \rho \, dV, \tag{K.4}
\]

\[
\Sigma = \iiint_{V} \sigma \, dV. \tag{K.5}
\]

Substitution of these expressions (K.4) and (K.5) into equation (K.3) gives,

\[
\frac{d}{dt} \iiint_{V} \rho \, dV = -\iiint_{V} (\nabla \cdot j) \, dV + \iiint_{V} \sigma \, dV. \tag{K.6}
\]

This equation (K.6) implies the following continuity equations in differential form,

\[
\frac{d\rho}{dt} = - (\nabla \cdot j) + \sigma. \tag{K.7}
\]

Here, \(\rho\) is the quantity \(q\) per unit volume and \(\sigma\) the creannihilation of \(q\) per unit volume.
L Amplified spontaneous emission

This appendix contains the first steps undertaken in describing the amplified spontaneous emission process. This text is not refined but should be seen as notes.

Spontaneous emission is the process in which a particle spontaneously makes the transition to a state with a lower energy thereby emitting a photon, with an energy equal to the transition energy. As a result, the occupation number of the upper state will decrease and of the lower state will increase. The spontaneously emitted photon propagates through the system and can interact with other particles. If the transition energy of these particles corresponds to the photon energy, the particle and photon can interact through stimulated emission or stimulated absorption. If stimulated absorption occurs the photon is absorbed by the particle and the particle makes a transition to a higher energy state. If stimulated emission occurs a photon is emitted by the particle, with the same energy and phase as the incoming photon and the particle makes a transition to a lower energy state. If spontaneous emission occurs between two states which are in Boltzmann equilibrium, then the states with which the spontaneously emitted photon can interact are distributed according to the Boltzmann distribution. This means that the state with lower energy has a higher occupation number than the state with higher energy. Therefore, the probability for stimulated absorption will be larger than for stimulated emission. As a result it is most probable for the spontaneously emitted radiation to be absorbed and decrease. However, if spontaneous emission occurs between two states which are not in Boltzmann equilibrium but are in population inversion, then the states with which the spontaneously emitted photon can interact are not distributed according to the Boltzmann distribution. This means that the state with lower energy has a lower occupation number than the state with higher energy. Therefore, the probability for stimulated emission will be larger than for stimulated absorption. As a result it is most probable for the spontaneously emitted radiation to amplify. Due to the high occupation number of the upper state, the probability for spontaneous emission to occur is also high. So then the spontaneous emitted radiation is amplified, which is called amplified spontaneous emission (ASE). As a consequence this ASE will decrease the population inversion. Often ASE is an undesired phenomenon because it gives limitations on the maximum achievable population inversion and the creation of non-coherent radiation. In the reservoir model for a CO₂-laser amplification the 0D-model for the state of the gas mixture is used in every grid point of a 1D space. The effect of ASE can be described as the effect of an auxiliary pump term. The time rate of change of the population of the upper state due to ASE is then,

\[
\left[ \frac{dn}{dt} \right]_{\text{ASE}} = - \int g_0 \cdot \Phi_{\text{ASE}} d\lambda.
\]  

(L.1)

Here, \( n \) is the occupation number of the considered state, \( \lambda \) the spectral wavelength, \( g_0 \) the small signal gain and \( \Phi_{\text{ASE}} \) the amplified spontaneous emission flux. The ASE flux \( d\Phi_{\text{ASE}} \) at position \( r_0 \) out of a spatial interval \( dr \) at position \( r \) with a spectral interval \( d\lambda \) within a solid angle interval \( d\Omega \) is,

\[
d\Phi_{\text{ASE}} = \frac{1}{\Omega_f} \frac{n(r)}{\tau_f} g(\lambda) G_{r\rightarrow r_0} dr d\lambda d\Omega
\]

(L.2)

Here, \( \Omega_f \) is the full solid angle, \( s \) the dimension of the space, \( \tau_f \) the lifetime of the state, \( g(\lambda) \) spectral distribution of the spontaneous emission and \( G_{r\rightarrow r_0} \) the gain over the trajectory from position \( r \) to \( r_0 \). The full solid angle is,

\[
\Omega_f = \frac{2\pi^2}{\Gamma\left(\frac{3}{2}\right)}
\]

(L.3)

The spectral distribution of the spontaneous emission is,

\[
g(\lambda) = \sum_{i=1}^{I} \beta_i g(\lambda - \lambda_i)
\]

(L.4)
Here, $I$ is the number of possible transitions due to spontaneous emission from the considered state, $\beta_i$ is the branching ratio of the $i$-th transition, and $g(\lambda - \lambda_i)$ is the line shape function with line width $\Delta \nu_i$ and line center $\nu_i$. Consider a space element in the space with dimension $s$. The magnitude of the space $d^sV$ within this element is given by $|\rho(r, r_0)|^{s-1} d\Omega dr$. Here, $|\rho(r, r_0)|^{s-1}$ is the distance from the origin to the space element, $d\Omega$ the infinitesimal spacial angle, and $dr$ the infinitesimal length of the space element in the direction of $r$. The case is considered where there is a one-dimensional space, monochromatic light, non-saturated gain, and exponential gain. Then,

$$s = 1$$  \hspace{1cm} (L.5)

$$\Omega_1^n = 2$$  \hspace{1cm} (L.6)

$$drd\Omega = \frac{d^sV}{|\rho(r, r_0)|^{s-1}} = dx$$  \hspace{1cm} (L.7)

$$r = x$$  \hspace{1cm} (L.8)

$$r_0 = x_0$$  \hspace{1cm} (L.9)

$$\int_{\lambda=\infty}^{\lambda=0} g(\lambda) d\lambda = \sum_{i=1}^{I} \beta_i (g(\lambda - \lambda_i) d\lambda = \sum_{i=1}^{I} \beta_i = 1$$  \hspace{1cm} (L.10)

$$G_{r\rightarrow r_0} = G_{x\rightarrow x_0} = e^{g_0(x_0 - x)}$$  \hspace{1cm} (L.11)

The ASE flux then reduces to,

$$d\Phi_{ASE} = \frac{n}{2\tau_f} e^{g_0(x_0 - x)} dx.$$  \hspace{1cm} (L.12)

Spontaneous emission can occur anywhere in the medium. To determine the ASE flux as a function of a position $x_0 = z$ in the one-dimensional, the contributions from every point in the space to the ASE flux in this position have to be summed,

$$\Phi_{ASE}(z) = \int d\Phi_{ASE} = \int_{x=0}^{x=z} \frac{n}{2\tau_f} e^{g_0(z-x)} dx + \int_{x=z}^{x=L} \frac{n}{2\tau_f} e^{g_0(L-x)} dx$$

$$= \frac{n}{2\tau_f} \left( \int_{x=0}^{x=z} e^{g_0(z-x)} dx + \int_{x=z}^{x=L} e^{g_0(x-z)} dx \right)$$

$$= \frac{n}{2\tau_f} \left( \left[ e^{g_0(z-x)} \right]_{x=0}^{x=z} + \left[ e^{g_0(x-z)} \right]_{x=z}^{x=L} \right)$$

$$= \frac{n}{2\tau_f} \left( \frac{1}{g_0} (-1 + e^{g_0z}) + \frac{1}{g_0} (e^{g_0(L-z)} - 1) \right)$$

$$= \frac{n}{2\tau_f} \left( e^{g_0z} + e^{g_0(L-z)} - 2 \right)$$  \hspace{1cm} (L.13)
This result shows that the ASE flux is the biggest closer to the boundaries of the space. Therefore, the depletion of the population of the upper state in population inversion will be bigger closer the the edges of the system. The expression,

\[
d^2P_{sp} = \frac{\hbar \nu_0 n d\Omega}{2\tau_f \Omega_f^2} g(\nu) G d\nu dx
\]

leads to,

\[
P_{sp} = \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} \frac{\hbar \nu_0 n}{2\tau_f} g(\nu) G d\nu dx
\]

\[
= \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} \frac{\hbar \nu_0 n}{2\tau_f} \sqrt{\frac{\ln(2) \nu}{\Delta \nu_{sp}}} e^{-\frac{(\nu-\nu_0)^2}{\Delta \nu_{sp}^2}} G d\nu dx
\]

\[
= \frac{\hbar \nu_0}{2\tau_f} \Delta \nu_{sp} \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} n G d\nu dx
\]

\[
= \frac{\hbar \nu_0}{2\tau_f} \Delta \nu_{sp} \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} nG_1 d\nu + \int_{x=z}^{x=L} nG_2 dx d\nu
\]

\[
= \frac{\hbar \nu_0}{2\tau_f} \Delta \nu_{sp} \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} e^{-\frac{(\nu-\nu_0)^2}{\Delta \nu_{sp}^2}} \left( \int_{x=z}^{x=L} nG_1 d\nu + \int_{x=z}^{x=L} nG_2 dx d\nu \right)
\]

\[
= \frac{\hbar \nu_0}{2\tau_f} \Delta \nu_{sp} \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} e^{-\frac{(\nu-\nu_0)^2}{\Delta \nu_{sp}^2}} \left( \int_{x=z}^{x=L} nG_1 d\nu + \int_{x=z}^{x=L} nG_2 dx d\nu \right)
\]

\[
= \frac{\hbar \nu_0}{2\tau_f} \Delta \nu_{sp} \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} e^{-\frac{(\nu-\nu_0)^2}{\Delta \nu_{sp}^2}} \left( \int_{x=z}^{x=L} nG_1 d\nu + \int_{x=z}^{x=L} nG_2 dx d\nu \right)
\]

\[
= \frac{\hbar \nu_0}{2\tau_f} \Delta \nu_{sp} \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} e^{-\frac{(\nu-\nu_0)^2}{\Delta \nu_{sp}^2}} \left( \int_{x=z}^{x=L} nG_1 d\nu + \int_{x=z}^{x=L} nG_2 dx d\nu \right)
\]

\[
= \frac{\hbar \nu_0}{2\tau_f} \Delta \nu_{sp} \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} e^{-\frac{(\nu-\nu_0)^2}{\Delta \nu_{sp}^2}} \left( \int_{x=z}^{x=L} nG_1 d\nu + \int_{x=z}^{x=L} nG_2 dx d\nu \right)
\]

\[
= \frac{\hbar \nu_0}{2\tau_f} \Delta \nu_{sp} \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} e^{-\frac{(\nu-\nu_0)^2}{\Delta \nu_{sp}^2}} \left( \int_{x=z}^{x=L} nG_1 d\nu + \int_{x=z}^{x=L} nG_2 dx d\nu \right)
\]

\[
= \frac{\hbar \nu_0}{2\tau_f} \Delta \nu_{sp} \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} e^{-\frac{(\nu-\nu_0)^2}{\Delta \nu_{sp}^2}} \left( \int_{x=z}^{x=L} nG_1 d\nu + \int_{x=z}^{x=L} nG_2 dx d\nu \right)
\]

\[
= \frac{\hbar \nu_0}{2\tau_f} \Delta \nu_{sp} \int_{\nu=\infty}^{\nu=L} \int_{x=0}^{x=L} e^{-\frac{(\nu-\nu_0)^2}{\Delta \nu_{sp}^2}} \left( \int_{x=z}^{x=L} nG_1 d\nu + \int_{x=z}^{x=L} nG_2 dx d\nu \right)
\]
However, this equation should be,

\[
P_{sp} = \frac{\hbar \nu_0}{2 \tau_f \sigma_0} \left( \frac{e^{\nu_0} + e^{\nu_0(L-z)}}{\sqrt{\nu_0(L-z)}} \right).
\]

(L.16)
\[\begin{align*}
L. AMPLIFIED SPONTANEOUS EMISSION
\end{align*}\]
Assuming that the gain is very large gives,

\[ P_{sp} \approx \frac{\hbar\nu_0}{2\tau_f \sigma_0} \left( \frac{(e^{g_0 z})^{\frac{1}{2}}}{(g_0 z e^{g_0 z})^{\frac{1}{2}}} + \frac{(e^{g_0 (L-z)})^{\frac{1}{2}}}{(g_0 (L-z) e^{g_0 (L-z)})^{\frac{1}{2}}} \right). \]

This blows up at the edges, so at the edges to a Taylor series for the exponential around \( z \) or,

\[ P_{sp} = \frac{\hbar\nu_0}{2\tau_f \sigma_0} \left( e^{g_0 z} \left( \frac{1}{(g_0 z)^{\frac{1}{2}}} + \frac{1}{(g_0 (L-z))^{\frac{1}{2}}} \right) \right). \]

Another way is to get the result,

\[ P_{sp} = \frac{\hbar\nu_0}{2\tau_f \sigma_0} \left( (e^{g_0 (L-z) - 1})^{\frac{1}{2}} \right). \]

Then the ASE at point \( z \) is the sum of the contribution of both sides.

\[ P_{sp} = \frac{\hbar\nu_0}{2\tau_f \sigma_0} \left( \frac{(e^{g_0 z} - 1)^{\frac{1}{2}}}{(g_0 z e^{g_0 z})^{\frac{1}{2}}} + \frac{(e^{g_0 (L-z)} - 1)^{\frac{1}{2}}}{(g_0 (L-z) e^{g_0 (L-z)})^{\frac{1}{2}}} \right). \]

To plot this we take,

\[ P_{sp} = \frac{(e^{g_0 z} - 1)^{\frac{1}{2}}}{(g_0 z e^{g_0 z})^{\frac{1}{2}}} + \frac{(e^{g_0 (1-z)} - 1)^{\frac{1}{2}}}{(g_0 (1-z) e^{g_0 (1-z)})^{\frac{1}{2}}}, \]

or,

\[ P_{sp} = \frac{(e^z - 1)^{\frac{1}{2}}}{(ze^z)^{\frac{1}{2}}} + \frac{(e^{1-z} - 1)^{\frac{1}{2}}}{((1-z)e^{1-z})^{\frac{1}{2}}}. \]

This blows up at the edges. so at the edges to a Taylor series for the exponential around \( z = 0 \) is used,

\[ P_{sp} = \frac{z}{(1+z)^{\frac{1}{2}}} + \frac{1-z}{(2+z)^{\frac{1}{2}}}, \]

\[ P_{sp} = \frac{0}{(1)^{\frac{1}{2}}} + \frac{1}{(2)^{\frac{1}{2}}} = \frac{1}{\sqrt{2}}. \]

If again the gain is assumed to be very large this gives,

\[ P_{sp} = \frac{\hbar\nu_0}{2\tau_f \sigma_0} \left( \frac{e^{g_0 z}}{\sqrt{g_0 z}} + \frac{e^{g_0 (L-z)}}{\sqrt{g_0 (L-z)}} \right). \]

To plot is we use,

\[ P_{sp} = \frac{e^{g_0 z}}{\sqrt{g_0 z}} + \frac{e^{g_0 (1-z)}}{\sqrt{g_0 (1-z)}}, \]
or,

\[ P_{sp} = e^z \sqrt{z} + \frac{e^{(1-z)}}{\sqrt{1-z}} \]  \hspace{1cm} (L.28)

This expression also blows up at the edges. A Taylor series again also gives that it blows up.

\[ P_{sp} = 1 + z \sqrt{z} + \frac{2 - z}{\sqrt{1-z}} \]  \hspace{1cm} (L.29)

So maybe not use a Taylor series for the exponential but something else to determine its behavior at the edges.

In thermal equilibrium the gain is negative and spontaneously emitted radiation is not probable to get amplified. If the gas is pumped to an extend that a population inversion exists the upper level of the population inversion has many more occupants than in thermal equilibrium. Therefore spontaneous emission is more likely to occur from this upper level to a lower level. All of the allowed transitions to lower levels are possible. Each of these transitions having their own transition energy, emitted photon frequency and line width. Therefore an average is taken over all these transitions and wavelengths. So then in that model the upper level spontaneously decays to this artificial lower level, thereby having reduced the problem to a two level system. The gain experienced by the spontaneously emitted photon depends on the gain coefficient. The gain coefficient depends on the resonance cross section and the population inversion. However the population of the lower state cannot be determined in this way so it is assumed to be zero because the population of the upper state is very high. When a spontaneously emitted photon is amplified, all the molecules which cause this amplification make the same transition as the initial one. Therefore the upper state gets depleted. The actual lower state of the particular transition is fed by this process. In this way the population inversion decreases.
Bibliography


