

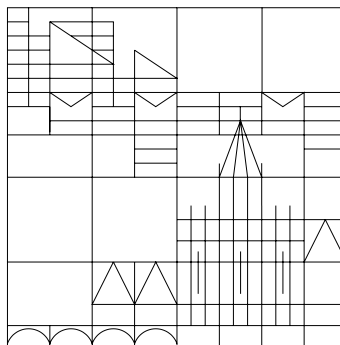
The Theory of the Manipulation of Molecules with Laser Beams

Theorie der Manipulation von Molekülen mit
Laserstrahlen

Diplomarbeit

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Für meine Eltern
Sigrid Rehfeld und Karl-Heinz Rehfeld
und für meine Freundin Margit
die mich das ganze Studium hindurch
unterstützt haben

Motivation

Jedes angeregte Atom oder Molekül emittiert früher oder später spontan ein Photon. Stimmt das? Bei der Betrachtung eines anderen Vorgangs, der Absorption eines Photons, stellt sich überraschenderweise heraus, daß es Zustände gibt, die Photonen einer bestimmten Mode nicht absorbieren, obwohl sie dies aufgrund der Wellenlänge und der Auswahlregeln eigentlich tun sollten.

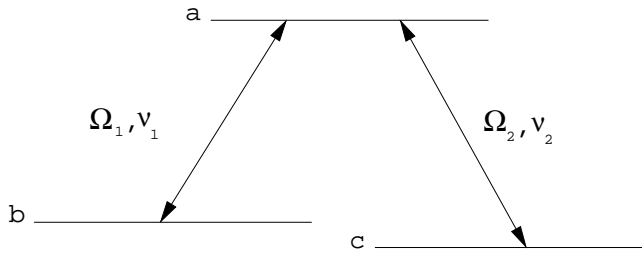


Abbildung 1: Termschema eines Λ Dark States.

Diese Zustände werden Dunkelzustände genannt. In Abb.1 ist ein Beispiel eines solchen Zustandes dargestellt. Ein Atom mit drei Niveaus wechselwirkt mit zwei Photonmoden der Frequenzen ν_1 und ν_2 . Es ist möglich eine Superposition der unteren Eigenzustände zu wählen, die unterbindet, daß ein Photon absorbiert wird. Dies kann in einer kurzen Rechnung näher verdeutlicht werden. Für resonante Moden hat der Hamiltonoperator im Wechselwirkungsbild folgende Gestalt:

$$H_{\text{int}} = \Omega_1|a\rangle\langle b| + \Omega_2|a\rangle\langle c| + \Omega_1^*|b\rangle\langle a| + \Omega_2^*|c\rangle\langle a|. \quad (1)$$

Setzt man den Zustand

$$|\Psi_{\text{dark}}\rangle \propto \Omega_1|c\rangle - \Omega_2|b\rangle \quad (2)$$

in die zugehörige Schrödingergleichung ein, so wird ersichtlich, daß kein Photon absorbiert wird:

$$H_{\text{int}}|\Psi_{\text{dark}}\rangle = 0. \quad (3)$$

Das Drei-Niveau-Atom bleibt trotz Wechselwirkung in der Superposition und wird nicht angeregt. Die beiden möglichen Übergänge interferieren miteinander destruktiv und verhindern so die Absorption.

Gibt es auf der anderen Seite einen angeregten Zustand, der spontane Emission unterbindet? Spontane Emission ist, im Gegensatz zu der oben diskutierten Absorption, kein kohärenter Vorgang und sie kann in sehr viele Moden erfolgen - nämlich in alle Moden des Vakuums. Es ist daher möglich die spontane Emissionsrate zu verändern, indem man die Modendichte ändert. Dies kann in Kavitäten (*engl.: cavities*) erreicht werden. Eine Kavität ist ein Raum der von beinahe ideal spiegelnden Flächen umgeben ist. Diese Flächen stellen Randbedingungen an das Photonen-Feld, die die Modenzahl begrenzen.

Läßt sich auch die spontane Emission im freien Raum verändern? In den letzten Jahren ist in einigen theoretischen Arbeiten die Möglichkeit diskutiert worden, spontane Emission in Atomen sowie in Molekülen durch Überlagerung von angeregten Zuständen und durch die Verwendung von Lasern zu modifizieren (unter anderem in [Zhu and Scully(1996)], [Agarwal(1997)], [Berman(1998)] und [Ficek and Swain(2001)]).

In Abb.2 ist ein einfaches Drei-Niveau-Atom dargestellt, daß mit dem Vakuum wechselwirkt. Der wesentliche Unterschied zu Abb.1 ist hier, daß \vec{k}_1 und \vec{k}_2 zwei beliebige Wellenvektoren darstellen. Sogar wenn nur resonante Moden betrachtet werden, wechselwirken viele Photonen-Moden mit dem Atom. Die Unterdrückung

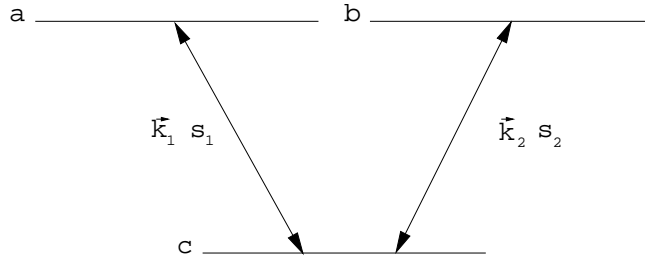


Abbildung 2: V- Schema eines 3-Niveau Atoms im Vakuum.

von spontaner Emission ist daher viel schwieriger als die Unterdrückung der Absorption. Später (in Kapitel 3) wird sich herausstellen, daß Übergänge mit orthogonalen Dipolmomenten nicht benutzt werden können, um die spontane Emission zu verändern. Übergänge mit parallelen oder antiparallelen Dipolmomenten können jedoch destruktiv oder konstruktiv miteinander interferieren und so die spontane Emissionsrate verringern oder verstärken. Aus diesem Grund behandeln alle oben genannten Veröffentlichungen ausschließlich Übergänge mit parallelen oder antiparallelen Dipolmomenten.

Diese Bedingung ist im allgemeinen nicht erfüllt für entartete Eigenzustände in Atomen.¹ Xia und seine Gruppe [Xia et al.(1996)] versuchten dieses Problem zu umgehen, indem sie gemischte Rydberg Zustände von N_2 benutzten, die durch Spin-Orbit Wechselwirkung überlagert sind und parallele oder antiparallele Dipolübergänge bei einer niedrigen Energieaufspaltung haben sollten. Sie beobachteten experimentell eine Unterdrückung der spontanen Emission aus dieser Überlagerung in einen tieferen Zustand. Leider konnte dieses Experiment in einem späteren Versuch von Li *et al.* [Li et al.(2000)] nicht wiederholt werden, und es bestehen Zweifel ob die Ergebnisse von Xia *et al.* stimmen.

In der vorliegenden Diplomarbeit werden elektronische Übergänge zwischen Superpositionen von Vibrationsniveaus des elektronisch angeregten Zustandes und Vibrationszuständen des elektronischen Grundzustandes untersucht. Die Vibration der Kerne verursacht eine Aufspaltung der elektronischen Zustände in viele Vibrationszustände. Die elektronischen Dipolmomente zwischen den Vibrationszuständen sind parallel, wenn sie den gleichen elektronischen Übergang haben. In dieser Arbeit werden deshalb nur zwei elektronische Zustände betrachtet, der Grundzustand und der erste angeregte elektronische Zustand. Vibrationsniveaus sind außerdem interessant, weil zwischen Vibrationszuständen keine Auswahlregeln existieren. Spontane

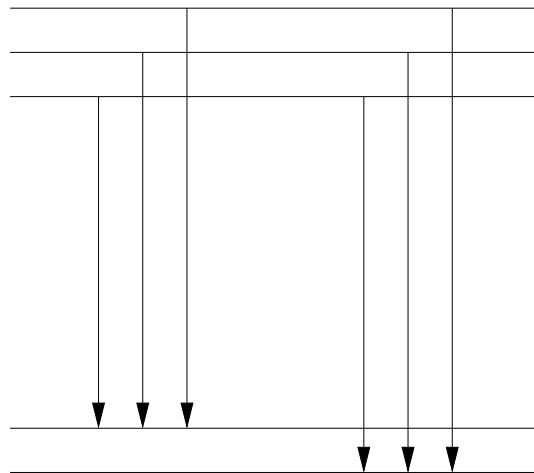
¹Die Phasen von Zustände mit unterschiedlicher Energie entwickeln sich unterschiedlich. Dies zerstört im Normalfall die gewünschte Superposition.

Emission kann in viele tiefere Vibrationsniveaus erfolgen. Falls es möglich wäre, die spontane Emission in ein bestimmtes Vibrationsniveau zu verstärken und in alle anderen zu unterbinden, würde sich das entsprechende Molekül in dieser Hinsicht wie ein Atom verhalten. Experimentelle Methoden wie z.B. Laserkühlen könnten benutzt werden. Soweit mir bekannt ist, ist die Verstärkung der spontanen Emissionsrate durch Überlagerung von Vibrationsniveaus des angeregten elektronischen Zustandes bisher nicht untersucht worden.

Aufbau der Arbeit

Das nächste Kapitel versorgt den Leser mit Hintergrundwissen über Mastergleichungen und zweiatomige Moleküle. Im ersten Teil 2.1 wird die Mastergleichung eines Systems (wie z.B. eines Atoms oder eines Moleküls) hergeleitet, das mit dem Vakuum wechselwirkt. Mastergleichungen spielen eine zentrale Rolle in meiner Diplomarbeit. Dieser Teil von Kapitel 2 trägt daher zum Verständnis meiner Diplomarbeit wesentlich bei.

Der zweite Teil des Kapitels vermittelt Grundwissen über zweiatomige Moleküle. Vibrationsniveaus werden dabei etwas tiefgreifender behandelt. Ein Leser, der



mit zweiatomigen Molekülen vertraut ist, kann diesen Teil überspringen.

Das nächste Kapitel, der Hauptteil meiner Diplomarbeit, benutzt die oben erwähnte Mastergleichung um die Bewegungsgleichung des Dichteoperators von Molekülen mit zwei elektronischen Zuständen, die jeweils in Vibrationsniveaus aufgespalten sind, zu untersuchen. In Abb.1.3 sieht man das Termschema eines zweiatomigen Moleküls mit drei Vibrationszuständen im angeregten elektronischen Zustand und zwei Vibrationszuständen im elektronischen Grundzustand. In der Wirklichkeit ist die Anzahl der Vibrationszustände meist erheblich höher².

Abbildung 3: Der energetisch höher liegende Zustand besteht aus einer Überlagerung der drei $|\mu\rangle$ Zustände. Die Übergänge dieser drei Niveaus nach $|\nu_0\rangle$ interferieren. Das gleiche gilt für Übergänge nach $|\nu_1\rangle$. Gibt es eine Superposition der $|\mu\rangle$ Zustände, die die Übergangswahrscheinlichkeit nach $|\nu_0\rangle$ erhöhen und nach $|\nu_1\rangle$ erniedrigen?

Die so erhaltene Mastergleichung wird dann dazu verwendet, eine Methode zu finden, die spontane Emissionsrate in ein bestimmtes unteres Vibrationsniveau zu

²10, 20 oder mehr

erhöhen, und die spontane Emission in andere zu unterdrücken. Das Molekül wird dazu in eine Überlagerung von Vibrationszuständen des angeregten elektronischen Zustandes gebracht, und dann wird versucht die Rate der spontanen Emission zu maximieren. Die Rate soll also nur zu einem bestimmten Zeitpunkt maximal sein. Die Zeitenwicklung des Dichteoperator wird bis dahin nicht betrachtet. Der letzte Teil dieses Kapitels behandelt schließlich die Zeitenwicklung des Dichteoperator für große Zeiten verglichen mit der Schwingungsdauer der Kerne.

Das Ergebnis von Kapitel 3 wird sein, daß die Maximierung stark von den Übergangswahrscheinlichkeiten zwischen einzelnen Vibrationsniveaus abhängt.³ Wenn viele solche Übergänge in die Rechnung mit eingehen, ist es schwierig zu verstehen warum die spontane Emissionsrate in manchen Molekülen verstärkt werden kann und in anderen nicht. Leider haben Moleküle viele mögliche Übergänge zwischen Vibrationsniveaus. Aus diesem Grund werden in Kapitel 4 numerische Berechnungen durchgeführt.

Kapitel 5 faßt letztendlich die Ergebnisse zusammen, beleuchtet sie in einem größerem Zusammenhang und zeigt mögliche Lösungen für die entstanden Probleme auf.

Im Anhang A wird gezeigt, daß nur extrem starke Laserfelder in der Lage sind, die spontane Emissionsrate in größerem Rahmen zu ändern. Anhang B führt Superoperatoren ein und enthält den Liouville Superoperator der in Kapitel 4 verwendet wird.

³Diese Übergangswahrscheinlichkeiten sind proportional zu sogenannten Franck Condon Faktoren (siehe 2.2).

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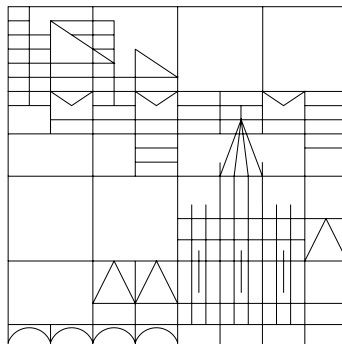
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There is a theory which states that if ever anybody discovers exactly what the Universe is for and why it is here, it will instantly disappear and be replaced by something even more bizarre and inexplicable. There is another theory which states that this has already happened.

Douglas Adams

Acknowledgements

At this place I would like to thank Prof. Audretsch and his group. Especially I wish to thank all the people I kept busy knocking on their doors and asking "I have a short question, do you have time...?" Here I must mention in first place and before all my advisor Peter Marzlin whom I certainly asked the most questions. He always has found time to answer my questions, helped me with my calculations, gave me physical insight and new ideas and last but not least he was never too busy to make a joke. These are the things that have made my life much easier during my diploma thesis. Speaking of an easier life I must also mention Jan Krüger who helped me with all the problems I had concerning Linux or C++. Matthias Söhn helped me with my numerous questions on Mathematica. And last but not least, I would like to thank Thomas Konrad, the only person whom I didn't bother by knocking on the door, simply because he has been my office mate; I certainly asked him many questions, too. Thank you. It was a really nice time in your group!

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Chapter 1

Introduction

1.1 Motivation

Every excited atom or molecule eventually emits spontaneously a photon. Or does it not? For an opposite and coherent process – the absorption of a photon – states are known which do not absorb a photon with a special wave vector

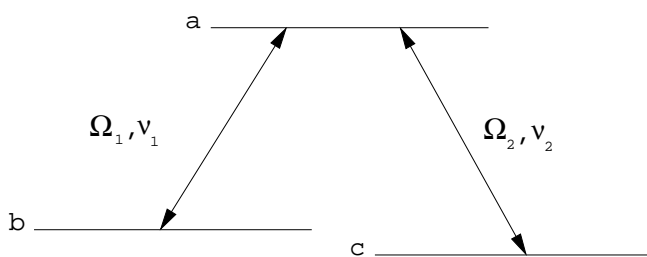


Figure 1.1: Level scheme for a Λ dark state.

even if the energy separation and dipole selection rules would facilitate it. These states are called *dark states*. What is meant to be a dark state can be seen in Fig.1.1 In this example a three level atom couples to two photon modes with frequencies ν_1 and ν_2 . A superposition of lower levels b

and c can be chosen that prevents the absorption of a photon. This can be shown in a short calculation. For resonant modes the interaction Hamiltonian of the system has the following form:

$$H_{\text{int}} = \Omega_1|a\rangle\langle b| + \Omega_2|a\rangle\langle c| + \Omega_1^*|b\rangle\langle a| + \Omega_2^*|c\rangle\langle a|. \quad (1.1)$$

It is obvious that in this case the state

$$|\Psi_{\text{dark}}\rangle \propto \Omega_1|c\rangle - \Omega_2|b\rangle \quad (1.2)$$

is the above mentioned superposition that prevents the absorption:

$$H_{\text{int}}|\Psi_{\text{dark}}\rangle = 0. \quad (1.3)$$

The three level atom stays in the superposition. No photon will be absorbed. The coherent trapping occurs due to the destructive quantum interference of the two transitions.

Does on the other hand exist an excited state which forbids or enhances spontaneous emission? Spontaneous emission is, in contrast to the above mentioned absorption, always related to many modes – the vacuum field. One way of changing the spontaneous emission rate is therefore to modify the vacuum by application of boundary conditions. This is a well proven fact and experimentally confirmed. Cavities can be used to achieve this. A *cavity* is a space enclosed by (almost) ideal mirrors. The boundary conditions of a cavity restricts the number of modes. In this means the spontaneous emission rate can be reduced.

But it is possible to modify the spontaneous emission in free space? In the last years several theoretical papers discussed the possibility to modify the spontaneous emission rate in atoms as well as in molecules by superposition of excited levels and by coupling laser fields to the atoms or molecules (among others [Zhu and Scully(1996)], [Agarwal(1997)], [Berman(1998)], and [Ficek and Swain(2001)]). A simple three level atom that couples to the vacuum can be seen in Fig.1.2.

The major difference to Fig.1.1 is that \vec{k}_1 and \vec{k}_2 are arbitrary wave vectors. Even if only resonant modes are considered, many modes couple to the atom. Spontaneous emission cancellation or suppression is therefore a much more complicated task. It will turn

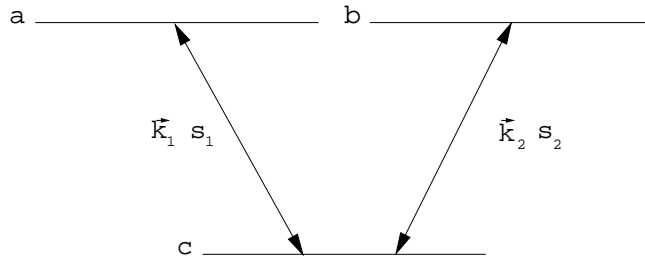


Figure 1.2: V- scheme for a 3 level atom that couples to the vacuum.

out later (see chapter 3) that transitions with orthogonal dipole moments cannot interfere in such a way that they change the spontaneous emission rate. Transitions with parallel or antiparallel dipole moments however can interfere destructively or constructively and lessen or enhance the transition probability. For this reason all the above mentioned papers deal with parallel or antiparallel dipole moments.

This requirement is in general not fulfilled in atoms, at least for degenerate energy levels.¹ Xia *et al.* [Xia et al.(1996)] tried to circumvent this problem by using mixed Rydberg states of N₂ (mixed by spin-orbit interaction) which should have parallel or anti-parallel dipole moments and a small energy separation. They experimentally observed spontaneous emission cancellation to a special lower level. Anyhow a later experiment of Li *et al.* [Li et al.(2000)] could not confirm these results and casts doubt on the results of Xia *et al.*

In my thesis electronic transitions from a superposition of vibrational levels in diatomic molecules is discussed. The vibration of the nuclei results in a splitting of electronic states into several vibrational levels. The corresponding electronic dipole moments are all parallel and the problem of orthogonal dipole moments does not occur. Vibrational levels are also interesting because for electronic transitions between vibrational levels no strict selection rules exist. Spontaneous emission into

¹Levels with different energy eigenvalues start to de-phase very fast and the intended superposition is destroyed.

many lower vibrational levels is possible. If it were possible to enhance the spontaneous emission rate to one special lower level and suppress the spontaneous emission to the other levels, the molecule would in this respect behave like an atom. Experimental methods that are used in the case of atoms, like for example *laser cooling* could be used. To my knowledge the enhancement or suppression of spontaneous emission by using a superposition of vibrational levels has not been discussed so far.

1.2 Thesis outline

The next chapter provides the reader with some necessary background knowledge. In section 2.1 master equations are introduced and the master equation of a system (like an atom or a molecule) interacting with the vacuum is derived. This master equation plays a central role in my thesis and I therefore strongly recommend to read this section.

The second part of the next chapter deals with diatomic molecules. Basic information about diatomic molecules is given. Vibrational levels are discussed in more detail. The experienced reader may skip this section.

The main part of my thesis uses the above mentioned master equation

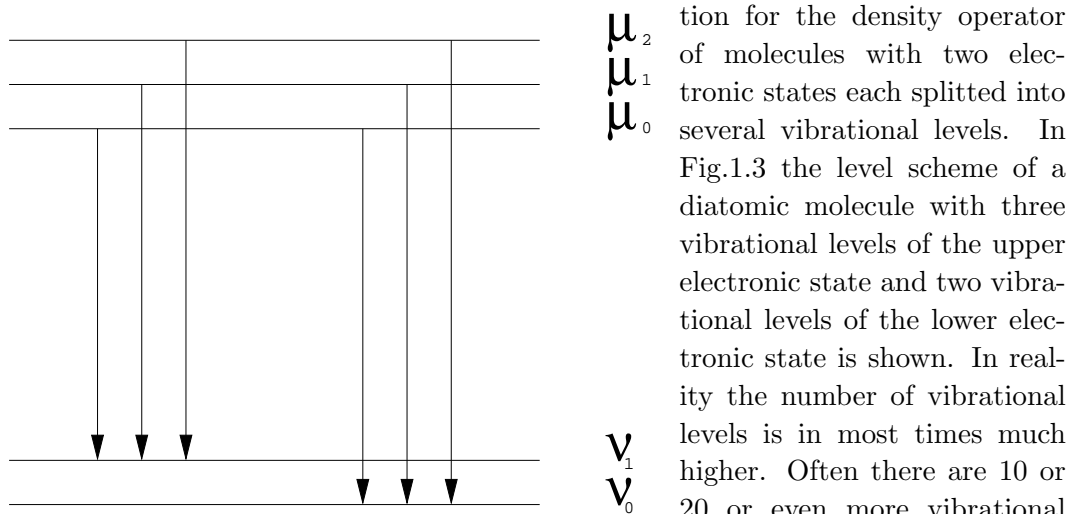


Figure 1.3: The upper state is in a superposition of three $|\mu\rangle$ -levels. The transitions of these three levels to $|\nu_0\rangle$ interfere. The same is true for the transitions to $|\nu_1\rangle$. Is there, for example, a superposition that favors the transition to $|\nu_0\rangle$ over the transition to $|\nu_1\rangle$?

to derive the equation of motion for the density operator of molecules with two electronic states each splitted into several vibrational levels. In Fig.1.3 the level scheme of a diatomic molecule with three vibrational levels of the upper electronic state and two vibrational levels of the lower electronic state is shown. In reality the number of vibrational levels is in most times much higher. Often there are 10 or 20 or even more vibrational states between two electronic states.

The resulting master equation is then used to find a method to maximize the spontaneous emission rate to one lower vibrational level and to suppress the rate to all other levels. The molecule is brought into a superposition of vibrational levels of the upper electronic state and then the spontaneous emission rate is tried to be maximized to one lower level. So far the time evolution of the density matrix is not considered. The last part of the main chapter

3 discusses the time dependence of the density operator for large times compared with the vibrational motion of the nuclei.

The outcome of chapter 3 will be that the maximization depends crucially on the transition probabilities between single vibrational levels.² If many transitions are included into the calculation, it is difficult to understand why the spontaneous emission rate in some molecules can be modified and in some not. Unfortunately, molecules do have many possible transitions between vibrational levels. For this reason in chapter 4 numerical calculations were performed to get a better understanding which molecules are suitable and which molecules are not.

Chapter 5 finally discusses the results in the greater context and points up some possible solutions for the arised problems.

Appendix A proves that only extremely strong laser fields can change the spontaneous emission rate considerably. Appendix B introduces super operators and provides the Liouville super operator for the time evolution used in chapter 4.

²These transition probabilities are proportional to so called Franck Condon factors (see 2.2).

Chapter 2

Background knowledge

In this chapter master equations are introduced and diatomic molecules are discussed. A general introduction on quantum optics is *not* given. Many excellent books cover this topic. I would like to mention [Loudon(1991)], [Scully and Zubairy(1997)], [Cohen-Tannoudji et al.(1992)], [Mandel and Wolf(1995)], [Milonni(1995)], [Cohen-Tannoudji et al.(1989)], and [Walls and Milburn(1995)].

2.1 The master equation approach

In this section a general formalism to derive *master equations* is introduced. A master equation is a differential equation describing the time evolution of a subsystem. In our case the system includes a molecule and the radiation field that couples to it. We are concerned with the time development of the molecule states. We are not interested in the radiation field. The master equation approach provides a useful method to derive the "equation of motion" for the molecule states in a "mean" radiation field.

In the derivation projection operators are used which project the overall density operator on a density operator solely for the radiation (the *reservoir*) or on a density operator only describing the state of the molecule (the subsystem we are interested in). These operators are applied to the equation describing the time evolution of the density operator of the combined system. This results in a coupled system of equations for the time evolution of the subsystem and the reservoir. The trick of the master equation approach is to formally integrate the time evolution of the reservoir. By this means the time evolution of the reservoir is eliminated and we have an equation describing only the time evolution of the states of the molecule. This technique, which is called *Zwanzig's projection operator technique*, is shown in a very comprehensive way in [Agarwal(1975)] or in [Mandel and Wolf(1995)]. For a more physical interpretation of master equations have a look at [Cohen-Tannoudji et al.(1992)]. Because the master equation approach plays an important role in chapter 3, a short derivation is sketched below.

Let ρ be the density operator characterizing the system consisting of the molecule and the radiation field. H is the Hamiltonian in the Schrödinger picture. The

Liouville super operator $\mathcal{L} = \frac{1}{\hbar}[H, \dots]$ describes the time evolution of the density operator.

$$i\dot{\rho} = \mathcal{L}\rho \quad (2.1)$$

Further let P be the time independent super operator projecting ρ on the molecule states and Q the super operator projecting ρ on the part of ρ which doesn't belong to P ρ . These operators have the following properties:

$$P^2 = P \quad Q^2 = Q \quad PQ = QP = 0. \quad (2.2)$$

The reduced density operators ¹ are defined as follows:

$$\sigma_M := P\rho \quad \sigma_R := Q\rho \equiv (1 - P)\rho. \quad (2.3)$$

Here σ_M stands for the reduced density operator representing the molecule and σ_R stands for the rest of ρ . A suggestive way of writing this is:

$$\rho = \begin{pmatrix} \boxed{\sigma_M} \\ \sigma_R \end{pmatrix}. \quad (2.4)$$

Now let the projection operators act on (2.1). This results in two coupled differential equations.

$$\dot{\sigma}_M(t) = -iP\mathcal{L}(\sigma_M(t) + \sigma_R(t)) \quad (2.5)$$

$$\dot{\sigma}_R(t) = -iQ\mathcal{L}(\sigma_M(t) + \sigma_R(t)) \quad (2.6)$$

So far the result is symmetric in σ_M and σ_R . Now the set of equations can be uncoupled by solving equation (2.6) for $\sigma_R(t)$ and inserting it into equation (2.5).

Equation 2.6 can be solved formally with the *method of variation of parameters*.

$$\sigma_R(t) = T e^{-iQ \int_0^t dt' \mathcal{L}(t')} A(t) =: U(0, t) A(t). \quad (2.7)$$

Here T is the time ordering operator. With this ansatz $\dot{\sigma}_R$ becomes:

$$\begin{aligned} \dot{\sigma}_R(t) &= -iQ\mathcal{L}(t)\sigma_R(t) + U(0, t)\dot{A}(t) \\ &\stackrel{!}{=} -iQ\mathcal{L}(t)\sigma_R(t) - iQ\mathcal{L}(t)\sigma_M(t). \end{aligned} \quad (2.8)$$

¹Actually the density operators introduced here are not really reduced, since they belong to a Hilbert space of the full dimensionality of both the molecule and the radiation. In the literature the reduced density operators are often defined without the radiation part. $\sigma_M = |0_R\rangle\langle 0_R|\sigma$. Here σ is really a reduced density operator of lower dimension. For further details have a look at the end of this section.

Solving equation (2.8) for $A(t)$ yields

$$A(t) = A(0) + \int_0^t d\tau U(\tau, 0) (-iQ\mathcal{L}(\tau)\sigma_M(\tau)). \quad (2.9)$$

This can be inserted into equation (2.7):

$$\begin{aligned} \sigma_R(t) &= U(0, t)A(0) - iU(0, t) \int_0^t d\tau U(\tau, 0)Q\mathcal{L}(\tau)\sigma_M(\tau) \\ &= U(0, t)A(0) - iU^{-1}(t, 0) \int_0^t d\tau U^{-1}(0, \tau)Q\mathcal{L}(\tau)\sigma_M(\tau) \\ &= U(0, t)A(0) - i \int_0^t d\tau U(\tau, t)Q\mathcal{L}(\tau)\sigma_M(\tau). \end{aligned} \quad (2.10)$$

With the substitution $\tau \rightarrow t - \tau$ the last equation becomes:

$$\sigma_R(t) = U(0, t)A(0) - i \int_0^t d\tau U(t - \tau, t)Q\mathcal{L}(t - \tau)\sigma_M(t - \tau). \quad (2.11)$$

The constant $A(0)$ can be fixed by the constraint that $\sigma_R(t = 0) \stackrel{!}{=} \sigma_R(0)$. So finally we get

$$\sigma_R(t) = U(0, t)\sigma_R(0) - i \int_0^t d\tau U(t - \tau, t)Q\mathcal{L}(t - \tau)\sigma_M(t - \tau). \quad (2.12)$$

The result for $\sigma_R(t)$ can now be inserted into equation (2.5):

$$\dot{\sigma}_M(t) = -iP\mathcal{L}(t)\sigma_M(t) - iP\mathcal{L}(t)U(0, t)\sigma_R(0) - P\mathcal{L}(t) \int_0^t d\tau U(t - \tau, t)Q\mathcal{L}(t - \tau)\sigma_M(t - \tau). \quad (2.13)$$

This equation is still exact. No approximations or assumptions were made. In (2.13) there is no $\sigma_R(t)$ -dependence anymore. Equation (2.13) is called *Zwanzig's generalized master equation*. Now let us assume a specific form for \mathcal{L} and P .²

$$\mathcal{L} = \mathcal{L}_M + \mathcal{L}_R + \mathcal{L}_{MR} \quad P = |0_R\rangle\langle 0_R| \text{Tr}_R \quad (2.14)$$

\mathcal{L}_M , \mathcal{L}_R , and \mathcal{L}_{MR} corresponds to H_M , H_R and H_{MR} in $H = H_M + H_R + H_{MR}$. These are the molecule Hamiltonian, the radiation Hamiltonian and the interaction Hamiltonian. The choice of P assures that the second term in (2.13) vanishes and that the reservoir is the vacuum. Furthermore assume

²Here often the notation $P = |0_R\rangle\langle 0_R| \otimes \text{Tr}_R$ is used.

$$\mathcal{L}_R = \sum_k \omega_k a_k^\dagger a_k \quad \text{and} \quad \mathcal{L}_{MR} \text{ is linear in } a_k \text{ and } a_k^\dagger. \quad (2.15)$$

These assumptions lead to the following useful equations:

$$\begin{aligned} [\mathbf{P}, \mathcal{L}_M] &= 0 \quad (\text{a}) & \mathbf{P}\mathcal{L}_R &= 0 \quad (\text{b}) \\ \mathbf{P}\mathcal{L}_{MR}\mathbf{P} &= 0 \quad (\text{c}) & \mathbf{Q}\mathcal{L}_M\mathbf{P} &= 0 \quad (\text{d}) \end{aligned} \quad (2.16)$$

The first equation (2.16a) is a consequence of the definition of \mathcal{L}_M . The special choice of \mathbf{P} , \mathcal{L}_R , and \mathcal{L}_{MR} leads to the two next equations (2.16b) and (2.16c). From $[\mathbf{P}, \mathcal{L}_M] = 0$ and $\mathbf{Q}\mathbf{P} = 0$ follows that $\mathbf{Q}\mathcal{L}_M\mathbf{P} = 0$. These equations can be used to simplify equation (2.13):

$$\dot{\sigma}_M(t) = -i\mathcal{L}_M(t)\mathbf{P}\rho(t) - \mathbf{P}(\mathcal{L}_M(t) + \mathcal{L}_{MR}(t)) \int_0^t d\tau U(t-\tau, t) \mathbf{Q}\mathcal{L}_{MR}(t-\tau)\mathbf{P}\rho(t-\tau). \quad (2.17)$$

In addition $\mathbf{Q}\mathcal{L}_{MR}\mathbf{P} = (1 - \mathbf{P})\mathcal{L}_{MR}\mathbf{P} = \mathcal{L}_{MR}\mathbf{P}$. This results in:

$$\dot{\sigma}_M(t) = -i\mathcal{L}_M(t)\mathbf{P}\rho(t) - \mathbf{P}(\mathcal{L}_M(t) + \mathcal{L}_{MR}(t)) \int_0^t d\tau U(t-\tau, t) \mathcal{L}_{MR}(t-\tau)\mathbf{P}\rho(t-\tau). \quad (2.18)$$

Since $[\mathcal{L}_M, \mathbf{P}] = 0$ and $\mathbf{P}U = 0$, the second $\mathcal{L}_M(t)$ can be removed without changing the result:

$$\dot{\sigma}_M(t) = -i\mathcal{L}_M(t)\mathbf{P}\rho(t) - \mathbf{P}\mathcal{L}_{MR}(t) \int_0^t d\tau U(t-\tau, t) \mathcal{L}_{MR}(t-\tau)\mathbf{P}\rho(t-\tau). \quad (2.19)$$

So far any simplification was due to the special choice of \mathcal{L} and \mathbf{P} . To further simplify equation (2.18) an approximation is used:

$$U(t-\tau, t) = \mathbf{T}e^{-i\mathbf{Q} \int_{t-\tau}^t dt' (\mathcal{L}_M(t') + \mathcal{L}_R(t') + \mathcal{L}_{MR}(t'))}$$

is replaced by

$$U_0(t-\tau, t) := \mathbf{T}e^{-i\mathbf{Q} \int_{t-\tau}^t dt' (\mathcal{L}_M(t') + \mathcal{L}_R(t'))}. \quad (2.20)$$

This corresponds to the *Born approximation*. The integral is now of first order in \mathcal{L}_{MR} . Since $[\mathbf{Q}, \mathcal{L}_M] = [1 - \mathbf{P}, \mathcal{L}_M] = 0$ and $[\mathbf{Q}, \mathcal{L}_R] = [1 - \mathbf{P}, \mathcal{L}_R] = 0$, $U_0(t-\tau, t)$ can be rewritten as

$$U_0(t-\tau, t) = \mathbf{Q}\mathbf{T}e^{-i \int_{t-\tau}^t dt' (\mathcal{L}_M(t') + \mathcal{L}_R(t'))}. \quad (2.21)$$

With the help of $P\mathcal{L}_{\text{MR}}Q = P\mathcal{L}_{\text{MR}}(1 - P) = P\mathcal{L}_{\text{MR}}$ the master equation finally assumes the following form:

$$\dot{\sigma}_{\text{M}}(t) = -i\mathcal{L}_{\text{M}}(t)\sigma_{\text{M}}(t) - P\mathcal{L}_{\text{MR}}(t) \int_0^t d\tau \tilde{U}_0(t - \tau, t) \mathcal{L}_{\text{MR}}(t - \tau) \sigma_{\text{M}}(t - \tau) \quad (2.22)$$

with

$$\tilde{U}_0(t - \tau, t) := T e^{-i \int_{t-\tau}^t dt' (\mathcal{L}_{\text{M}}(t') + \mathcal{L}_{\text{R}}(t'))}. \quad (2.23)$$

If \mathcal{L}_{M} , \mathcal{L}_{R} , and \mathcal{L}_{MR} are not time dependent, the master equation simplifies to

$$\dot{\sigma}_{\text{M}}(t) = -i\mathcal{L}_{\text{M}}\sigma_{\text{M}}(t) - P\mathcal{L}_{\text{MR}} \int_0^t d\tau e^{-i(\mathcal{L}_{\text{M}} + \mathcal{L}_{\text{R}})\tau} \mathcal{L}_{\text{MR}}\sigma_{\text{M}}(t - \tau). \quad (2.24)$$

This equation is used in chapter 3 to derive a master equation for the model molecule in vacuum. Often the master equation is used in the *interaction picture*.

$$\dot{\sigma}_{\text{M}}^{\text{I}} \equiv \frac{\partial}{\partial t} (e^{i\mathcal{L}_0 t} \sigma_{\text{M}}(t)) = -e^{i\mathcal{L}_0 t} P\mathcal{L}_{\text{MR}} \int_0^t d\tau e^{-i\mathcal{L}_0 \tau} \mathcal{L}_{\text{MR}} \sigma_{\text{M}}(t - \tau) \quad (2.25)$$

For the sake of simplicity $\mathcal{L}_0 := \mathcal{L}_{\text{M}} + \mathcal{L}_{\text{R}}$ and $H_0 := H_{\text{M}} + H_{\text{R}}$ is used. With the help of $e^{i\mathcal{L}_0 t} A = e^{i\frac{H_0}{\hbar} t} A e^{-i\frac{H_0}{\hbar} t}$, this yields:

$$\dot{\sigma}_{\text{M}}^{\text{I}} = -e^{i\frac{H_0}{\hbar} t} P\mathcal{L}_{\text{MR}} \int_0^t d\tau e^{-i\frac{H_0}{\hbar} \tau} \mathcal{L}_{\text{MR}} \sigma_{\text{M}}(t - \tau) e^{i\frac{H_0}{\hbar} \tau} e^{-i\frac{H_0}{\hbar} t}. \quad (2.26)$$

This finally results in the *master equation in the interaction picture*³:

$$\dot{\sigma}_{\text{M}}^{\text{I}} = -P e^{i\frac{H_0}{\hbar} t} \mathcal{L}_{\text{MR}} e^{-i\frac{H_0}{\hbar} t} \int_0^t d\tau e^{i\frac{H_0}{\hbar} (t-\tau)} \mathcal{L}_{\text{MR}} e^{-i\frac{H_0}{\hbar} (t-\tau)} e^{i\frac{H_0}{\hbar} (t-\tau)} \sigma_{\text{M}}(t - \tau) e^{-i\frac{H_0}{\hbar} (t-\tau)}$$

or

$$\dot{\sigma}_{\text{M}}^{\text{I}} = -P \mathcal{L}_{\text{MR}}^{\text{I}}(t) \int_0^t d\tau \mathcal{L}_{\text{MR}}^{\text{I}}(t - \tau) \sigma_{\text{M}}^{\text{I}}(t - \tau). \quad (2.27)$$

The equation also holds for time dependent \mathcal{L}_{MR} . This equation is used in appendix A.

In all these calculations σ_{M} is an operator on the Hilbert space describing the molecule and the reservoir. Yet the part describing the reservoir is trivial: $\sigma_{\text{M}} = |0_{\text{R}}\rangle\langle 0_{\text{R}}| \text{Tr}_{\text{R}} \rho = |0_{\text{R}}\rangle\langle 0_{\text{R}}| \sigma$. Here σ really "lives" on a lower dimensional Hilbert space, only describing the molecule. Often σ is called the reduced density operator. σ is used in chapter 3. The $|0_{\text{R}}\rangle\langle 0_{\text{R}}|$ -part in σ_{M} is very important, because, depending where it appears in the commutator, it cancels either a_k or a_k^\dagger in H_{MR} .

³ $[\frac{H_0}{\hbar}, P] = 0$

2.2 Diatomic Molecules

In this section some basic features of diatomic molecules will be introduced. Chapter 3, the main part of my thesis, deals with vibrational levels of the two lowest electronic states. Therefore in this section mainly the vibrational structure of molecular spectra is discussed. The Born-Oppenheimer approximation, the Franck Condon principle and Franck Condon factors are introduced. For further reading and background information on diatomic molecules I refer to the books of Haken [Haken and Wolf(1992)], Herzberg [Herzberg(1950)], Steinfeld [Steinfeld(1993)], and Hollas [Hollas(1998)]. A more theoretical treatment of diatomic molecules is given in [Mizushima(1975)]. Spectroscopic data of diatomic molecules can be found in [Khristenko et al.(1998)], [Radzig and Smirnov(1985)], [Herzberg(1950)], [Grigoriev and Meilikhov(1997)], and [NIST(2002)].

2.2.1 Spectra of diatomic molecules

The spectrum of a diatomic molecule is simpler than the spectrum of a polyatomic molecule, but on the other hand much more complicated than the spectrum of an atom. In a diatomic molecule, the two nuclei can vibrate against each other, or rotate around the center of mass. If the nuclei were not moving, the spectra of a diatomic molecule would resemble the spectra of an atom placed in a strong electric field (*Stark effect*). But they do move. The additional degrees of freedom result in a more complicated spectrum. The spectrum has a threefold structure: electronic, vibrational, and rotational. The energy contribution of the electronic configuration is the largest. In a coarse grained view, the spectrum consists of different bands each located at an electronic eigenvalue. A closer look reveals that these bands have a vibrational and rotational structure. The rotational motion is coupled to the vibrational motion, because the inertial tensor depends on the distance between the two nuclei.

The spectroscopic term of a molecule contains electronic, vibrational and rotational contributions.

$$E = T_e + G_\nu + F_{\nu,J} \quad (2.28)$$

Here the term T_e is the contribution of the electrons to the energy, G_ν the contribution of the vibrational motion of the nuclei, and $F_{\nu,J}$ the contribution due to the rotation of the nuclei.⁴

In a diatomic molecules electronic transitions between the two lowest electronic states are typically in the visible or ultra violet regime ($\omega_e = \Delta T(e \rightarrow e')/\hbar \approx 10^{15} \dots 10^{16}$). The energy difference between two neighboring vibrational states is often approximately one or two orders of magnitude smaller than the above mentioned energy difference ΔT_e . This means $\omega_{\text{vib}} = \Delta G(\nu \rightarrow \nu')/\hbar \approx 10^{13} - 10^{14}$ and

⁴The quantum number ν stands for a vibrational level and the number J is the quantum number of the angular momentum of the nuclei.

the corresponding photons are often in the infrared regime. The spectrum of two rotational levels within the same rotational band⁵ is typically in the microwave or far infrared ($\omega_{\text{rot}} = \Delta F(J \rightarrow J')/\hbar \approx 10^{11}$). For the spontaneous emission this means, since $\Gamma \propto \omega^3$, that $\Gamma_e \approx 10^3 \Gamma_{\text{vib}} \approx 10^{11} \Gamma_{\text{rot}}$. Thus, in a model with spontaneous emission between two electronic levels, spontaneous emission between rotational levels of the same band can be neglected. This also holds for vibrational transitions in the same electronic level, but with less accuracy.

2.2.2 The Born-Oppenheimer approximation

The *Born-Oppenheimer approximation* assumes that the wave function of the molecule is separable into nuclear and electronic parts. The Hamiltonian for diatomic molecules looks like:⁶

$$H = -\frac{\hbar^2}{2m_e} \sum_i \Delta_i - \sum_A \frac{\hbar^2}{2m_A} \Delta_A - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 R} + \sum_{i>j} \frac{e^2}{r_{ij}}. \quad (2.29)$$

The index i stands for the electrons and the index $A = 1, 2$ for the two nuclei. R denotes the distance between the two nuclei. $r_{Ai} = |\vec{r}_i - \vec{R}_A|$ stands for the distance between the i th electron and the A th nucleus. Using the ansatz

$$\Psi = \psi_e(\vec{r}, \vec{R})\chi(\vec{R}) \quad (2.30)$$

the Schrödinger equation becomes

$$\begin{aligned} \chi \left\{ -\frac{\hbar^2}{2m_e} \sum_i \Delta_i - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{i>j} \frac{e^2}{r_{ij}} \right\} \psi_e + \psi_e \left\{ -\sum_A \frac{\hbar^2}{2m_A} \Delta_A + \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 R} \right\} \chi \\ - \underbrace{\sum_A \frac{\hbar^2}{m_A} (\nabla_A \psi_e) \nabla_A \chi - \sum_A \frac{\hbar^2}{2m_A} \chi \Delta_A \psi_e}_{X: \text{ will be neglected}} = E_{\text{total}} \chi \psi_e. \end{aligned} \quad (2.31)$$

Assuming for the time being that X can be neglected, this results in two differential equations.

⁵i.e. they have the same vibrational eigenvalue

⁶omitting spin and hyperfine structure

$$\left(\overbrace{-\frac{\hbar^2}{2m_e} \sum_i \Delta_i}^{\text{kinetic energy of el.}} - \underbrace{\sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}_A|}}_{\text{el.-nucl. attract.}} + \overbrace{\sum_{i>j} \frac{e^2}{r_{ij}}}^{\text{el.-el. repulsion}} \right) \psi_e = W(R_A) \psi_e \quad (2.32)$$

$$\left(\overbrace{-\sum_A \frac{\hbar^2}{2m_A} \Delta_A}^{\text{kinetic energy of nucl.}} + \underbrace{\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 R}}_{\text{nucl.-nucl. repuls.}} + \overbrace{W(R_A)}^{\text{energy of the el.}} \right) \chi = E_{\text{total}} \chi. \quad (2.33)$$

effective potential $V(R)$

In equation (2.32) the transformation $\vec{r}_i \rightarrow \vec{r}_i + \vec{R}_1$ reveals that W really only depends on the internuclear distance vector $\vec{R} := \vec{R}_2 - \vec{R}_1$ and not on the two coordinates \vec{R}_1 and \vec{R}_2 . The resulting Hamiltonian of equation (2.32) is invariant under rotations around the internuclear axis:

$$-\frac{\hbar^2}{2m_e} \sum_i \Delta_i - \sum_i \frac{Z_1 e^2}{4\pi\epsilon_0 |\vec{r}_i|} - \sum_i \frac{Z_2 e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{R}|} + \sum_{i>j} \frac{e^2}{r_{ij}}. \quad (2.34)$$

When the coordinate system is chosen in which $\vec{R} = (0, 0, R)$, then it is obvious that the above Hamiltonian only depends on R . The energy $W(R)$ of the electrons is therefore calculated in the coordinate system with fixed nuclei.⁷

In the derivation of the two equations (2.32) and (2.33) the following approximation has been made:

$$\left| -\sum_A \frac{\hbar^2}{m_A} (\nabla_A \psi_e) \nabla_A \chi - \sum_A \frac{\hbar^2}{2m_A} \chi \Delta_A \psi_e \right| \ll W(R) \lesssim E_{\text{total}}. \quad (2.35)$$

It is possible to obtain a rough estimate for the order of error be made by neglecting (2.35). The electron wave function depends on the relative coordinate $\vec{r} - \vec{R}$. This means that $\Delta_A \psi_e \approx \Delta_i \psi_e$. Therefore $\frac{\hbar^2}{2m_A} \Delta_A \psi_e \approx \frac{m_e}{m_A} \frac{\hbar^2}{2m_e} \Delta_i \psi_e \approx \frac{m_e}{m_A} W(R)$. The last estimate is true because the kinetic energy of an electron is of the order of $W(R)$. Think for example of the virial theorem in classical mechanics. It states that the average kinetic energy is half the total energy in a $\frac{1}{r}$ potential.

The first term can be estimated by the following approximations:

$$\left| \frac{\hbar \nabla_A \psi_e}{\sqrt{m_A}} \right| \approx \left| \frac{\sqrt{2m_e W(R)}}{\sqrt{m_A}} \right| \quad \text{and} \quad \left| \frac{\hbar \nabla_A \chi}{\sqrt{m_A}} \right| \approx \left| \frac{\sqrt{2m_A W_{\text{nucl.}}(R_A)}}{\sqrt{m_A}} \right|. \quad (2.36)$$

In a classical gas of two types of particles (nuclei and electrons), $\sqrt{2m_A W_{\text{nucl.}}} \approx \sqrt{2m_e W(R)}$ would hold due to Dalton's law of partial pressures. So it is at least

⁷The fact that $W(R)$ is expressed in the coordinate system with fixed positions for the nuclei results later in the selection rules for the angular momenta of the nuclei (see (2.49)).

plausible to some extent that $\frac{\hbar^2}{m_A}(\nabla_A\psi_e)\nabla_A\chi$ is also of the order of $\frac{m_e}{m_A}W(R)$. The argumentation was in no way exact, but it is possible to gain the same results using expectation values for the above neglected terms.

The Born-Oppenheimer approximation therefore neglects terms of order $\frac{m_e}{m_A} \lesssim 5 \cdot 10^{-4}$. The worst case is H_2 . The heavier the molecule, the more justified is the approximation.

For given $W(R)$ equation (2.33) therefore describes the motion of the nuclei in an effective potential. Because the mass of the electrons is much smaller than the mass of the nuclei, the nuclei feel a "time averaged" electron potential. In first approximation the effective potential can be assumed to be harmonic around the equilibrium internuclear distance \bar{R} . In the literature the corresponding harmonic oscillator eigenfrequency is given to describe the vibrational structure of a given electronic state.⁸

The effective potential depends only on the distance R between the two particles.

$$V(R) := \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 R} + W(R) \approx \frac{1}{2}m\omega^2(R - \bar{R})^2 + V(\bar{R}). \quad (2.37)$$

In the harmonic approximation the reduced mass $m := \frac{m_1 m_2}{m_1 + m_2}$ was used. With the help of the relative coordinate \vec{R} and using the ansatz $\chi(\vec{R}) = P(R)\Phi(\vartheta, \varphi)$, the relative motion can be roughly described by the following equation:⁹

$$\left\{ -\frac{\hbar^2 \partial}{2mR^2 \partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{\vec{L}^2}{2mR^2} + V(R) \right\} P(R)\Phi(\vartheta, \varphi) = E_{\text{total}} P(R)\Phi(\vartheta, \varphi). \quad (2.38)$$

This equation looks like the Hamilton equation for an electron in the H atom with a general potential¹⁰ instead of the coulomb interaction. It is now possible to use the same formalism. From hydrogen we know that \vec{L}^2 can only assume $2L + 1$ discrete values $\hbar L(L + 1)$. It is therefore possible to get a differential equation only depending on R with L as an parameter. Usually, the vibrational motion is faster than the rotational motion. This means that a lot of vibrations occur during one period. A mean *moment of inertia*, depending only on the time-averaged internuclear distance¹¹, can be assumed. With the help of this approximation and the harmonic approximation, the total energy can be written as

$$E_{\text{total}} = V(\bar{R}) + \hbar\omega\left(\nu + \frac{1}{2}\right) + \frac{\hbar^2 J(J + 1)}{2\Theta(\bar{R})}. \quad (2.39)$$

Here ω is the eigenfrequency of the potential in the harmonic approximation. \bar{R} is the equilibrium internuclear distance and $\Theta(\bar{R})$ the mean moment of inertia.

⁸Often *anharmonic constants* are also given to further specify the potential.

⁹Here the Laplacian Δ is written in spherical coordinates.

¹⁰a radial potential

¹¹In the literature often the equilibrium distance is used. Strictly speaking, the time-averaged and the equilibrium internuclear distance need not be the same, but for most potentials they should not differ much.

2.2.3 Coupling to the electromagnetic field

The coupling of the electromagnetic field to a diatomic molecule can be described by the following interaction Hamiltonian:

$$H_{\text{int}} = (\vec{d} + \vec{D})\vec{E}. \quad (2.40)$$

Here \vec{d} is the *electronic dipole moment* and \vec{D} the dipole moment of the nucleus. The latter can be written as¹²

$$\vec{D} = \frac{m_1 Q_2 - m_2 Q_1}{m_1 + m_2} \vec{R} = m \left(\frac{Q_2}{m_2} - \frac{Q_1}{m_1} \right) \vec{R}. \quad (2.41)$$

So in the case of *homonuclear molecules*, the *nuclear dipole moment* is zero. The electronic dipole moment is

$$\vec{d} = \sum_n e \vec{r}_n. \quad (2.42)$$

In the Born-Oppenheimer approximation (see 2.2.2), the wave function can be written as a product of two wave functions. In addition, the nuclear wave function is the product of two wave functions $P(R)$ and $\Phi(\vartheta, \varphi)$.

$$\Psi = \psi_e(\vec{r}; R) \underbrace{P(R)\Phi(\vartheta, \varphi)}_{\chi(\vec{R})}. \quad (2.43)$$

The first wave function is the electronic wave function. The function depends on R parametrically. The second wave function only depends on the internuclear distance R . The third function is describing the angular dependence of the wave function.¹³ The probability of a transition between two different *electronic* states in the *dipole approximation* is proportional to $|\vec{M}_{\text{fi}}|^2$, where

$$\begin{aligned} \vec{M}_{\text{fi}} &= \int d^{3n}r d^3R \psi_{\text{ef}}^*(\vec{r}, R) \chi_{\text{f}}^*(\vec{R}) (\vec{d} + \vec{D}) \psi_{\text{ei}}(\vec{r}, R) \chi_{\text{i}}(\vec{R}) \\ &= \int d\Omega \int dR P_{\text{f}}^*(R) \Phi_{\text{f}}^*(\vartheta, \varphi) \overbrace{\left(\int d\vec{r} \psi_{\text{ef}}^* \vec{d} \psi_{\text{ei}} \right)}^{\vec{M}_{\text{fi}}^e(R)} \Phi_{\text{i}}(\vartheta, \varphi) P_{\text{i}}(R) \\ &\quad + \int d^3R \chi_{\text{f}}^* \underbrace{\vec{D} \chi_{\text{i}}}_{=0} \int d^3r \psi_{\text{ef}}^* \psi_{\text{ei}}. \end{aligned} \quad (2.44)$$

Because transitions between two different electronic levels are considered, the second part in (2.44) cancels due to the orthogonality of the ψ_e s.

¹² m is the reduced mass of the two nuclei.

¹³Assuming a fast vibrational motion compared with the rotational motion (see previous section).

The value of $\vec{M}_{\text{fi}}^e(R)$ is calculated in the coordinate system in which the nuclei are fixed. On the other hand the calculation in (2.44) is done in the lab frame. It is easy to express $\vec{M}_{\text{fi}}^e(R)$ in the lab frame, when the electronic dipole moment points in the direction of the internuclear axis

$$\hat{R} := \begin{pmatrix} \sin \vartheta \cos \varphi \\ \sin \vartheta \sin \varphi \\ \cos \vartheta \end{pmatrix}. \quad (2.45)$$

In this special case, $\vec{M}_{\text{fi}}^e(R)$ can be calculated easily:

$$\vec{M}_{\text{fi}}^e(R) = \hat{R} |\vec{M}_{\text{fi}}^e(R)|. \quad (2.46)$$

For the dipole matrix element this means:

$$\vec{M}_{\text{fi}} = \int d\Omega \Phi_{\text{f}}^*(\vartheta, \varphi) \hat{R} \Phi_{\text{i}}(\vartheta, \varphi) \int dR P_{\text{f}}^*(R) P_{\text{i}}(R) |\vec{M}_{\text{fi}}^e(R)|. \quad (2.47)$$

The operator \hat{R} is a vector operator. It satisfies the commutation relation

$$[L_i, R_j] = i\hbar \epsilon_{ijk} R_k. \quad (2.48)$$

The integral

$$\int d\Omega \Phi_{\text{f}}^*(\vartheta, \varphi) \hat{R} \Phi_{\text{i}}(\vartheta, \varphi)$$

is only non zero for

$$\begin{aligned} \Delta L &= \pm 1 \\ \Delta M &= 0, \pm 1. \end{aligned} \quad (2.49)$$

These are the usual selection rules. See for example [Cohen-Tannoudji et al.(1977)] for the derivation of the these rules.

If we assume furthermore that the R dependence of $M_{\text{fi}}^e(R)$ is small, it can be taken out of the integral. We obtain:

$$\begin{aligned} \vec{M}_{\text{fi}} &= |\vec{M}_{\text{fi}}^e| \int d\Omega \Phi_{\text{f}}^*(\vartheta, \varphi) \hat{R} \Phi_{\text{i}}(\vartheta, \varphi) \int dR P_{\text{f}}^*(R) P_{\text{i}}(R) \\ &= f_{\text{fi}} |\vec{M}_{\text{fi}}^e| \int d\Omega \Phi_{\text{f}}^*(\vartheta, \varphi) \hat{R} \Phi_{\text{i}}(\vartheta, \varphi). \end{aligned} \quad (2.50)$$

Here f_{fi} is the so called *Franck Condon integral* or *Franck Condon factor* .

$$f_{\text{fi}} := \int dR P_{\text{f}}^*(R) P_{\text{i}}(R). \quad (2.51)$$

In the literature often $F = |f_{fi}|^2$ is defined as the Franck Condon factor¹⁴. Nevertheless, in this thesis the Franck Condon factor is defined as above. In chapter 3 I do not consider rotational levels. Thus the calculations become easier. The above mentioned selection rule should in most times make sure that the results do not differ qualitatively from the correct calculations with rotational levels.

2.2.4 The Franck Condon principle

In equation (2.51) the Franck Condon factor was introduced. But what is the physical meaning of this factor? The best way, to understand this, is to look at a picture (Fig. 2.1).

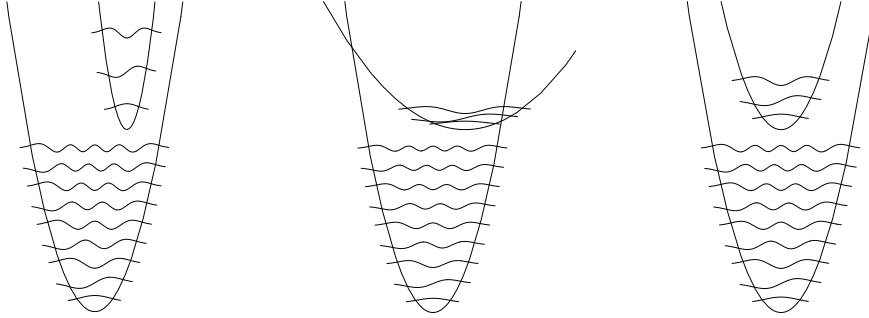


Figure 2.1: Eigenfunctions of different potentials. The overlap between upper and lower wave functions are the Franck Condon integrals. In the first two pictures all integrals including the lower ground state are quite small. The last picture shows two identical potentials. In this case the Franck Condon integrals can be expressed with the help of a unity matrix: $f_{\mu\nu} = \delta_{\mu\nu}$.

The Franck Condon factor is the inner product of two wave functions. One is the vibrational nuclear wave function $P_i(R)$ of the upper electronic state, the other belongs to the lower state. If we again adopt the classical picture, it is obvious that the "reduced particle" stays most of its time at the turning points, because there its velocity is not very high. Except for the vibrational ground state, this is also true in quantum mechanics for oscillator-like potentials. This means for example, that most likely a transition between a vibrational upper state and the vibrational ground state occurs, when the center of the ground state and one turning point of the upper state coincide. This rule is called *Franck Condon principle*.

Nevertheless, throughout this thesis the Franck Condon factors are calculated in the correct quantum mechanical way. The classical picture cannot work in the context of this thesis, since superpositions of excited vibrational wave functions are considered.

¹⁴Due to the fact that the transition probability is proportional to $|f_{fi}|^2$

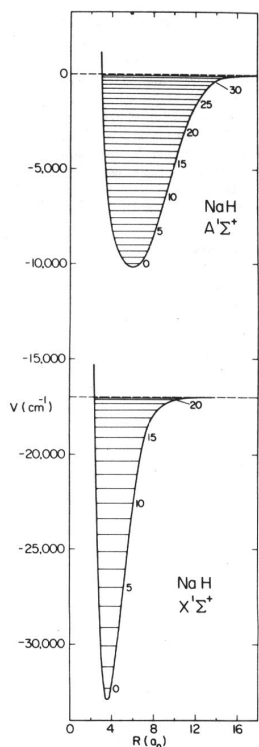


Figure 2.2: The potential energy curves of the two lowest lying electronic states of NaH . The shown vibrational levels are based on calculations. Taken from [Zemke(1984)].

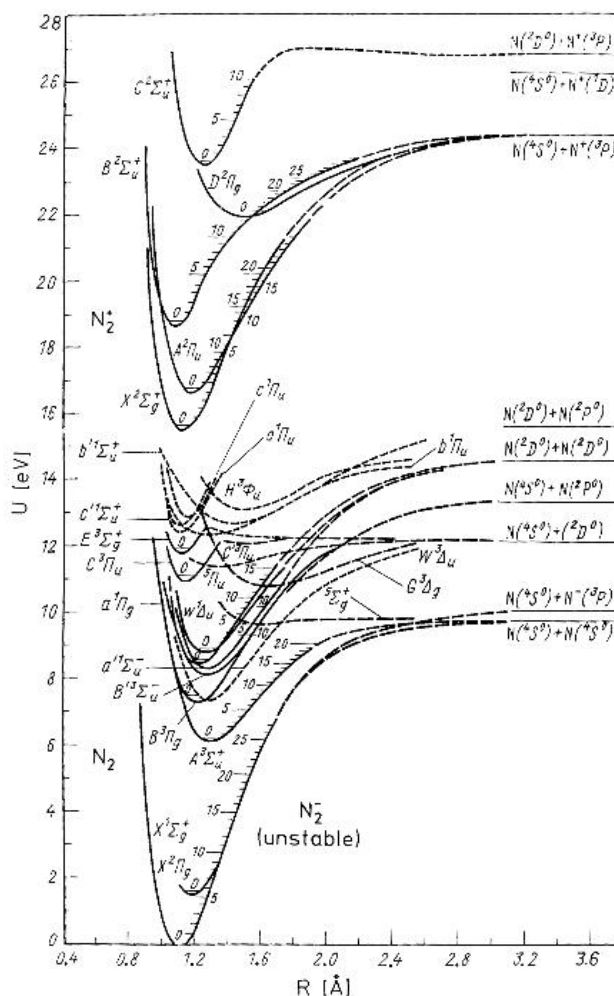


Figure 2.3: The low lying states of N_2 , N_2^+ , and N_2^- . Taken from [Radzig and Smirnov(1985)].

2.2.5 Examples, remarks, and notational conventions

Continuous states

In the real world, two different types of potentials can occur. Either the *dissociation energy* of the ground state is greater or less than the energy of the lowest excited state.(see Fig. 2.4 and Fig. 2.5) In the first case no continuous spectra is observed. A finite number of ground state levels lies below the excited states. In the second case, however, a transition to the continuum is possible. In this case the two atoms become separated. An example for such a molecule can be seen in Fig. 2.2.

Throughout my thesis only molecules with discrete emission spectra are considered. Examples can be found in Fig. 2.3(N_2), Fig. 2.7(OH), and Fig. 4.8(CN). In OH most upper vibrational levels have a non-zero transition probability to the continuum. Therefore OH is not the best choice for a superposition of several upper vibrational levels.

Some remarks on electronic levels

There are two principal approaches to derive the electronic levels of a diatomic molecule. Either the molecule is in first approximation treated as two atoms (*separated atom approach*) or the molecule is considered as one large atom (*united atom approach*). Correlation diagrams can be constructed in which the atomic orbitals of the united atom are correlated through the orbitals of the molecule with those of the separated atom (see for example [Haken and Wolf(1992)]).

To calculate the wave function of the molecule again two methods are mainly used. One is the *valence bond technique*, the other is the *molecular orbital technique* (MO). The first method starts with the atoms totally separated and brings them then to the equilibrium distance. There the nuclei and the electrons are allowed to interact. The second theory uses the so called *LCAO* - method. LCAO stands for *linear combination of atomic orbitals*. Two atomic orbitals together yield two molecular orbitals one with higher the other with lower energy.

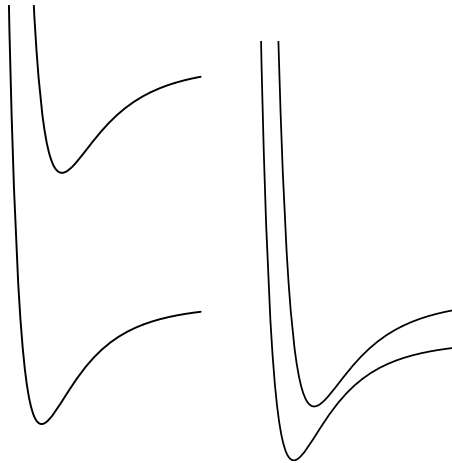


Figure 2.4:
Two adiabatic potentials. It is possible that the molecule ends up in a continuous state when it spontaneously emits a photon.

Figure 2.5:
Two adiabatic potentials. The molecule cannot dissociate by spontaneous emission.

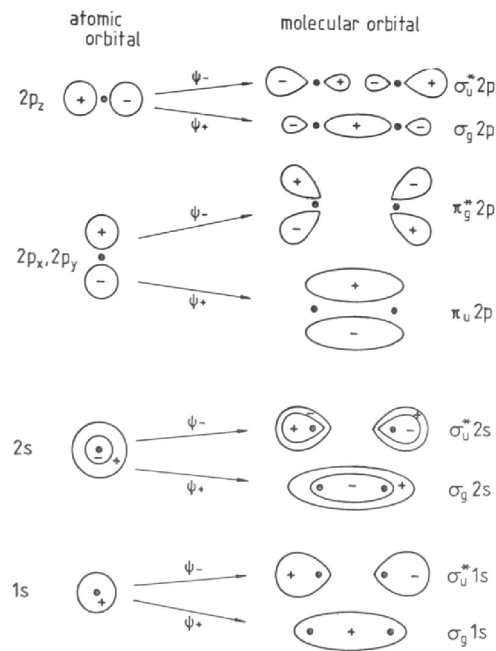


Figure 2.6: The formation of MOs from 1s, 2s, and 2p AOs. Taken from [Hollas(1998)].

The molecular orbitals with higher energy are called *antibonding states* and are labeled by an asterisk *. The antibonding states have a rather low electron density between the nuclei. The repulsion between the two positively charged nuclei is screened only weakly by the electrons (see Fig. 2.6). In *homonuclear molecules* antibonding states are often asymmetric to inversion. Namely in simplest LCAO

theory, the bonding and antibonding states can be written as¹⁵

$$\begin{aligned}\Psi_{\text{bind}} &\propto \Psi_1(\vec{r}_1) + \Psi_2(\vec{r}_2) \\ \Psi_{\text{anti}} &\propto \Psi_1(\vec{r}_1) - \Psi_2(\vec{r}_2).\end{aligned}\quad (2.52)$$

In this approximation it becomes clear that antibonding states are asymmetric and bonding states are symmetric to inversion. In homonuclear molecules symmetric states are labeled by g and asymmetric states by u . In hetero-nuclear molecules these labels cannot be used. To further specify the symmetry, the superscript $+$ is added if the state is symmetric under reflection at a plane through the two nuclei. The symbol $-$ stands for the corresponding antisymmetric state.

As mentioned before, the molecule resembles an atom placed in a strong electric field (Stark effect).¹⁶ Unless the spin orbit coupling is large, as would be the case if at least one of the nuclei had a high charge, the electrostatic field uncouples the \vec{l} and \vec{s} vectors of the electrons. \vec{l} and \vec{s} precess independently around the internuclear axis. Therefore \vec{l} is not a good quantum number anymore. But the component of the angular momentum along the internuclear axis is an eigenvalue. It is defined in the following form:

$$\lambda = |m_l| = 0, 1, 2, \dots, l \quad (2.53)$$

Therefore, all MOs with $\lambda > 0$ are doubly degenerate. Small Greek letters denote the angular momentum of an orbital: σ , π , δ , correspond to $\lambda = 0, 1, 2$, for example.

These molecular orbitals are filled with electrons as in the case of atoms. In filled orbitals, the angular momenta of the electrons add up to zero. The angular momenta and spins of the remaining electrons are in general nonzero and interact with each other. If \vec{l} and \vec{s} are weakly coupled, a good approximation is the following: All

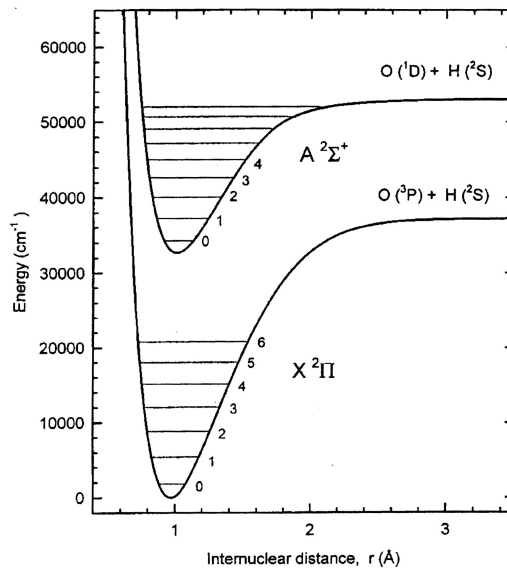


Figure 2.7: Adiabatic potentials of the electronic ground state and the first excited state of OH . Taken from [Luque and Crosley(1998)].

¹⁵ Ψ_1 and Ψ_2 represent the atom wave functions. This approach can be found in many textbooks, for example in [Hollas(1998)].

¹⁶In the frame in which the nuclei rest. The electronic dipole matrix element $\vec{M}_{fi}^e(R)$ is calculated in this frame (see 2.2.3).

angular momenta are coupled to give a resultant \vec{L}_e and all spins couple to \vec{S} . The state itself is described by capital Greek letters $\Sigma, \Pi, \Delta, \dots$, representing $\Lambda := \sum \lambda = 0, 1, 2, \dots$. The number $\Omega := |\Lambda + \tilde{\Sigma}|$ is the quantum number of the total electronic angular momentum.¹⁷

These quantum numbers in the MO framework are used like the corresponding quantum numbers in atoms to describe the electronic state of a molecule. The notation is the following:¹⁸

$${}^{2S+1}\Lambda_{\tilde{\Sigma}+\Lambda}. \quad (2.54)$$

For example, the term symbol ${}^4\Pi_{-\frac{1}{2}}$ stands for $\Lambda = 1$, $S = 3/2$, and $\tilde{\Sigma} = -3/2$.

Another notational convention is often used for low lying electronic states:

The electronic ground state is labeled X and higher states of the same multiplicity are called A, B, C, ... in order of increasing energy. States of different multiplicity are called a, b, c, ... (see [Hollas(1998)] page 312).

¹⁷Here $\tilde{\Sigma} = S, S-1, \dots, -S$ is used as the quantum number of S in the unfilled orbital. In the literature this quantity is often labeled Σ .

¹⁸For example see [Hollas(1998)] page 311.

Chapter 3

The model

In this chapter spontaneous emission in a molecule is discussed. My model expects the molecule to be in its two lowest electronic states and includes the vibrational levels for both states. For reasonable temperatures the assumption that only the vibrational levels of the two lowest electronic states are populated is justified quite well.¹ In section 3.1 the master equation in vacuum is derived. In the derivation it is first assumed that all vibrational states of the ground state of the molecule lie energetically below the vibrational states of the excited state. Then in section 3.2 this constraint is removed. In later sections the master equation in the Born-Oppenheimer approximation is introduced. In the last two parts of this chapter it is discussed whether a superposition of upper states can enhance the spontaneous emission rate at the time $t = 0$. Finally, the time evolution of the population of this special vibrational level of the ground state is discussed.

3.1 Master equation of a system with two distinct sets of eigenstates

The derivation of the *master equation* starts with the Hamiltonian in the *rotating wave approximation*. The correct way would be to apply the rotating wave approximation to the master equation. The application of the rotating wave approximation on the Hamiltonian results in a small frequency shift which is negligible in our case, since we are mainly interested in the decay of the system. Further details concerning this frequency shift are discussed in [Agarwal(1975)].

In the Schrödinger picture the time evolution of the reduced density operator σ_M of the molecule is given by the master equation (2.24).² Equation (2.24) describes the interaction of a system with the vacuum. (For the derivation see 2.1). In this case

¹In the thermodynamic equilibrium $E_{eg} \approx k_B T$ holds. Therefore for $T < 10^3$ K very few molecules are in higher states. E_{eg} is the energy separation of the electronic ground state and the first electronic state.

²Here σ_M is still an operator acting on the radiation field. For this reason σ in $\sigma_M =: |0_R\rangle\langle 0_R|\sigma$ is used from now on. σ only acts on the molecule. (See also 2.1.)

the system is a molecule with vibrational levels for the electronic ground state e and the first excited state g :

$$\dot{\sigma}(t) = -i\mathcal{L}_{\text{mol}}\sigma(t) - \frac{1}{\hbar^2}\text{Tr}_{\text{R}}\left([V, \int_0^t d\tau e^{-i\tau\mathcal{L}_0}[V', |0_{\text{R}}\rangle\langle 0_{\text{R}}|\sigma(t-\tau)]]\right) \quad (3.1)$$

with³

$$\mathcal{L}_{\text{mol}} := \frac{1}{\hbar}[H_{\text{mol}}, \dots] := \left[\sum_{\mu} \mu|\mu\rangle\langle\mu| + \sum_{\nu} \nu|\nu\rangle\langle\nu|, \dots\right] \quad (3.2)$$

$$\mathcal{L}_0 := \mathcal{L}_{\text{mol}} + \sum_{\vec{k}, s} \omega_{\vec{k}} a_{\vec{k}s}^{\dagger} a_{\vec{k}s}, \dots \quad (3.3)$$

$$V := V_0 \sum_{\vec{k}, s} \sum_{\mu} \sum_{\nu} \sqrt{\omega_{\vec{k}}} a_{\vec{k}s} a_{\vec{k}s}^{\dagger} \vec{\epsilon}_{\vec{k}s} \vec{d}_{\mu\nu} |\mu\rangle\langle\nu| + \text{H.C.} \quad (3.4)$$

$$V' := V_0 \sum_{\vec{k}_1, s_1} \sum_{\mu_1} \sum_{\nu_1} \sqrt{\omega_{\vec{k}_1}} a_{\vec{k}_1 s_1} a_{\vec{k}_1 s_1}^{\dagger} \vec{\epsilon}_{\vec{k}_1 s_1} \vec{d}_{\mu_1 \nu_1} |\mu_1\rangle\langle\nu_1| + \text{H.C.} \quad (3.5)$$

$$V_0 := \sqrt{\frac{\hbar}{2\epsilon_0 V}}. \quad (3.6)$$

Here $|\mu\rangle$ is a vibrational state in the excited electronic level e and $|\nu\rangle$ is a vibrational state in the electronic ground state g . Both include the electronic wavefunction as well. This definition of $|\mu\rangle$ and $|\nu\rangle$ is used throughout this thesis. μ and ν stand for the frequencies of the associated vibrational excitations. Often μ and ν are also used as indices.⁴ $\vec{d}_{\mu\nu}$ is the dipole matrix element between level μ and level ν . The subscript R stands for radiation.⁵

It is necessary to attach more importance to the rotating wave approximation than it is usually done. As can be seen in Fig. 3.1, it is possible that the energy of $|\nu\rangle$ states is greater than the energy of $|\mu\rangle$ states. The rotating wave approximation on the other hand states that a photon is created when the molecule loses energy and a photon is destroyed when the molecule gains energy. The fact that the states are still arbitrary forbids therefore to assume that a $\mu \rightarrow \nu$ transition is associated with the creation of a photon. If $\mu < \nu$, a photon is destroyed instead. The same problem arises of course the other way around. All the same, the rotating wave approximation can be written in a nice way. The trick is simply to distinguish the two cases $\mu > \nu$ and $\mu < \nu$. The above expression (equation (3.4) and (3.5)) for the interaction potential V assumed implicitly $\mu > \nu$. Since μ and ν are still arbitrary, it is possible to simply exchange μ and ν in V . The resulting interaction potential, let us call it $V_{\mu \leftrightarrow \nu}$, then includes the condition $\mu < \nu$. A simple way of writing the true interaction Hamiltonian in the rotating wave approximation for arbitrary μ and ν is therefore:

³H.C. stands for "hermitian conjugated".

⁴For example, instead of writing $\sigma_{n_{\mu} n_{\mu_1}}$, the short hand notation $\sigma_{\mu\mu_1}$ is used.

⁵Later, quantities like $R_{\mu\nu}^{\mu_1\nu_1}$ and $r_{\mu\nu}^{\mu_1\nu_1}$ are introduced. These quantities have nothing to do with the index R .

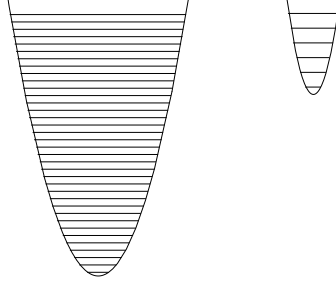


Figure 3.1: Example: The potentials for the electronic ground state and the first excited state. On left are the eigenvalues of the $|\nu\rangle$ states and on the right are the eigenvalues of the $|\mu\rangle$ states shown. It is obvious that in general not always $\mu > \nu$. In this example the Franck Condon factors are all very close to zero.

$$V_{\text{arbitrary}} = \Theta(\mu - \nu)V + \Theta(\nu - \mu)V_{\mu \leftrightarrow \nu}. \quad (3.7)$$

Instead of V and V' the interaction Hamiltonians $V_{\text{arbitrary}}$ and $V'_{\text{arbitrary}}$ must be used in (3.1), if the constraint $\mu > \nu$ does *not* apply.

Nevertheless, it is a good thing to associate the creation of a photon with the transition $\mu \rightarrow \nu$. The arbitrary choice of $\mu > \nu$ or $\mu < \nu$ is simply confusing. Therefore from now on it is assumed that

$$\text{Assumption for the time being: } \mu > \nu. \quad (3.8)$$

Since (3.1) is linear in V and V' the resulting master equation can be easily generalized later. This is also the reason why V' contains primed variables.⁶ Of course, simply renaming the variables does not change the interaction Hamiltonian in any way, but in this way it is easy to use the linearity of the Hamiltonian later.

But now the master equation for the case $\mu > \nu$ is derived. Recalling the form of (3.1)

$$\dot{\sigma}(t) = -i\mathcal{L}_{\text{mol}}\sigma(t) - \frac{1}{\hbar^2}\text{Tr}_{\text{R}}\left([V, \int_0^t d\tau e^{-i\tau\mathcal{L}_0}[V', |0_{\text{R}}\rangle\langle 0_{\text{R}}|\sigma(t-\tau)]]\right),$$

it must be stressed, that $e^{-i\tau\mathcal{L}_0}$ is applied to the commutator on the right and not only to V' , namely,

$$\begin{aligned} \dot{\sigma}(t) = & -i\mathcal{L}_{\text{mol}}\sigma(t) - \frac{1}{\hbar^2}\text{Tr}_{\text{R}}\left(\left[\sum_{\vec{k}} \sum_s \sum_{\mu} \sum_{\nu} \omega_k \vec{\epsilon}_{\vec{k}s} a_{\vec{k}s} \vec{d}_{\mu\nu} |\mu\rangle\langle \nu| + \text{H.C.}, \int_0^t d\tau (e^{-i\tau\frac{H_0}{\hbar}} \right. \right. \\ & \left. \left. [\sum_{\vec{k}_1} \sum_{s_1} \sum_{\mu_1} \sum_{\nu_1} \epsilon_{\vec{k}_1 s_1} a_{k_1 s_1} \vec{d}_{\mu_1 \nu_1} |\mu_1\rangle\langle \nu_1| + \text{H.C.}, |0_{\text{R}}\rangle\langle 0_{\text{R}}|\sigma(t-\tau)] e^{i\tau\frac{H_0}{\hbar}} \right]\right). \end{aligned} \quad (3.9)$$

⁶This will become apparent in section 3.2.

The trace Tr_R of the radiation field in the Fock basis is:

$$\text{Tr}_R A := \sum_{n, \vec{k}, s} \langle n, \vec{k}, s | A | n, \vec{k}, s \rangle. \quad (3.10)$$

If there are not as many creation operators $a_{\vec{k}s}^\dagger$ as there are annihilation operators $a_{\vec{k}s}$ in A , the trace is zero. All terms with $\vec{k} \neq \vec{k}_1$ or $s \neq s_1$ become therefore zero.⁷ The fourfold sum over \vec{k} , \vec{k}_1 , s , and s_1 can be simplified to a sum over only \vec{k} and s .

This twofold sum can be simplified even further. With the help of $a|0\rangle = 0$ and $\langle \mu | \nu_1 \rangle = \langle \mu_1 | \nu \rangle = 0$ ⁸ the equation can be simplified to the following form:

$$\begin{aligned} \dot{\sigma}(t) = & -i\mathcal{L}_{\text{mol}}\sigma(t) - \frac{V_0^2}{\hbar^2} \text{Tr}_R \left\{ \sum_{\mu, \nu, \mu_1, \nu_1} \left(\right. \right. \\ & + \sum_{\vec{k}s} (\omega_k \vec{\epsilon}_{\vec{k}s}^* a_{\vec{k}s}^\dagger \vec{d}_{\mu\nu} | \mu \rangle \langle \nu | \int_0^t d\tau (e^{-i\tau \frac{H_0}{\hbar}} \vec{\epsilon}_{\vec{k}s}^* a_{\vec{k}s}^\dagger \vec{d}_{\mu_1 \nu_1}^* | \nu_1 \rangle \langle \mu_1 | |0_R\rangle \langle 0_R| \sigma(t-\tau) e^{i\tau \frac{H_0}{\hbar}})) \\ & - \sum_{\vec{k}s} (\omega_k \vec{\epsilon}_{\vec{k}s}^* a_{\vec{k}s}^\dagger \vec{d}_{\mu\nu}^* | \nu \rangle \langle \mu | \int_0^t d\tau (e^{-i\tau \frac{H_0}{\hbar}} |0_R\rangle \langle 0_R| \sigma(t-\tau) \vec{\epsilon}_{\vec{k}s} a_{\vec{k}s} \vec{d}_{\mu_1 \nu_1} | \mu_1 \rangle \langle \nu_1 | e^{i\tau \frac{H_0}{\hbar}})) \\ & - \left(\int_0^t d\tau \sum_{\vec{k}s} \omega_k (e^{-i\tau \frac{H_0}{\hbar}} \vec{\epsilon}_{\vec{k}s}^* a_{\vec{k}s}^\dagger \vec{d}_{\mu_1 \nu_1}^* | \nu_1 \rangle \langle \mu_1 | |0_R\rangle \langle 0_R| \sigma(t-\tau) e^{i\tau \frac{H_0}{\hbar}}) \vec{\epsilon}_{\vec{k}s} a_{\vec{k}s} \vec{d}_{\mu\nu} | \mu \rangle \langle \nu | \right) \\ & \left. \left. + \left(\int_0^t d\tau \sum_{\vec{k}s} \omega_k (e^{-i\tau \frac{H_0}{\hbar}} |0_R\rangle \langle 0_R| \sigma(t-\tau) \vec{\epsilon}_{\vec{k}s} a_{\vec{k}s} \vec{d}_{\mu_1 \nu_1} | \mu_1 \rangle \langle \nu_1 | e^{i\tau \frac{H_0}{\hbar}}) \vec{\epsilon}_{\vec{k}s}^* a_{\vec{k}s}^\dagger \vec{d}_{\mu\nu}^* | \nu \rangle \langle \mu | \right) \right) \right\}. \end{aligned} \quad (3.11)$$

Let us calculate the trace now. The projector $|0_R\rangle \langle 0_R|$ simplifies the trace considerably. Because never two $a_{\vec{k}s}^\dagger$ or $a_{\vec{k}s}$ appear⁹, all parts of the trace including $n = 2$ or more photons is zero. A closer look reveals that for the first and the last addend only $\langle 0, \vec{k}, s | \dots | 0, \vec{k}, s \rangle_R$ remains. For the second and the third addend $\langle 1, \vec{k}, s | \dots | 1, \vec{k}, s \rangle_R$ is the only part of the trace that does not cancel. This results in:

⁷If for example A includes $a_{\vec{k}s}$ and $a_{\vec{k}_1 s_1}^\dagger$ and $k \neq k_1$ or $s \neq s_1$, then different modes are destroyed and created. The resulting Fock states are orthogonal.

⁸Remember: $|\mu\rangle$ and $|\nu\rangle$ include the electronic parts of the wave functions!

⁹which means that never two photons of the same kind are destroyed or created.

$$\begin{aligned}
\dot{\sigma}(t) = & -i\mathcal{L}_{\text{mol}}\sigma(t) - \frac{V_0^2}{\hbar^2} \left\{ \sum_{\mu,\nu,\mu_1,\nu_1} \left(\right. \right. \\
& + \sum_{\vec{k}_s} (\omega_k \vec{\epsilon}_{\vec{k}_s}^* \vec{d}_{\mu\nu} |\mu\rangle \langle \nu| \int_0^t d\tau (e^{-i\tau(\frac{1}{\hbar}H_{\text{mol}}+\omega_k)} \vec{\epsilon}_{\vec{k}_s}^* \vec{d}_{\mu_1\nu_1}^* |\nu_1\rangle \langle \mu_1| \sigma(t-\tau) e^{i\tau\frac{1}{\hbar}H_{\text{mol}}})) \\
& - \sum_{\vec{k}_s} (\omega_k \vec{\epsilon}_{\vec{k}_s}^* \vec{d}_{\mu\nu}^* |\nu\rangle \langle \mu| \int_0^t d\tau (e^{-i\tau\frac{1}{\hbar}H_{\text{mol}}} \sigma(t-\tau) \vec{\epsilon}_{\vec{k}_s} \vec{d}_{\mu_1\nu_1} |\mu_1\rangle \langle \nu_1| e^{i\tau(\frac{1}{\hbar}H_{\text{mol}}+\omega_k)})) \\
& - \left(\int_0^t d\tau \sum_{\vec{k}_s} \omega_k (e^{-i\tau(\frac{1}{\hbar}H_{\text{mol}}+\omega_k)} \vec{\epsilon}_{\vec{k}_s}^* \vec{d}_{\mu_1\nu_1}^* |\nu_1\rangle \langle \mu_1| \sigma(t-\tau) e^{i\tau\frac{1}{\hbar}H_{\text{mol}}} \vec{\epsilon}_{\vec{k}_s} \vec{d}_{\mu\nu} |\mu\rangle \langle \nu|) \right. \\
& \left. \left. + \left(\int_0^t d\tau \sum_{\vec{k}_s} \omega_k (e^{-i\tau\frac{1}{\hbar}H_{\text{mol}}} \sigma(t-\tau) \vec{\epsilon}_{\vec{k}_s} \vec{d}_{\mu_1\nu_1} |\mu_1\rangle \langle \nu_1| e^{i\tau(\frac{1}{\hbar}H_{\text{mol}}+\omega_k)} \vec{\epsilon}_{\vec{k}_s}^* \vec{d}_{\mu\nu}^* |\nu\rangle \langle \mu|) \right) \right) \right\}. \tag{3.12}
\end{aligned}$$

Now it is time to use the *Markov approximation* to simplify the result. In the Markov approximation the time evolution of σ is dominated by H_{mol} .

$$\sigma(t-\tau) \approx e^{i\tau\frac{H_{\text{mol}}}{\hbar}} \sigma(t) e^{-i\tau\frac{H_{\text{mol}}}{\hbar}}. \tag{3.13}$$

In addition the Markov approximation includes that the upper limit in the time integral goes to infinity. This yields

$$\begin{aligned}
\dot{\sigma}(t) = & -i\mathcal{L}_{\text{mol}}\sigma(t) - \frac{V_0^2}{\hbar^2} \left\{ \sum_{\mu,\nu,\mu_1,\nu_1} \left(\right. \right. \\
& + \sum_{\vec{k}_s} (\omega_k \vec{\epsilon}_{\vec{k}_s}^* \vec{d}_{\mu\nu} |\mu\rangle \langle \nu| \int_0^t d\tau (e^{-i\tau(\nu+\omega_k)} \vec{\epsilon}_{\vec{k}_s}^* \vec{d}_{\mu_1\nu_1}^* |\nu_1\rangle \langle \mu_1| e^{i\tau\mu_1} \sigma(t-\tau)) \\
& - \sum_{\vec{k}_s} (\omega_k \vec{\epsilon}_{\vec{k}_s}^* \vec{d}_{\mu\nu}^* |\nu\rangle \langle \mu| \int_0^t d\tau (\sigma(t-\tau) e^{-i\tau\mu_1} \vec{\epsilon}_{\vec{k}_s} \vec{d}_{\mu_1\nu_1} |\mu_1\rangle \langle \nu_1| e^{i\tau(\nu_1+\omega_k)})) \\
& - \left(\int_0^t d\tau \sum_{\vec{k}_s} \omega_k (e^{-i\tau(\nu_1+\omega_k)} \vec{\epsilon}_{\vec{k}_s}^* \vec{d}_{\mu_1\nu_1}^* |\nu_1\rangle \langle \mu_1| e^{i\tau\mu_1} \sigma(t-\tau) \vec{\epsilon}_{\vec{k}_s} \vec{d}_{\mu\nu} |\mu\rangle \langle \nu|) \right. \\
& \left. \left. + \left(\int_0^t d\tau \sum_{\vec{k}_s} \omega_k (\sigma(t-\tau) e^{-i\tau\mu_1} \vec{\epsilon}_{\vec{k}_s} \vec{d}_{\mu_1\nu_1} |\mu_1\rangle \langle \nu_1| e^{i\tau(\nu+\omega_k)} \vec{\epsilon}_{\vec{k}_s}^* \vec{d}_{\mu\nu}^* |\nu\rangle \langle \mu|) \right) \right) \right\}. \tag{3.14}
\end{aligned}$$

To further simplify the equation, the orthogonality of the wave functions can be used.¹⁰

¹⁰like $\langle \nu_1 | \nu \rangle = \delta_{\nu_1\nu}$

$$\begin{aligned}
\dot{\sigma}(t) = & -i\mathcal{L}_{\text{mol}}\sigma(t) - \frac{V_0^2}{\hbar^2} \sum_{\mu, \mu_1, \nu} \left(\sum_{\vec{k}, s} \int_0^t d\tau \omega_k \vec{\epsilon}_{\vec{k}s} \vec{d}_{\mu\nu} \vec{\epsilon}_{\vec{k}s}^* \vec{d}_{\mu_1\nu}^* e^{-i\tau(\omega_k - (\mu_1 - \nu))} \right) |\mu\rangle \langle \mu_1| \sigma(t) \\
& + \sum_{\mu, \mu_1, \nu, \nu_1} \left(\sum_{\vec{k}, s} \int_0^t d\tau \omega_k \vec{\epsilon}_{\vec{k}s}^* \vec{d}_{\mu\nu}^* \vec{\epsilon}_{\vec{k}s} \vec{d}_{\mu_1\nu_1} e^{i\tau(\omega_k - (\mu_1 - \nu_1))} \right) |\nu\rangle \langle \mu| \sigma(t) |\mu_1\rangle \langle \nu_1| \\
& + \sum_{\mu, \mu_1, \nu, \nu_1} \left(\int_0^t d\tau \sum_{\vec{k}, s} \omega_k \vec{\epsilon}_{\vec{k}s}^* \vec{d}_{\mu_1\nu_1}^* \vec{\epsilon}_{\vec{k}s} \vec{d}_{\mu\nu} e^{-i\tau(\omega_k - (\mu_1 - \nu_1))} \right) |\nu_1\rangle \langle \mu_1| \sigma(t) |\mu\rangle \langle \nu| \\
& - \sum_{\mu, \mu_1, \nu} \left(\int_0^t d\tau \sum_{\vec{k}, s} \omega_k \vec{\epsilon}_{\vec{k}s} \vec{d}_{\mu_1\nu} \vec{\epsilon}_{\vec{k}s}^* \vec{d}_{\mu\nu}^* e^{i\tau(\omega_k - (\mu_1 - \nu))} \right) \sigma(t) |\mu_1\rangle \langle \mu|. \tag{3.15}
\end{aligned}$$

Now it is time to sum over s . For two general operators the following equation holds:

$$\sum_s (\vec{A}\vec{\epsilon}_s)(\vec{B}\vec{\epsilon}_s^*) = A_i B_j (\delta_{ij} - \frac{k_i k_j}{k^2}). \tag{3.16}$$

This is true, because¹¹

$$\vec{\epsilon}_1 \circ \vec{\epsilon}_1^* + \vec{\epsilon}_2 \circ \vec{\epsilon}_2^* + \hat{k} \circ \hat{k} = 1 \tag{3.17}$$

and

$$(\vec{A}\vec{\epsilon}_s)(\vec{B}\vec{\epsilon}_s^*) = (\vec{A}\vec{\epsilon}_s)(\vec{\epsilon}_s^* \vec{B}) = \vec{A}^\Gamma (\vec{\epsilon}_s \circ \vec{\epsilon}_s^*) \vec{B}. \tag{3.18}$$

The sum over \vec{k} can be rewritten as:

$$\sum_{\vec{k}} = \int d\Omega \sum_k. \tag{3.19}$$

The integral in (3.19) can also be integrated.

$$\int d\Omega (\delta_{ij} - \frac{k_i k_j}{k^2}) = \frac{8\pi}{3} \delta_{ij}. \tag{3.20}$$

This can be verified by simply inserting the components of

$$\vec{k} = \begin{pmatrix} \sin \vartheta \cos \varphi \\ \sin \vartheta \sin \varphi \\ \cos \vartheta \end{pmatrix} \tag{3.21}$$

into the above quotient $(k_i k_j)/k^2$ and integrating the left hand side of equation (3.20).

¹¹Here \circ stands for the outer product.

Altogether this yields:

$$\sum_{\vec{k}} \sum_s (\vec{A}\vec{\epsilon}_s)(\vec{B}\vec{\epsilon}_s^*) = \frac{8\pi}{3} \sum_k A_i B_j \delta_{ij}. \quad (3.22)$$

From now on k is not a vector anymore, but a real number. Using this equation to simplify (3.15) results in

$$\begin{aligned} \dot{\sigma}(t) = & -i\mathcal{L}_{\text{mol}}\sigma(t) - \frac{8\pi V_0^2}{3\hbar^2} \sum_{\mu, \mu_1, \nu} \left(\sum_k \int_0^t d\tau \omega_k \vec{d}_{\mu\nu} \vec{d}_{\mu_1\nu}^* e^{-i\tau(\omega_k - (\mu_1 - \nu))} \right) |\mu\rangle \langle \mu_1 | \sigma(t) \\ & + \sum_{\mu, \mu_1, \nu, \nu_1} \left(\sum_k \int_0^t d\tau \omega_k \vec{d}_{\mu\nu}^* \vec{d}_{\mu_1\nu_1} e^{i\tau(\omega_k - (\mu_1 - \nu_1))} \right) |\nu\rangle \langle \mu | \sigma(t) |\mu_1\rangle \langle \nu_1 | \\ & + \sum_{\mu, \mu_1, \nu, \nu_1} \left(\int_0^t d\tau \sum_k \omega_k \vec{d}_{\mu_1\nu_1}^* \vec{d}_{\mu\nu} e^{-i\tau(\omega_k - (\mu_1 - \nu_1))} \right) |\nu_1\rangle \langle \mu_1 | \sigma(t) |\mu\rangle \langle \nu | \\ & - \sum_{\mu, \mu_1, \nu} \left(\int_0^t d\tau \sum_k \omega_k \vec{d}_{\mu_1\nu} \vec{d}_{\mu\nu}^* e^{i\tau(\omega_k - (\mu_1 - \nu))} \right) \sigma(t) |\mu_1\rangle \langle \mu|. \end{aligned} \quad (3.23)$$

At this point it becomes clear that for orthogonal dipole moments the above equation decouples. In the case of orthogonal dipole moments only terms with $\mu = \mu_1$ and $\nu = \nu_1$ would remain. The equation would be totally uncoupled and all modes would just decay exponentially. Luckily, in our model the electronic dipole moments are *all* parallel. Using the definition of $R_{\mu\nu}^{\mu_1\nu_1}$ below, the following master equation is obtained:

$$\begin{aligned} \dot{\sigma}(t) = & -\frac{i}{\hbar} [H_0, \sigma] - \sum_{\mu, \mu_1, \nu} R_{\mu\nu}^{\mu_1\nu*} |\mu\rangle \langle \mu_1 | \sigma(t) + \sum_{\mu, \mu_1, \nu, \nu_1} R_{\mu\nu}^{\mu_1\nu_1} |\nu\rangle \langle \mu | \sigma(t) |\mu_1\rangle \langle \nu_1 | \\ & + \sum_{\mu, \mu_1, \nu, \nu_1} R_{\mu\nu}^{\mu_1\nu_1*} |\nu_1\rangle \langle \mu_1 | \sigma(t) |\mu\rangle \langle \nu | - \sum_{\mu, \mu_1, \nu} R_{\mu\nu}^{\mu_1\nu} \sigma(t) |\mu_1\rangle \langle \mu|. \end{aligned} \quad (3.24)$$

Here $R_{\mu\nu}^{\mu_1\nu_1}$ is defined by (assuming that the order of the k - and the time integral can be changed)

$$R_{\mu\nu}^{\mu_1\nu_1} := \Theta(\mu - \nu) \Theta(\mu_1 - \nu_1) \frac{8\pi V_0^2}{3\hbar^2} \int_0^\infty d\tau \sum_k \omega_k \vec{d}_{\mu\nu}^* \vec{d}_{\mu_1\nu_1} e^{i\tau(\omega_k - (\mu_1 - \nu_1))}. \quad (3.25)$$

The *Heaviside function* Θ is used to stress that in the derivation the constraint $\mu > \nu$ was used for all levels. In this way the definition of $R_{\mu\nu}^{\mu_1\nu_1}$ can than later also be used for the general case.

In the case of vacuum modes the sum over k can be calculated:

$$\sum_k \longrightarrow \frac{V}{(2\pi c)^3} \int_0^\infty d\omega \omega^2. \quad (3.26)$$

and therefore

$$R_{\mu\nu}^{\mu_1\nu_1} = \Theta(\mu - \nu)\Theta(\mu_1 - \nu_1)\frac{1}{6\pi^2\hbar\epsilon_0c^3}\int_0^\infty d\tau\int_0^\infty d\omega\omega^3\vec{d}_{\mu\nu}^*\vec{d}_{\mu_1\nu_1}e^{i\tau(\omega-(\mu_1-\nu_1))}. \quad (3.27)$$

To evaluate the ω -integral it is necessary to go to a new variable:

$$\omega' = \omega - (\mu_1 - \nu_1). \quad (3.28)$$

$$R_{\mu\nu}^{\mu_1\nu_1} = \Theta(\mu - \nu)\Theta(\mu_1 - \nu_1)\frac{1}{6\pi^2\hbar\epsilon_0c^3}\vec{d}_{\mu\nu}^*\vec{d}_{\mu_1\nu_1}\int_{-(\mu_1-\nu_1)}^\infty d\omega'\omega'^3\underbrace{\int_0^\infty d\tau e^{i\tau\omega'}}_{\int_0^\infty d\tau e^{i\tau\omega'} = \pi\delta(\omega') + i\frac{P}{\omega'}}. \quad (3.29)$$

The imaginary term with the principal value P of the above integral can be included into the energy of the molecule.

$$R_{\mu\nu}^{\mu_1\nu_1} = \Theta(\mu - \nu)\Theta(\mu_1 - \nu_1)\frac{1}{6\pi^2\hbar\epsilon_0c^3}\vec{d}_{\mu\nu}^*\vec{d}_{\mu_1\nu_1}\Theta(\mu_1 - \nu_1)(\mu_1 - \nu_1)^3. \quad (3.30)$$

The Heaviside function $\Theta(\mu_1 - \nu_1)$ that comes from the δ function does not yield any more information.

The final result is:

$$\begin{aligned} \dot{\sigma}(t) &= -\frac{i}{\hbar}[H_0, \sigma] - \sum_{\mu, \mu_1, \nu} R_{\mu\nu}^{\mu_1\nu*}|\mu\rangle\langle\mu_1|\sigma(t) + \sum_{\mu, \mu_1, \nu, \nu_1} R_{\mu\nu}^{\mu_1\nu_1}|\nu\rangle\langle\mu|\sigma(t)|\mu_1\rangle\langle\nu_1| \\ &+ \sum_{\mu, \mu_1, \nu, \nu_1} R_{\mu\nu}^{\mu_1\nu_1*}|\nu_1\rangle\langle\mu_1|\sigma(t)|\mu\rangle\langle\nu| - \sum_{\mu, \mu_1, \nu} R_{\mu\nu}^{\mu_1\nu}\sigma(t)|\mu_1\rangle\langle\mu| \end{aligned} \quad (3.31)$$

$$R_{\mu\nu}^{\mu_1\nu_1} := \Theta(\mu - \nu)\Theta(\mu_1 - \nu_1)\frac{(\mu_1 - \nu_1)^3}{6\pi^2\hbar\epsilon_0c^3}\vec{d}_{\mu\nu}^*\vec{d}_{\mu_1\nu_1} \quad (3.32)$$

This is the master equation for a system with eigenstates $|\mu\rangle$ and $|\nu\rangle$ with $\mu > \nu$. For arbitrary energy levels μ, ν it also describes correctly the spontaneous emission rate in a system at time $t = 0$ with the molecule initially being in a superposition of μ levels. This is true because no transitions $\nu \rightarrow \mu$ are possible, when the ν levels are not populated.

3.2 The master equation without constraint $\mu > \nu$

As discussed at the beginning of section 3.1, it is possible to generalize the hitherto result to the case $\mu < \nu$ OR $\mu > \nu$.¹² To obtain the *general master equation*, V and V' must be replaced by

¹²OR being the logic OR.

$$\begin{aligned}
V_{\text{arbitrary}} &= \Theta(\mu - \nu)V + \Theta(\nu - \mu)V_{\mu \leftrightarrow \nu} \\
V'_{\text{arbitrary}} &= \Theta(\mu_1 - \nu_1)V' + \Theta(\nu_1 - \mu_1)V'_{\mu_1 \leftrightarrow \nu_1}.
\end{aligned} \tag{3.33}$$

The definition of (3.32) can be used:

$$R_{\mu\nu}^{\mu_1\nu_1} := \Theta(\mu - \nu)\Theta(\mu_1 - \nu_1)\frac{(\mu_1 - \nu_1)^3}{6\pi^2\hbar\epsilon_0c^3}\vec{d}_{\mu\nu}^*\vec{d}_{\mu_1\nu_1}.$$

It is important to understand that, if the constraint $\mu > \nu$ is dropped, for example $R_{\nu\mu}^{\nu_1\mu_1}$ is not necessarily zero, because $R_{\nu\mu}^{\nu_1\mu_1}$ is¹³

$$R_{\nu\mu}^{\nu_1\mu_1} = \Theta(\nu - \mu)\Theta(\nu_1 - \mu_1)\frac{(\nu_1 - \mu_1)^3}{6\pi^2\hbar\epsilon_0c^3}\vec{d}_{\nu\mu}^*\vec{d}_{\nu_1\mu_1}. \tag{3.34}$$

The Heaviside functions $\Theta(\nu - \mu)$ or $\Theta(\nu_1 - \mu_1)$ are not necessarily zero in this case.

Equation (3.31) becomes¹⁴

$$\begin{aligned}
\dot{\sigma}(t) &= -\frac{i}{\hbar}[H_0, \sigma] - \sum_{\mu, \mu_1, \nu} R_{\mu\nu}^{\mu_1\nu*} |\mu\rangle\langle\mu_1| \sigma(t) + \sum_{\mu, \mu_1, \nu, \nu_1} R_{\mu\nu}^{\mu_1\nu_1} |\nu\rangle\langle\mu| \sigma(t) |\mu_1\rangle\langle\nu_1| \\
&+ \sum_{\mu, \mu_1, \nu, \nu_1} R_{\mu\nu}^{\mu_1\nu_1*} |\nu_1\rangle\langle\mu_1| \sigma(t) |\mu\rangle\langle\nu| - \sum_{\mu, \mu_1, \nu} R_{\mu\nu}^{\mu_1\nu} \sigma(t) |\mu_1\rangle\langle\mu| \\
&- \sum_{\nu, \mu_1, \mu} R_{\nu\mu}^{\mu_1\mu*} |\nu\rangle\langle\mu_1| \sigma(t) + \sum_{\nu, \mu_1, \mu, \nu_1} R_{\nu\mu}^{\mu_1\nu_1} |\mu\rangle\langle\nu| \sigma(t) |\mu_1\rangle\langle\nu_1| \\
&+ \sum_{\nu, \mu_1, \mu, \nu_1} R_{\nu\mu}^{\mu_1\nu_1*} |\nu_1\rangle\langle\mu_1| \sigma(t) |\nu\rangle\langle\mu| - \sum_{\nu, \mu_1, \mu} R_{\nu\mu}^{\mu_1\mu} \sigma(t) |\mu_1\rangle\langle\nu| \\
&- \sum_{\mu, \nu_1, \nu} R_{\mu\nu}^{\nu_1\nu*} |\mu\rangle\langle\nu_1| \sigma(t) + \sum_{\mu, \nu_1, \nu, \mu_1} R_{\mu\nu}^{\nu_1\mu_1} |\nu\rangle\langle\mu| \sigma(t) |\nu_1\rangle\langle\mu_1| \\
&+ \sum_{\mu, \nu_1, \nu, \mu_1} R_{\mu\nu}^{\nu_1\mu_1*} |\mu_1\rangle\langle\nu_1| \sigma(t) |\mu\rangle\langle\nu| - \sum_{\mu, \nu_1, \nu} R_{\mu\nu}^{\nu_1\nu} \sigma(t) |\nu_1\rangle\langle\mu| \\
&- \sum_{\nu, \nu_1, \mu} R_{\nu\mu}^{\nu_1\mu*} |\nu\rangle\langle\nu_1| \sigma(t) + \sum_{\nu, \nu_1, \mu, \mu_1} R_{\nu\mu}^{\nu_1\mu_1} |\mu\rangle\langle\nu| \sigma(t) |\nu_1\rangle\langle\mu_1| \\
&+ \sum_{\nu, \nu_1, \mu, \mu_1} R_{\nu\mu}^{\nu_1\mu_1*} |\mu_1\rangle\langle\nu_1| \sigma(t) |\nu\rangle\langle\mu| - \sum_{\nu, \nu_1, \mu} R_{\nu\mu}^{\nu_1\mu} \sigma(t) |\nu_1\rangle\langle\nu|.
\end{aligned} \tag{3.35}$$

This equation looks so complicated because the eigenstates of the molecule are divided into two distinct sets of states. If there was only one variable describing the state, the equation would look much simpler, but on the other hand would be less meaningful. In the Born-Oppenheimer approximation the equation will simplify a little bit due to orthogonal nuclear wavefunctions (see section 3.4).

¹³I write this here explicitly to stress that the position of the indices in $R_{\mu\nu}^{\mu_1\nu_1}$ is important.

¹⁴Since $[V + V_{\leftrightarrow}, [V' + V'_{\leftrightarrow}, A]] = [V, [V', A]] + [V_{\leftrightarrow}, [V', A]] + [V, [V'_{\leftrightarrow}, A]] + [V_{\leftrightarrow}, [V'_{\leftrightarrow}, A]]$.

3.3 Master equation in the Born-Oppenheimer approximation

In this section the master equation is simplified by using the Born-Oppenheimer approximation. Again, first the case $\mu > \nu$ is considered. In the Born-Oppenheimer the dipole matrix elements assume the following form:

$$\vec{d}_{\mu\nu} = f_{\mu\nu} \vec{d}_{\text{eg}}. \quad (3.36)$$

Here $f_{\mu\nu}$ is the *Franck Condon integral* (see (2.50)). \vec{d}_{eg} is the dipole moment of the electronic wave function. Since there are only two electronic levels, the dipole moment is either \vec{d}_{eg} or $\vec{d}_{\text{ge}} = \vec{d}_{\text{eg}}^*$. That means that each of the $R_{\mu\nu}^{\mu_1\nu_1}$ is proportional to $|\vec{d}_{\text{eg}}|^2$.

The master equation becomes:

$$\begin{aligned} \dot{\sigma}(t) = & -\frac{i}{\hbar} [H_0, \sigma] + \frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2 \hbar \epsilon_0 c^3} \left(- \sum_{\mu, \mu_1, \nu} r_{\mu\nu}^{\mu_1\nu*} |\mu\rangle \langle \mu_1| \sigma(t) \right. \\ & + \sum_{\mu, \mu_1, \nu, \nu_1} r_{\mu\nu}^{\mu_1\nu_1} |\nu\rangle \langle \mu| \sigma(t) |\mu_1\rangle \langle \nu_1| + \sum_{\mu, \mu_1, \nu, \nu_1} r_{\mu\nu}^{\mu_1\nu_1*} |\nu_1\rangle \langle \mu_1| \sigma(t) |\mu\rangle \langle \nu| \\ & \left. - \sum_{\mu, \mu_1, \nu} r_{\mu\nu}^{\mu_1\nu} \sigma(t) |\mu_1\rangle \langle \mu| \right) \end{aligned} \quad (3.37)$$

with

$$r_{\mu\nu}^{\mu_1\nu_1} := \Theta(\mu_1 - \nu_1) \Theta(\mu - \nu) f_{\mu\nu}^* f_{\mu_1\nu_1} (\mu_1 - \nu_1)^3. \quad (3.38)$$

Now one can insert the density operator

$$\begin{aligned} \sigma(t) = & \sum_{\mu_3, \mu_4} \sigma(t)_{\mu_3\mu_4} |\mu_3\rangle \langle \mu_4| + \sum_{\mu_3, \nu_4} \sigma(t)_{\mu_3\nu_4} |\mu_3\rangle \langle \nu_4| \\ & + \sum_{\nu_3, \mu_4} \sigma(t)_{\nu_3\mu_4} |\nu_3\rangle \langle \mu_4| + \sum_{\nu_3, \nu_4} \sigma(t)_{\nu_3\nu_4} |\nu_3\rangle \langle \nu_4|. \end{aligned} \quad (3.39)$$

This results in differential equations describing the time evolution of the matrix elements of the density operator:

$$\dot{\sigma}_{\mu_A\mu_B} = -i(\mu_A - \mu_B)\sigma_{\mu_A\mu_B} - \frac{|\vec{d}_{eg}|^2}{6\pi^2\hbar\epsilon_0c^3} \left(\sum_{\mu,\nu} (r_{\mu_A\nu}^{\mu\nu*}\sigma_{\mu\mu_B} + r_{\mu_B\nu}^{\mu\nu}\sigma_{\mu_A\mu}) \right) \quad (3.40)$$

$$\dot{\sigma}_{\nu_A\nu_B} = -i(\nu_A - \nu_B)\sigma_{\nu_A\nu_B} + \frac{|\vec{d}_{eg}|^2}{6\pi^2\hbar\epsilon_0c^3} \left(\sum_{\mu,\mu_1} (r_{\mu\nu_A}^{\mu_1\nu_B} + r_{\mu_1\nu_B}^{\mu\nu_A*})\sigma_{\mu\mu_1} \right) \quad (3.41)$$

$$\dot{\sigma}_{\mu_A\nu_B} = -i(\mu_A - \nu_B)\sigma_{\mu_A\nu_B} - \frac{|\vec{d}_{eg}|^2}{6\pi^2\hbar\epsilon_0c^3} \left(\sum_{\mu,\nu} r_{\mu_A\nu}^{\mu\nu*}\sigma_{\mu\nu_B} \right) \quad (3.42)$$

$$\dot{\sigma}_{\nu_A\mu_B} = -i(\nu_A - \mu_B)\sigma_{\nu_A\mu_B} - \frac{|\vec{d}_{eg}|^2}{6\pi^2\hbar\epsilon_0c^3} \left(\sum_{\mu,\nu} r_{\mu_B\nu}^{\mu\nu}\sigma_{\nu_A\mu} \right) \quad (3.43)$$

It is interesting that the *coherences*¹⁵ connecting the upper states with lower states (like $\sigma_{\mu_A\nu_B}$) are not coupled with matrix elements connecting levels of the same electronic state (for example $\sigma_{\mu_A\mu_B}$). If one is interested in the probability of finding a molecule in a specific state (for example $|\sigma_{\mu_A\mu_A}|^2$), these coherences need not to be regarded.

3.4 Master equation in the Born-Oppenheimer approximation without the constraint $\mu > \nu$

Having a closer look at the r_{cd}^{ab} in (3.32), it is clear that if a and b are either both vibrational states of the excited electronic level or both of them belong to the ground state, then $\vec{d}_{ab} = 0$. Due to this fact, four of the 16 parts in equation (3.35) are zero in the Born-Oppenheimer approximation. Because in equation (3.38) the constraint $\mu > \nu$ was already explicitly included into $r_{\mu\nu}^{\mu_1\nu_1}$, the same definition for $r_{\mu\nu}^{\mu_1\nu_1}$ can be used in this general case. The Θ -functions insure that no error is made.

With the density operator (3.39), the time dependence of the density matrix is described by the following set of differential equations:

¹⁵Coherences are the non-diagonal matrix elements of the density operator.

$$\begin{aligned} \dot{\sigma}_{\mu_A\mu_B} = & -i(\mu_A - \mu_B)\sigma_{\mu_A\mu_B} - \frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2\hbar\epsilon_0c^3} \left\{ \sum_{\mu,\nu} (r_{\mu_A\nu}^{\mu\nu*}\sigma_{\mu\mu_B} + r_{\mu_B\nu}^{\mu\nu}\sigma_{\mu_A\mu}) \right. \\ & \left. - \sum_{\nu,\nu_1} (r_{\nu\mu_A}^{\nu_1\mu_B} + r_{\nu_1\mu_B}^{\nu\mu_A*})\sigma_{\nu\nu_1} \right\} \end{aligned} \quad (3.44)$$

$$\begin{aligned} \dot{\sigma}_{\nu_A\nu_B} = & -i(\nu_A - \nu_B)\sigma_{\nu_A\nu_B} - \frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2\hbar\epsilon_0c^3} \left\{ \sum_{\nu,\mu} (r_{\nu_A\mu}^{\nu\mu*}\sigma_{\nu\nu_B} + r_{\nu_B\mu}^{\nu\mu}\sigma_{\nu_A\nu}) \right. \\ & \left. - \sum_{\mu,\mu_1} (r_{\mu_1\nu_B}^{\mu_1\nu_A} + r_{\mu_1\nu_A}^{\mu_1\nu_B*})\sigma_{\mu\mu_1} \right\} \end{aligned} \quad (3.45)$$

$$\begin{aligned} \dot{\sigma}_{\mu_A\nu_B} = & -i(\mu_A - \nu_B)\sigma_{\mu_A\nu_B} - \frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2\hbar\epsilon_0c^3} \left\{ \sum_{\mu,\nu} (r_{\mu_A\nu}^{\mu\nu*}\sigma_{\mu\nu_B} + r_{\nu_B\mu}^{\nu\mu}\sigma_{\mu_A\nu}) \right. \\ & \left. - \sum_{\nu,\mu} (r_{\nu\mu_A}^{\mu\nu_B} + r_{\mu\nu_B}^{\nu\mu_A*})\sigma_{\nu\mu} \right\} \end{aligned} \quad (3.46)$$

$$\begin{aligned} \dot{\sigma}_{\nu_A\mu_B} = & -i(\nu_A - \mu_B)\sigma_{\nu_A\mu_B} - \frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2\hbar\epsilon_0c^3} \left\{ \sum_{\mu,\nu} (r_{\mu_B\nu}^{\mu\nu}\sigma_{\nu_A\mu} + r_{\nu_A\mu}^{\nu\mu*}\sigma_{\nu\mu_B}) \right. \\ & \left. - \sum_{\nu,\mu} (r_{\nu\mu_B}^{\mu\nu_A*} + r_{\mu\nu_A}^{\nu\mu_B})\sigma_{\mu\nu} \right\} \end{aligned} \quad (3.47)$$

Since here the constraint $\mu > \nu$ was dropped, the resulting set of equations above is invariant under exchange of μ and ν .

3.5 Maximization of the rate to $\sigma_{\nu_A\nu_B}$ at $t = 0$

In this section it will be shown that the spontaneous emission rate at the time $t = 0$ can be enhanced. The enhancement depends on the involved Franck Condon factors. Sometimes it is rather small, sometimes it can be large. A more quantitatively discussion can be found in chapter 4.

To simplify the calculation the states are assumed to be only in vibrational levels of the upper electronic state at time $t = 0$. In this case equation (3.41) can be used. At time $t = 0$ no ν states are populated and therefore no $\nu \rightarrow \mu$ transitions can occur.

$$\dot{\sigma}_{\nu_A\nu_B} = -i(\nu_A - \nu_B)\sigma_{\nu_A\nu_B} + \underbrace{\frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2\hbar\epsilon_0c^3} \left(\sum_{\mu,\mu_1} (r_{\mu\nu_A}^{\mu_1\nu_B} + r_{\mu_1\nu_B}^{\mu\nu_A*})\sigma_{\mu\mu_1} \right)}_{X : \text{ to be maximized}}. \quad (3.48)$$

It is important to recall that in general the $\sigma_{\mu\mu_1}$ s cannot be chosen arbitrarily. There is an additional set of differential equations (namely (3.40)) describing the change of $\sigma_{\mu\mu_1}$ s:

$$\dot{\sigma}_{\mu_A\mu_B} = -i(\mu_A - \mu_B)\sigma_{\mu_A\mu_B} - \frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2\hbar\epsilon_0c^3} \left(\sum_{\mu,\nu} (r_{\mu_A\nu}^{\mu\nu*}\sigma_{\mu\mu_B} + r_{\mu_B\nu}^{\nu\mu}\sigma_{\mu_A\mu}) \right)$$

But, because the rate to $\sigma_{\nu_A\nu_B}$ is to be maximized for a fixed time $t = 0$, these equations need not be considered.

3.5.1 Pure system

First a pure system is considered. At time $t = 0$ the system is in a superposition of upper states. Is it possible to enhance the spontaneous emission to $\sigma_{\nu_A\nu_B}$ by using a superposition of upper states?

Let be

$$\chi_{\mu}^{\mu_1} := \chi_{\mu\nu_A}^{\mu_1\nu_B} := r_{\mu\nu_A}^{\mu_1\nu_B} + r_{\mu_1\nu_B}^{\mu\nu_A*}. \quad (3.49)$$

χ is always hermitian and in the case of real Franck Condon factors it is even symmetric. In addition there is the constraint $\sum_{\mu} \sigma_{\mu\mu} - 1 = 0$.

Therefore the following expression is to be maximized¹⁶:

$$\sum_{\mu\mu_1} \chi_{\mu}^{\mu_1} \sigma_{\mu\mu_1} + \lambda (\sum_{\mu} \sigma_{\mu\mu} - 1). \quad (3.50)$$

Since the system is a pure state, we can use $\sigma_{\mu\mu_1} = c_{\mu} c_{\mu_1}^*$

Instead of taking the real and the imaginary part of c as independent variables it is possible to take c and c^* as independent.

$$\partial_{c_{\alpha}^*} \left(\sum_{\mu\mu_1} \chi_{\mu}^{\mu_1} c_{\mu} c_{\mu_1}^* + \lambda (\sum_{\mu} c_{\mu} c_{\mu}^* - 1) \right) = 0. \quad (3.51)$$

This results in

$$\sum_{\mu} \chi_{\mu}^{\alpha} c_{\mu} + \lambda c_{\alpha} = 0. \quad (3.52)$$

This is an eigenvalue problem for the Matrix χ_{μ}^{α} . The eigenvector of the above equation with the maximal eigenvalue is the superposition of upper states that maximizes the spontaneous emission rate into level (or more general the coherence) $\sigma_{\nu_A\nu_B}$.

3.5.2 Mixed system

Let us now consider the case where the system is in a mixed state. In this case the simple form of $\sigma_{\mu\mu_1}$ can not be assumed. If the maximization effect is a pure quantum mechanical effect, the result should be the same as in (3.52).

In the matrix notation the problem has the following form:

$$\text{Tr}(\chi\sigma) = \text{maximal} \quad \text{with the constraint} \quad \text{Tr}(\sigma) = 1. \quad (3.53)$$

¹⁶Using the method of Lagrangian multipliers.

In order to easily determine the trace of the first expression the argument should be diagonal. If χ is diagonalizable¹⁷, this can be achieved by changing the basis:

$$\mathbf{A}^{-1}(\chi\sigma)\mathbf{A} = \mathbf{A}^{-1}\chi\mathbf{A}\mathbf{A}^{-1}\sigma\mathbf{A}. \quad (3.54)$$

Define

$$\tilde{\sigma} = \mathbf{A}^{-1}\sigma\mathbf{A} \quad \text{and} \quad \tilde{\chi} = \mathbf{A}^{-1}\chi\mathbf{A}. \quad (3.55)$$

Then the problem becomes:

$$\sum_i \tilde{\chi}_i \tilde{\sigma}_{ii} = \text{maximal} \quad \text{with the constraint} \quad \sum_i \tilde{\sigma}_{ii} = 1. \quad (3.56)$$

Let us assume that there is one index n for which $\tilde{\chi}_i$ is maximal. Then (3.56) is maximal for $\tilde{\sigma}_{ii} = 0$ ($i \neq n$) and $\tilde{\sigma}_{nn} = 1$. We know the diagonal elements of $\tilde{\sigma}$, but what about the non diagonal elements? Actually these elements are all zero. The proof is the following:

$$\text{Tr}(\tilde{\sigma}^2) = \sum_{ij} \tilde{\sigma}_{ij}\tilde{\sigma}_{ji} = \sum_{ij} \tilde{\sigma}_{ij}\tilde{\sigma}_{ij}^* = \underbrace{|\tilde{\sigma}_{nn}|^2}_1 + \sum_{ij \neq n} |\tilde{\sigma}_{ij}|^2. \quad (3.57)$$

For a pure or mixed system $\text{Tr}(\tilde{\sigma}^2) \leq 1$ always holds. The last term in (3.57) has to be zero. A sum of positive numbers is only zero if all numbers are zero. Thus, all non diagonal elements are zero.

Now we know how $\tilde{\sigma}$ looks like: It has one 1 on the diagonal and all the rest is 0. $\tilde{\sigma}$ is therefore a projector. But we should know σ instead of $\tilde{\sigma}$. The Matrix \mathbf{A} for the basis transformation must be found.

$$\tilde{\chi} = \mathbf{A}^{-1}\chi\mathbf{A} \quad (3.58)$$

or

$$\chi\mathbf{A} = \mathbf{A}\tilde{\chi}. \quad (3.59)$$

This means

$$\mathbf{A}\tilde{\chi} = (\tilde{\chi}_1\vec{a}_1, \tilde{\chi}_2\vec{a}_2, \dots, \tilde{\chi}_N\vec{a}_N) \quad (3.60)$$

and

$$\chi\mathbf{A} = (\chi\vec{a}_1, \chi\vec{a}_2, \dots, \chi\vec{a}_N). \quad (3.61)$$

¹⁷ $\chi\chi^\dagger = \chi^\dagger\chi$

Here \vec{a} are the column vectors of \mathbf{A} . Remember $\tilde{\chi}_i$ are numbers. Now compare the columns. The problem is equivalent to solve the following eigenproblem.

$$\chi \vec{a} = \tilde{\chi} \vec{a}. \quad (3.62)$$

Remember that the n th eigenvalue is the largest. Then $\tilde{\sigma}$ is a projector on the n th basis vector. In our case χ is hermitian. Then all eigenvectors \vec{a}_i are orthogonal. (If eigenvalues are degenerate the eigenvectors can be chosen to be orthogonal.) That means that the matrix \mathbf{A} is orthogonal.

Now we can calculate $\sigma = \mathbf{A} \tilde{\sigma} \mathbf{A}^{-1}$.

$$\sigma_{il} = \sum_{jk} a_{ij} \tilde{\sigma}_{jk} a_{lk}^*. \quad (3.63)$$

Because of the special form of $\tilde{\sigma}$ is $j = k = n$.

$$\sigma_{il \text{ max}} = a_{in} a_{ln}^*. \quad (3.64)$$

This can be compared with the result in 3.5.1. Obviously it is the same. The conclusion is that if χ is hermitian, only a pure system can maximize the spontaneous emission in a special lower state.

In context with chapter 4 it is important to mention, that this procedure maximizes the *absolute transition rate*, i.e. the rates to the other levels are not considered. In chapter 4 the relative rate is calculated.

3.5.3 A simple picture

In the case of $\Delta\omega := \mu_{\text{max}} - \mu_{\text{min}} \ll \omega_{\text{eg}}$ (see Fig. 3.2 for the definition) there is even a simpler way of maximizing the spontaneous emission rate at the time $t = 0$. Given these requirements and assuming $\nu_0 := \nu_A = \nu_B$, $\chi_{\mu}^{\mu_1}$ simply becomes $2\omega_{\text{eg}}^3 f_{\mu_1 \nu_0} f_{\mu \nu_0}^*$.¹⁸

$$\chi_{\mu}^{\mu_1} \approx 2\omega_{\text{eg}}^3 f_{\mu_1 \nu_0} f_{\mu \nu_0}^*. \quad (3.65)$$

Keeping this in mind, let us go on to a more handwaving approach of the maximization. Let $|\check{\mu}'\rangle = \sum_{\mu} c_{\mu} |\check{\mu}\rangle$ be a state representing a superposition of electronically excited states.¹⁹ μ stands for an upper eigenstate. $\{|\check{\mu}\rangle\}$ forms a basis for a vector space representing all possible superpositions. Let ν_0 be the lower level of interest. If one picks only one lower and one upper state, the spontaneous emission rate is predominantly given by the corresponding Franck Condon factor times the energy difference to the power of three. Given the fact of small $\Delta\omega$, the rates of the upper levels are mainly determined by the corresponding Franck Condon factors. If this

¹⁸Here ν_A and ν_B define the matrix element $\sigma_{\nu_A \nu_B}$ that should be maximized.

¹⁹The $\check{\cdot}$ marks that only the nuclear wave functions $P(R)$ are considered.

idea is applied to the superposition, it is possible to find the superposition that maximizes the spontaneous emission by maximizing the corresponding overlap²⁰:

$$f_{\mu'\nu_0} = \left(\sum_{\mu} c_{\mu} \langle \check{\mu} | \right) | \check{\nu}_0 \rangle = \sum_{\mu} c_{\mu} f_{\mu\nu_0}. \quad (3.66)$$

$$\partial_{c_{\check{\mu}}} \left(\sum_{\mu} c_{\mu} f_{\mu\nu_0} - \lambda \left(\sum_{\mu} |c_{\mu}|^2 - 1 \right) \right) = 0. \quad (3.67)$$

Here again the method of the is applied. The above expression has a maximum for $c_{\check{\mu}} = \lambda^{-1} f_{\check{\mu}\nu_0}$. The factor λ insures the normalization of the $c_{\check{\mu}}$ s. If the set of upper states formed a complete set of orthonormal eigenvectors for the space of bound states, then the state $|\check{\nu}_0\rangle$ could be expressed in the basis $\{|\check{\mu}\rangle\}$. Naturally, since all eigenstates are normalized, the maximal overlap between the superposition and the state $|\check{\nu}_0\rangle$ is assured, when the superposition has the same shape as $|\check{\nu}_0\rangle$. In this case the spontaneous emission rate to $|\check{\nu}_0\rangle$ is the same as in a two-level atom. But since the number of excited eigenstates which are involved is restricted, this never²¹ happens. The best choice for an subset of upper eigenstates is therefore to choose such eigenstates that have a good overlap with $|\check{\nu}_0\rangle$.

In order to verify this argumentation, $c_{\check{\mu}} = \lambda^{-1} f_{\check{\mu}\nu_0}$ can be inserted in equation (3.52)

$$\sum_{\check{\mu}} \chi_{\check{\mu}}^{\alpha} c_{\check{\mu}} + \lambda' c_{\alpha} = 0 \quad (3.68)$$

of section 3.5.1.

$$\sum_{\check{\mu}} 2\omega_{\text{eg}}^3 f_{\alpha\nu_0} f_{\check{\mu}\nu_0}^* \lambda^{-1} f_{\check{\mu}\nu_0} + \lambda' \lambda^{-1} f_{\alpha\nu_0} = 0. \quad (3.69)$$

This equation is true for

$$\lambda' = -2\omega_{\text{eg}}^3 \sum_{\check{\mu}} |f_{\check{\mu}\nu_0}|^2. \quad (3.70)$$

The maximal spontaneous emission rate to the level ν_0 is therefore:

$$\Gamma_{\text{max}} = \frac{|\vec{d}_{\text{eg}}|^2}{6\pi^2 \hbar \epsilon_0 c^3} \lambda' = \frac{|\vec{d}_{\text{eg}}|^2}{3\epsilon_0 \pi \hbar^2 c^3} \omega_{\text{eg}}^3 \left(\sum_{\check{\mu}} |f_{\check{\mu}\nu_0}|^2 \right). \quad (3.71)$$

²⁰This overlap can be understood as the "Franck Condon integral" of the superposition.

²¹Actually it could happen, if $|\check{\nu}_0\rangle$ is exactly a linear combination of the finite subset of upper states of concern. Then the corresponding Franck Condon factor would be 1, and, since the other ν levels are orthogonal, there would be no transition into other lower levels.

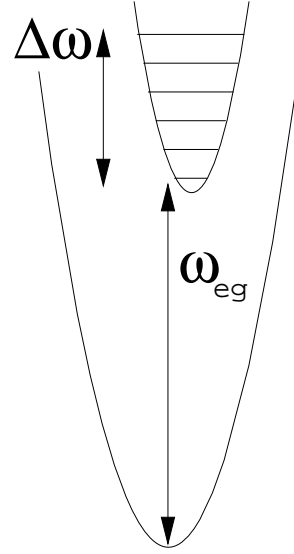


Figure 3.2: Definition of ω_{eg} and $\Delta\omega$.

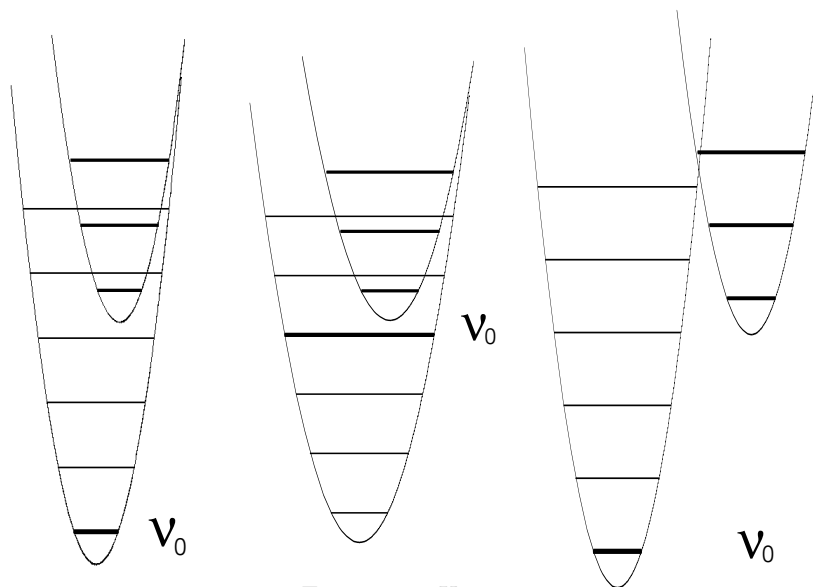
Figure 3.3: \checkmark

Figure 3.4: X

Figure 3.5: X

An interesting effect is that the better the overlap between the superposition and the lower state the smaller is the overlap between the other lower levels. This is true because the lower levels are all orthogonal.

3.5.4 Discussion of the simple picture

The above approximation should be a good approximation for a lot of molecules. Nevertheless, if ν_0 is a higher vibrational level of the electronic ground state or higher vibrational levels of the first electronic state are needed, it is possible that the approximation $\Delta\omega \ll \omega_{eg}$ is not valid anymore. This can be seen in Fig. 3.3 - 3.5.

In Fig. 3.4 and Fig. 3.5 the condition $\Delta\omega \ll \omega_{eg}$ is not satisfied. In these cases the ω^3 dependence of the transition rates is dominant. In Fig. 3.4 for example, the contribution of the highest μ level to the transition rate is much higher than the contribution of the lowest one. Anyhow, the *relative transition rate* is much more important. This means: How likely is a transition to level ν_0 compared to the likelihood to other lower levels. If a superposition includes higher μ levels, the transition rate to other ν levels should be enhanced as well, simply due to the greater energy difference. This is shown numerically in chapter 4 on the basis of a few examples.

3.6 Master equation for times $t \gg \tau_{\text{vib}}$

So far, all the previous master equations were in the Schrödinger picture. To better understand the master equations (for example (3.35)) they can be written formally with the help of super operators²² \mathbf{A} and \mathbf{B} :

$$\dot{\sigma} = -i\mathbf{A}\sigma + \mathbf{B}\sigma \quad (3.72)$$

Here \mathbf{A} and \mathbf{B} are real matrices. The decay of the system and the coupling between different matrix elements of σ is described in \mathbf{B} . \mathbf{A} has matrix elements like $\mu_A - \mu_B$. The typical order of magnitude of these matrix elements is therefore 10^{14} . Using typical electronic dipole moments, \mathbf{B} has matrix elements of the order of 10^7 . So it is clear that the evolution of σ is described by two timescales. Define

$$\tau_{\text{vib}} := \mathcal{O}\left(\frac{2\pi}{\mu_A - \mu_B}\right) \approx 10^{-14} \text{ s}. \quad (3.73)$$

For $t \gg \tau_{\text{vib}}$ the master equation can be simplified extremely. Unfortunately, this simplification will also cancel the effect of the superposition of the states.

To show this, the master equation is handled best in the *interaction picture*. Starting point is the general master equation (3.35). The interaction picture is achieved in the same way as in 2.1. Since the radiation field is already traced out, H_0 does not depend on it any more:

$$H_0 = \hbar\left(\sum_{\mu} \mu|\mu\rangle\langle\mu| + \sum_{\nu} \nu|\nu\rangle\langle\nu|\right). \quad (3.74)$$

The usual relation between the density operator in the Schrödinger picture and the density operator in the interaction picture is assumed.

$$\sigma = e^{-i\frac{H_0}{\hbar}t}\sigma_{\text{I}}e^{i\frac{H_0}{\hbar}t} \quad \text{or} \quad \sigma_{\text{I}} = e^{i\frac{H_0}{\hbar}t}\sigma e^{-i\frac{H_0}{\hbar}t} \quad (3.75)$$

²²A short introduction on super operators is given in B.1.

Using this in (3.35), yields

$$\begin{aligned}
\dot{\sigma}_I = & - \sum_{\mu, \mu_1, \nu} R_{\mu\nu}^{\mu_1\nu*} |\mu\rangle\langle\mu_1| \sigma_I e^{-i(\mu_1-\mu)t} + \sum_{\mu, \mu_1, \nu, \nu_1} R_{\mu\nu}^{\mu_1\nu_1} |\nu\rangle\langle\mu| \sigma_I |\mu_1\rangle\langle\nu_1| e^{i(\mu_1-\nu_1-\mu+\nu)t} \\
& + \sum_{\mu, \mu_1, \nu, \nu_1} R_{\mu\nu}^{\mu_1\nu_1*} |\nu_1\rangle\langle\mu_1| \sigma_I |\mu\rangle\langle\nu| e^{-i(\mu_1-\nu_1-\mu+\nu)t} - \sum_{\mu, \mu_1, \nu} R_{\mu\nu}^{\mu_1\nu} \sigma_I |\mu_1\rangle\langle\mu| e^{i(\mu_1-\mu)t} \\
& - \sum_{\nu, \mu_1, \mu} R_{\nu\mu}^{\mu_1\mu*} |\nu\rangle\langle\mu_1| \sigma_I e^{-i(\mu_1-\nu)t} + \sum_{\nu, \mu_1, \mu, \nu_1} R_{\nu\mu}^{\mu_1\nu_1} |\mu\rangle\langle\nu| \sigma_I |\mu_1\rangle\langle\nu_1| e^{i(\mu_1-\nu_1-\nu+\mu)t} \\
& + \sum_{\nu, \mu_1, \mu, \nu_1} R_{\nu\mu}^{\mu_1\nu_1*} |\nu_1\rangle\langle\mu_1| \sigma_I |\nu\rangle\langle\mu| e^{-i(\mu_1-\nu_1-\nu+\mu)t} - \sum_{\nu, \mu_1, \mu} R_{\nu\mu}^{\mu_1\mu} \sigma_I |\mu_1\rangle\langle\nu| e^{i(\mu_1-\nu)t} \\
& - \sum_{\mu, \nu_1, \nu} R_{\mu\nu}^{\nu_1\nu*} |\mu\rangle\langle\nu_1| \sigma_I e^{-i(\nu_1-\mu)t} + \sum_{\mu, \nu_1, \nu, \mu_1} R_{\mu\nu}^{\nu_1\mu_1} |\nu\rangle\langle\mu| \sigma_I |\nu_1\rangle\langle\mu_1| e^{i(\nu_1-\mu_1-\mu+\nu)t} \\
& + \sum_{\mu, \nu_1, \nu, \mu_1} R_{\mu\nu}^{\nu_1\mu_1*} |\mu_1\rangle\langle\nu_1| \sigma_I |\mu\rangle\langle\nu| e^{-i(\nu_1-\mu_1-\mu+\nu)t} - \sum_{\mu, \nu_1, \nu} R_{\mu\nu}^{\nu_1\nu} \sigma_I |\nu_1\rangle\langle\mu| e^{i(\nu_1-\mu)t} \\
& - \sum_{\nu, \nu_1, \mu} R_{\nu\mu}^{\nu_1\mu*} |\nu\rangle\langle\nu_1| \sigma_I e^{-i(\nu_1-\nu)t} + \sum_{\nu, \nu_1, \mu, \mu_1} R_{\nu\mu}^{\nu_1\mu_1} |\mu\rangle\langle\nu| \sigma_I |\nu_1\rangle\langle\mu_1| e^{i(\nu_1-\mu_1-\nu+\mu)t} \\
& + \sum_{\nu, \nu_1, \mu, \mu_1} R_{\nu\mu}^{\nu_1\mu_1*} |\mu_1\rangle\langle\nu_1| e^{-i(\nu_1-\mu_1-\nu+\mu)t} \sigma_I |\nu\rangle\langle\mu| - \sum_{\nu, \nu_1, \mu} R_{\nu\mu}^{\nu_1\mu} \sigma_I |\nu_1\rangle\langle\nu| e^{i(\nu_1-\nu)t}.
\end{aligned} \tag{3.76}$$

This is the same equation as (3.35) without \mathcal{L}_0 and with time dependent Franck Condon factors.²³ In the interaction picture, the nuclear wave functions therefore "wobble" in the potential with different frequencies $\omega_{\text{wobble}} = \frac{E}{\hbar}$. Again four terms cancel in the Born-Oppenheimer approximation.²⁴

Now a tricky approximation is made. We know, that the exponential functions vary on a time scale of 10^{-14} s, but the time scale of the decay itself is of the order of 10^{-7} s. To obtain $\sigma_I(t)$ the equation above must be integrated. Equation (3.76) can be converted into a *coarse grained differential equation*. This means, that all changes of σ on a small time scale are filtered or averaged out. Each term in the equation above is of the form

$$\dot{\sigma}_I(t) = a e^{i\omega t} \sigma_I(t). \tag{3.77}$$

It is possible to convolute this equation with a symmetric normalized²⁵ function, for example with a Gaussian function:

$$g(t' - t) := \frac{1}{\sqrt{2\pi}\Delta} e^{-\frac{(t'-t)^2}{2\Delta^2}}. \tag{3.78}$$

Important for this function is also that $g(t' - t) \approx 0$ for $|t' - t| > \Delta$.

²³This equation can be achieved in the same way as the master equation in the interaction picture in 2.1. It turns out that a simple substitution $R_{cd}^{ab} \rightarrow R_{cd}^{ab} e^{i(a-b-c+d)t}$ leads to the interaction picture.

²⁴the terms with $e^{\pm i(\mu_1-\nu)t}$ and $e^{\pm i(\nu_1-\mu)t}$

²⁵ $g(t' - t) = g(t - t')$ and $\int_{-\infty}^{\infty} dt' g(t' - t) = 1$

$$\int_{-\infty}^{\infty} dt' g(t' - t) \dot{\sigma}_I(t') = a \int_{-\infty}^{\infty} dt' g(t' - t) e^{i\omega t'} \sigma_I(t'). \quad (3.79)$$

It is important that $\tau_{\text{vib}} \approx 10^{-14}$ s $\ll \Delta \ll \Delta T \approx \frac{1}{|a|} \approx 10^{-7}$ s. Here ΔT is the time scale where σ_I changes due to spontaneous emission. Assuming $\sigma_I(t')$ as well as $\dot{\sigma}_I(t')$ are slowly varying functions²⁶ on a time scale of Δ and using the *mean value theorem*²⁷ yields

$$\begin{aligned} \dot{\sigma}_I(\bar{t}) \underbrace{\int_{-\infty}^{\infty} dt' g(t' - t)}_1 &= a \sigma_I(\bar{t}) \int_{-\infty}^{\infty} dt' g(t' - t) e^{i\omega t'} \\ &= \sigma_I(\bar{t}) a e^{i\omega t} \int_{-\infty}^{\infty} dt' g(t' - t) e^{i\omega(t' - t)} \\ &= \sigma_I(\bar{t}) a e^{i\omega t} \int_{-\infty}^{\infty} d\tau g(\tau) e^{i\omega\tau} \\ &= \sigma_I(\bar{t}) \frac{a}{\sqrt{2\pi\Delta}} e^{i\omega t} \int_{-\infty}^{\infty} d\tau e^{-\frac{\tau^2}{2\Delta^2}} (\cos(\omega\tau) + i \sin(\omega\tau)) \\ &= \sigma_I(\bar{t}) a e^{i\omega t} e^{-\frac{\omega^2 \Delta^2}{2}}. \end{aligned} \quad (3.80)$$

Here $e^{i\omega t}$ is bounded. Because $\omega^2 \Delta^2 = \frac{2\pi\Delta^2}{\tau_{\text{vib}}} \gg 1$ the right hand side is zero except for $\omega \approx 0$. But in this case $e^{i\omega t} e^{-\frac{\omega^2 \Delta^2}{2}} = 1$. The equation above simplifies to

$$\dot{\sigma}_I(\bar{t}) = a \sigma_I(\bar{t}) \delta_\omega. \quad (3.81)$$

□

Here δ_ω is the Kronecker δ . This means δ is a function and *not* a distribution. For

²⁶ $\sigma_I(t' + \Delta) \approx \sigma_I(t')$, but $\sigma_I(t' + \Delta T) \neq \sigma_I(t')$

²⁷Strictly speaking, the mean value theorem only can be applied to strictly monotone functions. If applied to non monotone but bounded functions, which are constructed out of a finite number of monotone pieces on a given interval, the mean value theorem results in different possible \bar{t} s. If anyhow the function goes to zero fast enough (due to $g(t' - t)$) then $\bar{t} \in (t - \mathcal{O}(\Delta), t + \mathcal{O}(\Delta))$. If the above integral is exact zero, then \bar{t} needs not lie in the mentioned interval, but a \bar{t} can be chosen, that lies in the interval. Altogether, this means that \bar{t} is accurate enough for the coarse grained equation.

example $\delta_0 \equiv 1$. The result (3.81) can be used to simplify equation (3.76):

$$\begin{aligned}
\dot{\sigma}_{\text{I}} = & - \sum_{\mu, \mu_1, \nu} R_{\mu\nu}^{\mu_1\nu*} |\mu\rangle \langle \mu_1 | \sigma_{\text{I}} \delta_{\mu_1 - \mu} + \sum_{\mu, \mu_1, \nu, \nu_1} R_{\mu\nu}^{\mu_1\nu_1} |\nu\rangle \langle \mu | \sigma_{\text{I}} |\mu_1\rangle \langle \nu_1 | \delta_{\mu_1 - \nu_1 - \mu + \nu} \\
& + \sum_{\mu, \mu_1, \nu, \nu_1} R_{\mu\nu}^{\mu_1\nu_1*} |\nu_1\rangle \langle \mu_1 | \sigma_{\text{I}} |\mu\rangle \langle \nu | \delta_{\mu_1 - \nu_1 - \mu + \nu} - \sum_{\mu, \mu_1, \nu} R_{\mu\nu}^{\mu_1\nu} \sigma_{\text{I}} |\mu_1\rangle \langle \mu | \delta_{\mu_1 - \mu} \\
& + \sum_{\nu, \mu_1, \mu, \nu_1} R_{\nu\mu}^{\mu_1\nu_1} |\mu\rangle \langle \nu | \sigma_{\text{I}} |\mu_1\rangle \langle \nu_1 | \delta_{\mu_1 - \nu_1 - \nu + \mu} \\
& + \sum_{\nu, \mu_1, \mu, \nu_1} R_{\nu\mu}^{\mu_1\nu_1*} |\nu_1\rangle \langle \mu_1 | \sigma_{\text{I}} |\nu\rangle \langle \mu | \delta_{\mu_1 - \nu_1 - \nu + \mu} \\
& + \sum_{\mu, \nu_1, \nu, \mu_1} R_{\mu\nu}^{\nu_1\mu_1} |\nu\rangle \langle \mu | \sigma_{\text{I}} |\nu_1\rangle \langle \mu_1 | \delta_{\nu_1 - \mu_1 - \mu + \nu} \\
& + \sum_{\mu, \nu_1, \nu, \mu_1} R_{\mu\nu}^{\nu_1\mu_1*} |\mu_1\rangle \langle \nu_1 | \sigma_{\text{I}} |\mu\rangle \langle \nu | \delta_{\nu_1 - \mu_1 - \mu + \nu} \\
& - \sum_{\nu, \nu_1, \mu} R_{\nu\mu}^{\nu_1\mu*} |\nu\rangle \langle \nu_1 | \sigma_{\text{I}} \delta_{\nu_1 - \nu} + \sum_{\nu, \nu_1, \mu, \mu_1} R_{\nu\mu}^{\nu_1\mu_1} |\mu\rangle \langle \nu | \sigma_{\text{I}} |\nu_1\rangle \langle \mu_1 | \delta_{\nu_1 - \mu_1 - \nu + \mu} \\
& + \sum_{\nu, \nu_1, \mu, \mu_1} R_{\nu\mu}^{\nu_1\mu_1*} |\mu_1\rangle \langle \nu_1 | \delta_{\nu_1 - \mu_1 - \nu + \mu} \sigma_{\text{I}} |\nu\rangle \langle \mu | - \sum_{\nu, \nu_1, \mu} R_{\nu\mu}^{\nu_1\mu} \sigma_{\text{I}} |\nu_1\rangle \langle \nu | \delta_{\nu_1 - \nu}. \quad (3.82)
\end{aligned}$$

Inserting the density operator (3.39) yields the matrix elements:

$$\dot{\sigma}_{\mu_A \mu_B}^{\text{I}} = - \sum_{\nu} (R_{\mu_A \nu}^{\mu_A \nu*} + R_{\mu_B \nu}^{\mu_B \nu}) \sigma_{\mu_A \mu_B}^{\text{I}} + \sum_{\nu, \nu_1} (R_{\nu \mu_A}^{\nu_1 \mu_B} + R_{\nu_1 \mu_B}^{\nu \mu_A*}) \sigma_{\nu \nu_1}^{\text{I}} \delta_{\nu_1 - \nu + \mu_A - \mu_B} \quad (3.83)$$

$$\dot{\sigma}_{\nu_A \nu_B}^{\text{I}} = - \sum_{\mu} (R_{\nu_A \mu}^{\nu_A \mu*} + R_{\nu_B \mu}^{\nu_B \mu}) \sigma_{\nu_A \nu_B}^{\text{I}} + \sum_{\mu, \mu_1} (R_{\mu \nu_A}^{\mu_1 \nu_B} + R_{\mu_1 \nu_B}^{\mu \nu_A*}) \sigma_{\mu \mu_1}^{\text{I}} \delta_{\mu_1 - \mu + \nu_A - \nu_B}. \quad (3.84)$$

Since the coherences between μ and ν states are not coupled to the $\sigma_{\nu\nu_1}^{\text{I}}$ and $\sigma_{\mu\mu_1}^{\text{I}}$ matrix elements, the last two sets of differential equations are not mentioned anymore. Here it is important to keep in mind, that $R_{cd}^{ab} \propto \Theta(a-b)\Theta(c-d)$. For the sake of simplicity assume again $\mu > \nu$. Then the time evolution of the probabilities looks like

$$\dot{\sigma}_{\mu\mu}^{\text{I}} = - \sum_{\nu} (R_{\mu\nu}^{\mu\nu*} + R_{\mu\nu}^{\mu\nu}) \sigma_{\mu\mu}^{\text{I}} \quad (3.85)$$

$$\dot{\sigma}_{\nu\nu}^{\text{I}} = \sum_{\mu} (R_{\mu\nu}^{\mu\nu} + R_{\mu\nu}^{\mu\nu*}) \sigma_{\mu\mu}^{\text{I}}. \quad (3.86)$$

The time evolution of the probabilities depends only on the probabilities and not on coherences. This implies, that a superposition cannot change the spontaneous emission rate on a time scale $t \gg \tau_{\text{vib}}$. If the systems starts in a superposition, the spontaneous emission rate to a certain level ν is just the sum of all transition rates of the eigenstates contributing to the superposition.

It is necessary to keep in mind that the Kronecker δ acts on frequencies not on indices. This means, that for degenerate upper levels with different(!) nuclear wave functions, there is a possibility to improve the transition to a special lower state - even for times $t \gg \tau_{\text{vib}}$. It is possible that this kind of enhancement could work in *polyatomic molecules*. But to verify this, one must derive a master equation for polyatomic molecules and must check whether the approximations made in this chapter are also valid. Anyway it is not unlikely that, even if this was the case, the corresponding Franck Condon factors for all but one level of the degenerate levels are zero or very small due to their symmetry properties.

For $\mu_A \neq \mu_B$ or $\nu_A \neq \nu_B$ (this means coherences are considered) the corresponding equations (3.83) and (3.84) are not as simple as the above equations for the probabilities. Again assuming $\mu > \nu$ and an initial wave function that is a superposition of only μ states, yields $\dot{\sigma}_I = 0$ if the condition described by the Kronecker δ never applies. When for example $\mu_A - \mu_B = \nu - \nu_1$, then the Kronecker δ in (3.83) becomes 1. For simplicity assume, that exactly one energy difference between the μ states equals exactly one energy difference of the ν states. Without loss of generality, assume $\mu_C - \mu_D = \nu_A - \nu_B$. From (3.84) we know that

$$\dot{\sigma}_{\nu_A \nu_B}^I = +(R_{\mu_C \nu_A}^{\mu_D \nu_B} + R_{\mu_D \nu_B}^{\mu_C \nu_A*}) \sigma_{\mu_C \mu_D}^I. \quad (3.87)$$

That means that, even for times $t \gg \tau_{\text{vib}}$, there are coherences between the lower levels. The density matrix is partially still a superposition, not a completely mixed state. But is important to recall that the degeneracy does not change the result for the probabilities.

Chapter 4

Numerical calculations

4.1 Maximization at $t = 0$ for harmonic potentials

So far, we know that using a superposition instead of a single upper state can result in an enhanced spontaneous emission rate. Since there are so many variables that influence the spontaneous emission rate (all Franck Condon integrals and all energy eigenvalues), it is difficult to understand when it is possible to obtain a reasonable enhancement of the spontaneous emission rate and when not. The Franck Condon integrals and energy eigenvalue themselves depend on the shape of the upper and the lower adiabatic potential. A way to circumvent this problem is therefore to choose some meaningful parameters for the potentials. The change of the spontaneous emission rate due to the variation of these parameters gives us more information what kind of potentials are suited to enhance the spontaneous emission rate.

I decided to examine harmonic potentials and chose $\Delta x := x_{0e} - x_{0g}$ and ω_e as parameters. Δx is the distance between the two minima of the potentials and ω_e is the frequency characterizing the upper potential. The frequency of the ground state ω_g and the energy separation of the two harmonic potentials $\Delta E_{eg} := V_e^{\min}(x_{0e}) - V_g^{\min}(x_{0g})$ are fixed values. For these fixed values I used constants of real molecules, N_2 and CN. The first was chosen, because the energy separation E_{eg} is quite large and the second because of the small energy separation.

The form of the two potentials is

$$V_{g/e} = \frac{1}{2}m\omega_{g/e}^2(x - x_{0g/e})^2 + V_{g/e}^{\min}(x_{0g/e}). \quad (4.1)$$

Here m is the reduced mass of the two nuclei. I chose x_{0g} to be zero and x_{0e} to be positive.¹ Of interest is the maximal relative rate to the absolute ground state $|\nu_0\rangle$.

¹The fact that x_{0e} is positive does not matter, because a negative choice would just negate all Franck Condon integrals. This is true because all harmonic potentials are symmetric. If the potentials were not symmetric, the sign of Δx would matter. Think for example of Lennard Jones potentials (Fig.4.17).

The relative transition rate to $|\nu_0\rangle$ is:

$$\Gamma^{\text{rel}}(\text{superposition of upper levels}) := \frac{\Gamma_0(\text{superposition of upper levels})}{\sum_{\nu} \Gamma_{\nu}(\text{superposition of upper levels})}. \quad (4.2)$$

Γ_{ν} denotes the rate calculated for a specific superposition of upper levels into a special lower level ν . The ideal superposition of upper levels is of course different for different potentials, and therefore for different Δx and ω_e . Ideal means in this case the superposition that maxi-

mizes the transition rate to ν_0 . The corresponding relative transition rate $\Gamma_{\text{max}}^{\text{rel}}$ becomes therefore a function of Δx and ω_e as well. The superposition can be calculated as described in section 3.5. The superposition maximizes the *absolute transition rate* to ν_0 , but the *relative transition rate* is displayed.

	in N ₂	in calculations
ω_{eg}	9.45661×10^{15}	9.45661×10^{15}
ω_e	2.7513×10^{14}	$1 \times 10^{-14} - 6 \times 10^{-14}$
ω_g	4.4428×10^{14}	4.4428×10^{14}
Δx	$0.189 \times 10^{-10} \text{m}$	$0 \text{ m} - 0.3 \times 10^{-10} \text{m}$
mass	7.003 amu	7.003 amu

Figure 4.1: N₂. Physical quantities used in the calculations.

This results in some strange effects in the graphs. These effects are discussed in 4.1.2.

In the following figures $\Gamma_{\text{max}}^{\text{rel}}(\Delta x, \omega_e)$ is plotted as a three dimensional plot with the relative transition rate to ν_0 on the z -Axes. I always tried to use meaningful parameters close to real molecules.

4.1.1 Large ω_{eg}

First, molecules with a large electronic energy difference were examined. N₂ can be taken as an example (see Fig. 2.3). The data of N₂ can be seen in Fig.4.1. The intervals for Δx and ω_e were chosen in such a way that the corresponding parameters of the N₂ molecule lie within these intervals. For the energy separation between the two lowest electronic levels, 9.9727×10^{-19} Joule was used. That corresponds to $\omega_{\text{eg}} = 9.4566 \times 10^{15}$. The adiabatic potential curve of the first excited electronic state of N₂ in the harmonic approximation is described by $\omega_e = 2.7513 \times 10^{14}$. In the calculations ω_e was varied between 1×10^{-14} and 6×10^{-14} . In the plots in Fig.4.4 - 4.7 N₂ is therefore located somewhere in the middle. For ω_g the value 4.4428×10^{14} was used. The separation of the two minima (Δx) was varied between 0 and $3 \times 10^{-11} \text{m}$. The difference between the equilibrium internuclear distance of the upper and the equilibrium internuclear distance of the ground state is for N₂ $0.189 \times 10^{-10} \text{m}$. Therefore N₂ is represented somewhere in the middle of the Δx axis in the plots in Fig.4.4 - 4.7. The reduced mass of N₂ is 7.003 amu ² ($1.1629 \times 10^{-26} \text{kg}$). All the data was taken from [Radzig and Smirnov(1985)].

In the "simple picture" (see 3.5.3) one would expect a good enhancement for a superposition of at least 10 levels. From Fig.4.2 it is plausible that there is a superposition of the first 10 upper levels that produce a strong overlap with ν_0 . Fig.4.7

²1 amu = $1.66053 \times 10^{-27} \text{kg}$

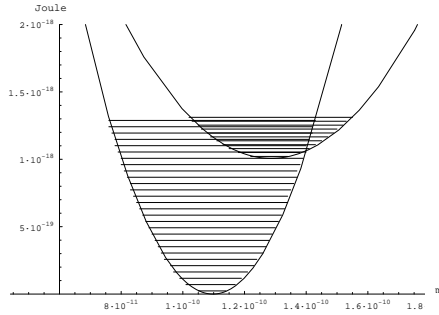


Figure 4.2: N_2 in the harmonic approximation. All units in SI units. 10 vibrational levels of the excited state are shown.

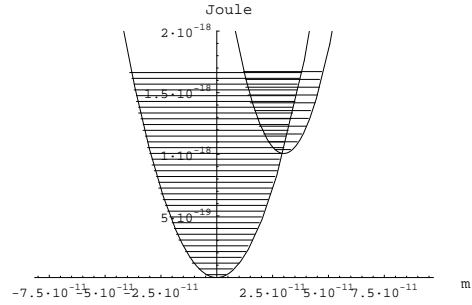


Figure 4.3: These potentials correspond to the right upper corner of Fig.4.4 - 4.7. All units in SI units. 10 vibrational levels of the excited state are shown.

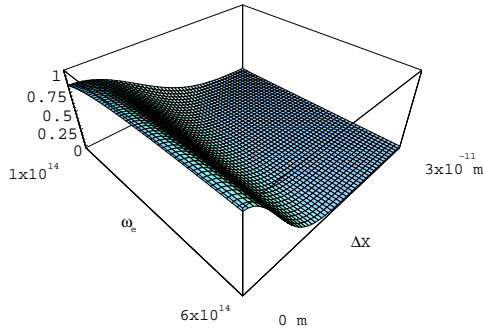


Figure 4.4: Large ω_{eg} . Probability that spontaneous emission occurs from μ_0 to ν_0 . $0 \text{ m} < \Delta x < 3 \times 10^{-11} \text{ m}$, $1 \times 10^{14} < \omega_e < 6 \times 10^{14}$

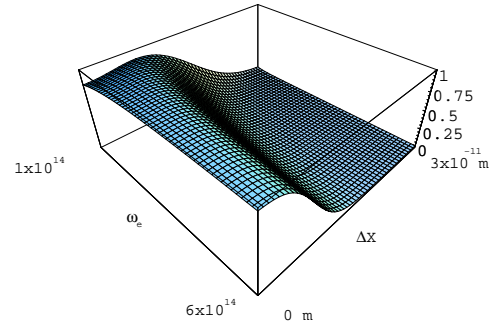


Figure 4.5: Large ω_{eg} . Probability that spontaneous emission occurs from a superposition of μ_0 and μ_1 to ν_0 . $0 \text{ m} < \Delta x < 3 \times 10^{-11} \text{ m}$, $1 \times 10^{14} < \omega_e < 6 \times 10^{14}$

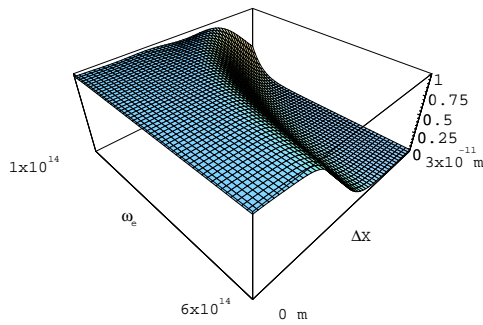


Figure 4.6: Large ω_{eg} . Probability that spontaneous emission occurs from a superposition of $\mu_0 - \mu_4$ to ν_0 . $0 \text{ m} < \Delta x < 3 \times 10^{-11} \text{ m}$, $1 \times 10^{14} < \omega_e < 6 \times 10^{14}$

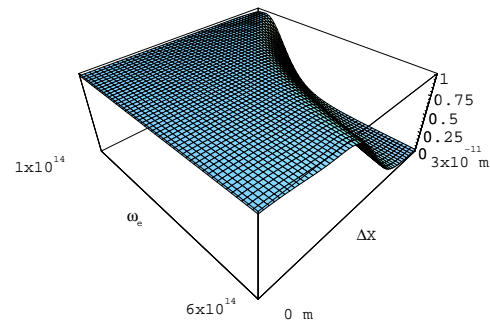


Figure 4.7: Large ω_{eg} . Probability that spontaneous emission occurs from a superposition of $\mu_0 - \mu_9$ to ν_0 . $0 \text{ m} < \Delta x < 3 \times 10^{-11} \text{ m}$, $1 \times 10^{14} < \omega_e < 6 \times 10^{14}$

confirms that the "simple picture" approach is justified in this case. The graph in Fig.4.7 reveals a considerable enhancement of the relative rate to the level ν_0 at the

coordinates $(\Delta x, \omega_e)$ where N_2 should be found.

4.1.2 Small ω_{eg}

In this section the case $\Delta\omega \lesssim \omega_{eg}$ is discussed. The two lowest states of CN are taken as an example (see Fig.4.8). The harmonic approximation made here can be seen in Fig.4.10.

The parameters can be seen in Fig.4.9. They differ from the parameters in the previous section, but the intervals for Δx and ω_e are the same. In the 3D plots in Fig.4.12 - Fig.4.15 a strange effect appears. There are parameters Δx and ω_e for which the relative spontaneous emission rate gets worse for superpositions consisting of more states! (Compare for example Fig.4.13 and Fig.4.15.) This seems to be very unlogically. The superposition is however not the superposition that maximizes the relative spontaneous emission rate, but the superposition which maximizes the absolute spontaneous emission rate. Since the spontaneous emission rate between two levels μ and ν is larger the larger the energy difference is, it is possible that a level μ_n with a small overlap with the lower level ν_0 plays an important role in the superposition, simply because energy eigenvalue of this level is so high. If the overlap of this level with the other ν levels is even larger, the relative spontaneous emission rate to ν_0 becomes smaller when this additional upper level is taken into the superposition. In other words: the absolute rate to ν_0 is enhanced, but the absolute rate to the other levels is enhanced even more. This results in a smaller relative rate to ν_0 .

4.1.3 Discussion

The 3D plots of the previous section allow some conclusions. For a given number of states in the superposition, the spontaneous emission rate depends strongly on the distance Δx between the potentials. An explanation is the following: if Δx is so large that none of the wave functions of the superposition have a significant overlap with the lower level, then any superposition has a very small overlap as well. This is the case when only the exponential outer part of the oscillator eigenfunction (which is $\propto \exp(-x^2/(2\sigma^2))$) do overlap. As soon as the

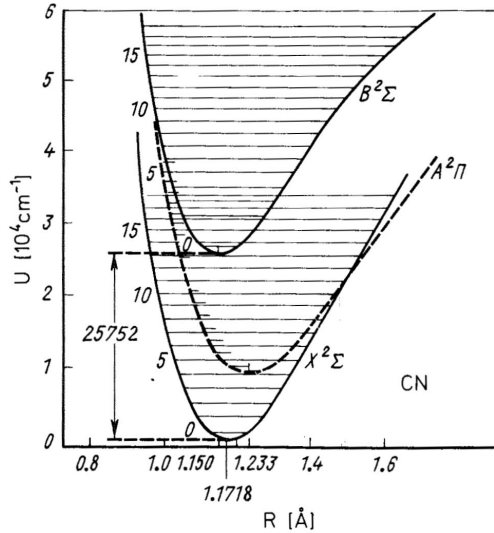


Figure 4.8: The adiabatic potential curves for the lowest electronic states of CN. In my calculations the B state is not considered at all. The graph is taken from [Radzig and Smirnov(1985)].

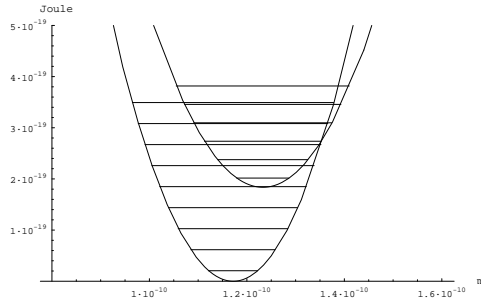


Figure 4.10: Potentials for the CN molecule in the harmonic approximation. All units in SI units.

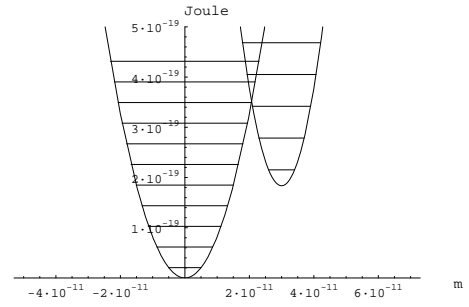


Figure 4.11: Small ω_{eg} . Worst case. Overlap between the wave functions is very small due to large Δx and large ω_e . This corresponds to the upper right corner of Fig.4.12 - Fig.4.15

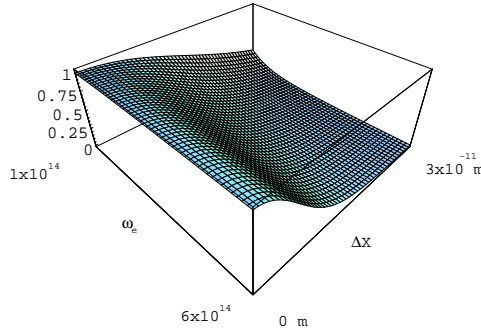


Figure 4.12: Small ω_{eg} . Probability that spontaneous emission occurs from μ_0 to ν_0 . $0 \text{ m} < \Delta x < 3 \times 10^{-11} \text{ m}$, $1 \times 10^{14} < \omega_e < 6 \times 10^{14}$

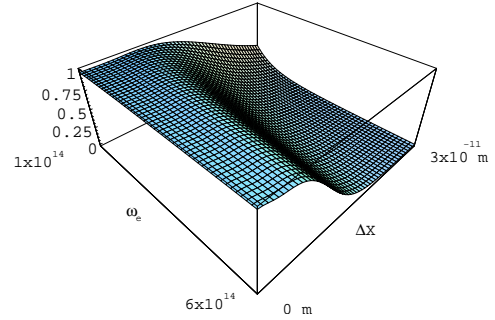


Figure 4.13: Small ω_{eg} . Probability that spontaneous emission occurs from a superposition of μ_0 and μ_1 to ν_0 . $0 \text{ m} < \Delta x < 3 \times 10^{-11} \text{ m}$, $1 \times 10^{14} < \omega_e < 6 \times 10^{14}$

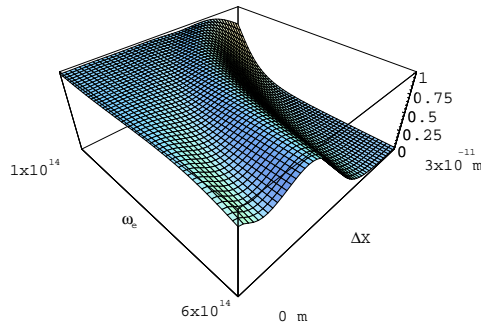


Figure 4.14: Small ω_{eg} . Probability that spontaneous emission occurs from a superposition of $\mu_0 - \mu_4$ to ν_0 . $0 \text{ m} < \Delta x < 3 \times 10^{-11} \text{ m}$, $1 \times 10^{14} < \omega_e < 6 \times 10^{14}$

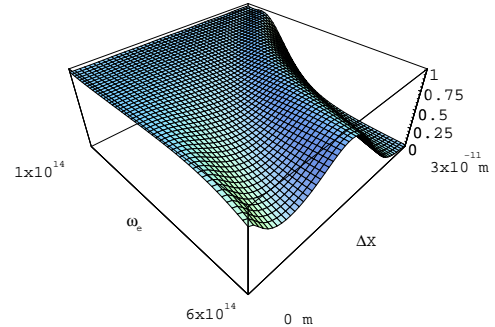


Figure 4.15: Small ω_{eg} . Probability that spontaneous emission occurs from a superposition of $\mu_0 - \mu_9$ to ν_0 . $0 \text{ m} < \Delta x < 3 \times 10^{-11} \text{ m}$, $1 \times 10^{14} < \omega_e < 6 \times 10^{14}$

	in CN	in calculations
ω_{eg}	1.74149×10^{15}	1.74149×10^{15}
ω_e	3.4143×10^{14}	$1 \times 10^{-14} - 6 \times 10^{-14}$
ω_g	3.8965×10^{14}	3.8965×10^{14}
Δx	$0.061 \times 10^{-10} \text{m}$	$0 \text{ m} - 0.3 \times 10^{-10} \text{m}$
mass	6.47 amu	6.47 amu

Figure 4.9: CN. Physical quantities used in the calculations.

upper eigenfunction does not cover all of the lower wave function, the superposition cannot do better. Therefore the maximization becomes better for smaller ω_e . This corresponds to a shallow potential.

4.1.4 Implementation

Most calculations were done by a C++ program that I wrote. *Mathematica* was used to calculate the coefficients of the oscillator eigenfunctions. The coefficients of the monomials of $e^{\frac{1}{2}x^2} \text{os}[n, x]$ were just written in a file and read in from my C++ program.³

The program then produced the exact solution of the harmonic potentials by shifting and rescaling the corresponding oscillator eigenfunctions depending on the parameters Δx and ω_e . The integration itself was done numerically by a *Gauss Legendre Integration* (see. [Press et al.(1994)]). Since all wave functions can be chosen to be real, all Franck Condon integrals are real. These Franck Condon integrals are used to calculate the elements of the matrix χ .

Recall the definition of χ :

$$\chi_{\mu\nu A}^{\mu_1\nu B} = r_{\mu\nu A}^{\mu_1\nu B} + r_{\mu_1\nu B}^{\mu\nu A*}$$

³Here $\text{os}[n, x]$ are just the normalized oscillator eigenfunctions.

$\text{os}[n, x] := e^{-\frac{1}{2}x^2} \frac{1}{\sqrt{2^n n! \pi^{\frac{1}{4}}}} \text{HermiteH}[n, x]$.

HermiteH is a Mathematica function for Hermite polynomials.

distance Δx is small enough to ensure a overlap of the "inner part" of the oscillator eigenfunctions, the spontaneous emission rate of the superposition rises considerably and stays large for smaller Δx .

The ω_e -dependence can be interpreted even simpler. A large ω_e results in a narrow upper wave function. If the broadest

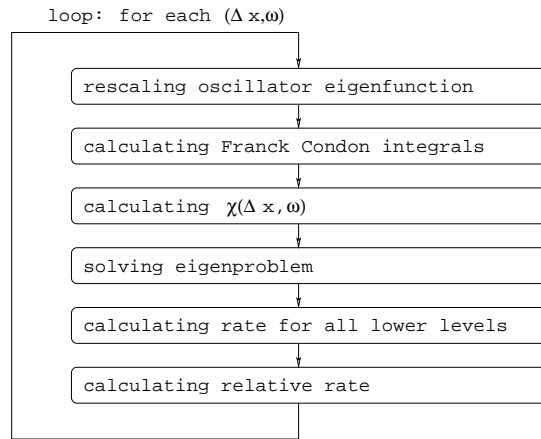


Figure 4.16: Flow chart of the program that calculates the data for the 3D plots.

with

$$r_{\mu\nu}^{\mu_1\nu_1} = \Theta(\mu_1 - \nu_1)\Theta(\mu - \nu)f_{\mu\nu}^*f_{\mu_1\nu_1}(\mu_1 - \nu_1)^3.$$

This matrix has the dimension m , where m is the number of upper levels. The indices ν_A and ν_B are parameters that specify the lower level (or if $\nu_A \neq \nu_B$ the coherence) to that the spontaneous emission rate should be maximized. The eigenvector of χ with the largest eigenvalue represents the superposition that maximizes the rate.⁴(See also 3.5.) We are only interested in the probability and not in the coherences. This implies $\nu_A = \nu_B$. The relative rate to ν_0 is

$$\Gamma_{\max}^{\text{rel}} = \frac{\Gamma_0(\text{max. superpos.})}{\sum_{\nu} \Gamma_{\nu}(\text{max. superpos.})} = \frac{\sum_{\mu\mu_1} \chi_{\mu\nu_0}^{\mu_1\nu_0} a_{\mu} a_{\mu_1}^*}{\sum_{\nu} \sum_{\mu\mu_1} \chi_{\mu\nu}^{\mu_1\nu} a_{\mu} a_{\mu_1}^*}. \quad (4.3)$$

Here $a_{\mu} := a(\nu_0)_{\mu}$ is the μ th component of the eigenvector of χ with the largest eigenvalue.

*DSYEVR*⁵, a *LAPACK* routine, was used to find the eigenvalues and the eigenvectors of the matrix χ . For further information about LAPACK have a look at [LAPACK(2002)]. LAPACK routines are Fortran routines. The integration of DSYEVR into the C++ program was done with the help of the *Template Numerical Toolkit (TNT)*. The home page of TNT can be found at [TNT(2002)]. Unfortunately the TNT project seems to stagnate.

4.2 Example: Maximization for molecules with Lennard Jones potentials

In this section the transition rates for Lennard Jones potentials are calculated. Lennard Jones potentials are not symmetric and the separation of the energy levels is not constant. If the symmetry and the equally spaced energy levels of the harmonic potentials in the previous section produced some special effect, this effect cannot occur here. The Lennard Jones potential has the following form:

$$V(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right). \quad (4.4)$$

The minimum of this potential is at $(2^{\frac{1}{6}}\sigma, -\epsilon)$.

4.2.1 Large ω_{eg}

For the case $\omega_{\text{eg}} \gg \Delta\omega$ I used again the N_2 molecule. The minimum of the ground state adiabatic potential curve of N_2 is $\text{X}(1.0977 \times 10^{-10} \text{ m}, -1.536 \times 10^{-18} \text{ Joule})$. The first excited state has a minimum at $\text{A}(1.287 \times 10^{-10} \text{ m}, -0.528 \times 10^{-18} \text{ Joule})$. Here I put the zero line of the energy $1.536 \times 10^{-18} \text{ Joule}$ above the minimum of

⁴The elements of the vector are the coefficients of the superposition.

⁵DSYEVR is specialized in solving eigenproblems of symmetric matrices.

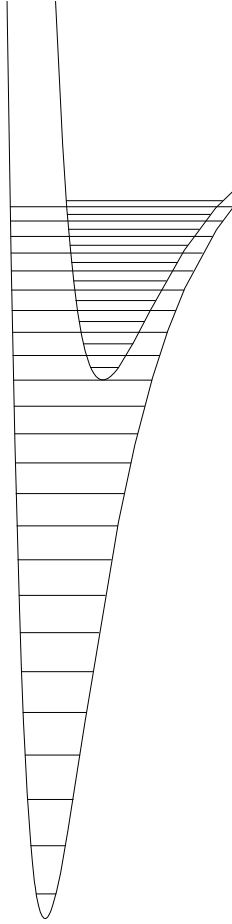


Figure 4.17: Lennard Jones potential fit for a N_2 -like molecule. 10 upper and 24 lower levels are displayed.

the potential of the ground state and further assumed that the dissociation energies for the X and the A state are the same.⁶ The latter assumption is based on Fig. 2.3. The dissociation energies of X and A states in diatomic molecules are in general *not* the same. The calculation yields Fig.4.17. The fit is not very good, because in the real molecule (see Fig. 2.3) there are 24 ν states below the lowest μ state in contrast to 15 states in Fig.4.17. However, I discuss these potentials here, because it is a nice example that reveals some important features of

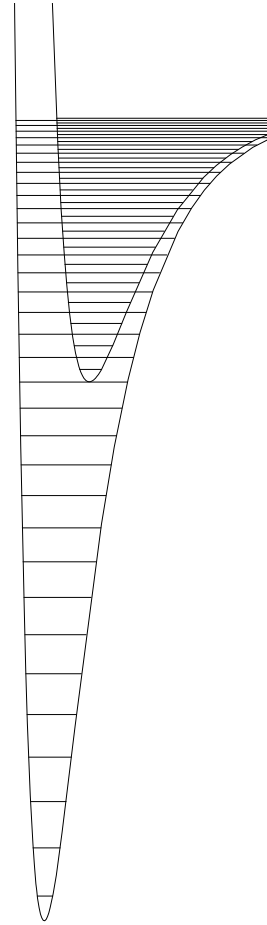


Figure 4.18: Lennard Jones potential fit for a N_2 -like molecule. 20 upper and 34 lower levels are displayed. Here the limits of my calculations can be seen. The most upper levels are perturbed by the borders of the integration area.

μ	coefficient		
0	-0.0199706	1	0.0497566
2	-0.0921149	3	0.145751
4	-0.208351	5	0.277065
6	-0.348873	7	0.420842
8	-0.490309	9	0.554976

Figure 4.19: N_2 -like molecule. Coefficients for the superposition of 10 levels.

⁶I assumed $\epsilon_X = 1.536 \times 10^{-18}$ Joule and $\epsilon_A = \epsilon_X - \hbar\omega_{eg} = 0.528 \times 10^{-18}$ Joule

the maximization of the spontaneous emission rate.

First a superposition of 10 levels is examined. In this case 24 ν levels are below the highest μ level. This can also be seen in Fig.4.17. The superposition that maximizes the spontaneous emission to ν_0 can be seen in Fig.4.19. The calculated relative spontaneous emission rate from μ_0 to ν_0 is 3.998×10^{-5} . The relative spontaneous emission rate of the superposition $\mu_0 - \mu_9$ to ν_0 is 0.01488.

It is possible to improve the result by taking 20 upper levels. Then 34 ν levels are lying below level μ_{19} (Fig.4.18).⁷ With the help of 20 levels, the relative transition rate can be enhanced up to 0.05285 (again compared to 3.998×10^{-5} for a $\mu_0 - \nu_0$ transition).

From the shape of the potentials it is clear that the transition rate cannot be enhanced significantly more. The very steep border of the upper potential forbids an overlap of the upper wave functions with the left part of the ν_0 ground state function. If the minimum of the upper potential was located at smaller R , the overlap would be much better. The spontaneous emission rate cannot be enhanced considerably in molecules that have a steep repulsive part in the upper potential⁸ and whose equilibrium internuclear distance of the upper state is much larger than the equilibrium distance of the lower potential.

μ	coefficient	μ	coefficient
0	-0.00856741	1	0.0211726
2	-0.0388972	3	0.061105
4	-0.0867675	5	0.114673
6	-0.143575	7	0.172295
8	-0.199787	9	0.225166
10	-0.247727	11	0.266941
12	-0.282446	13	0.294026
14	-0.301595	15	0.305178
16	-0.30489	17	0.300917
18	-0.293499	19	0.28292

Figure 4.20: N₂-like molecule. Coefficients for the superposition of 20 levels.

4.2.2 CN-like molecules

A better approximation can be achieved, when at the minimum $r_0 = 2^{-\frac{1}{6}}\sigma$ of the Lennard Jones potential the curvature⁹ has the same value as in the harmonic potential. If $V(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right)$, then $V''(r) = 4\epsilon\left(156\frac{\sigma^{12}}{r^{14}} - 42\frac{\sigma^6}{r^8}\right)$. And $V''(r_0) = \frac{36\epsilon}{r_0^2}$. Therefore the curvature at r_0 and the knowledge of r_0 is enough to determine the Lennard Jones potential. From Fig.4.9 it is also known that $E_{eg} = \hbar\omega_{eg} = 1.8365 \times 10^{-19}$ Joule. From [Radzig and Smirnov(1985)] we get $r_0^X = 1.172 \times 10^{-10}$ m and $r_0^A = 1.233 \times 10^{-10}$ m. Now it is possible to calculate the

⁷ Unfortunately, for such high lying levels the algorithm to find the energy eigenvalues is not ideal. The borders of the integration area shift the energy eigenvalues and change the eigenfunctions of the uppermost levels. For more information about the implementation have a look at 4.2.3. One could have chosen a more sophisticated calculation, but the results are anyway only qualitative.

⁸for example the left part of the upper potential in Fig.4.18

⁹The curvature of a harmonic potential at its minimum is $m\omega_{e/g}^2$. With $m = 1.0743 \times 10^{-26}$ kg for the reduced mass of CN.

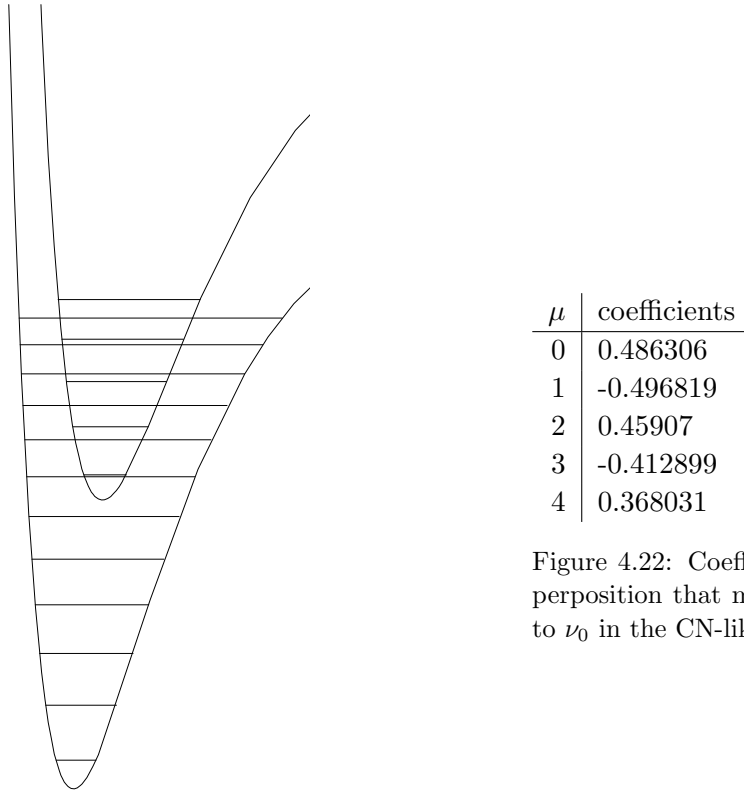


Figure 4.21: Lennard Jones potential fit for a CN-like molecule. 5 upper and 12 lower levels are displayed.

Lennard Jones potentials for the two lowest levels of CN.¹⁰

They are also shown in Fig.4.21. The relative transition rate to ν_0 can be almost doubled with only five upper levels. The $\mu_0 \rightarrow \nu_0$ rate is 0.560712. If the superposition of $\mu_0 - \mu_4$ is taken, the transition rate can be enhanced to 0.944259. The coefficients of the superposition are shown in Fig. 4.22.

4.2.3 Implementation

The Lennard Jones Potentials for the N₂-like molecule were calculated by using r_0 and reading the dissociation limit from Fig.2.3. For CN a better approximation was obtained by using the curvature at r_0 . The potentials then were discretized by taking the potential at 5000 equally spaced points. The space in between the points was $\Delta = 10^{-13}$ m for both molecules. For the first molecule the interval (0.5×10^{-10} m -

¹⁰I write them here explicitly, because they are also used in 4.3:

$$V_X(r) = 2.48946 \times 10^{-18} \left(\frac{1.679079 \times 10^{-120}}{r^{12}} - \frac{1.29579 \times 10^{-60}}{r^6} \right) \text{ Joule m}$$

$$V_A(r) = 1.8365 \times 10^{-19} + 2.11558 \times 10^{-18} \left(\frac{3.08671 \times 10^{-120}}{r^{12}} - \frac{1.75690 \times 10^{-60}}{r^6} \right) \text{ Joule m}$$

5.5×10^{-10} m) was used. For the CN molecule (0.8×10^{-10} m - 5.8×10^{-10} m) was used. Then the Laplace operator was replaced by the discrete Laplace operator

$$\text{Laplacian} = \frac{1}{\Delta^2} \begin{pmatrix} -2 & 1 & 0 & \cdots & \cdots \\ 1 & -2 & 1 & 0 & \cdots \\ 0 & 1 & -2 & 1 & 0 \\ \cdots & 0 & 1 & -2 & 1 \\ \cdots & \cdots & 0 & 1 & -2 \end{pmatrix}. \quad (4.5)$$

This form can be derived from the discrete definition of the derivative:

$$f'(x_0) = \frac{f(x_0 + \frac{\Delta}{2}) - f(x_0 - \frac{\Delta}{2})}{\Delta} \quad (4.6)$$

$$\begin{aligned} f''(x_0) &= \frac{f'(x_0 + \frac{\Delta}{2}) - f'(x_0 - \frac{\Delta}{2})}{\Delta} \\ &= \frac{1}{\Delta^2} (f(x_0 + \Delta) - 2f(x_0) + f(x_0 - \Delta)). \end{aligned} \quad (4.7)$$

The resulting Hamilton equation is just an algebraic equation. The eigenvalues and eigenvectors were found using *DSTEVR*, a LAPACK routine which is specialized on real tridiagonal matrices. The resulting eigenvectors were just multiplied to get the Franck Condon integrals.¹¹ The Franck Condon integrals and the energy eigenvalues were written to a file. A C++ program, similar to the program in 4.1.4, used this file to calculate the matrix χ . Again the LAPACK routine *DSYEV*R was used to find the eigen vectors that represent the superposition that maximizes the transition.

The relative rate to ν_0 was calculated in the same manner as in 4.1.4.

4.3 Time dependent calculation for a *CN*-like molecule

So far the relative transition rate was only calculated at the time $t = 0$. In section 3.6 it was shown that for large times the effect of the superposition should get smaller and smaller. In this section the population $P_{\nu_0}(t)$ of ν_0 is calculated as a function of time. The differential equation (3.47) is integrated numerically with the help of the Runge-Kutta algorithm. The result can be seen in Fig.4.23 and in Fig.4.24. The latter is just a magnified plot of the same graph.

The numerical calculations are in perfect agreement with the results from section 3.6. For $t \gg \tau_{\text{vib}}$ the spontaneous emission rate to ν_0 should be just additive, i.e. the rate to ν_0 should be just the sum $\sum_{\mu} \Gamma_{\nu_0}^{\mu}$, where $\Gamma_{\nu_0}^{\mu}$ is just the rate of one single state μ to ν_0 . Exactly this behavior can be seen in Fig.4.23.

The transition rate of the superposition differs only on a time scale τ_{vib} significantly from the rates of single states. On this time scale it should be possible to enhance (or suppress) spontaneous emission to special levels. Often the enhancement or suppression can be even considerable.

¹¹inner product

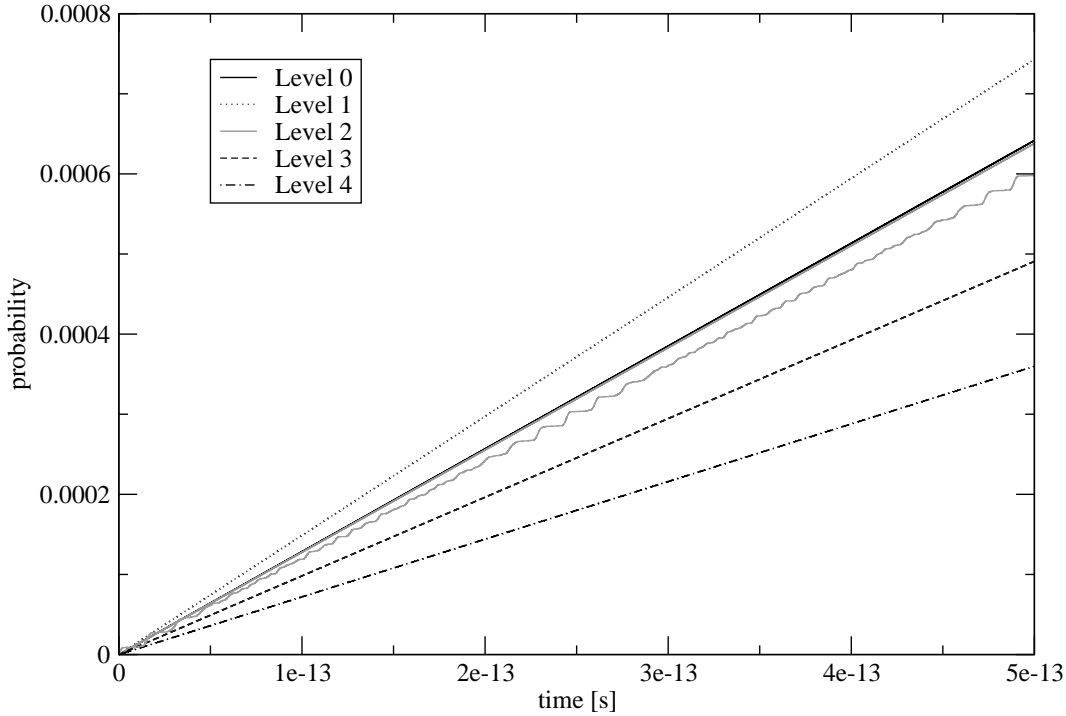


Figure 4.23: The population of level ν_0 of CN for $t \in (0s, 5 \times 10^{-13}s)$. The straight lines stand for the population if the molecule initially is in state $\mu \in [0, 4]$. In this case, there is no interference and the time evolution of the population is just like $1 - e^{-\Gamma_{\nu_0}^{\mu} t}$. The wavy line is the line when the molecule is initially in the calculated superposition. For large times it must lie between the straight lines. Exactly this can be seen here.

4.3.1 Implementation

The integration of the differential equation (3.47) was performed by a self written C++ program. The Liouville super operator was expressed in its matrix form.¹² The resulting set of coupled first order linear differential equations was integrated by a simple fourth-order *Runge-Kutta* algorithm¹³. The Liouville operator in the case of our CN molecule of the previous section has the dimension $K = M^2 + N^2 = 5^2 + 12^2 = 169$. The formula for the dimension K is derived in appendix B. M is the number of states contributing to the superposition and N is the number of lower states. When five upper levels are considered, it is necessary to include 12 lower levels, because a transition to each of these levels is possible energetically (see also Fig.4.21). The calculation a step size of $\Delta = 10^{-17}s$ was used.

¹²Actually, there does not exist a special matrix form, different representations are possible. In our case the matrix can even have a lower dimension than in the general case. For details have a look at appendix B.

¹³There are different fourth-order Runge-Kutta algorithms. The algorithm used here is the "classical" one (see [Press et al.(1994)]).

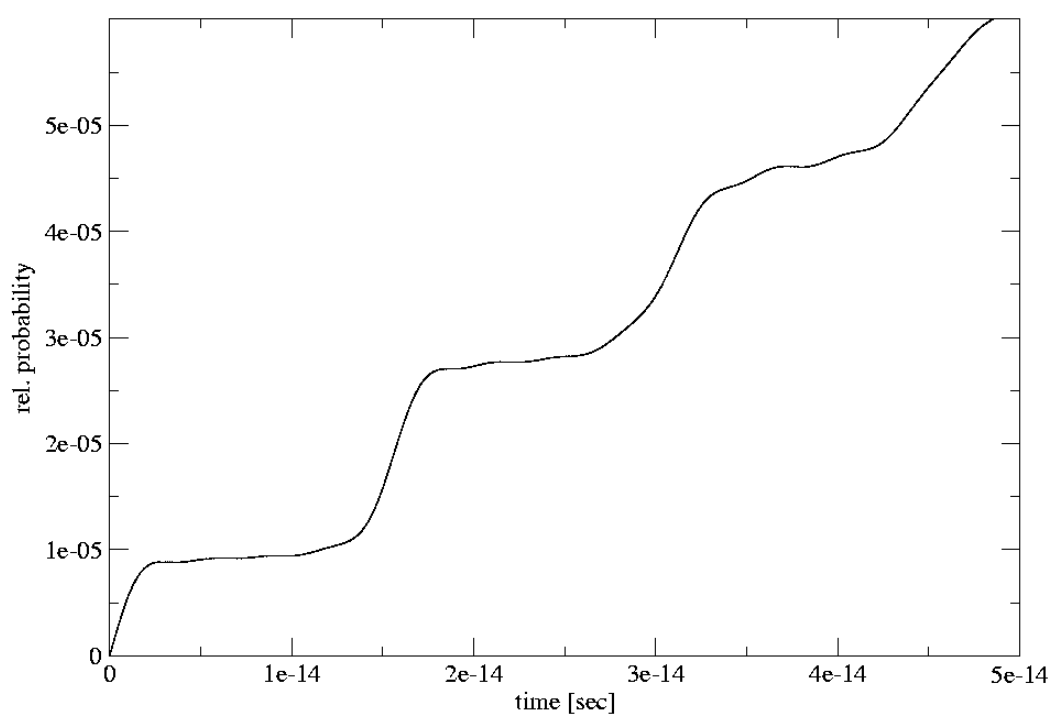


Figure 4.24: The population of ν_0 of *CN* for $t \in (0s, 5 \times 10^{-14}s)$.

Chapter 5

Conclusion

In my calculations I demonstrated that spontaneous emission to a special lower vibrational state in a molecule can be sometimes considerably enhanced. The enhancement depends crucially on the involved Franck Condon factors. An good enhancement is only possible if there exists a superposition of wave functions in the upper electronic state that has a significant overlap with the lower wave function of concern. For large energy separation of the electronic levels E_{eg} ¹ the superposition that maximizes the transition rate to ν_0 is easy to find. The coefficient for a level $|\check{\mu}\rangle$ in the superposition is just the scalar product of this level with $|\check{\nu}_0\rangle$.² In the general case, the problem turned out to be a simple eigenvalue problem for the matrix χ (see (3.52)) which comprises only the involved Franck Condon integrals and the energy eigenvalues of the respective states. The enhancement described in this paragraph however only works for times $t \ll \tau_{vib}$. (see (3.73)). This is the time scale on which the wave functions of the upper states start to de-phase considerably due to different energy eigenvalues.

In chapter 4 some example calculations for the maximization effect above were carried out. First the adiabatic potentials of the molecule were considered to be harmonic and the maximization of the relative spontaneous emission rate to the lower ground state was calculated for different harmonic potentials using the displacement Δx of the two minima and the frequency ω_e as parameters.³ This yielded some qualitative results about the question when it is possible to enhance the spontaneous emission rate to the lower ground state.

Later the Lennard Jones potential was used to approximate the adiabatic potentials of N_2 and CN .⁴ The corresponding Franck Condon integrals were calculated and again the transition rate to the lower ground state maximized by a superposition. For CN this worked quite well. With a superposition of five upper levels the relative

¹ compared with the energy separation between the lowest excited state and the highest populated excited state

²Again the $\check{\cdot}$ stresses that this is the nuclear wave function $P(R)$. The electronic part of the wave function is not included.

³The potential of the upper state was assumed to be a harmonic potential with energy eigenvalues that are separated by $\hbar\omega_e$.

⁴The calculation was done without rotational levels.

spontaneous emission rate could be enhanced from approximately 56% to 94%. But for N_2 even ten upper levels could not form a superposition that produced a relative spontaneous emission rate larger than 6%. A closer look at the N_2 -potentials revealed that due to the steep rise of the potential for small R the upper wave functions have a small overlap with the lower wave function. The latter has a smaller mean internuclear distance \bar{R} and a considerable part of the wave function lies beyond the steep rise of the upper potential. This results in a small overlap for all upper wave functions with the ground state wave function of the lower electronic state. (See Fig. 4.17.)

At the end of chapter 4 the population of the ground state of the lower level of CN is calculated as a function of time. As expected the transition rate cannot be enhanced on a time scale much larger than τ_{vib} . It turns out that the different energies of the upper levels in the superposition result in a rather complicated oscillatory variation around the expected transition rate which is only the sum of the transition rates of the single upper levels weighted with the corresponding Franck Condon factors times the coefficient of the superposition.

Finally, the question should be posed if the calculation can be used in some experimental setup or what kind of further refinement of the model could be thought of. It should be stressed that even with the present model a modification of the spontaneous emission rate on the time scale τ_{vib} is possible. Unfortunately τ_{vib} is around 10^{-14} s and therefore very small. The most natural way of reducing the time constraint, is just to look for molecules with very shallow adiabatic excited state potentials. This would result in a larger τ_{vib} . It can however not be expected that this can change τ_{vib} more than one or two orders of magnitude.

Another way to remove the time constraint could be to couple a strong laser to the molecule. As shown in appendix A, a weak laser cannot change the spontaneous emission rate noticeable. Short laser pulses could be used to counter the de-phasing of the wave functions of the upper levels. Unfortunately this laser pulses would have to be very short (order of 10^{-16} – 10^{-15} s or shorter) and should be repeated with a frequency of approximately 10^{14} s $^{-1}$. In a review article Steinmeyer *et al.* [Steinmeyer et al.(1999)] mention that sub-10-fs laser (pulse duration less than 10^{-14} s) already exist. But to my knowledge no laser can repeat the pulses fast enough.

Another possible way could be to couple a *strong* lasers permanently to the system to counteract the de-phasing. Here the problem is probably that *continuous wave lasers* are not strong enough. All the above thoughts on strong laser interaction are *not* based on any calculations of my part. It is possible that the above suggestions do not even work theoretically, despite experimentally.

The summary of my thesis is that spontaneous emission enhancement in vibrating molecules is in principle possible, but probably only on very small time scale.

Appendix A

Spontaneous emission in weak laser fields

The following section discusses the reason why it is feasible to work without dressed states even when a laser is involved. It will be shown that when the photon-atom interaction ¹ is not too large, the term describing the laser field can be added as an extra term to the master equation. In order to simplify the calculation a two level atom is considered.

The following Hamiltonian describes the system:

$$H = \hbar \frac{\omega_A}{2} \sigma_3 + \hbar \Omega (\mathbf{S}_+ e^{-i\omega_L t} + \mathbf{S}_- e^{i\omega_L t}) + \hbar \sum_k \omega_k a_k^\dagger a_k + \hbar \sum_k (g_k \mathbf{S}_+ a_k + g_k^* \mathbf{S}_- a_k^\dagger). \quad (\text{A.1})$$

Here the first part is the energy of the atom, the second part the interaction of the atom with a classical field (the laser field), the third part the energy of the photon field (in our case the vacuum), and the last part the interaction between the photon field and the atom. \mathbf{S}_+ and \mathbf{S}_- are lowering and raising operators for the two level atom:

$$\mathbf{S}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \mathbf{S}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \quad (\text{A.2})$$

The basis is chosen such that

$$\vec{e} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \vec{g} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (\text{A.3})$$

are the excited state e and the ground state g of the two-level atom.

¹as well as the photon-molecule interaction

To show the additive character of the laser field term, equation (A.1) will first be expressed in the interaction picture. Then the master equation in the interaction picture will be derived (using results from 2.1). The assumptions mentioned above lead to approximations during the derivation of the master equation. Finally the master equation will be transformed back to the Schrödinger picture and the additive character of the laser field term will become apparent.

The interaction of the photon field with the atom is considered as the perturbation. The laser field is included into H_0 . Since the considered photon field is the vacuum field, this is a sensible assumption. The calculations are much simpler if a time independent H_0 is used. In order to obtain this, a unitary transformation U is applied to equation (A.1).

$$U = \begin{pmatrix} e^{-i\omega_L t} & 0 \\ 0 & 1 \end{pmatrix}. \quad (\text{A.4})$$

U has the following useful properties:

$$U^\dagger \mathbf{S}_+ e^{-i\omega_L t} U = \mathbf{S}_+ \quad (\text{A.5})$$

$$U^\dagger \mathbf{S}_- e^{i\omega_L t} U = \mathbf{S}_- \quad (\text{A.6})$$

$$U^\dagger \sigma_3 U = \sigma_3 \quad (\text{A.7})$$

$$-i\hbar U^\dagger \dot{U} = -\frac{\omega_L}{2}(\sigma_3 + 1). \quad (\text{A.8})$$

Application of this unitary transformation to a state in the Hamilton equation yields in

$$i\hbar(\dot{U}|\varphi\rangle + U|\dot{\varphi}\rangle) = HU|\varphi\rangle.$$

This is equivalent to

$$i\hbar|\dot{\varphi}\rangle = (U^\dagger HU - i\hbar U^\dagger \dot{U})|\varphi\rangle =: \tilde{H}|\varphi\rangle \quad (\text{A.9})$$

with

$$\begin{aligned} \tilde{H} = & \hbar \left(-\frac{\omega_L}{2} 1 - \frac{\Delta}{2} \sigma_3 + \Omega(\mathbf{S}_+ + \mathbf{S}_-) + \sum_k \omega_k a_k^\dagger a_k \right. \\ & \left. + \sum_k (g_k \mathbf{S}_+ e^{i\omega_L t} a_k + g_k^* \mathbf{S}_- e^{-i\omega_L t} a_k^\dagger) \right). \end{aligned} \quad (\text{A.10})$$

Here is $\Delta = \omega_L - \omega_A$ is the detuning of the laser frequency with respect to the eigenfrequency of the atom. For the sake of simplicity, the \sim on \tilde{H} will be dropped.

The *dressed state picture* can be understood as the *interaction picture* where the laser field is incorporated in H_0 :

$$H_0 = H_{\text{AL}} + H_{\text{R}} \quad (\text{A.11})$$

$$H_{\text{AL}} = -\hbar \frac{\omega_{\text{L}}}{2} 1 - \frac{\Delta}{2} \sigma_3 + \Omega(\mathbf{S}_+ + \mathbf{S}_-) \quad (\text{A.12})$$

$$H_{\text{R}} = \hbar \sum_k a_k^\dagger a_k \omega_k. \quad (\text{A.13})$$

The Hamiltonian has therefore the following form:

$$H = \underbrace{\left(-\hbar \frac{\omega_{\text{L}}}{2} 1 - \frac{\Delta}{2} \sigma_3 + \Omega(\mathbf{S}_+ + \mathbf{S}_-) \right)}_{H_{\text{AL}}} + \underbrace{\hbar \sum_k a_k^\dagger a_k \omega_k}_{H_{\text{R}}} + \underbrace{\hbar \sum_k (g_k \mathbf{S}_+ e^{i\omega_{\text{L}}} a_k + g_k^* \mathbf{S}_- e^{-i\omega_{\text{L}}} a_k^\dagger)}_{H_{\text{int}}}. \quad (\text{A.14})$$

Application of $U_{\text{I}} := e^{-iH_0 t} = e^{-iH_{\text{AL}} t} e^{-iH_{\text{R}} t}$ on the state in the Schrödinger equation results in the Schrödinger equation in the interaction picture.

$$\begin{aligned} i\hbar |\dot{\Psi}\rangle &= (-i\hbar U_{\text{I}}^\dagger \dot{U}_{\text{I}} + U_{\text{I}}^\dagger \tilde{H} U_{\text{I}}) |\Psi\rangle \\ &= (-H_0 + H_0) |\Psi\rangle + U_{\text{I}}^\dagger \underbrace{\hbar \sum_k (g_k \mathbf{S}_+ e^{i\omega_{\text{L}}} a_k + g_k^* \mathbf{S}_- e^{-i\omega_{\text{L}}} a_k^\dagger)}_{H_{\text{int}}^{\text{I}}} U_{\text{I}} |\Psi\rangle. \end{aligned} \quad (\text{A.15})$$

A closer look at H_0 reveals that H_{AL} only works on the two dimensional subspace describing the atom. H_{R} only affects the radiation field. In addition H_{AL} and H_{R} commute. When \mathbf{S}_+ and \mathbf{S}_- are expressed in the basis of the eigenvectors of H_{AL} , the effect of the transformation U_{IS} on \mathbf{S}_+ or \mathbf{S}_- in H_{int} is simple.

H_{AL} has the eigenvalues

$$\frac{E_{\pm}}{\hbar} = -\frac{\omega_{\text{L}}}{2} \pm \underbrace{\sqrt{\left(\frac{\Delta}{2}\right)^2 + \Omega^2}}_W \quad \text{always } W \geq \frac{\Delta}{2} \quad (\text{A.16})$$

and the eigenvectors:

$$\varphi_{\pm}^{\text{AL}} = \frac{1}{\sqrt{2W}} \begin{pmatrix} \frac{\Omega}{\sqrt{W \pm \frac{\Delta}{2}}} \\ \pm \sqrt{W \pm \frac{\Delta}{2}} \end{pmatrix}. \quad (\text{A.17})$$

Therefore the matrix for the basis transformation to the basis of eigenvectors of H_{AL} has the following form:

$$\mathbf{A} = \frac{1}{\sqrt{2W}} \begin{pmatrix} \frac{\Omega}{\sqrt{W+\frac{\Delta}{2}}} & \sqrt{W+\frac{\Delta}{2}} \\ \frac{\Omega}{\sqrt{W-\frac{\Delta}{2}}} & -\sqrt{W-\frac{\Delta}{2}} \end{pmatrix}. \quad (\text{A.18})$$

The inverse transformation looks like this:

$$\mathbf{A}^{-1} = \frac{1}{\sqrt{2W}} \begin{pmatrix} \frac{\Omega}{\sqrt{W+\frac{\Delta}{2}}} & \frac{\Omega}{\sqrt{W-\frac{\Delta}{2}}} \\ \sqrt{W+\frac{\Delta}{2}} & -\sqrt{W-\frac{\Delta}{2}} \end{pmatrix}. \quad (\text{A.19})$$

Now \mathbf{S}_+ and \mathbf{S}_- can be expressed in the basis of the eigenvectors of H_{AL} :

$$\mathbf{S}_+^{\text{AL}} = \mathbf{A}\mathbf{S}_+\mathbf{A}^{-1} \quad \mathbf{S}_-^{\text{AL}} = \mathbf{A}\mathbf{S}_-\mathbf{A}^{-1} \quad (\text{A.20})$$

$$\mathbf{S}_+^{\text{AL}} = \begin{pmatrix} \frac{\Omega}{2W} & \frac{1}{2}(\frac{\Delta}{2W} - 1) \\ \frac{1}{2}(\frac{\Delta}{2W} + 1) & -\frac{\Omega}{2W} \end{pmatrix} \quad \mathbf{S}_-^{\text{AL}} = \begin{pmatrix} \frac{\Omega}{2W} & \frac{1}{2}(\frac{\Delta}{2W} + 1) \\ \frac{1}{2}(\frac{\Delta}{2W} - 1) & -\frac{\Omega}{2W} \end{pmatrix}. \quad (\text{A.21})$$

In Dirac notation this means:²

$$\mathbf{S}_+ = \frac{\Omega}{2W} (|+\rangle\langle+| - |-\rangle\langle-|) + \frac{1}{2}(\frac{\Delta}{2W} - 1)|+\rangle\langle-| + \frac{1}{2}(\frac{\Delta}{2W} + 1)|-\rangle\langle+| \quad (\text{A.22})$$

$$\mathbf{S}_- = \frac{\Omega}{2W} (|+\rangle\langle+| - |-\rangle\langle-|) + \frac{1}{2}(\frac{\Delta}{2W} + 1)|+\rangle\langle-| + \frac{1}{2}(\frac{\Delta}{2W} - 1)|-\rangle\langle+| \quad (\text{A.23})$$

Now \mathbf{S}_+ and \mathbf{S}_- are expressed in terms of $|\pm\rangle\langle\pm|$. The states $|\pm\rangle$ are the eigenstates of H_{AL} .³

Now it is necessary to calculate the effect of U_I^\dagger and U_I on a_k and $|\pm\rangle\langle\pm|$ which appear in H_{int} . Since U_I^\dagger appears on the left hand side and U_I on the right hand side, only the parts of U_I that do not commute with a_k or $|\pm\rangle\langle\pm|$ must be considered. The other parts cancel each other. For the a_k this is the radiation part $e^{-iH_R t}$ of U_I . For $|\pm\rangle\langle\pm|$ it is $e^{-iH_{AL} t}$.

²The above index AL was used to stress that $\mathbf{S}_\pm^{\text{AL}}$ is expressed in the basis of the eigenvectors of H_{AL} . The Dirac notation however is a basis free notation.

³In the old basis the states $|\pm\rangle$ are $\tilde{\varphi}_\pm^{\text{AL}}$.

$$\begin{aligned}
U_I^\dagger a_k U_I &= e^{i\omega_k t a_k^\dagger a_k} a_k e^{-i\omega_k t a_k^\dagger a_k} \\
&= \sum_{n=0}^{\infty} \frac{(i\omega_k t)^n}{n!} K_n \quad K_0 = a_k \text{ and } K_{n+1} = [a_k^\dagger a_k, K_n] \\
&= e^{-i\omega_k t} a_k.
\end{aligned} \tag{A.24}$$

Expressed in $|+\rangle\langle+|$ and $|-\rangle\langle-|$ H_{AL} has the following form:

$$H_{\text{AL}} = \hbar \left(\frac{\omega_L}{2} + W(|+\rangle\langle+| - |-\rangle\langle-|) \right). \tag{A.25}$$

With the help of this $e^{-iH_{\text{AL}}t}$ can be simplified even more⁴:

$$\begin{aligned}
e^{-iH_{\text{AL}}t} &= e^{-\frac{i}{2}\omega_L t} e^{-itW(|+\rangle\langle+| - |-\rangle\langle-|)} \\
&= e^{-\frac{i}{2}\omega_L t} (|+\rangle\langle+| e^{-itW} + |-\rangle\langle-| e^{itW}).
\end{aligned} \tag{A.26}$$

$U_I^\dagger |\pm\rangle\langle\pm| U_I$ can easily be calculated:

$$\begin{aligned}
U_I^\dagger |+\rangle\langle+| U_I &= |+\rangle\langle+| \\
U_I^\dagger |-\rangle\langle-| U_I &= |-\rangle\langle-| \\
U_I^\dagger |+\rangle\langle-| U_I &= e^{2itW} |+\rangle\langle-| \\
U_I^\dagger |-\rangle\langle+| U_I &= e^{-2itW} |-\rangle\langle+|.
\end{aligned} \tag{A.27}$$

Using (A.22) for \mathbf{S}_+ and (A.23) for \mathbf{S}_- , the Schrödinger equation (A.15) becomes in the interaction picture:

$$i\hbar |\dot{\Psi}_I\rangle = H_{\text{int}}^I |\Psi_I\rangle \tag{A.28}$$

with

$$H_{\text{int}}^I = \sum_k \left\{ g_k e^{-i(\omega_k - \omega_L)t} a_k \mathbf{S}_+^I(t) + g_k^* e^{i(\omega_k - \omega_L)t} a_k^\dagger \mathbf{S}_-^I(t) \right\} \tag{A.29}$$

and

$$\mathbf{S}_-^I(t) = \frac{\Omega}{2W} (|+\rangle\langle+| - |-\rangle\langle-|) + \frac{1}{2} \left(\frac{\Delta}{2W} - 1 \right) |+\rangle\langle-| e^{2itW} + \frac{1}{2} \left(\frac{\Delta}{2W} + 1 \right) |-\rangle\langle+| e^{-2itW} \tag{A.30}$$

$$\begin{aligned}
\mathbf{S}_+^I(t) = \mathbf{S}_-^{\dagger I}(t) &= \frac{\Omega}{2W} (|+\rangle\langle+| - |-\rangle\langle-|) + \frac{1}{2} \left(\frac{\Delta}{2W} + 1 \right) |+\rangle\langle-| e^{2itW} \\
&\quad + \frac{1}{2} \left(\frac{\Delta}{2W} - 1 \right) |-\rangle\langle+| e^{-2itW}.
\end{aligned} \tag{A.31}$$

⁴since $|\pm\rangle\langle\pm|$ are projectors

With the definition of the Liouville super operator

$$\mathcal{L}^I = \frac{1}{\hbar}[H_{\text{int}}^I, \dots] \quad (\text{A.32})$$

the result for the master equation in the interaction picture (see equation (2.27)) can be used:

$$\begin{aligned} |0_{\text{R}}\rangle\langle 0_{\text{R}}|\dot{\sigma}_{\text{I}} &= -\text{P}\mathcal{L}^I(t) \int_0^t d\tau \mathcal{L}^I(t-\tau) |0_{\text{R}}\rangle\langle 0_{\text{R}}|\sigma_{\text{I}}(t-\tau) \\ &= -\frac{1}{\hbar^2} |0_{\text{R}}\rangle\langle 0_{\text{R}}|\text{Tr}_{\text{R}}[H_{\text{int}}^I(t), \int_0^t d\tau [H_{\text{int}}^I(t-\tau), |0_{\text{R}}\rangle\langle 0_{\text{R}}|\sigma_{\text{I}}(t-\tau)]]]. \end{aligned} \quad (\text{A.33})$$

This reduces to (see also chapter 3):

$$\begin{aligned} \dot{\sigma}_{\text{I}} &= \frac{1}{\hbar^2} \int_0^t d\tau (- \langle 0_{\text{R}}|H_{\text{int}}^I(t)H_{\text{int}}^I(t-\tau)|0_{\text{R}}\rangle\langle 0_{\text{R}}|\sigma_{\text{I}}(t-\tau)|0_{\text{R}}\rangle \\ &\quad + \langle 1_{\text{R}}|H_{\text{int}}^I(t)|0_{\text{R}}\rangle\langle 0_{\text{R}}|\sigma_{\text{I}}(t-\tau)H_{\text{int}}^I(t-\tau)|1_{\text{R}}\rangle \\ &\quad + \langle 1_{\text{R}}|H_{\text{int}}^I(t-\tau)|0_{\text{R}}\rangle\langle 0_{\text{R}}|\sigma_{\text{I}}(t-\tau)H_{\text{int}}^I(t)|1_{\text{R}}\rangle \\ &\quad - \langle 0_{\text{R}}||0_{\text{R}}\rangle\langle 0_{\text{R}}|\sigma_{\text{I}}(t-\tau)H_{\text{int}}^I(t-\tau)H_{\text{int}}^I(t)|0_{\text{R}}\rangle) \\ &= -\frac{1}{\hbar^2} \int_0^t d\tau (G(\tau)\mathbf{S}_+^I(t)\mathbf{S}_-^I(t-\tau)\sigma_{\text{I}}(t-\tau) - G(-\tau)\mathbf{S}_-^I(t)\sigma_{\text{I}}(t-\tau)\mathbf{S}_+^I(t-\tau) \\ &\quad - G(\tau)\mathbf{S}_-^I(t-\tau)\sigma_{\text{I}}(t-\tau)\mathbf{S}_+^I(t) + G(-\tau)\sigma_{\text{I}}(t-\tau)\mathbf{S}_+^I(t-\tau)\mathbf{S}_-^I(t)) \end{aligned} \quad (\text{A.34})$$

with

$$G(\tau) = \sum_{ks} |g_k|^2 e^{-i(\omega_k - \omega_{\text{L}})\tau}. \quad (\text{A.35})$$

In the *Markov approximation* the border of the time integral is replaced by ∞ and the evolution of the reduced density operator is mainly determined by H_0 . In the interaction picture this means $\sigma_{\text{I}}(t-\tau) \approx \sigma_{\text{I}}(t)$. The above equation becomes

$$\begin{aligned} \dot{\sigma}_{\text{I}} &= -\frac{1}{\hbar^2} \int_0^\infty d\tau (G(\tau)\mathbf{S}_+^I(t)\mathbf{S}_-^I(t-\tau)\sigma_{\text{I}}(t) - G(-\tau)\mathbf{S}_-^I(t)\sigma_{\text{I}}(t)\mathbf{S}_+^I(t-\tau) \\ &\quad - G(\tau)\mathbf{S}_-^I(t-\tau)\sigma_{\text{I}}(t)\mathbf{S}_+^I(t) + G(-\tau)\sigma_{\text{I}}(t)\mathbf{S}_+^I(t-\tau)\mathbf{S}_-^I(t)). \end{aligned} \quad (\text{A.36})$$

Inserting $\mathbf{S}_-^I(t)$ and $\mathbf{S}_+^I(t)$ by using (A.30) and (A.31) results in many terms.

Now the approximation for weak laser fields comes into consideration. Recall the definition of W and Δ :

$$W = \sqrt{\Omega^2 + \left(\frac{\Delta}{2}\right)^2} \quad \Delta = \omega_L - \omega_A.$$

Weak laser field means small Ω . However, the detuning Δ can be arbitrary large. Then W is not small. The above mentioned terms are proportional to

$$\sum_{ks} |g_k|^2 e^{\pm i(\omega_k - \omega_L \pm (2W \text{ or } 0))\tau}. \quad (\text{A.37})$$

First consider the case with Δ having the same order of magnitude as Ω . That means the *detuning* Δ is small. Then W is small as well and $\omega_L \approx \omega_A$. The τ -dependence of the terms can be described as:

$$\sum_{ks} |g_k|^2 e^{-i(\omega_k - \omega_A)\tau}. \quad (\text{A.38})$$

For *large* Δ but small Ω the same holds, but the proof is much more cumbersome. In the approximation $\Omega \ll \Delta$, W becomes

$$W = \sqrt{\Omega^2 + \left(\frac{\Delta}{2}\right)^2} = \left|\frac{\Delta}{2}\right| \sqrt{1 + \underbrace{\left(\frac{2\Omega}{\Delta}\right)^2}_{\ll 1}} \approx \left|\frac{\Delta}{2}\right|. \quad (\text{A.39})$$

Let us calculate the first term in A.34:

$$\begin{aligned} \mathbf{S}_+^I(t) \mathbf{S}_-^I(t - \tau) &= \frac{\Omega^2}{4W^2} (|+\rangle\langle +| + |-\rangle\langle -|) \\ &+ \frac{\Omega}{4W} \left(\frac{\Delta}{2W} - 1\right) |-\rangle\langle +| e^{2iWt} - \frac{\Omega}{4W} \left(\frac{\Delta}{2W} + 1\right) |-\rangle\langle +| e^{-2iWt} \\ &+ e^{2iW\tau} \left(\frac{\Delta}{2W} - 1\right) |+\rangle\langle -| \left(\frac{1}{4} \left(\frac{\Delta}{2W} - 1\right) + \frac{\Omega}{4W} e^{-2iWt}\right) \\ &- e^{-2iW\tau} \left(\frac{\Delta}{2W} + 1\right) |-\rangle\langle +| \left(\frac{1}{4} \left(\frac{\Delta}{2W} + 1\right) + \frac{\Omega}{4W} e^{2iWt}\right) \quad (\text{A.40}) \end{aligned}$$

Here the first three terms can be neglected because $\Omega/W \ll 1$. One of the two last terms cancels as well, depending on the sign of Δ . For positive Δ is $\frac{\Delta}{2W} - 1 \approx 0$. For negative Δ cancels $\frac{\Delta}{2W} + 1$.

Inserting (A.40) into equation (A.34) yields

$$\begin{aligned}
\dot{\sigma}_I = & -\frac{1}{\hbar^2} \int_0^\infty d\tau \times \\
& \left\{ \sum_{ks} |g_k|^2 e^{-i(\omega_k - \omega_L)\tau} \left(+ e^{2iW\tau} \left(\frac{\Delta}{2W} - 1 \right) |+\rangle \langle -| \left(\frac{1}{4} \left(\frac{\Delta}{2W} - 1 \right) + \frac{\Omega}{4W} e^{-2iWt} \right) \right. \right. \\
& \quad \left. \left. - e^{-2iW\tau} \left(\frac{\Delta}{2W} + 1 \right) |-\rangle \langle +| \left(\frac{1}{4} \left(\frac{\Delta}{2W} + 1 \right) + \frac{\Omega}{4W} e^{2iWt} \right) \right) \right\} + \dots
\end{aligned} \tag{A.41}$$

Assume Δ to be positive. In this case the first term of equation (A.41) cancels. The second remains

$$\dot{\sigma}_I = -\frac{1}{\hbar^2} \int_0^\infty d\tau \left\{ - \sum_{ks} |g_k|^2 e^{-i(\omega_k - \omega_L + \omega_L - \omega_A)\tau} \left(\frac{\Delta}{2W} + 1 \right) |-\rangle \langle +| \left(\dots \right) \right\} + \dots \tag{A.42}$$

A negative choice of Δ yields

$$\dot{\sigma}_I = -\frac{1}{\hbar^2} \int_0^\infty d\tau \left\{ - \sum_{ks} |g_k|^2 e^{-i(\omega_k - \omega_L + \omega_L - \omega_A)\tau} \left(\frac{\Delta}{2W} - 1 \right) |+\rangle \langle -| \left(\dots \right) \right\} + \dots \tag{A.43}$$

The frequency of the laser field drops out. Now the integration is done in the same manner as in chapter 3. The part

$$\int_0^\infty d\tau e^{-i(\omega_k - \omega_A)\tau},$$

which is obtained for small and for large Δ , results in a δ function $\delta(\omega_k - \omega_A)$.⁵

The coupling constant g_k is proportional to $\sqrt{\omega_k}$ and the integration over k yields a factor ω_k^2 . With the delta function this results in a term that is proportional to ω_A^3 . For the other three terms similar calculations exist. The spontaneous emission rate is

$$\Gamma \propto \omega_A^3. \tag{A.44}$$

Thus, the spontaneous emission rate does not depend on the laser field, but only on the transition of the atom.

We know now that weak laser fields cannot change the spontaneous emission rate considerably. The effect of the laser can just be added to the master equation without laser. The laser only generates an oscillation between the two states, but does not change the spontaneous emission rate. \square

⁵The principal value of the integral results again in a frequency shift and does not contribute to the spontaneous emission (see also chapter 3).

Appendix B

The Liouville super operator for the model

B.1 Super operators

A super operator is an operator which acts on an operator and not on a state. The Liouville operator

$$i\mathcal{L}\rho = \frac{1}{\hbar}[H, \rho]. \quad (\text{B.1})$$

is an example for a super operator acting on a density operator. The density operator is the argument. If the operator on which the super operator acts can be expressed as a finite dimensional matrix and the super operator is linear as well, there is a simple way of understanding the nature of super operators. Actually, the super operator can be understood as being a matrix. In this case, the operator must be described as a vector. To further clarify this principle a short example is given:

$$\sigma := \begin{pmatrix} \sigma_{00} & \sigma_{01} \\ \sigma_{10} & \sigma_{11} \end{pmatrix} \quad (\text{B.2})$$

$$(\text{B.3})$$

$$\mathcal{L} := \frac{1}{\hbar}[H, \dots]. \quad (\text{B.4})$$

If one writes σ as a vector, then \mathcal{L} can be expressed as a matrix. Then $\mathcal{L}\sigma$ becomes $\mathcal{L}_{\text{mat}}\sigma_{\text{vec}}$ with

$$\sigma_{\text{vec}} := \begin{pmatrix} \sigma_{00} \\ \sigma_{01} \\ \sigma_{10} \\ \sigma_{11} \end{pmatrix} \quad (\text{B.5})$$

and

$$\mathcal{L}_{\text{mat}} := \frac{1}{\hbar} \begin{pmatrix} 0 & -H_{10} & H_{01} & 0 \\ -H_{01} & H_{00} - H_{11} & 0 & H_{01} \\ H_{10} & 0 & H_{11} - H_{00} & -H_{10} \\ 0 & H_{10} & -H_{01} & 0 \end{pmatrix}. \quad (\text{B.6})$$

Here

$$H = \begin{pmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{pmatrix} \quad (\text{B.7})$$

was assumed. Therefore, in this example H is a linear operator that acts on a two dimensional complex vector space. It is easy to verify that each component of the vector σ_{vec} in $\mathcal{L}_{\text{mat}}\sigma_{\text{vec}}$ transforms like the corresponding matrix element of σ in $\mathcal{L}\sigma$.

It is important that a super operator is in general *not* hermitian or unitary even if the operators used in it¹ have these properties.

B.2 The super operator of the model

In section 4.3 the time evolution for the density matrix was calculated. This was done by using the *Runge-Kutta* algorithm. If the Liouville super operator is used in its matrix form (see appendix B.1), then the algorithm can be implemented easily.

From equation (3.47) it is clear, that $\sigma_{\mu\mu}$ -like matrix elements are not coupled to $\sigma_{\mu\nu}$ -like matrix elements. Or in short hand notation

$$\sigma = \begin{pmatrix} \boxed{\sigma_{\mu_{a_1}\mu_{a_2}}} & \sigma_{\mu_{b_1}\nu_{b_2}} \\ \sigma_{\nu_{c_1}\mu_{c_2}} & \boxed{\sigma_{\nu_{d_1}\nu_{d_2}}} \end{pmatrix} \quad (\text{B.8})$$

only the boxed matrix elements are coupled. Therefore it is not necessary to take $\sigma_{\mu\nu}$ elements into account. This fact reduces the dimensionality of the corresponding "Liouville matrix". The vector $\vec{\sigma}_{\text{vec}}$ can then be written as

$$\vec{\sigma}_{\text{vec}} = \begin{pmatrix} \sigma_{\mu_0\mu_0} \\ \sigma_{\mu_0\mu_1} \\ \dots \\ \sigma_{\mu_{M-1}\mu_{M-1}} \\ \sigma_{\nu_0\nu_0} \\ \dots \\ \sigma_{\nu_{N-1}\nu_{N-1}} \end{pmatrix} = \begin{pmatrix} \sigma_0^{\text{vec}} \\ \sigma_1^{\text{vec}} \\ \dots \\ \dots \\ \sigma_{K-1}^{\text{vec}} \end{pmatrix}. \quad (\text{B.9})$$

¹here H

Here M denotes the number of vibrational levels in the excited electronic state and N the number of vibrational levels in the electronic ground state. The corresponding vector space has the dimension $K = M^2 + N^2$.²

When it comes to the implementation, it must be possible to differentiate between the index μ and the frequency μ . For the index, I used m for upper states and n for lower states. The frequencies are still written as μ and ν . To simplify the representation of \mathcal{L}_{mat} , I introduced some new variables.³

$$\mu_{\text{L}}(a) := \mu_{m_{\text{L}}(a)} \quad m_{\text{L}}(a) := (\text{int})a/M \quad (\text{B.10})$$

$$\mu_{\text{R}}(a) := \mu_{m_{\text{R}}(a)} \quad m_{\text{R}}(a) := a \pmod{M} \quad (\text{B.11})$$

$$\nu_{\text{L}}(a) := \nu_{n_{\text{L}}(a)} \quad n_{\text{L}}(a) := (\text{int})(a - M^2)/N \quad (\text{B.12})$$

$$\nu_{\text{R}}(a) := \nu_{n_{\text{R}}(a)} \quad n_{\text{R}}(a) := (a - M^2) \pmod{N} \quad (\text{B.13})$$

Here a is the index in σ_a^{vec} . The above definitions make it easy to assign the vector element σ_a^{vec} to the corresponding matrix element of σ .

$$a < M^2 \quad \text{then} \quad \sigma_a^{\text{vec}} = \sigma_{m_{\text{L}}(a)m_{\text{R}}(a)} \quad (\text{B.14})$$

$$a \geq M^2 \quad \text{then} \quad \sigma_a^{\text{vec}} = \sigma_{n_{\text{L}}(a)n_{\text{R}}(a)}. \quad (\text{B.15})$$

The definitions on the right of (B.10) to (B.13) provide rules how to map the index a onto the two indices μ and μ_1 in $\sigma_{\mu\mu_1}$ or onto the two indices ν and ν_1 in $\sigma_{\nu\nu_1}$. The definitions on the left of (B.10) to (B.13) calculate the frequencies that belong to the indices. The subscript L stands for "left index" and is therefore in the usual notation convention the row-index. The subscript R stands for "right index", the column index.

If for example the molecule has two upper levels and one lower level, then the density matrix is

$$\sigma = \begin{pmatrix} \sigma_{\mu\mu} & \sigma_{\mu\mu_1} & \sigma_{\mu\nu} \\ \sigma_{\mu_1\mu} & \sigma_{\mu_1\mu_1} & \sigma_{\mu_1\nu} \\ \sigma_{\nu\mu} & \sigma_{\nu\mu_1} & \sigma_{\nu\nu} \end{pmatrix}. \quad (\text{B.16})$$

In vector form this matrix becomes

$$\vec{\sigma}^{\text{vec}} = \begin{pmatrix} \sigma_{\mu\mu} \\ \sigma_{\mu\mu_1} \\ \sigma_{\mu_1\mu} \\ \sigma_{\mu_1\mu_1} \\ \sigma_{\nu\nu} \end{pmatrix} = \begin{pmatrix} \sigma_0^{\text{vec}} \\ \sigma_1^{\text{vec}} \\ \sigma_2^{\text{vec}} \\ \sigma_3^{\text{vec}} \\ \sigma_4^{\text{vec}} \end{pmatrix}. \quad (\text{B.17})$$

²If all σ matrix elements were taken into account, the vector space would have the dimension $(M + N)^2 = M^2 + N^2 + 2MN$.

³Here mod stands for *modulus* and (int) means "entire value of".

In this case $M = 2$ and $N = 1$ and for example $m_R(a = 1) = \mu_1$ and $n_R(a = 4) = \nu$. $n_R(a = 3)$ or $m_L(a = 4)$ are in this example not defined.⁴

With the help of these variables, the Liouville super operator which belongs to equation (3.47) can be written in matrix form:

$$\begin{aligned}
 \mathcal{L}_{ab} = & \delta_{ab} \left\{ -i\Theta(M^2 - a - \frac{1}{2})(\mu_L(a) - \mu_R(a)) - i\Theta(a - M^2 + \frac{1}{2})(\nu_L(a) - \nu_R(a)) \right\} \\
 & - \bar{D}\Theta(M^2 - a - \frac{1}{2})\Theta(M^2 - b - \frac{1}{2}) \left\{ \delta(m_R(a) - m_R(b)) \sum_{\nu} (r_{\mu_L(a)\nu}^{\mu_L(b)\nu})^* \right. \\
 & \quad \left. + \delta(m_L(a) - m_L(b)) \sum_{\nu} r_{\mu_R(a)\nu}^{\mu_R(b)\nu} \right\} \\
 & + \bar{D}\Theta(M^2 - a - \frac{1}{2})\Theta(b - M^2 + \frac{1}{2}) \left\{ r_{\nu_L(b)\mu_L(a)}^{\nu_R(b)\mu_R(a)} + (r_{\nu_R(b)\mu_R(a)}^{\nu_L(b)\mu_L(a)})^* \right\} \\
 & + \bar{D}\Theta(a - M^2 + \frac{1}{2})\Theta(M^2 - b - \frac{1}{2}) \left\{ r_{\mu_L(b)\nu_L(a)}^{\mu_R(b)\nu_R(a)} + (r_{\mu_R(b)\nu_R(a)}^{\mu_L(b)\nu_L(a)})^* \right\} \\
 & - \bar{D}\Theta(a - M^2 + \frac{1}{2})\Theta(b - M^2 + \frac{1}{2}) \left\{ \delta(n_R(a) - n_R(b)) \sum_{\mu} (r_{\nu_L(a)\mu}^{\nu_L(b)\mu})^* \right. \\
 & \quad \left. + \delta(n_L(a) - n_L(b)) \sum_{\mu} r_{\nu_R(a)\mu}^{\nu_R(b)\mu} \right\} \tag{B.18}
 \end{aligned}$$

Expressions like $\delta(m_R(a) - m_R(b))$ are zero except for $m_R(a) - m_R(b) = 0$. Since $m_R(a)$ and $m_R(b)$ are integers, the δ stands for Kronecker's δ . Θ stands for the *Heaviside function*. The $1/2$ is just added to avoid any ambiguity concerning $\Theta(0)$. Any real number between 0 and 1 could have been added. \bar{D} stands for $|\vec{d}_{eg}|^2/6\epsilon_0\pi\hbar^2c^3$. It is just a constant.

The above matrix form of the Liouville super operator looks very complicated. Nevertheless, used in a computer language like C or C++, the super operator can simply be expressed with some nested loops and **if** statements.

⁴ $m_R(a)$ and $m_L(a)$ are only defined for $a < M^2$ and $n_L(a)$ and $n_R(a)$ only for $a \geq M^2$.

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