Turun yliopisto
University of Turku

TIME-DEPENDENT QUANTUM SYSTEMS

Jaakko Lehto

TURUN YLIOPISTON JULKAISUJA - ANNALES UNIVERSITATIS TURKUENSIS
Sarja - ser. AI osa - tom. 561 | Astronomica - Chemica - Physica - Mathematica | Turku 2017

Turun yliopisto
University of Turku

TIME-DEPENDENT QUANTUM SYSTEMS

Jaakko Lehto

TURUN YLIOPISTON JULKAISUJA – ANNALES UNIVERSITATIS TURKUENSIS
Sarja - ser. A I osa - tom. 561 | Astronomica - Chemica - Physica - Mathematica | Turku 2017

University of Turku

Faculty of Mathematics and Natural Sciences
Department of Physics and Astronomy

Supervised by

Kalle-Antti Suominen
Professor
Department of Physics and Astronomy
University of Turku
Finland

Reviewed by

Vladimir Akulin
Professor
Laboratoire Aimé-Cotton
CNRS
France

Stéphane Guérin
Professor
Laboratoire Interdisciplinaire
Carnot de Bourgogne
CNRS
France

Opponent

Jonas Larson
University Lecturer
Department of Physics
University of Stockholm
Stockholm

ISBN 978-951-29-6854-1 (PRINT)
ISBN 978-951-29-6855-8 (PDF)
ISSN 0082-7002 (Print)
ISSN 2343-3175 (Online)
Painosalama Oy - Turku, Finland 2017

Acknowledgments

Theoretical research may have seemed like a solitary activity at times, but in reality, the completion of this work owes very much to many people.

Firstly, I would like to thank my supervisor, professor Kalle-Antti Suominen, for his guidance and patience over the whole thesis project. I appreciate the fact that you have always been very open to new ideas and could find the time to discuss them and share your knowledge even in your often busy schedule.

I would also like to extend my best thanks to professor Artur Ishkhanyan for discussions and especially for exemplifying me from the very early on the work ethic and the mindset of a true theoretical physicist.

I am also grateful for the many teachers and colleagues I have had the pleasure to meet along the way, in Turku and elsewhere. Special thanks to the people from the corridor, both former and current, and in both the "noisy" and the "quiet" rooms. You have made this journey more interesting.

Recreational activities provided by WFAT and TTR and other oddly abbreviated and obscure consortia are also gratefully acknowledged. In other words, thank you to all of my friends for providing me enough real-world data not to get stuck in only the theoretical simulations.

I also thank the Väisälä Fund, the Magnus Ehrnrooth Foundation and the Academy of Finland (grant nr. 268745) for the financial support during my PhD studies.

Finally, I wish to give my warmest thanks to my family for all the support over the years and especially to my fiancée Pauliina for her love and constant encouragement that made all the difference.

Turku, May 2017

Jaakko Lehto

Contents

Abstract **7**

Tiivistelmä **9**

List of articles **11**

1 Introduction **12**

2 Coherent dynamics of TLS **18**
2.1 The Schrödinger equation 18
2.2 Two-level systems 20
2.2.1 The diabatic basis 21
2.2.2 The adiabatic basis 23
2.3 Differential equations 25
2.3.1 2nd order ODE for amplitudes 25
2.3.2 Bloch equations 26
2.4 Analytically solvable models 27
2.4.1 Rabi model 28
2.4.2 Landau-Zener model 29
2.4.3 Rosen-Zener model 32
2.4.4 Other analytically solvable models 33
2.5 Parabolic and superparabolic models 34
2.6 Time-independent Schrödinger equation 36

3 Approximative approaches **39**
3.1 Perturbation methods 39
3.2 Area theorem 41
3.3 Independent crossing approximation 42
3.4 Adiabatic approximation 43
3.5 DDP theory 45

3.5.1 History and description of the method 45
3.6 Zhu-Nakamura theory 49
3.6.1 Stokes constants 49
3.6.2 Zhu-Nakamura formulas for general models 51

4 Plane-curve representation of TLS **53**
4.1 Basics of the differential geometry of plane curves 54
4.2 Two-state level-crossing model as a plane curve 56
4.2.1 Examples 57

5 CPI and zero-area pulses **62**
5.1 History and general results 62
5.2 The effect of symmetries 66
5.3 Two-level phase-jump models 67
5.4 Propagators in different bases 69
5.5 Universal formula 71
5.6 Zero-area models and DDP theory 73

6 Conclusion **75**

Original publications **83**

Abstract

This thesis discusses different aspects of time-dependent two-level quantum systems and their coherent dynamics. In the introductory chapters, we present some basic models used to study them and some basic results related to the level-crossing problems generally.

As these systems are only rarely analytically solvable, some emphasis is put on the existing approximative theories. In particular, the generalization of the method of Dykhne, Davis and Pechukas (DDP), originally developed for problems in near-adiabatic region, is studied further. In the DDP theory, the final populations of different states are determined by the complex zero points of the eigenenergies. Superparabolic level-crossing models are introduced in this thesis and they prove to be simple but versatile test models for these studies. It is shown that, by considering all of the zero points, one can obtain accurate approximations also for highly non-adiabatic regions.

In Chapter 4, a general differential geometric framework for time-dependent level-crossing models is developed and its basic character is discussed. A natural way of associating a plane curve to a time-dependent two-level model is introduced. This association allows one to use all of the mathematical results concerning plane curves to study these models. As an example, we use the Four-vertex theorem to discuss the adiabatic limit of certain type of systems.

We also consider the prospect of enhancing the population transfer by transforming the time-dependent coupling pulse into a zero-area coupling. This is done either smoothly or by an abrupt jump in the phase of the coupling. It has been shown earlier, that one can obtain a complete population inversion (CPI) in a robust way with strong, non-resonant zero-area pulses. We study this in the more general time-dependent setting in Chapter 5, where also the energy levels are driven in a time-dependent fashion. This allows to transport the CPI phenomenon from the strong coupling region towards more moderate couplings. As an example of the smooth case, we

consider the SechTanh-model, and show that even the nearest-zero DDP approximation can be used, despite the highly non-adiabatic origin of the phenomenon. We develop an approximative scheme also for the phase-jump case, using the parabolic model as an example. As a limiting case, we derive an approximative formula for the transition probability, which has some universal character and which proves to be useful in the most interesting case where the robust CPI is obtained. It is shown that even the highly suppressed transitions in tunnelling cases can be strongly enhanced in the phase-jump scenario.

Tiivistelmä

Tässä väitöskirjatyössä tarkastellaan kvanttimekaanisten kaksitasosysteemien eli kubittisysteemien koherenttia dynamiikkaa eri näkökulmista. Alun johdantoluvuissa esitellään lyhyesti tähän tarkoitukseen käytettyjä malleja ja niihin liittyviä perustuloksia.

Nämä systeemit ratkeavat analyyttisesti vain hyvin erityisissä tapauksissa, ja työssä painotetaankin jonkin verran olemassaolevia approksimatiivisia teorioita. Tutkimme erityisesti Dykhnen, Davisin ja Pechukas'n (DDP) teoriaa ja sen yleistystä. Tässä teoriassa systeemin transitiotodennäköisyys saadaan määrättyä sen analyyttisesti jatkettujen energiatasojen kompleksisten nollakohtien avulla. Alkuperäisessä muodossaan teoria soveltuu lähinnä adiabaattisten ongelmien tutkimiseen. Tässä työssä osoitetaan kuitenkin edelleen kuinka koko nollakohtarakenteen huomioiminen voi mahdollistaa tarkan approksimaation saamisen kaikille parametrialueille.

Luvussa 4 kehitellään uudenlaista differentiaaligeometrista kehystä ajasta riippuvien kubittisysteemien tutkimiseksi ja esitellään luonteva yhteys eri mallien ja tasokäyrien välille. Tämän avulla differentiaaligeometrian tuloksia voidaan käyttää mallien dynamiikan tutkimiseen. Esimerkkinä esitetään neliverteksiteoreeman soveltaminen tiettyjen mallien adiabaattisen rajan tutkimiseen.

Luvussa 5 puolestaan tutkitaan mahdollisuutta parantaa transitiotodennäköisyyksiä muuntamalla ajasta riippuva pulssi nk. nollapinta-alan pulssiksi. Aiemmin on osoitettu, että tietyillä voimakkailla ja ei-resonanteilla pulsseilla jopa täydellinen populaatioinversio on tällä tavalla mahdollista. Luvussa 5 tutkimme asiaa yleisempien mallien kannalta, jolloin myös systeemin energiatasot voivat riippua ajasta. Pulssin häviävä pinta-ala tuotetaan tässä tapauksessa nopealla vaihehypyllä. Käy ilmi, että tällöin populaatioinversioon tarvittava kytkennän suuruus voi olla selkeästi pienempi. Lisäksi johdamme yksinkertaisen ja tarkan approksimatiivisen kaavan transitioille. Tämän avulla voidaan osoittaa tiettyjä näiden mallien yleisiä piirteitä, esimerkiksi se, kuinka voimakkaasti vaimen-

netut tunnelointitransitiotkin saadaan todennäköisiksi käyttämällä tätä menetelmää. Lopuksi tutkimme myös DDP-teorian soveltuvuutta näihin selkeästi epäadiabaattisiin malleihin käyttäen esimerkkinä SechTanh-mallia ja osoitamme sen käyttökelpoisuuden jopa karkeimmassa lähimmän nollakohdan approksimaatiossa.

List of articles

This thesis consists of an introductory review and the following five articles:

I J. Lehto and K.-A. Suominen
Superparabolic level-glancing models for two-state quantum systems
Physical Review A 86, 033415 (2012) (8 pages)

II J. Lehto
Zhu-Nakamura theory and the superparabolic level-glancing models
Physical Review A 88, 043404 (2013) (8 pages)

III J. Lehto and K.-A. Suominen
Geometry of adiabatic Hamiltonians for two-level quantum systems
Journal of Physics A: Mathematical and Theoretical 48, 235301 (2015) (13 pages)

IV J. Lehto and K.-A. Suominen
Time-dependent two-level models and zero-area pulses
Physica Scripta 91, 013005 (2016) (8 pages)

V J. Lehto and K.-A. Suominen
Two-level parabolic model with phase-jump coupling
Physical Review A 94, 013404 (2016) (7 pages)

Chapter 1

Introduction

The 20th century revolutionized our understanding of the Nature and in particular the way it operates on atomic and molecular scales. As with any revolution, the history of quantum theory is complex and manifold but in any case the first major steps were taken by Planck in 1900 and Einstein in 1905 explaining the spectral distribution of blackbody radiation [1] and photoelectric effect [2], respectively. To do this, they assumed that light was emitted and absorbed only in discrete quanta of energy. Later, in 1913, Bohr extended the quantization principle to include internal energy states of atoms [3], explaining this way the discrete spectral lines observed in spectroscopy. Many perplexities followed in the efforts to understand and describe the newly-found phenomena until the agreeable mathematical setting of quantum theory was obtained at the turn of 1920s and 1930s.

We have come a long way since those days, but we still find it often very hard to get our classical-sized heads, used to classical environments, around the full implications of the theory. The seemingly weird reality implied by quantum theory is best exemplified in such phenomena as the interference of different alternatives when a system is measured in a superposition state (as met, for example, in the famous two-slit experiment) or the measurement outcomes of entangled particles which are found to be correlated even in the absence of any direct interaction between the particles at the time of the measurement. These features, combined with the fact that quantum theory can be seen to assign physical meaning only in the probabilities to find the system in some specified state, has often led to confusion. Yet, we know that it seems to agree with all the experiments that are performed, and even many of its more surprising predictions are experimentally confirmed with a spectacular precision.

For a long time it was sufficient to consider mostly time-independent

models and problems in quantum mechanics. One was interested in calculating, for example, energy levels of different atoms and molecules and it was also mostly these kinds of stationary properties that were within the reach of experimentalists to confirm. During the recent decades, however, we have seen great advances in experimental techniques. In particular, the remarkable development of laser technology has allowed the study of genuinely time-dependent processes in quantum systems in a new way [4, 5, 6]. Nowadays one can design and tailor the shapes of laser pulses and their frequencies more or less at will. They can be, for example, manufactured into such a short pulses as to allow observing and controlling molecular or chemical processes happening in their natural time scales. In conjunction with (and, of course largely due to) the development of experimental physics, there has also emerged new theoretical ideas. In particular the quantum information and computation paradigm has led to important insights in understanding quantum theory [7]. All in all, it can be said that we are currently in the middle of a second quantum revolution. Unlike in the first one, which was more about the stationary properties of the material world, as mentioned earlier, the focus in the current revolution is to take full advantage of the laws of quantum physics and its fundamental features to make new quantum technologies and devices, while at the same time, of course, advancing our understanding of the nature further.

The above-mentioned development has highlighted the importance of being able to coherently control and manipulate quantum systems in a precise way. One of the basic tasks then is to obtain an efficient population transfer from well-defined initial state to the desired final state. This requires the ability to theoretically simulate and solve the dynamics of the quantum systems of interest. In the experiments before the invention of lasers, one could use only incoherent radiation sources to excite quantum systems. Such schemes lacked the efficiency and selectivity and could often be described effectively by rate equations or perturbative calculations. Such approaches, in contrast, are not sufficient when we study the effects of coherent external fields on quantum systems. The most important features characteristic to laser radiation are that it can be practically monochromatic, including extremely narrow range of frequencies and it maintains a definite phase relation for an extended period of time, the very reason why it is termed coherent. It can then be tuned to match the Bohr frequency between only the states of interest, and then the narrow spectrum enables the selectivity and efficiency of the population transfer. Moreover, the coherence of the radiation allows one to prepare and probe many novel quantum

states, such as superpositions, that are not possible with incoherent radiation. The correct description for the evolution of the quantum system is then the time-dependent Schrödinger equation. Solving the equation for a time-dependent external field is a very difficult problem in general and subject to many approximations.

Despite the relatively minor emphasis on the genuine time-dependency in quantum mechanics historically, there have been some important results from very early on. One of the most important of these is the quantum adiabatic theorem, which originally dates back to 1928 and to the work of Born and Fock [8]. It basically addresses the borderline between dynamics and statics considering interactions that change infinitely slowly. Often one can divide the system into two interacting subsystems where one is evolving in a much more shorter time-scale compared with the other and the meaning of "infinitely slowly" refers to the ratio of these time-scales. It follows that the fast subsystem will react practically instantly to any change in the slow system. Then, generally speaking, we can refer to the set of variables of the slow system as the adiabatic parameters and to the states of the fast system as the adiabatic states. When adiabaticity holds, there are no transitions between these states.

Although many interesting processes take place in nearly adiabatic conditions, none of them happen, strictly speaking, infinitely slowly. It is therefore a task of foremost importance to study the way the adiabaticity breaks down and estimate the probability of non-adiabatic transitions. In quantum theory, the intrinsic time-scale of the system is usually related to the gaps in the energy spectrum. Indeed, for a time-dependent and discrete spectrum we consider here, there can be points where the energy levels either cross or have a near miss, so-called avoided level-crossing, and the non-adiabatic transitions in the system are concentrated in the vicinity of these points. Furthermore, the amount of excitation that results is sensitive to the way these crossings are traversed and this has led to the study of different level-crossing models.

Because of the fact that transitions usually happen effectively at these points, where only two different energy-levels have a crossing and the system is in resonance with the external driving field, the essential features of the dynamics can often be understood with the help of two-level systems and this two-level approximation is also used throughout this thesis. We also neglect the granularity of the driving field and describe it classically as having definite given time-dependencies, so the approach is therefore essentially a semiclassical one and similar to the NMR techniques in spin

manipulation. This obviously is valid for laser fields which are often very intense. The description is not however restricted to them and we study the time-dependent two-level problem on a general level and it is the power of quantum theory that the results can be utilized in any physical system that fulfils these approximations.

In fact, the history of the study of analytic two-level models is almost as long as the quantum adiabatic theorem. The paradigmatic Landau-Zener (LZ) model was introduced in 1932 by several people independently: Landau, Zener and Stückelberg considered different phenomena related to atomic collisions [9, 10, 11], while Majorana introduced the same model in his study of atoms in time-dependent magnetic field [12][a]. It basically consists of a two-level system whose energy levels corresponding to the bare states are driven through the resonance in a way that is linear in time while the coupling between these states remains constant during the process. Despite the crude time-dependency of its model functions, the LZ model with its exactly solvable dynamics has proved to be a very useful one, sometimes even surprisingly so. Of course, also LZ model does have its limits [13, 14, 15, 16] and different solvable models with simple time-dependencies, for example given in terms of hyperbolic functions, have been considered over the years [17, 18]. However, the analytically solvable models are still rare. Nevertheless, analytical results are worth looking for, since they usually offer more complete understanding, for example on the parameter dependence of the problem, than numerical simulations. It can be even said that analytically solvable models have been central in the advancement of the understanding of coherent dynamics, each new model describing some paradigmatic situation.

One of the motivations behind this thesis was to understand models with parabolic-type level-crossings better. Indeed, the two-state parabolic model can be seen as the next one in order after LZ model, yet its complete analytical solution is not known[b]. This is unfortunate, as the model encompasses many different types of behaviour depending on its parameters and arises in many applications.

A partial solution to the problem has been obtained quite recently when Zhu and Nakamura were able to calculate the Stokes constants for the corresponding differential equation [20]. This solves the scattering problem,

[a] And the model should, perhaps, more correctly be called as the Landau-Zener-Stückelberg-Majorana model.

[b] More precisely, the problem can be reduced to the Heun class of differential equations whose solutions, the Heun functions, are not currently well-enough characterized [19].

i.e., gives the transition probabilities after infinite times. The constants themselves were given by rather tedious and complicated expressions and are therefore of limited utility. Realizing this, however, Zhu and Nakamura devised general approximative formulas for the constants that were given in relatively simple form by elementary functions only [21]. The resulting Zhu-Nakamura theory, summed up by these formulas, is meant as a general theory for non-adiabatic quantum dynamics. However, the formulas contain "experimental" modifications of parameters, for example, so despite the stated generality of the theory and the demonstrations of its usefulness [22], the region of validity of the formulas must not be taken for granted.

Indeed, another theme of this thesis is also to better understand the validity of different approximative theories of non-adiabatic transitions. Another widely used approximative scheme is the Dykhne-Davis-Pechukas (DDP) theory which takes into account the analytic structure of the Hamiltonian by considering the zero points of the eigenenergies in the complex plane [23, 24]. The behavior of the analytically continued eigenenergies give an expression for the probability of transitions between the eigenstates that is asymptotically correct in the adiabatic limit. Originally, the theory considered only the case where there was only a single complex zero point near the real axis, so only its influence on the dynamics was felt. However, many models have multiple complex zeros, even infinite in number, in various distances from the real axis, so naturally the question raises which zero points have the most effect on the dynamics and which ones can be excluded from considerations. The work of Joye and co-workers have studied the mathematical aspect of the problem and, to a great extent, answered this question [25, 26]. On the other hand, regardless of these rigorous results, it is known that sometimes the full summation of the contributions from all the zero points leads to the exact result [27]. We study further the prospect of expanding the validity of the DDP approach by considering more than just the zero points closest to the real axis.

Because of the long history and apparent simplicity of the time-dependent two-level problem, one could think that everything would have already been said on them, so to speak, and there would be nothing new left to study on them. This, however, is not the case and the third aspect of our studies encompasses topics of more general nature that can be used in understanding and controlling the dynamics of simple quantum systems. We have found that there is a natural correspondence between two-level models and plane curves that has previously gone unnoticed and that one can understand some aspects of the dynamics, particularly issues concern-

ing he adiabatic limit, with the help of the differential geometry of these plane curves.

Another recent and quite surprising result is the complete population inversion effect (CPI) related to models of zero pulse area (ZPA), obtained by Vitanov and co-workers [28, 29]. It offers an efficient and robust way of enhancing the population transfer between desired states, simply by replacing the coupling pulse by a sufficiently strong off-resonant coupling with zero temporal area, in a clear distinction to the area theorem in the resonant case. We have considered this highly non-adiabatic effect in a more general setting, identifying some universal features of it. In particular, the strongly suppressed transitions in adiabatic processes or in Zener tunnelling can become substantial even for small coupling values if one introduces rapid phase changes in the coupling pulse. In this way, it gives another useful tool for obtaining reliable state transfer, in addition, for example, to the conventional rapid adiabatic passage.

This Thesis is organized in the following way. In Chapter 2 we introduce the very basic concepts, equations and models that are important in the description of the dynamics of time-dependent two-level systems. In Chapter 3 we continue by giving information on the various approximative approaches that are needed in practice when dealt with such systems. Chapter 4 features an entirely novel but simple connection between the time-dependent quantum systems and parametrized plane curves and explains how some differential geometrical results can be used study phenomena related especially to non-adiabatic quantum transitions. Also Chapter 5 considers a simple and unexpected recently-found phenomenon, namely, the robust complete population inversion related to off-resonant zero-area pulses, and studies this further by introducing the time-dependent phase-jump models. Chapter 6 summarizes the results and concludes the Thesis.

Chapter 2

Coherent dynamics of two-level quantum systems

In this chapter, we present the basic mathematical formalism used in the description of the coherent dynamics of quantum systems.

2.1 The Schrödinger equation

The time evolution of a closed quantum system is given by the time-dependent Schrödinger equation,

$$i\hbar\partial_t|\psi(t)\rangle = H|\psi(t)\rangle, \tag{2.1}$$

where $|\psi(t)\rangle$ is the state vector of the system at time t and H is a hermitian linear operator, the Hamiltonian, representing the energy of the system. The Hamiltonian in equation (2.1) is independent of time, reflecting the conservation of energy in closed systems. In this thesis, we use the convention to work in physical units in which $\hbar$, the reduced Planck constant, is fixed to unity, $\hbar = 1$. The state vectors are normalized to have a unit length and they belong to a Hilbert space describing the physical states of the system[a]. Any state vector can be expanded in terms of the basis vectors $|i\rangle$ as

$$|\psi(t)\rangle = \sum_i c_i(t)|i\rangle. \tag{2.2}$$

[a]Distinct physical state vectors are actually rays in the Hilbert space, since the observable properties are not altered if a vector is multiplied by a phase factor, i.e., a complex number with unit modulus.

The square modulus of a complex coefficient in this expansion, $|c_i(t)|^2$, gives the probability that the system, if measured at time t, is found in the state $|i\rangle$. The normalization of the vector then corresponds to the fact that these probabilities sum up to one.

In addition to generating the evolution, the Hamiltonian also determines, through its eigenvalues, the observable energy values E_i. These are also called as the energy levels of the system. The corresponding eigenstates form a basis where the dynamics is in particularly simple form: if equation (2.2) is given in this basis, the coefficients are simply given as

$$c_i(t) = \exp(-iE_i t)\, c_i(0), \tag{2.3}$$

and there are no transitions between the eigenstates because the probabilities associated with different eigenstates remain constant, i.e. $|c_i(t)|^2 = |c_i(0)|^2$. Because of this, systems with time independent Hamiltonians cannot be used to describe very interesting dynamics. Either nothing exciting happens to the system under study, or else the Hamiltonian has to include a too large system to make it isolated, and thus time independent, making its evolution too complex and intractable

However, many important realistic processes can be incorporated into this framework in a straightforward way by simply considering explicit time-dependency in the Hamiltonians[b]. These are usually obtained when we take into account the interaction of the system with a coherent environment. The basic structures in the mathematical description of the dynamics are still as introduced above, but now all the quantities such as the energy levels and eigenstates all depend explicitly on time and the dynamics is far richer. In fact, with time-dependent Hamiltonians, it is only in very special cases or after numerous approximations that we are able to solve the dynamics analytically. Before discussing these, we still consider formally some aspects of coherent dynamics.

The connection of the state vector at time t, $|\psi(t)\rangle$, to the initial one, $|\psi(t_0)\rangle$, is given by the unitary matrix, called propagator, as

$$|\psi(t)\rangle = U(t, t_0)\, |\psi(t_0)\rangle, \tag{2.4}$$

which implies that the proper initial condition is $U(t_0, t_0) = 1$ for any t_0. This allows one to write the Schrödinger equation also in the matrix form

$$i\partial_t U(t, t_0) = H(t) U(t, t_0). \tag{2.5}$$

[b] This way one can incorporate also dissipative dynamics (with non-hermitian Hamiltonians) [30, 31, 32] or even effects of quantal environments [5, 33] but these aspects are not considered further in this thesis.

The formal solution to this equation can be obtained iteratively and written as the series

$$U(t,t_0) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^{t} \mathrm{dt}_1 \int_{t_0}^{t_1} \mathrm{dt}_2 \ldots \int_{t_0}^{t_{n-1}} \mathrm{dt}_\mathrm{n} H(t_1)H(t_2)\ldots H(t_n)$$
$$\equiv \mathcal{T} \exp\left(-i \int_{t_0}^{t} \mathrm{ds} H(s)\right), \qquad (2.6)$$

where $\mathcal{T}$ is the time-ordering operator. This form, however, is not usually the most useful one in practice because the Hamiltonians at different times do not generally commute, $[H(t_1), H(t_2)] \neq 0$.

Another formal way to think about the time-dependent Schrödinger equation is to note that any given unitary matrix U is an exact solution to equation (2.5) when $H = i(\partial_t U)U^\dagger$. This opposite viewpoint constitutes a starting point for a so-called reverse engineering approach [34] where one starts with desired evolution of the system and obtains the Hamiltonian that generates this evolution. The challenge is then just to end up with Hamiltonians that are relevant to the physical situation at hand or, indeed, ones that can actually be produced in a experimental situation. In any case, this approach allows also the incorporation of additional features, such as fast [35] and robust [36] control, into the discussion.

2.2 Two-level systems

The concept of a two-level system (TLS) has always played a very important role in quantum mechanics. While it forms an exact representation for the spin degrees of freedom of a particle with spin$-\frac{1}{2}$, and to which the description of any TLS can be reduced to, in many cases the essential changes in a coherently-driven multiple-level system also happen effectively between just two levels and the description of its dynamics can then be reduced to a two-level system. An example of a such case is the atom-laser interaction, where the frequency of the electric field of a laser is tuned to a near-resonance to match the energy difference of two electronic states. Two-level systems are also central to quantum computation where one tries to devise TLS in different physical implementations to act as quantum bits, or qubits for short, that are used to store and manipulate data.

In the following we introduce the basic concepts used in the study of the dynamics of TLS. Particularly important are the various different representations of the system in different bases. For time-dependent systems we frequently have to consider general transformations that also

themselves depend on time. If the operator $R(t)$ transforms the basis as $|\tilde{\psi}(t)\rangle = R(t)|\psi(t)\rangle$, the original Hamiltonian transforms generally[c] as

$$\tilde{H}(t) = R(t)H(t)R^{\dagger}(t) - iR(t)\partial_t R^{\dagger}(t), \tag{2.7}$$

where the second term arises from the time-dependency of the transformation.

2.2.1 The diabatic basis

An obvious way to choose the basis for a time-dependent system is to take those states which refer to the energy eigenstates of the free system, that is, the system in the absence of the external field. The resulting basis is called diabatic[d], sometimes also referred to as the bare state basis. We take the complex functions $C_1(t)$ and $C_2(t)$ to denote the probability amplitudes basis states, so any state is written as $|\psi(t)\rangle = (C_1(t), C_2(t))^T$.

The basis is particularly useful to describe the dynamics when the field is changing very rapidly. Also, the connection to the external parameters is straightforward and simply described in this basis. In addition to the basic requirement that the physically observable quantities are hermitian, the structure of the general two-level Hamiltonian can be still specified further. Firstly, it can take the traceless form by defining the (time-dependent) zero point for energy in the middle of the two energy levels[e].

$$H(t) = \vec{B}(t) \cdot \vec{\sigma} \tag{2.8}$$

$$= \begin{pmatrix} Z(t) & X(t) - iY(t) \\ X(t) + iY(t) & -Z(t) \end{pmatrix}, \tag{2.9}$$

where $\vec{B}(t)$ is the field vector having the real functions $X(t)$, $Y(t)$ and $Z(t)$ as its Cartesian components and $\vec{\sigma}$ is the vector having Pauli matrices as its components. In what follows, it is sometimes useful to have these field vector components in the spherical coordinates in which case the Hamiltonian is given by

$$H(t) = E(t) \begin{pmatrix} \cos(\theta(t)) & \sin(\theta(t))e^{-i\phi(t)} \\ \sin(\theta(t))e^{+i\phi(t)} & -\cos(\theta(t)) \end{pmatrix}, \tag{2.10}$$

[c] Not just in the two-level case.

[d] This terminology originates from the collisional framework but is widely used in other contexts as well [22].

[e] Mathematically this corresponds to equipping the basis vectors only with extra phase factor so the resulting basis may still be called diabatic.

where $E(t) = \sqrt{X^2(t) + Y^2(t) + Z^2(t)}$ is the length of the field vector and the angles $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi]$ are defined by

$$\tan(\theta(t)) = \frac{\sqrt{X^2(t) + Y^2(t)}}{Z(t)}, \qquad \tan(\phi(t)) = \frac{Y(t)}{X(t)}. \tag{2.11}$$

As a simple example of the transformation of Eq. (2.7) we can consider the time-dependent phase transformation $|\tilde{\psi}(t)\rangle = R_\alpha(t)|\psi(t)\rangle$, where

$$R_\alpha(t) = \begin{pmatrix} e^{+i\alpha(t)/2} & 0 \\ 0 & e^{-i\alpha(t)/2} \end{pmatrix}, \tag{2.12}$$

which induces different phase dependency on the basis vectors. This is often called as the transformation to the rotating frame but, nevertheless, also here the identification of the new basis states with the original diabatic states can be maintained. The Hamiltonian in this form is obtained through equation (2.7) explicitly as

$$\tilde{H}(t) = \begin{pmatrix} Z(t) - \frac{\dot{\alpha}}{2} & V(t)e^{-i(\phi(t)-\alpha(t))} \\ V(t)e^{+i(\phi(t)-\alpha(t))} & -Z(t) + \frac{\dot{\alpha}}{2} \end{pmatrix}, \tag{2.13}$$

where it is also defined $V(t) = \sqrt{X^2(t) + Y^2(t)}$. We are free to choose the phase factor as $\alpha(t) = \phi(t)$ and this means that in all cases it is sufficient to consider Hamiltonians that are traceless and real:

$$H(t) = \begin{pmatrix} \varepsilon(t) & V(t) \\ V(t) & -\varepsilon(t) \end{pmatrix}, \tag{2.14}$$

where $\varepsilon(t) = Z(t) - \frac{\dot{\phi}}{2}$.

On the other hand, taking the traceless and real Hamiltonian of (2.14) as the starting point, we can perform the same transformation of equation (2.12) to the rotating frame. Now if we choose the function $\alpha(t) = 2\int^t Z(s)\mathrm{ds}$ which removes the diagonal terms in (2.14), we will end up with the Hamiltonian

$$\tilde{H}(t) = \begin{pmatrix} 0 & V\,(t)\, e^{+i\alpha(t)} \\ V\,(t)\, e^{-i\alpha(t)} & 0 \end{pmatrix}. \tag{2.15}$$

Here the only non-zero elements are the off-diagonal ones which couple the two states, while the unperturbed energies are eliminated, and this is actually the interaction representation. However, also in this representation the basis states differ only by phase factors from the original diabatic basis

and therefore lead to same transition probabilities. This just shows that there are many equivalent pictures and which one to consider depends on the situation at hand. In any case, there is generally two independent functions characterizing a two-level model, not more. For special classes of models this may be restricted further. For example, if $V(t) \neq 0$ for all t this function can be incorporated in a new time-variable

$$s(t) = \int^t V(u)\mathrm{du}, \tag{2.16}$$

which is equivalent of choosing $V(t) \equiv 1$ and replacing t by s in equation (2.15).

2.2.2 The adiabatic basis

Another canonical choice for the basis consists of the eigenstates of the Hamiltonian in the diabatic basis. This is not obtained by a simple phase transformation and it mixes these bare states in an essential and time-dependent way. It is obtained by the time-dependent basis transformation $|\psi_A(t)\rangle = R(t)|\psi_D(t)\rangle$ where the unitary matrix is constructed by placing the eigenstates as its columns, and for Hamiltonian in Eq. (2.14) it is explicitly expressed as

$$R(t) = \begin{pmatrix} \cos(\frac{\theta(t)}{2}) & -\sin(\frac{\theta(t)}{2}) \\ \sin(\frac{\theta(t)}{2}) & \cos(\frac{\theta(t)}{2}) \end{pmatrix}, \tag{2.17}$$

where $\tan[\theta(t)] = V(t)/\varepsilon(t)$. This leads to the Schrödinger equation in the adiabatic basis, which reads

$$i\frac{d}{dt}\begin{pmatrix} a_+(t) \\ a_-(t) \end{pmatrix} = \begin{pmatrix} E(t) & i\gamma(t) \\ -i\gamma(t) & -E(t) \end{pmatrix}\begin{pmatrix} a_+(t) \\ a_-(t) \end{pmatrix}, \tag{2.18}$$

where $|\psi(t)\rangle = a_+(t)|\chi_+(t)\rangle + a_-(t)|\chi_-(t)\rangle$ and the fact that the transformation is time-dependent induces a gauge term in the adiabatic Hamiltonian that couples the adiabatic basis states. This term is called adiabatic coupling $\gamma(t)$ and is given by

$$\begin{aligned} \gamma(t) &\equiv -\langle\chi_+(t)|\dot{\chi}_-(t)\rangle \\ &= \tfrac{\varepsilon(t)\dot{V}(t)-\dot{\varepsilon}(t)V(t)}{2(\varepsilon^2(t)+V^2(t))} \\ &= \tfrac{\dot{\theta}(t)}{2}, \end{aligned} \tag{2.19}$$

where the overhead dot stands for time derivation. The function $E(t) = \sqrt{\varepsilon^2(t) + V^2(t)}$ gives the adiabatic energy levels as $E_\pm(t) = \pm E(t)$.

This is usually a particularly good choice when the diabatic basis is not, namely, in the case when the external field is changing slowly, as discussed in 3.4. Then the dynamics is called adiabatic and its solution can be approximated with the adiabatic states. Often this corresponds to the parameter region of strong coupling. This adiabatic basis transformation also has fundamental role in both the Dykhne-Davis-Pechukas theory (section 3.5) and in the plane-curve representation of time-dependent two-level problems, to be dealt with in chapter 4.

The general solution for the two-level model can be given in the unitary propagator form as

$$U(t) = \begin{pmatrix} u_1(t) & u_2(t) \\ -u_2^*(t) & u_1^*(t) \end{pmatrix}, \tag{2.20}$$

where the functions $u_1(t)$ and $u_2(t)$ are the Cayley-Klein parameters [4]. These functions of course depend on the basis that is used and this is made explicit by denoting U_D and U_A to indicate whether the quantities are given in the diabatic or adiabatic basis, respectively. In many applications, it is sufficient to consider often slightly simpler problem of calculating only the transition probability to some specified state $|\varphi\rangle$,

$$P(t) = |\langle\varphi|\psi(t)\rangle|^2 = |\langle\varphi|U(t,t_0)\psi(t_0)\rangle|^2, \tag{2.21}$$

and quite often one is only interested even in the final (or asymptotic) transition probability, corresponding to limits $t_0 \to -\infty$ and $t \to +\infty$. This is denoted simply by P. Furthermore, usually both the initial and specified states are one of the basis states. In the two-level case we almost exclusively consider the initial conditions in the diabatic basis as $|C_2(t_0)| = 1$, $C_1(t_0) = 0$ and the specified state as the another basis state, $|\varphi\rangle = |1\rangle$, which means that in this case

$$P_D(t) = |C_1(t)|^2. \tag{2.22}$$

If, at initial and final times, we have $|\varepsilon(t)| \gg |V(t)|$, it follows from Eq. (2.17) that the bases coincide in the initial and final times, although possibly swapping labels (the initial diabatic ground state may correspond to the excited state in the final time). It follows that we have either $P_D = P_A$ or $P_D = 1 - P_A$. The latter case is particularly important and used in the so-called rapid adiabatic passage (RAP), where a system is driven in a coherent and adiabatic fashion which leads to $P_A = 0$. Because in the latter case we then have $P_D = 1$, a perfect population transfer between two diabatic states of the system can realised in this way.

2.3 Differential equations

The Schrödinger equation for a two-level system can be reduced to a second-order complex scalar differential equation, and one common strategy for its solution is to try to transform the equation into a form for which the solutions are known. The model functions describing the time-dependence of the external field are typically assumed to be analytic and quite often they are of such form that the differential equation belongs to the class of hypergeometric differential equations, basically the most general class of ODEs in mathematical physics for which the solutions are currently well-characterized. In this section we present some of the general forms of these equations. These differential equations are also the basis for the numerical investigations used in this thesis.

2.3.1 2nd order ODE for amplitudes

The two-level Schrödinger equation consists of two coupled differential equations, first-order in time, for the probability amplitudes of the state vector. These can be decoupled, yielding a single second-order differential equation for either one of the probability amplitudes. If this is chosen to be the amplitude of the state labeled as 1, the differential equation obtained with the real-symmetric traceless Hamiltonian (2.14) is given by

$$\ddot{C}_1(t) - \frac{\dot{V}(t)}{V(t)}\dot{C}_1(t) + \left[i\dot{\varepsilon}(t) - i\varepsilon(t)\frac{\dot{V}(t)}{V(t)} + \varepsilon^2(t) + V^2(t) \right] C_1(t) = 0, \quad (2.23)$$

and similar equation holds for state 2 but with $\varepsilon(t)$ and $\dot{\varepsilon}(t)$ replace by $-\varepsilon(t)$ and $-\dot{\varepsilon}(t)$.

In the rotating frame one gets a form that is sometimes more simple,

$$\ddot{\tilde{C}}_1(t) - \left(2i\varepsilon(t) + \frac{\dot{V}(t)}{V(t)} \right) \dot{\tilde{C}}_1(t) + V^2(t)\tilde{C}_1(t) = 0, \quad (2.24)$$

In particular, for many interesting models we have $V(t) = \text{const.}$ and, after the additional change of independent variable, Eq. (2.16), this equation simplifies to

$$\ddot{\tilde{C}}_1(t) - 2i\varepsilon(t)\dot{\tilde{C}}_1(t) + \tilde{C}_1(t) = 0. \quad (2.25)$$

2.3.2 Bloch equations

Another way to describe the dynamics of the TLS is the Bloch vector formalism, due to Feynman, Vernon and Hellwarth [37]. It takes into account the fact that the overall phase of the state vector does not have a physical meaning, so the number of real variables describing the state of a TLS can be reduced by one and both the state of the system and the Hamiltonian can be represented by vectors in three-dimensional abstract space. This assigns an intuitive geometric picture to the situation and also allows the inclusion of terms responsible for decoherence and dissipation. The three-vector $\vec{R}(t)$, called the Bloch vector, describing completely the state of the system is defined as

$$u(t) = 2\mathrm{Re}\left[C_1^*(t)C_2(t)\right] = \sin\theta(t)\cos\phi(t) \tag{2.26}$$

$$v(t) = 2\mathrm{Im}\left[C_1^*(t)C_2(t)\right] = \sin\theta(t)\sin\phi(t) \tag{2.27}$$

$$w(t) = |C_1(t)|^2 - |C_2(t)|^2 = \cos\theta(t), \tag{2.28}$$

where the first two components, $u(t)$ and $v(t)$, are termed coherences and $w(t)$ is the population difference. These definitions are illustrated in Fig. 2.1. The populations of the basis states are obtained from the third coordinate as

$$|C_1(t)|^2 = \frac{1}{2}\left[1 + w(t)\right], \quad |C_2(t)|^2 = \frac{1}{2}\left[1 - w(t)\right] \tag{2.29}$$

With these definitions, one obtains a dynamical equation that is equivalent to the time-dependent Schrödinger equation.

$$\frac{d}{dt}\begin{pmatrix} u \\ v \\ w \end{pmatrix} = -2\begin{pmatrix} 0 & -\varepsilon & 0 \\ \varepsilon & 0 & V \\ 0 & -V & 0 \end{pmatrix}\begin{pmatrix} u \\ v \\ w \end{pmatrix}, \tag{2.30}$$

and this is generally of the form of torque equation $\partial_t \vec{R} = \vec{B} \times \vec{R}$ and for Eq. (2.30) we have $\vec{B}(t) = 2\left(V(t), 0, -\varepsilon(t)\right)$. As is clear from the Eqs. (2.26-2.28), the Bloch vector for coherent evolution is of constant length, so for pure state $|\vec{R}(t)| = 1$ and it can be pictured as a curve on a unit sphere, the Bloch sphere.

It useful also to note the similarity of Eqs. (2.30) with Frenet-Serret equations for a frame moving along a space curve [38]. Then the functions $-2\varepsilon(t)$ and $2V(t)$ have the roles of the curvature and torsion of the curve, respectively.

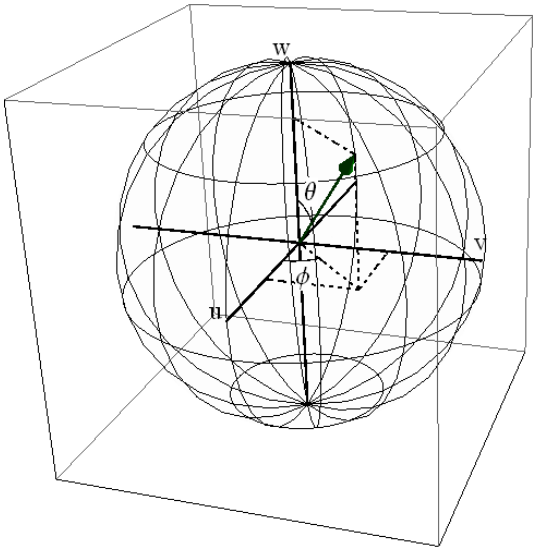

Figure 2.1: The Bloch vector and the Bloch sphere defined by Eq. (2.26-2.28).

Also, the adiabaticity (see Sec. 3.4) has a simple geometric interpretation in this representation. As mentioned above, Eq. (2.30) describes generally a situation where the Bloch vector precesses around the torque vector (the field vector $\vec{B}(t)$). If the field vector is changing in time, this can lead to transitions even if the Bloch vector of the system was originally parallel with the field. If, however, the direction of the field changes only slowly compared to the precession rate $|\vec{B}(t)| = \sqrt{\varepsilon^2(t) + V^2(t)}$ of the Bloch vector around it, things are different. In this limit, if the Bloch vector is initially parallel to $\vec{B}$, it adiabatically follows the direction of this field vector in its subsequent evolution and does not precess [39]. The same applies also for antiparallel initial condition.

2.4 Analytically solvable models

The models that are amenable to exact solution, in one form or another, of the equations presented in the previous section are important but exceedingly rare special cases. However, the exact solutions offer, for example, the dependencies of the system's dynamics on its parameters in a particularly transparent way and may reveal important insights into more general

situations. Here we introduce the basic models that are frequently treated in this thesis.

2.4.1 Rabi model

The (semiclassical) Rabi model is defined by functions

$$\varepsilon(t) = \varepsilon_0, \qquad V(t) = V_0, \tag{2.31}$$

where ε_0 and V_0 are real constants which can be chosen to be nonnegative. This model is not really a time-dependent model at all, but nonetheless it is a paradigmatic simple model for coherent excitation amenable for exact solution. Originally it was introduced by Rabi in the studies of magnetic resonance [40] but one is led to it also when one considers the two-level atom interacting with a monochromatic constant-amplitude laser field in the dipole and rotating wave approximations [39], for example.

Its solution in the diabatic basis is given by

$$u_1(t) = \cos\left[E\,(t-t_0)\right] - i\frac{\varepsilon_0}{E}\sin\left[E\,(t-t_0)\right], \tag{2.32}$$

and

$$u_2(t) = -i\frac{V_0}{E}\sin\left[E\,(t-t_0)\right], \tag{2.33}$$

where $E = \sqrt{\varepsilon_0^2 + V_0^2}$. In many cases the system is considered to be prepared in the ground state at the initial state, so that $C_2(t_0) = 1$ and $C_1(t_0) = 0$. The transition probability is then given by the non-diagonal term in the propagator,

$$P(t) = \frac{V_0^2}{\varepsilon_0^2 + V_0^2}\sin^2\left[E\,(t-t_0)\right], \tag{2.34}$$

which shows that the transition probability is oscillating in time with a frequency depending on the eigenenergy. This is usually expressed by saying that the system is experiencing Rabi flopping. The formula shows also that complete population transfer is obtained only when the system is in resonance ($\varepsilon_0 = 0$). This behavior is demonstrated in the Fig. 2.2. The resonance behavior is generalized for other systems in the area theorem discussed in section 3.2. For general initial conditions one of course gets the contribution from both of the functions (2.32) and (2.32).

It is interesting to study the more general initial conditions. For generality, it is sufficient to take $C_1(t_0) = \sqrt{p}e^{i\alpha}$ and $C_2(t_0) = \sqrt{1-p}$, where p

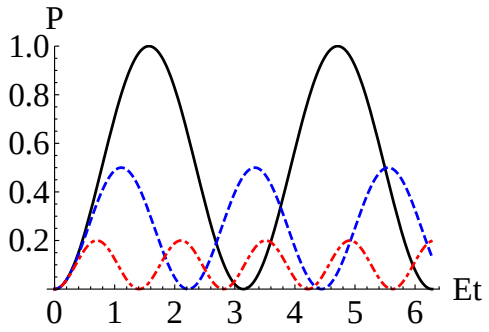

Figure 2.2: The time-dependence of the transition probability for the initial conditions $C_g(t=0)=1$ and given by Eq. (2.34) for three different values of the detuning: $\varepsilon_0 = rV_0$ where $r=0$ (black, solid), $r=1$ (blue, dashed) or $r=2$ (red, dotdashed).

is the initial population of the excited state and α is the phase difference between the probability amplitudes initially. The excited state population at time t can be given in a concise form which shows the effect of the initial condition as

$$\begin{aligned} P(t) &= \left(\tfrac{V_0}{E}\right)^2 S^2(t) + p\left[C^2(t) + \tfrac{\varepsilon_0^2 - V_0^2}{\varepsilon_0^2 + V_0^2} S^2(t)\right] \\ &+ \sqrt{p(1-p)}\left(\tfrac{2V_0 S(t)}{E}\right)\left[\tfrac{\varepsilon_0}{E}\cos(2\alpha)S(t) - \sin(2\alpha)C(t)\right] \qquad (2.35) \\ &= p + (1-2p)\left(\tfrac{V_0}{E}\right)^2 S^2(t) + \sqrt{p(1-p)}\tfrac{2V_0}{E}S(t) \\ &\quad \times \left[\tfrac{\varepsilon_0}{E}\cos(2\alpha)S(t) - \sin(2\alpha)C(t)\right], \qquad (2.36) \end{aligned}$$

where $C(t) = \cos\left[E\,(t-t_0)\right]$ and $S(t) = \sin\left[E\,(t-t_0)\right]$. This solution obviously reduces to equation (2.34) when there is no initial excitation.

2.4.2 Landau-Zener model

The Landau-Zener model is given by

$$\varepsilon(t) = \varepsilon_0 t, \qquad V(t) = V_0, \qquad (2.37)$$

where ε_0 and V_0 are again real constants. This gives a model for the time-dependencies of the system: diabatic energy levels cross each other once, at time $t=0$, in a linear manner while coupling remains constant for all

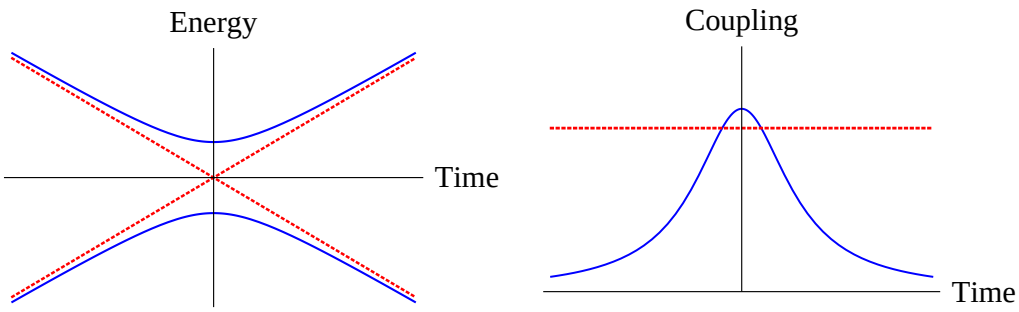

Figure 2.3: The schematic Landau-Zener model functions. The time-dependence of the energy and the coupling in the diabatic basis are drawn with dashed red line while the corresponding quantities in the adiabatic basis are drawn with blue solid line.

times. In the adiabatic basis, we have an avoided crossing at $t = 0$, as usual, and the adiabatic coupling is pulse-shaped having the maximum at the crossing point.

Landau considered the problem first [9] with contour integration methods and calculated the asymptotic transition probability as

$$P_A = \exp\left(\frac{-\pi V_0^2}{\varepsilon_0}\right), \tag{2.38}$$

whereas Zener was able to reduce the solution of the full problem to the equation for parabolic cylinder functions (PCF). Indeed, with the simple independent variable transformation $z = \sqrt{2\varepsilon_0}e^{-i\pi/4}t$, the Eq. (2.23) for the LZ model leads to an equation of the form

$$\frac{\mathrm{d}^2 C_2}{\mathrm{d}z^2} + \left(n + \frac{1}{2} - \frac{z^2}{4}\right) C_2 = 0, \tag{2.39}$$

where it is defined $n = (i\Lambda)/2)$ and $\Lambda = V_0^2/\varepsilon_0$ is the LZ parameter. The equation is exactly of the form of the Weber differential equation for which the parabolic cylinder functions $D_n(z)$ are the solutions [41]. The general solution to the equation can be given, for example, in the form

$$C_2(z) = aD_n(z) + bD_n(-z), \tag{2.40}$$

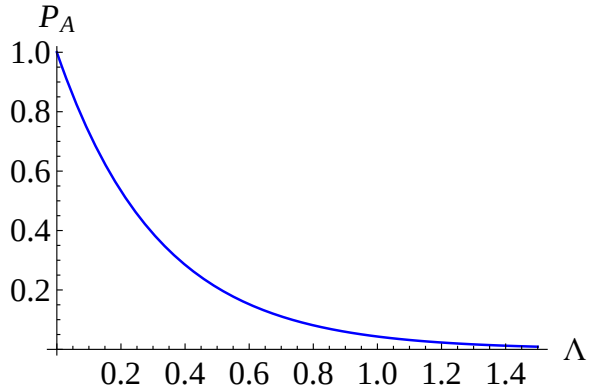

Figure 2.4: The final probability of transitions between adiabatic states, given by Eq. (2.38).

from which the dynamics of the system can be calculated for any initial conditions. Zener simply considered the initial conditions $|C_1(-\infty)| = 1$, $C_2(-\infty) = 0$ and was similarly interested only in the asymptotic transition probability P. In this way, from the asymptotics of PCFs, the expression of Eq. (2.38) is again obtained. Also, one can consider the asymptotics of the solutions with general initial conditions (2.40) and determine the S-matrix of the process defined as $S = U(\infty, -\infty)$.

Taken the rather crude time-dependencies in the definition of the LZ model, it has been often puzzled why it is then that the LZ model and the formula (2.38) is so unexpectedly useful in practise in many situations [13, 14, 15, 16]. Firstly, it is clear that, when considering a single process where the energy levels are crossed only once and the system starts from one of the basis states, only the transition probability matters and the phases do not play any role. Furthermore, one can take the analytic behaviour of the model functions into account and Taylor expand the energy levels at the crossing point. Now, if one can assume that the time-dependency of the coupling is much slower than of the energy levels and that the transition happens almost immediately at the crossing point, one can treat the coupling as constant and retain only the linear term in the expansion for the levels (assuming that their first derivative does not vanish at the crossing as happens in the so-called level glancing). This can be taken as a justification for the use of LZ model for the cases where the transitions happen rapidly. This simple picture does not explain, however, why the LZ formula often works also when the adiabatic limit is approached, but conditions for its

application can be given also in this case [14, 15].

In any case, the unphysical features of the model, in particular the constant diabatic coupling that never switches off, lead to infinities in the phases of the scattering matrix. Again, these do not show up when the conventional initial condition of single input state is used. This also applies when the initial state is a completely incoherent mixed state or when the system is in adiabatic or sudden limit [16]. In many modern applications, however, such as in quantum information processing, one constantly has to work with superposition states as intermediate states and to manipulate them further. For coherent superposition states the infinite interaction energy of LZ model shows up as a failure of converge of components in the density matrix of the system, as shown in [16], which limits the use of LZ model in such applications. However, in adiabatic basis the coupling does stop and we use the scattering matrix in the form [50],

$$S_A = \begin{pmatrix} \sqrt{1-R^2}e^{i\phi_S} & -R \\ R & \sqrt{1-R^2}e^{-i\phi_S} \end{pmatrix}, \tag{2.41}$$

which contains no such infinities and where $R = \exp(-\pi\Lambda/2)$ is the amplitude of the LZ transition and

$$\phi_S = \frac{\pi}{4} + \frac{\Lambda}{2}\ln\left(\frac{\Lambda}{2e}\right) + \arg\left[\Gamma\left(1 - i\Lambda/2\right)\right] \tag{2.42}$$

is the Stokes phase.

2.4.3 Rosen-Zener model

The third model we consider, although in brief, is the Rosen-Zener model (RZ) which is a paradigmatic no-crossing model for pulsed excitation. It is defined by

$$\varepsilon(t) = \varepsilon_0, \qquad V(t) = V_0\mathrm{sech}(t/T), \tag{2.43}$$

where ε_0, V_0 and T are real constants which can be taken to be positive. The constant T characterizes the length of the interaction. It was originally considered by Rosen and Zener in their time-dependent theory of double Stern-Gerlach process in [17]. The final transition probability for the model is given by

$$P = \sin^2\left[\pi V_0 T\right]\mathrm{sech}^2\left[\pi\varepsilon_0 T\right], \tag{2.44}$$

and plotted in Fig. 2.5. It shows that the effect of the detuning of the energy levels and the coupling on transition probability factorizes. As the

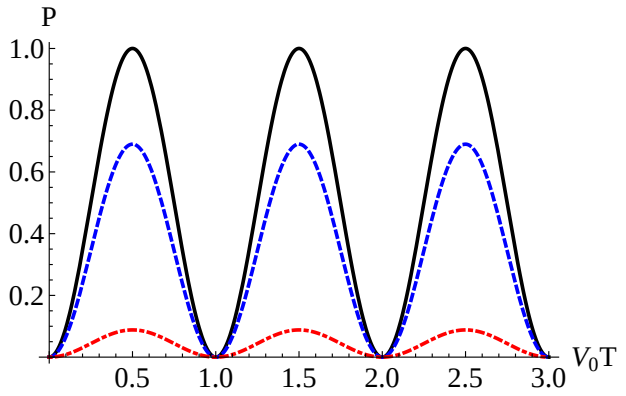

Figure 2.5: The final probability of transitions for Rosen-Zener model, given by Eq. (2.44), is plotted for three different detunings: $\varepsilon_0 T = 0$ (black solid line), $\varepsilon_0 T = 0.1$ (blue dashed line) and $\varepsilon_0 T = 0.3$ (red dot-dashed line).

detuning, $2\varepsilon_0$, grows, it controls the maximum of the transition probability which tends monotonically from unity to zero, as seen in the second factor of Eq. (2.44). The first factor shows that, for a fixed detuning the transition probability oscillates sinusoidally, as in the Rabi model, when the coupling is varied. In particular, the argument of the first factor in Eq. (2.44) is proportional to the total pulse area,

$$A = 2\int_{-\infty}^{+\infty} V(t)\mathrm{d}t = 2\pi V_0 T. \tag{2.45}$$

Furthermore, it also follows from this factor that the probability goes periodically to zero when either V_0 or T is varied as the condition for this is that $V_0 T$ must be an integer.

2.4.4 Other analytically solvable models

There exists some other well-known analytically solvable two-state models that are not explicitly made use of in this thesis but which are mentioned here for completeness. Some of these can be reduced to each other as a special or a limiting case and the solution belongs to the class of hypergeometric functions in all of the cases [4, 41].

Especially interesting in this respect are the two Demkov-Kunike models [18, 42] (denoted by DK1 and DK2, respectively) are defined with

$$\varepsilon(t) = \varepsilon_0 + \varepsilon_1 \tanh(t/T), \qquad V(t) = V_0 \mathrm{sech}(t/T), \tag{2.46}$$

for DK1 and where T is the time-scale parameter and for DK2 with

$$\varepsilon(t) = \varepsilon_0 + \varepsilon_1 \tanh(t/T), \qquad V(t) = V_0. \tag{2.47}$$

Others include Gaussian model [43, 44], the exponential models of Nikitin [45] and Demkov [46], Carroll-Hioe [43] and Allen-Eberly [39] models, to name a few. Important is also the class of models by Bambini and Berman [47] which have used to study some general properties of coherent excitation, such as the effect of asymmetric pulses [48]. There is also a systematic way to derive new classes of solvable models based on a certain class property of transformations, initiated by Ishkhanyan [51].

2.5 Parabolic and superparabolic models

In many ways, the next natural model to consider after the LZ model would be the parabolic model, where the diabatic energies behave quadratically while the coupling is kept constant also in this model

$$\varepsilon(t) = \varepsilon_0 t^2 - c, \qquad V(t) = V_0, \tag{2.48}$$

where ε_0 and V_0 are positive constants and c can be any real number. Depending on the value of c, we have three separate cases. If $c > 0$, the system undergoes two separate crossings at $t_c = \pm\sqrt{c/\varepsilon_0}$. If $c < 0$ the diabatic levels do not cross and the transitions can happen only by tunnelling through the non-zero energy barrier separating the levels. Finally, if $c = 0$ we have a case where the energy levels only touch each other temporally at $t = 0$ and this case is called as level glancing. The time-dependencies of the energy levels and couplings related to these different cases are shown in Fig. 2.6. The model has been introduced in the context of slow atomic collisions [54, 22] and it has served also as a simple model to study the loss of coherence in open system dynamics [52] or the failure of the LZ linearisation scheme [53]. Recently it has been applied also to laser-controlled molecular dynamics [55] and in Dirac cone physics [56].

The model exhibits dynamics that is both qualitatively and quantitatively different from the dynamics of the LZ model. In addition to the exponential suppression of the transition probability in the strong coupling region, it also has a oscillating component. In the double-crossing case these would be easy to associate with the interference arising from the two separate crossing points of the diabatic energy levels and the accumulation of the dynamic phase between the crossings. However, the oscillations persist

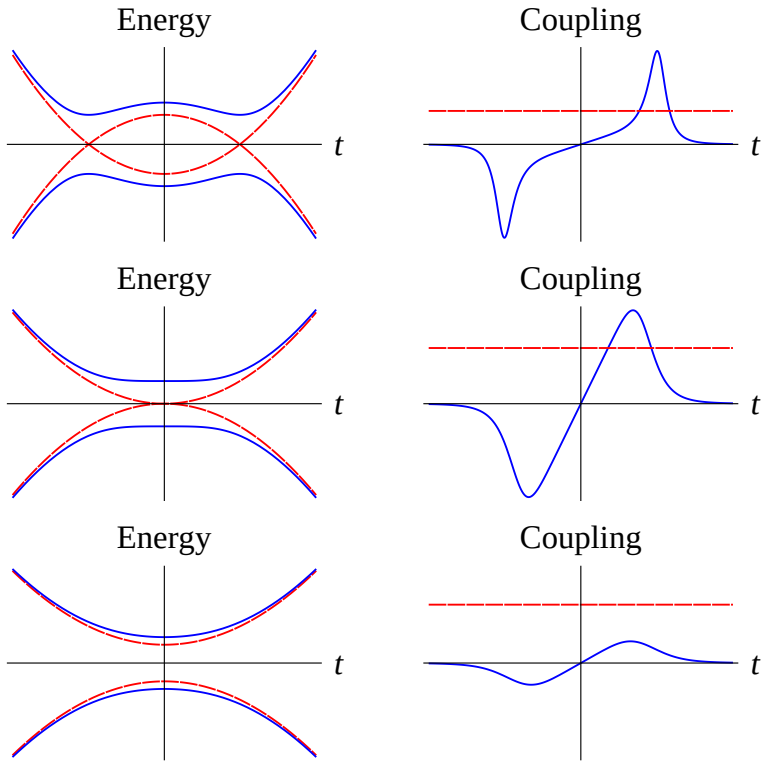

Figure 2.6: Schematics of the time-dependencies of the energy levels (left panel) and coupling (right panel) in the parabolic model for the different cases. In the uppermost plots we have the double-crossing ($c = 1$), the middle plots are for the level glancing ($c = 0$) and the lowermost plots are for the tunneling case ($c = -1$). Other parameters are the same for each plot, in this case they are $\varepsilon_0 = 1$ and $V_0 = 0.6$. The quantities in the adiabatic basis are drawn with blue solid line while the same quantities in the diabatic basis are drawn with dashed red lines.

also to the level-glancing case, where no such simple picture exists in the diabatic basis. In the adiabatic basis, however, the different cases are not too dissimilar and the adiabatic coupling, for example, has two clear peaks in each case. The oscillations can also be understood as a consequence of the interference between different complex transition points, the zeros of eigenenergies, in the framework of the Dykhne-Davis-Pechukas (DDP) theory, explained in Sec. 3.5. The number of the zeros and their structure remain similar, regardless of the value of c, so some oscillations are to be expected in each case although they may be washed out by the exponential term.

We consider also a straightforward generalization of these models to the so-called superparabolic models which have the model functions

$$\varepsilon(t) = \varepsilon_0 t^{2N} - c, \qquad V(t) = V_0, \tag{2.49}$$

where N is a positive integer. The energy levels and the coupling of higher superparabolic models ($N > 1$) are very similar to the parabolic model ($N = 1$), only flatter around the time $t = 0$. Much of what was said above applies to these models but, nonetheless, they also serve as a good models to test different phenomena related to level-crossings and in particular the approximative theories, such as the DDP theory (Sec. 3.5 and paper I) and the Zhu-Nakamura theory (paper II). Also, the paper V and Ch. 5.4 concerns on the study of a variant of the superparabolic models where the coupling changes rapidly and enhances the population transfer considerably.

2.6 Time-independent Schrödinger equation

Although we are mostly interested in purely time-dependent level-crossing models such as those arising in connection with the coherent excitation with laser fields, in order to understand fully the importance and historical developments of these models and their applications, some aspects of the nonadiabatic transitions in time-independent setting must be introduced. This is also needed to discuss the Zhu-Nakamura theory in Sec. 3.6.

The time-independent interacting two-level model, with diabatic states φ_1 and φ_2 is subject to the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi_1}{dR^2} + [V_1(R) - (E - E_X)]\,\varphi_1 = V_{12}(R)\varphi_2 \tag{2.50}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi_2}{dR^2} + [V_2(R) - (E - E_X)]\,\varphi_2 = V_{12}(R)\varphi_1, \tag{2.51}$$

where $V_1(R)$ and $V_2(R)$ are the diabatic potentials, that depend on the state of the system as well as the coordinate R, and $E - E_X$ is the energy of the system with the fixed reference value E_X. In contrast to the usual eigenvalue equation that is called time-independent Schrödinger equation, there is also the term $V_{12}(R)$ that is the diabatic coupling that induces transitions between the states. The most typical application of these equations is the electronic transitions in atomic and molecular collisions and there the problem related to the nonadiabatic dynamics is more often called the curve-crossing problem.

The dependence of the potentials can depend a lot on the nature of the physical system, but as the transitions are also in this case usually concentrated near the points where the difference between the potentials is small, it is natural, as in the time-dependent case, to consider as the model functions the linear dependence $V_1(R) = -F_1(R - R_X)$, $V_2(R) = -F_2(R - R_X)$ where R_X is the point where the potential curves cross. We take the energy zero point E_X to be this crossing point energy value. Also, the coupling is assumed to vary only slowly and taken to be a constant, $V_{12}(R) = A$. This defines the time-independent LZ problem. Although the relative signs of the slopes F_1 and F_2 could be arbitrary, we consider only the case $F_1 F_2 > 0$ because only it has a direct counterpart in the time-dependent theory. In this context, the case with same slopes is also called as being Landau-Zener type [22]. With no loss in generality we can require that $F_1 > 0$, $V_{12} > 0$ and $F_1 > F_2$.

As the coupled Eqs. (2.50) and (2.51) are two second-order differential equations, or equivalently a single fourth-order equation, its solution is more difficult than the time-dependent Schrödinger equation for TLS. By transforming the coupled Eqs. (2.50) and (2.51) into a momentum representation and redefining the variables suitably [54, 22] we can reduce these coupled first-order equations to a second-order differential equation for, say, the state corresponding to φ_1, to a equation of the form

$$y''(z) + q(z)y(z) = 0, \tag{2.52}$$

where

$$q(z) = \frac{1}{4} - ia^2 z + \frac{1}{4}(a^2 z^2 - b^2)^2, \tag{2.53}$$

where the parameters are defined as

$$a^2 = \frac{\hbar^2}{2m} \frac{F\,(F_1 - F_2)}{(2V_{12})^2}, \qquad b^2 = \frac{(F_1 - F_2)}{2FV_{12}}\,(E - E_X) \tag{2.54}$$

and we have defined $F = \sqrt{F_1|F_2|}$. The independent variable is $z = (2V_{12}k)/F$ where k is the momentum.

The physical meaning of these reduced parameters are as follows: the parameter a^2 represents the effective coupling strength and b^2 is the effective collision energy. From Eq. (2.54) one can see that a^2 is always non-negative but that b^2 can be both positive or negative, depending on whether the energy E is higher or lower than the crossing point energy E_X, respectively.

Some important simplifying approximations can be made, though, by assuming that the nuclear motion follows some well-defined common trajectories. For example, we could follow the method in the original paper of Zener [10] and assume that the relative nuclear motion is along a straight line and the velocity is constant, so that $R(t) = vt$ and $v^2 = 2(E - E_X)/m$. This reduces the problem to the familiar time-dependent LZ model and with the current variables we would get the transition probability as

$$p_{LZ} = \exp\left[-\frac{\pi}{4a|b|}\right]. \tag{2.55}$$

As is well known, this formula works only for energies much larger than the crossing point energy E_X, because in a collision the transition point is traversed twice, once when in-coming and once on the way out (or, if the energy is lower than the crossing point energy, there is no crossing at all). If E is too close to E_X, the two transitions start to overlap and this simple consideration is not valid.

In any case it is useful to note that the Eq. (2.52) is actually exactly of the same form as the Schrödinger equation for the time-dependent parabolic model and this connection is important in the context of Zhu-Nakamura theory in 3.6.

Chapter 3

Approximative approaches to the solution of coherent dynamics

3.1 Perturbation methods

An important special case that greatly simplifies the theory of the population transfer in quantum systems is the limit where the interaction is too weak for any appreciable excitation to occur. Then one can use the time-dependent perturbation theory to understand the dynamics of the system. This approximation method is sufficient to describe the excitation that occurs with broadband radiation sources, for example. Therefore, it is well-known and has been used for a long time, so we review only some of its basic results.

It is now most convenient to consider the system in the interaction basis. From the Schrödinger equation with the Hamiltonian (2.15) we obtain

$$i\tilde{C}_2(t) = i\tilde{C}_2(t_0) + \int_{t_0}^{t} V(s) \exp\left(-2i \int^{s} \varepsilon(u)\mathrm{du}\right) \tilde{C}_1(s)\mathrm{ds} \tag{3.1}$$

If it assumed that at the initial time, t_0, the system is completely in the first state, i.e. $C_1(t_0) = 1$ and $C_2(t_0) = 0$, then, by the assumption of weak coupling, these initial values are changed only very little by the interaction. To the first order, we have that $\tilde{C}_1(t) \approx 1$ for all t, and the Eq. (3.1) reduces to

$$\tilde{C}_2(t) = -i \int_{t_0}^{t} V(s) \exp\left(-2i \int^{s} \varepsilon(u)\mathrm{du}\right) \mathrm{ds}. \tag{3.2}$$

Some observations are in order: if the external field is in resonance with the TLS so that $\varepsilon(t) \equiv 0$, then the amplitude $\tilde{C}_2(t)$ is proportional to the

area of the pulse, that already appeared in Eq. (2.45) and to which more attention is paid on in Sec. 3.2. The final probability of transition in this lowest-order approximation is obtained as

$$P_D^{\mathrm{1st}} = |\tilde{C}_2(\infty)|^2 = |C_2(\infty)|^2 = \left| \int_{-\infty}^{+\infty} V(t) \exp\left(-2i \int^t \varepsilon(s)\mathrm{ds} \right) \mathrm{dt} \right|^2 . \tag{3.3}$$

This is often also referred to as the first Born approximation. It is seen from this result that for the case of constant detuning, zero or not, the transition probability is essentially the Fourier transform of the coupling function $V(t)$, evaluated at the detuning frequency. It also means that, to the first order, transitions are absent when the coupling pulse has no frequency component corresponding to the detuning.

An important class of models is those where the coupling function is taken constant $V(t) = V_0$. For those[a], we get from Eq. (3.3)

$$P_D^{\mathrm{1st}} = V_0^2 \left[\left(\int_{-\infty}^{+\infty} \cos\left(2 \int^t \varepsilon(s)\mathrm{ds} \right) \mathrm{dt} \right)^2 + \left(\int_{-\infty}^{+\infty} \sin\left(2 \int^t \varepsilon(s)\mathrm{ds} \right) \mathrm{dt} \right)^2 \right] . \tag{3.4}$$

From this we see that as function of the coupling strength, it is proportional to V_0^2. The second factor has an interesting geometrical interpretation that can offer more intuition on the behaviour of the system in the limit of weak coupling. It is the square of the length of a two-dimensional vector which traces out a plane curve where the signed curvature of the curve[b] is given by the detuning, $2\varepsilon(t)$. The curve in question starts from the origin, so choosing such a function $\varepsilon(t)$ that it returns there, in the limit $t \to +\infty$, gives another condition for the absence of transitions to the first order. For LZ model, the integrals in Eq. (3.4) are the Fresnel integrals that appear in an analogous fashion in Fresnel diffraction. For the case that we have a more general monomial, $\varepsilon(t) = at^n$, as it is the case for superparabolic models, the curves in question are the generalized Cornu spirals [38].

The weak-coupling approximation is often of very limited applicability. Even if it somehow would give correct estimate for the transitions beyond its expected validity of very small V_0 and P, it diverges as V_0^2 when the

[a] Actually, what follows could be applied also to more general models with $V(t) \neq 0$ by using the independent variable transformation (2.16) first.

[b] More details and the definitions regarding plane curves can be found in Sec. 4, and references therein, where we consider a completely different application of their differential geometry to the two-level problem.

coupling increases and soon gives values that exceed unity. At least the latter defect can be corrected by considering the Magnus approximation. The Magnus expansion [63, 65] can be used to obtain approximative solutions to non-autonomous differential equations that keep certain characteristic features of the exact solution, in this case the unitarity. The first Magnus approximation can be obtained from (3.3) in the form [64]

$$P_D^{Magnus} = \sin^2\left(\sqrt{P_D}\right), \tag{3.5}$$

which is obviously between 0 and 1.

3.2 Area theorem

Another important result in the theory of coherent excitation is the area theorem, which says that when the system is excited resonantly, the population depends on the area of the exciting pulse. The main thing of importance to notice here is that it is really only the time-integral of the interaction, i.e. the area, and not other details such as the shape of the pulse, that affects the final population. Indeed, if $C_1(t_0) = 1$, then a solution to the Schrödinger equation (2.23) with $\varepsilon(t) \equiv 0$ is

$$C_2 = \sin\left(\int_{t_0}^{t} V(s)\mathrm{ds}\right), \tag{3.6}$$

and therefore the population of the second state at any given time is given by

$$P(t) = \sin^2\left(\frac{A(t,t_0)}{2}\right), \tag{3.7}$$

where the pulse area $A(t,t_0)$ accumulated between times t_0 and t is defined as

$$A(t,t_0) = 2\int_{t_0}^{t} V(s)\mathrm{ds}, \tag{3.8}$$

and the factor of 2 in the definition arises from our definition of the Hamiltonian, Eq. (2.14). This convention is in place, in particularly in NMR and quantum computing, where one commonly employs so-called π and $\pi/2$ pulses, for example. If $A = \pi(2k+1)$ where k is integer, one obtains complete population inversion (CPI). Similarly, if $A = 2\pi k$ returns the population into the initial state whereas with $A = \pi(k+\frac{1}{2})$ one can prepare equal superposition of the basis states.

Manifestations of the area theorem result were already present in the expressions (2.34) and (2.44) for the resonant case. It should be also noted that the first Magnus approximation, Eq. (3.5) agrees with the area theorem in the resonant case. The area theorem is an important simple principle in designing pulses that produce the desired amount of excitation but the problem with it is that it is not robust against parameter fluctuations, i.e. small changes in the shape of the pulse can alter the area and therefore the amount of excitation considerably. This can be contrasted with the adiabatic approximation and the adiabatic passage method, as explained in the following sections.

3.3 Independent crossing approximation

Many dynamical processes can be decomposed into a sequence of simpler basic events which often are solvable. The combination of the propagators related to these basic events, form often a good approximation for the dynamics of the original process. The basic events sufficient to our purposes consist of transition or scattering matrices related to traversing a level crossing and of matrices related to the evolution of dynamical phases between the level-crossing events.

A particularly simple illustration of the technique is the reduction of the double-crossing parabolic-type models to two LZ crossings. All of the superparabolic models, defined by Eq. (2.49), have two level crossings, at times $t_* = \pm(c/\varepsilon_0)^{1/N}$. If the transitions are well-localized in the vicinity of the level crossing, we can linearize the energy levels around these points and consider the process to consist of two LZ crossings and obtain the total propagator for the process as

$$S_A^{tot} = S_{A,2} U_{\varphi_{dyn}} S_{A,1}, \tag{3.9}$$

where the $S_{A,i}$, $i = 1, 2$ corresponds to the two LZ events and are given by Eq. (2.41) but where the rate parameter in the variable Λ is replaced with the one obtained from the linear term in the Taylor expansion around the crossing point, namely with

$$\varepsilon_0^{LZ} \equiv 2n\varepsilon_0 t_*^{2N-1}. \tag{3.10}$$

The matrix $U_{\varphi_{dyn}}$ takes into account the difference of the dynamical phase accumulated between the levels in the duration between the crossings, since

only this has effect on the dynamics. This is given by

$$U_{\varphi_{dyn}}(t) = \begin{pmatrix} e^{+i\varphi_{dyn}} & 0 \\ 0 & e^{-i\varphi_{dyn}} \end{pmatrix}, \tag{3.11}$$

where

$$\varphi_{dyn} = \int_{-t_*}^{t*} \mathrm{d}s \sqrt{(\varepsilon_0 s^2 - c)^2 + V_0^2}. \tag{3.12}$$

In addition, one must occasionally take into account some additional structure of the model. The adiabatic coupling of the parabolic model is an odd function of time, so the off-diagonal elements of the second scattering matrix, $S_{A,2}$, have to be equipped with extra minus sign accordingly. This actually is important, making the oscillatory part of the final transition probability,

$$P = 4R^2(1-R^2)\sin^2\left(\varphi_{dyn} + \phi_S\right), \tag{3.13}$$

sine instead of cosine.

3.4 Adiabatic approximation

The notion of adiabaticity has had an important role in many areas of physics. The adiabatic theorem of quantum mechanics[c], in particular, gives us the dynamics in the limiting case when the Hamiltonian is changing very slowly.

It was stated first by Born and Fock [8] for the case that the spectrum of the Hamiltonian $H(t/T)$ is discrete and nondegenerate. If the system starts initially from an eigenstate $|n(t_0)\rangle$, then in any later time t it is found, in the limit $T \to \infty$, in the state

$$\psi_n(t) = \exp\left(-iT\int_{t_0}^{t} \mathrm{d}s E_n(s) - \int_{t_0}^{t} \mathrm{d}s \langle n(s)|\dot{n}(s)\rangle\right)|n(t)\rangle, \tag{3.14}$$

where in the following we can use the so-called Born-Fock gauge and fix the second term in the exponent as $\langle n(s)|\dot{n}(s)\rangle = 0$. For cyclic evolutions this term would give rise to the Berry phase and therefore such a fixing can not be done in general [49, 81]. In any case, what the adiabatic theorem says is

[c] To be more specific, we consider solely the time-adiabatic approximation, for which the whole term adiabatic approximation is often taken as a synonym for. There, however, exists other settings for adiabatic approximation such as in the space-adiabatic methods [66].

that, if the system starts in an eigenstate and the corresponding eigenvalue is separated from the rest of the spectrum, then at any later time the system is found in an eigenstate corresponding to the same eigenvalue, up to deviations of the order $1/T$. Equivalently, non-adiabatic transitions out of this eigenstate are bounded by a term of the order of $1/T^2$, so the transition probability vanishes in the limit $T \to \infty$. The adiabatic theorem was later generalized by Kato [61], by removing the overly restrictive assumptions on the spectrum.

As no change takes place infinitely slowly, it would be much more useful to obtain an answer to the question, how is the adiabatic limit approached. An important special case is the models with analytic Hamiltonians and for them, a more refined estimate can be obtained. Let $\epsilon = 1/T$ be the small parameter in the adiabatic domain. Then the nonadiabatic transition probability after infinite time is given by the asymptotic expression

$$P_A \sim \exp\left(-c/\epsilon\right), \ \epsilon \to 0, \tag{3.15}$$

where c is a positive constant, so the non-adiabatic transitions are exponentially suppressed. Sometimes this is also expressed by saying that the nonadiabatic phenomena are beyond any order in the perturbation parameter ϵ [62].

Adiabatic theorem can be easily demonstrated for a two-level system. Let us assume again, that there is a characteristic time-scale T which controls the rate of the variation of the diabatic Hamiltonian, so that the Hamiltonian can be written $H(\epsilon t)$. Now making the change of variables $\tau = \epsilon t$, the time is measured with this natural time-scale and the Schrödinger equation (2.5) is transformed to

$$i\epsilon\partial_\tau \tilde{\psi}(\tau) = H(\tau)\tilde{\psi}(\tau), \tag{3.16}$$

where $\tilde{\psi}(\tau) \equiv \psi(\tau/\epsilon)$. Now the limit that the system changes infinitely slowly, the adiabatic limit, corresponds to $\epsilon \to 0$. Because the parameter ϵ multiplies only the left-hand side of the equation (3.16)[d], the transformation (2.17) to the adiabatic basis (which has the effect of diagonalizing the Hamiltonian) leaves the dependence on it only in gauge term arising from the time-dependence of the transformation, i.e., in the off-diagonal

[d] Although in this form, the small parameter ϵ appears to be in similar position as the Planck constant $\hbar$, the quasi-classical and adiabatic limits are not always equivalent [60]. The equation also shows that the limit $\epsilon \to 0$ is actually singular for the Eq. (3.16).

elements of the resulting Hamiltonian. Adiabatic Hamiltonian is then explicitly given by

$$H_A(\tau) = \begin{pmatrix} E(\tau) & i\epsilon\gamma(\tau) \\ -i\epsilon\gamma(\tau) & -E(\tau) \end{pmatrix}, \tag{3.17}$$

where $E(\tau)$ and $\gamma(\tau)$ are the adiabatic energy level and coupling defined earlier. Clearly, when

$$\frac{|\gamma(t)|}{E(t)} \ll T, \tag{3.18}$$

for all t, the transitions between the adiabatic states are suppressed.

Continuing this diagonalization iteratively one might expect to suppress the effect of the nondiagonal terms in the Hamiltonian. Indeed, in every one of the new so-called superadiabatic bases that results from this, the nonadiabatic coupling is of higher order with respect to ϵ (explicitly, it is proportional to ϵ^n in the nth superadiabatic basis, where $n = 1$ is the adiabatic basis). In this way, one would obtain a perturbation series with respect to parameter ϵ for the nonadiabatic transitions, which contradicts Eq. (3.15). The resolution comes from the fact that the resulting series does not actually converge but is only asymptotic. Instead of continuing the iteration indefinitely, one can find an optimal superadiabatic basis where the coupling is the smallest, after which it starts to grow factorially in higher-order bases [67, 76].

It is also important to consider, what is the adiabatic parameter and adiabatic limit in the less clear-cut case that there is no single time-scale parameter T given explicitly and so the Hamiltonian is not given in the form $H(t/T)$. Quite often the adiabatic limit is also the strong coupling limit, like in the case of LZ model where the parameter controlling the adiabaticity is given by the combination V_0^2/ε_0. This question is dealt further with for more general models in Sec. 4 with the tools of differential geometry of plane curves.

3.5 Dykhne-Davis-Pechukas theory

3.5.1 History and description of the method

It was already in the seminal papers of Landau [9] and Stückelberg [11] that the complex plane zero of the adiabatic energies and its importance to the nonadiabatic transitions was realised. Later, in early 1960's, Dykhne elaborated this connection further and showed that in the adiabatic limit generally, for analytic time-dependent Hamiltonian, the transitions between

two neighbouring adiabatic levels $E_{\pm}(t) = \pm E(t)$ can be given by the formula [23]

$$P_A = \exp\left(-2T\mathrm{Im}D(t_c)\right), \tag{3.19}$$

where

$$D(t) = 2\int_0^t E(s)\mathrm{ds}, \tag{3.20}$$

and t_c is the complex zero, so that $E(t_c) = 0$. This is also called as the complex crossing or transition point. The formula (3.19) exhibits many intriguing features. It gives nonperturbative expression for the transitions in the adiabatic limit, proving the fact mentioned in Sec. 3.4 that this effect is indeed beyond all orders in adiabatic parameter $\epsilon = 1/T$ for analytic models. It was also peculiar that it makes no reference to the form of adiabatic coupling, which is, after all, causing the transition.

The Dykhne's formula (3.19) was put on a more rigorous basis some 15 years later, by Davis and Pechukas [24] and therefore it is nowadays called as the Dykhne-Davis-Pechukas (DDP) formula. Assuming that, for any t in the extended real line (that is, including the limits $t = \pm\infty$) $E(t)$ has only avoided crossings, that there is a unique complex crossing point t_c nearest to the real axis (other singular points are assumed to be well-separated from this point) and that $E(t)$ is analytic in a region from the real axis to the crossing point, they were able to prove that the Eq. (3.19) is the correct asymptotic transition probability in the adiabatic limit.

Davis and Pechukas were able to show that, in the adiabatic limit, the change in the amplitude, i.e. the nonadiabatic transition, is located in the close vicinity of the complex crossing point. They considered the analytic continuation to the upper complex plane ($\mathrm{Im}(t) > 0$) of the time-dependent Schrödinger equation in the adiabatic basis in the form

$$\dot{a}_+(t) = \quad \gamma(t)e^{-iTD(t)}a_-(t) \tag{3.21}$$

$$\dot{a}_-(t) = \quad -\gamma(t)e^{iTD(t)}a_+(t), \tag{3.22}$$

with the initial condition $a_-(-\infty) = 1$. By integrating the equation along the level line defined by $\mathrm{Im}D(t) = \text{const.} = \mathrm{Im}D(t_c)$, also called as Stokes lines, the solution of the equation and the growth of the amplitude $a_+(t)$ can be controlled. Assuming that t_c is a simple zero of $E^2(t)$, then, in the leading order, near t_c we have $E(t) = \text{const.} \times \sqrt{t - t_c}$ and t_c is a branch point for the complex-continued eigenenergy function. By local analysis, it can be shown that there are three Stokes lines emanating from a crossing point with equal angles and these can be constructed, for example, by the

algorithm provided in [77]. Similarly, for adiabatic coupling it was shown that near t_c its leading order is given by

$$\gamma(t) = \pm\frac{1}{4i(t-t_c)}, \tag{3.23}$$

that is, it has a simple pole at the crossing. This also explains the absence of any dependence on the nonadiabatic coupling in the Eq. (3.19), showing that its contribution, in the leading order, is actually same for any model. These both behaviors can be generalized in a straightforward way when the complex zero of $E^2(t)$ is not simple [67].

Despite being a method derived explicitly to systems in the adiabatic region, applying the DDP method to LZ model gives actually the exact expression for the probability of non-adiabatic transition after infinite time, Eq. (2.38), no matter what the parameter values are. The LZ model has one complex crossing point on each of the upper and lower complex planes, namely, at $t_c^+ = \pm iV_0/\varepsilon_0$. The DDP phase integral corresponding to the crossing point on the upper half plane then reads

$$D(t_c^+) = 2\int_0^{iV_0/\varepsilon_0} \sqrt{\varepsilon_0^2 t^2 + V_0^2}\mathrm{dt} = i\frac{\pi V_0^2}{\varepsilon_0}, \tag{3.24}$$

which when applied to Eq. (3.19) gives the exact formula of Eq. (2.38).

In the case that there are many zero points t_c, Eq. (3.19) has to be complemented accordingly and there exists some rigorous results on the matter [25, 26]. However, as discussed already in Refs. [24, 78] and studied later by Suominen and co-workers in [27, 13] and Paper I, a useful generalization into multiple-crossing case is to include the contribution of all the zero points t_c^k on the half plane as a coherent sum. This leads to the following formula as a generalization of the DDP formula,

$$P_{DDP} = \left|\sum_{k=1}^{N} \Gamma_k e^{iD\left(t_c^k\right)}\right|^2, \tag{3.25}$$

where

$$\Gamma_k = 4i \lim_{t\to t_c^k} \left(t - t_c^k\right)\gamma(t), \tag{3.26}$$

and $\gamma(t)$ is the nonadiabatic coupling defined in Eq. (2.19). From Eq. (3.25) one can be see that the existence of multiple zero points t_c^k, $k = 1, 2, 3, \ldots$ leads to oscillations in the final state populations as the parameters are varied.

As an intriguing fact, one can note that this definition leads to the exact solution for the final transition probability when applied to the Demkov-Kunike models (with the static detuning $\varepsilon_0 \equiv 0$, see Sec. 2.4.4). This involves a summation of infinite number of crossing points and careful consideration of branch points and poles [27], but is nevertheless impressive result, even more than the more well-known corresponding result for the LZ model in the single crossing point case and gives a strong motivation to study the DDP theory further.

The most important applications of the theory are of course to those cases where no analytic solutions are known. For example, in Paper I the generalization of the DDP model is applied to the superparabolic level-glancing models defined by Eq. (2.49). This type of model with a level-glancing has been troublesome for other approximate approaches in the past and it is not amenable for linearization in the LZ approach, for example [22, 79, 53].

For the superparabolic level-glancing models $E^2(t) = t^{4N} + V_0^2$ (where it is chosen $\varepsilon_0 \equiv 1$), so that the number of complex crossing points on a half plane is $2N$. The crossing points are located symmetrically with respect to real and imaginary axes and each crossing point can also be paired up with another crossing point with the same imaginary part. These paired-up points are also connected by a Stokes line. These facts are demonstrated in Fig. 3.1. However, taking only the one pair of crossing points closest to the real axis, as the original DDP theory suggests, gives only a rather poor approximation. Or rather, it gives a good approximation where it should, in the adiabatic limit where the transition probability itself is very small, which is not necessarily the most interesting region for many applications. In any case, the generalized DDP formula can be obtained with little extra effort, and it turns out, that by including all the points in the expression, one obtains a good approximation of the probability of non-adiabatic transitions for the whole parameter value, not just the adiabatic limit. Indeed, in the region of the applicability of the generalized DDP approximation, we can have $P_A \approx 1$.

For the superparabolic level-glancing models

$$t_c^k = V_0^{\frac{1}{2N}} e^{i\pi(2k-1)/(4N)}, \qquad k = 1, 2, 3, \ldots, 2N, \tag{3.27}$$

and

$$D(t_c^k) = \frac{V_0}{2N} B\left(\frac{1}{4N}, \frac{3}{2}\right) t_c^k, \qquad k = 1, 2, 3, \ldots, 2N, \tag{3.28}$$

where $B(x, y)$ is the beta function. The generalized DDP formula for the

superparabolic level-glancing models reads

$$P_{DDP} = \left|\sum_{k=1}^{2N}(-1)^k e^{iD\left(t_c^k\right)}\right|^2$$
$$= 4\left|\sum_{k=1}^{N}(-1)^k e^{-\eta\sin\left[\frac{\pi}{4N}(2k-1)\right]}\sin\left[\eta\cos\tfrac{\pi}{4N}(2k-1)\right]\right|^2, \quad (3.29)$$

where, in the second row, the pairing of the zero points with equal imaginary part is done, as explained above, and it is also defined

$$\eta = \frac{1}{4N}B\left(\frac{1}{4N},\frac{3}{2}\right)V_0^{(2N+1)/(2N)}. \quad (3.30)$$

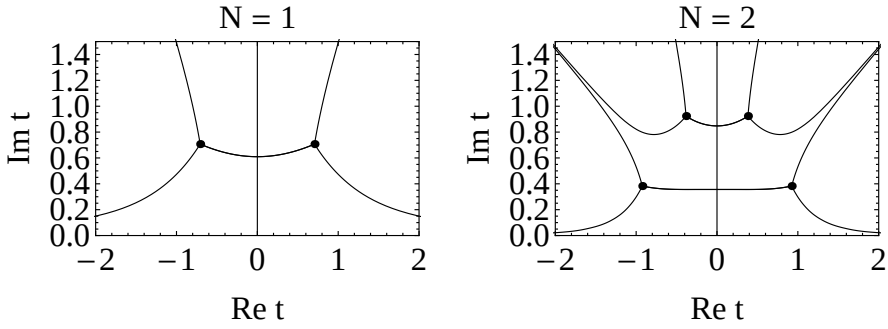

Figure 3.1: An example of the structure of the upper half-plane complex crossing points (black dots) and the Stokes lines (solid lines) for the parabolic (on left, $N = 1$) and first superparabolic (on right, $N = 2$) models. The parameters are here chosen as $\varepsilon_0 = V_0 = 1$

Now every term in the sum in the second line of Eq. (3.29) corresponds to zero points at a certain distance from the real axis and one can study their contribution to the transition probability (3.29) more clearly.

The DDP method is also recently generalized to models with dissipation [32].

3.6 Zhu-Nakamura theory

3.6.1 Stokes constants

Since most of the differential equations that are of interest in physics evade exact analytical solution, the construction of asymptotic approximations

is a very important task. For example, for the general second-order linear differential equation

$$\frac{\mathrm{d}^2 y}{\mathrm{dz}^2} + q(z)y = 0, \tag{3.31}$$

which is one the most important examples, in quantum physics particularly, one often considers the so-called first-order WKB-solutions [68]

$$y_{\pm}(z) = q^{-1/4}(z) \exp\left(i \int^{z} q^{1/2}(\tilde{z}) \mathrm{d}\tilde{\mathrm{z}}\right). \tag{3.32}$$

It may be noted that even if the function $q(z)$ is single-valued and analytic, so that also the exact solution must be, but has a zero, the approximate solutions (3.32) blow up in that point due to amplitude factor $q^{-1/4}$ and are not single-valued around the point which is also a branch point for $q^{1/2}$ and $q^{1/4}$. Therefore, it is clear that the solutions can not be valid over the whole complex plane. However, typical application in physics involves knowing the same solution over extended regions. If one fixes a linear combination of the approximative solutions (3.32) to fulfill a particular boundary value and traces this solution over to other regions, one finds that the same solution must be represented with different linear combinations in different sectorial regions. This is the important Stokes phenomenon [69] which takes place in the vicinity of the line boundaries of the sectors. The asymptotic expansion of the analytic continuation of the solution is no longer the one given by the analytic continuation of the terms of the asymptotic expansion when crossing the line [70]. Or to phrase it differently: given a linear combination of functions representing a certain solution in a certain region of the complex plane, the problem is to decide which linear combination appropriately approximates the solution in some other region [71]. Connecting the coefficients of the different linear combinations is a problem of global nature, also called as the connection problem, and it is much harder than the local problem of obtaining the functions (3.32). As its result one can construct the so-called F-matrix which has the Stokes constants as its elements and which can be used to map the asymptotic solutions from one region to another [71]. When the differential equation is the time-dependent Schrödinger equation, this amounts to obtaining the scattering matrix.

As an indication of the difficulty of the problem, it was only quite recently that the Stokes constants of the asymptotic solutions of Eq. (3.31) with the function $q(z)$ being a quartic polynomial, was solved by Zhu and Nakamura [20], despite this being an important special case for many physical applications. In a nutshell, they generalized the results of Hinton [72]

and Sibuya [73] and obtained the Stokes constants for a certain class of differential equations, the quartic polynomial among them, and also showed that all of the Stokes constants could be given in terms of only one of them. Furthermore, a convergent series expression for the one Stokes constant was found.

Zhu and Nakamura were originally interested in the nonadiabatic transitions occurring in curve crossings. For the Landau-Zener type curve crossing (see Sec. 2.6) the above results give that the S-matrix is given by

$$S_D = \begin{pmatrix} 1+U_1U_2 & -U_2 \\ -U_2 & 1-U_1^*U_2 \end{pmatrix}, \tag{3.33}$$

where U_1 and U_2 are the Stokes constants and they have the relation

$$U_2 = \frac{2i\mathrm{Im}U_1}{1+|U_1|^2}. \tag{3.34}$$

If we now define

$$p = \frac{1}{1+|p|^2}, \tag{3.35}$$

which is equivalent to

$$U_1 = \left(\frac{1-p}{p}\right)^{1/2} e^{i\varphi}, \tag{3.36}$$

where $\varphi = \arg U_1$, we get the probability of transitions of the process in the familiar form

$$P \equiv |U_2|^2 = 4p(1-p)\sin^2(\arg U_1). \tag{3.37}$$

Because the identification between the linear curve crossing and the time-dependent parabolic level-crossing models, reviewed in Sec. 2.6, the above formulas provide the exact solution for the scattering problem for either of the models. Unfortunately, to use the explicit expressions, given in terms of series expansions, for the one Stokes constant needed are very cumbersome and therefore the result is not transparent for analysis [22, 74, 75]. It should be also noted that, the Stokes constants for this problem have been derived very recently with alternative methods in [75], where the authors obtain the constants in a more compact form.

3.6.2 Zhu-Nakamura formulas for general models

Due to the limited practical applicability of the Stokes constant expressions for the case of a quartic coefficient function, Zhu and Nakamura have considered modifications of the semiclassical approximation to obtain them in

a form which is more readily utilized. The collection of formulas obtained this way and their application can be taken as the main content of the so-called Zhu-Nakamura theory.

Most theoretical approaches to the level-crossing problems require a model for the time or other parameter dependencies of the energy curves to describe the dynamics. For example, in DDP approach one would use analytic models and the contour integrals of the energies in the complex plane to calculate the transition probabilities. In addition of technical difficulties of performing these calculations in practice, the method may seem somewhat detached from the experimentalist's realm where in the case of curve-crossing problem, for example, the interaction potential and its dependence on some real parameters might be available only as a discrete set of numerical data points.

In contrast, the final formulas of Zhu-Nakamura are given in terms of elementary functions of the basic parameters. These formulas contain some experimental or "ad hoc" modifications and can be found, for example, in the appendices of [22]. They are said to be generally applicable to any model and there are some demonstrations of this [21]. However, the applicability of the Zhu-Nakamura theory should not be taken for granted and the paper II studies some of its obvious shortcomings.

Chapter 4

Plane-curve representation of two-level systems

The methods of differential geometry and topology are nowadays extensively used tools both in classical and quantum physics, and even in engineering [80]. Many theories can be cast in the geometric setting in a very natural and effective way. Primary example of geometric theory from classical physics is of course the general relativity where the gravitational field strength is understood as the curvature of spacetime. In modern quantum theories, geometric methods have numerous applications, from geometric phases to gauge theories [81], for example.

In contrast to these all the more abstract notions, there are many more elementary geometric tools used to understand quantum dynamics. After all, one of the advantages of geometric methods is their appeal to one's intuition and ability to provide mental pictures of complex phenomena. An example of such tool is the Bloch sphere representation of qubit, discussed in Sec. 2.3.2, which allows picturing the dynamics of a TLS as a curve on a sphere. In this section, we are going to discuss another geometric framework, which is even more elementary. As discussed in Sec. 2.2, to describe a model of TLS driven by an external field, it is sufficient to use two independent functions. These are the diabatic coupling and detuning, for example. This suggests a connection between two-state level-crossing models and parametric plane curves. Indeed, there is a simple and straightforward way to define a plane curve from the two functions so that a natural correspondence with the quantities of the two-state model and those appearing in the theory of plane curves can be established. This correspondence lets us discuss some aspects of the adiabatic limit from this new, geometric, viewpoint. This is hardly surprising, as the way to associate a model with a

curve is more or less directly implied by the diabatic-adiabatic basis transformation.

What on the other hand is surprising, is that this connection seems to have gone completely unnoticed previously. There are some papers discussing somewhat similar elementary applications of differential geometry of plane [82] or space curves [83, 84] and nonadiabatic dynamics of TLS but the association of a plane curve to a specific two-level model is different.

4.1 Basics of the differential geometry of plane curves

In order to establish the connection, some basic definitions and standard results in the theory of plane curves must be considered first. It is sufficient here to introduce them in a rather informal fashion, more thorough discussions can be found in many excellent books, for example [38, 85].

A parametrized curve in itself is a very intuitive concept but more formally it can be defined as (piecewise-) differentiable function $\vec{\alpha} : I \to \mathbb{R}^n$, where $I = (a, b)$ is an open, possibly infinite, interval in $\mathbb{R}$. We are only interested in plane curves ($n = 2$) and these can be also given as parametrized vectors,

$$\vec{\alpha}(t) = (x(t), y(t)) \,, \tag{4.1}$$

where $x(t)$ and $y(t)$ are two real functions and $t \in I$. Of course, the derivative of a curve is obtained by componentwise differentiation and $\dot{\alpha}$ and $\ddot{\alpha}$ are called, naturally enough, the velocity and acceleration of a curve α, respectively. Also, the norm of the velocity vector, $v(t) = \|\dot{\alpha}(t)\|$, is called speed. A natural requirement for a curve to be well-behaved, is that $v(t) \neq 0$ for all t. Such curves are called regular.

There is a certain ambiguity with the above definition for a curve, which is that two distinct functions can give arise to two curves that actually trace the same point set on a plane. From intuitive point of view, and indeed in common language, it is taken that these should then define the one and the same curve. Let $\alpha : (a, b) \to \mathbb{R}^2$ and $\beta : (c, d) \to \mathbb{R}^2$ be two curves and assume that there exists a differentiable function $h : (c, d) \to (a, b)$ such that $\dot{h}(t) > 0$ ($\dot{h}(t) < 0$) for all $c < t < d$ and $\beta = \alpha \circ h$. Then it is said that β is a positive (negative) reparametrization of α and we think of these curves as equivalent. The different signs in the reparametrization tells only whether the direction of the traversal along the curve is the same. It is also clear, that any quantity of the curve that is purely geometric, should not

depend nontrivially on the parametrization. For example, the length of a curve defined by

$$L[\vec{\alpha}] = \int_a^b \|\vec{\alpha}'(u)\| du \tag{4.2}$$

obviously should not, and does not, depend on any way the curve is parametrised. A closely related quantity is the arc-length function of curve which can be defined as follows: fix a number $c \in (a, b)$ and let the upper limit of integration be the variable t. Then the function in question is

$$l[\vec{\alpha}, c](t) = \int_c^\tau \|\vec{\alpha}'(u)\| du. \tag{4.3}$$

If a curve $\vec{\alpha}(t)$ is regular, there exists a re-parametrized unit-speed curve $\vec{\beta}(s)$, i.e. $\|\vec{\beta}'(s)\| = 1$. The unit-speed parameter is essentially unique (up to a sign and a change of origin) and is usually denoted by s. Because $l[\vec{\beta}, c](s) = s - c$, unit-speed curves are parametrized by their arc length. The use of unit-speed parametrization simplifies many of the formulas in differential geometry.

The single most important quantity one can associate with a plane curve is its curvature $\kappa[\alpha](t)$. It measures the way the plane curve differs from a straight line, being identically zero only for a line and constant if and only if the curve is an arc of a circle. A formula for a regular curve is given by

$$\kappa[\alpha](t) = \frac{\dot{x}(t)\ddot{y}(t) - \ddot{x}(t)\dot{y}(t)}{\left(\dot{x}^2(t) + \dot{y}^2(t)\right)^{3/2}}. \tag{4.4}$$

To see more clearly the meaning of the curvature function, one can associate two orthonormal vectors on each point of a unit-speed curve, the tangent vector $\vec{t}(s)$ and a vector obtained by rotating this by $\pi/2$, namely the normal vector $\vec{n}(s)$. Then the curve can be obtained from the Frenet equation

$$\frac{d}{ds}\begin{pmatrix} \vec{t}(s) \\ \vec{n}(s) \end{pmatrix} = \begin{pmatrix} 0 & \kappa(s) \\ -\kappa(s) & 0 \end{pmatrix}\begin{pmatrix} \vec{t}(s) \\ \vec{n}(s) \end{pmatrix}. \tag{4.5}$$

The content of the fundamental theorem on plane curves is that curvature determines the plane curve essentially uniquely, meaning up to Euclidean motions and reparametrizations. A curve with any desired curvature can be realized with the unit-speed construction

$$\begin{aligned} \vec{\alpha}(s) &= \left(\int \cos\tilde{\theta}(s)ds + c,\ \int \sin\tilde{\theta}(s)ds + d\right), \\ \tilde{\theta}(s) &= \int \kappa(s)ds + \tilde{\theta}_0, \end{aligned} \tag{4.6}$$

where c, d and $\tilde{\theta}_0$ are constants. The function $\tilde{\theta}(s)$ is also called the turning angle of the curve and it is the angle between the x-axis and the tangent vector of the curve at point t.

Finally, we mention one important and celebrated result related to the global behavior of plane curves which are simple and closed, known as the four-vertex theorem (FVT). Closed curves are are such that for some parameter $t_1 \neq t_0$ we have $\vec{\alpha}(t_1) = \vec{\alpha}(t_0)$. If a closed curve does not cross itself, we say that it is also simple. Vertices are the points of local minima and maxima of the curvature function. Now, the four-vertex theorem says that the curvature function of any simple closed plane curve, other than a circle, must have at least four vertices. One should also note that if we relax the condition of simplicity, the curve can have less than four vertices.

4.2 Two-state level-crossing model as a plane curve

As discussed in Sec. 2.2 and in particular with connection to Eq. (2.14), a diabatic Hamiltonian is defined, once the two time-dependent functions, $\varepsilon(t)$ and $V(t)$, are chosen. We associate with each such Hamiltonian a plane curve whose components are given simply as integrals in the following way

$$x(t) = \int_0^t \varepsilon(u)du, \quad y(t) = \int_0^t V(u)du, \tag{4.7}$$

the parameter t being the physical time. With this definition, the curvature of the curve is simply related to the functions in the Hamiltonian and given by

$$\kappa[\vec{\alpha}](t) = \frac{2\gamma(t)}{E(t)}, \tag{4.8}$$

as is obvious when we look at the formulas (2.19) and (4.4). The adiabatic coupling is directly proportional to curvature and the adiabatic condition (3.18) can be simply translated to

$$\kappa[\vec{\alpha}](s) \ll 1. \tag{4.9}$$

Furthermore, the speed of the curve is now just given by $E(t)$ and the existence of only avoided crossings means that the curve (4.7) is regular. The unit-speed parametrization is given by the change of the time variable to the natural time-scale,

$$s(t) = \int^t E(u)du, \tag{4.10}$$

where the time is measured by the accumulation of the dynamic phase. In this parametrization, the curvature and its relation to the adiabatic coupling simplifies further as the denominators in (4.8) and (4.4) become unity. Then from (2.19) it follows that curvature is given by

$$\kappa[\vec{\alpha}](t) = \frac{d\theta(s)}{ds}. \tag{4.11}$$

When θ is replaced with $\tilde{\theta}$, met earlier in Eq. (4.6), this equation is of exactly same form as the equation between the curvature and turning angle of a unit-speed plane curve in the theory of plane curves, so what this equation shows, is that the angle in (2.17) is the same as the turning angle of a curve, up to a constant.

This shows that there is a counterpart in the theory of differential geometry of plane curves for all the basic quantities in the two-state level-crossing problem and this differential geometric setting gives us a new viewpoint and a language with which to address the problem. A simple change in language would hardly be enough, but the important point here is that now one can use all the result of the theory of plane curves, a well-known and well-established field, to study the level-crossing problem as the following simple examples show.

4.2.1 Examples

Most of the time-dependent two-level models met regularly in quantum dynamics give rise to very simple plane curves. In Rabi model, for example, the nonadiabatic coupling plays no role, the adiabatic states are not coupled, and the corresponding plane curve is a straight line. The LZ model, parabolic model and their generalizations, where the diabatic coupling is constant and the detuning is polynomial, lead to algebraic curves shown in Figs. 4.1. Occasionally, the studied TLS models give rise to some famous plane curves. For example, the the Sech-Tanh model studied in Sec. 5.1 corresponds to the so-called "Witch of Agnesi" curve [38].

The simplicity of the curves comes from the natural physical requirement that the interactions must vanish sufficiently fast in the limits $t \to \pm\infty$. Therefore the curves have straight lines as their asymptotes and any twists on the curve are localized on one place, usually around $t = 0$. As a one further remark on Fig. 4.1, we note that one can directly see from the figure whether the diabatic states swap their labels during the interaction (see Sec. 2.2). The difference between the initial and final turning angle for LZ model is $\Delta\theta = \pi$, the curve returns to the same direction

it comes from. This reflects the fact that diabatic states swap their levels for LZ model. Similarly, for superparabolic models we have $\Delta\theta = 0$ and there is no swapping.

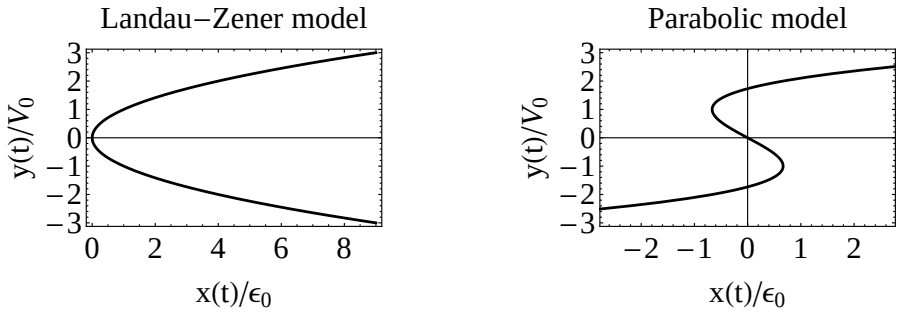

Figure 4.1: The plane curves corresponding to LZ model (left) and parabolic models (right).

The important point in introducing the plane curve representation of TLS is that now one can try to exploit any result in the theory of differential geometry of plane curves to study the coherent dynamics of TLS. Because the connection between adiabatic coupling and curvature in the representation, it is useful to study how approaching the adiabatic limit is understood with the help of the plane curves. Clearly the adiabatic limit now corresponds to the limit of vanishing curvature, meaning that when we change the system parameters, we have $\kappa \longrightarrow 0$. So the curve becomes a straight line, at least locally. In the case of simple closed curves, things are not always so straightforward, which can be understood on the basis of the four-vertex theorem.

Take for an example a model where both of the components of the external field vector oscillate trigonometrically,

$$\varepsilon(t) = \frac{\varepsilon_0}{\omega_1}\cos(\omega_1 t + \delta), \qquad V(t) = \frac{V_0}{\omega_2}\cos(\omega_2 t), \tag{4.12}$$

so that the corresponging parametrized plane curve is given by

$$x(t) = \varepsilon_0 \sin(\omega_1 t + \delta), \qquad y(t) = V_0 \sin(\omega_2 t), \tag{4.13}$$

When we choose the frequencies to be the same, $\omega_1 = \omega_2$, this defines an ellipse. For convenience, we can also choose $\delta = \pi/2$ so that the minor and major axes of ellipse coincide with the coordinate axes. Clearly, ellipse is

a simple closed plane curve and as such, the FVT can be applied to it. An ellipse has actually exactly four vertices, at points $t = 0$, π/ω, $\pi/(2\omega)$ and $(3\pi)/(2\omega)$. The curvature of the ellipse is given by

$$\kappa[\alpha](t) = \frac{\varepsilon_0 V_0}{\left[\varepsilon_0^2 \sin^2(\omega t) + V_0^2 \cos^2(\omega t)\right]^{3/2}}. \tag{4.14}$$

When $\varepsilon_0 \neq V_0$ (the ellipse is not a circle), two of the vertices correspond to minima of the curvature and two correspond to maxima. In general $\kappa(0) = \kappa(\frac{\pi}{\omega}) = \varepsilon_0/V_0^2$ and $\kappa(\frac{\pi}{2\omega}) = \kappa(\frac{3\pi}{2\omega}) = V_0/\varepsilon_0^2$, but which are minima and which maxima, depend on the parameters. If the ellipse is more flat initially in the y-direction, so that $\varepsilon_0 \geq V_0$, then the peaks of the curvature at $\kappa(0) = \kappa(\frac{\pi}{\omega})$ will be made smaller by making the ratio ε_0/V_0 smaller. However, at some point the parameter ε_0 ceases to be larger than V_0, after which the maxima of the curvature switches to points $t = \pi/\omega$ and $(3\pi)/(2\omega)$ and further reduction of ε_0 will actually increase the curvature of the new maxima. This description is summarized in Fig. 4.2. The only way one can make the curvature disappear identically and to suppress the transitions between the adiabatic states is first to fulfil the condition $\varepsilon_0 = V_0$ which makes the curve to be a circle and then increase the value of the parameters while still fulfilling the condition. Because the curvature of a circle is constant and inversely proportional to its radius, the curvature can indeed be made to vanish this way.

By considering Eq. (4.13) with general parameters, not just with $\omega_1 = \omega_2$, for example, one can note that it is a general definition for the Lissajous curve and has many familiar and interesting curves as its special case. For example, in addition to the ellipse and circle met above, fixing $\omega_1 = \omega_2$ and $\delta = 0$ gives a straight line and $\omega_1 = 2\omega_2$ and $\delta = \pi/2$ gives an arc of parabolic shape. Some general properties of Lissajous curves should be noted. Firstly, they are constricted to a rectangular box around origin with length of the sides given by ε_0 and V_0. They are closed curves only if ω_1/ω_2, the number of "lobes" of the curve in each coordinate direction are then given by the numerator and denominator of the rational number in question. Furthermore, they depend sensitively on the ratio of $\beta \equiv \omega_1/\omega_2$. A fairly dramatic example related to the ellipse and circle example above. Let $\varepsilon_0 = V_0$ and $\omega_1 = \omega_2$ so that $\beta = 1$ which defines a circle. The corresponding curvature is constant. However, if the parameters of the system are altered only very slightly, for example so that $\beta = 0.9$, the curve and its curvature function are altered dramatically, see Fig. 4.3.

The change could be even arbitrarily small, for example we could have

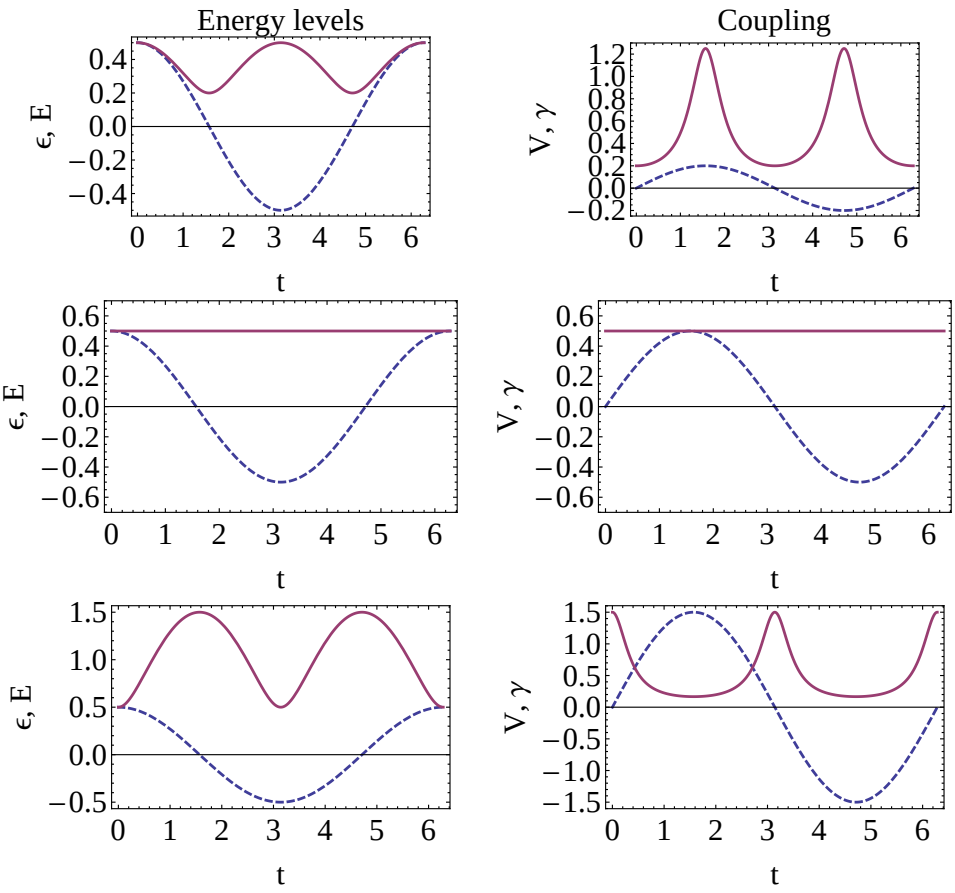

Figure 4.2: A plot of the energy levels (left panel) and couplings (right panel) of the system corresponding to the ellipse curve defined by (4.13). The diabatic quantities are drawn with blue and dashed line while the adiabatic ones are drawn with purple solid line. The plotted cases are, from top down: $\varepsilon_0 \geq V_0$, $V_0 = \varepsilon_0$ and $\varepsilon_0 \leq V_0$. The respective amplitudes of the coupling are: $V_0 = 0.2$, $V_0 = 0.5$ and $V_0 = 1.5$. In all of the plots it is chosen $\varepsilon_0 = 0.5$.

taken $\beta = 99/100$. The model equivalent to Eq. (4.12) was considered in [86] in the diabatic basis and its behavior was indeed found to be surprising, depending sensitively on the value of β. This demonstrates in a small way how one can search for interesting phenomena in the coherent dynamics of TLS by starting from the plane curve representation.

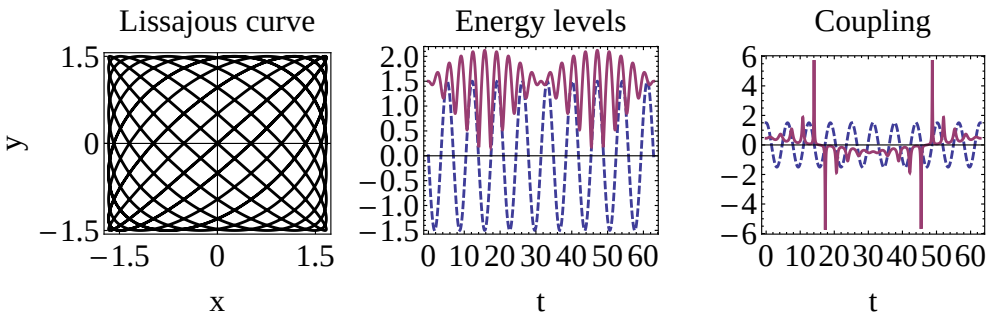

Figure 4.3: Left: A Lissajous curve defined by Eq. (4.12) with $\varepsilon_0 = V_0 = 1.5$, $\delta = \pi/2$ and $\beta = \omega_1/\omega_2 = 0.9$. Middle and right: The energy levels and the couplings of the Lissajous system, respectively. The purple solid line is for the adiabatic quantities, while the blue dashed line is for the corresponding diabatic ones.

Chapter 5

Complete population inversion and zero-area pulses

5.1 History and general results

Often when one considers different schemes of coherent excitation, there are simple heuristic guidelines in action. For example, to obtain complete population inversion (CPI), one needs to have the external field in resonance with the initial and target states of the system. For highly detuned pulses the excitation is negligible. Another example is the area theorem discussed in 3.2; the temporal area of the resonant pulse must be odd multiples of π in order for CPI to take place. On the other hand, zero-area pulses, or pulses with area multiple of 2π, are of self-cancelling nature. For them, the population is restored to the initial state (Complete Population Return, CPR) after the completion of the pulse. However, combining two separate obvious results can lead to a result which feels very counter-intuitive, at least initially.

Therefore, it does not come as a total surprise that it was only quite recently noted, that by combining the two above-mentioned undesirable features for effective population transfer, namely off-resonant pulse of zero area, one ends up with just that: a very effective and robust way to transfer population between two states! This effect was first studied for smooth zero-area pulses with constant non-zero detuning [28], and later found also for models where the zero-area coupling is produced by changing the pulse amplitude with an abrupt jump. Indeed, the effect can be obtained under quite general requirements and it is highly non-adiabatic in its origin. Here we present first shortly the original route that led to this finding, following

broadly the derivation in the Ref. [28], and then consider aspects related to CPI and zero-area pulses in more general time-dependent models.

Assume constant bare state energies, $\varepsilon(t) = \varepsilon_0$, and a smooth coupling $V(t) = V_0 f(t)$ where the pulse-shape function is assumed to be odd, so as to make it to be of zero area, $f(-t) = -f(t)$ and $f(0) = 0$. In Ref. [28], they consider also few specific exemplary pulse forms. One of them, a model with coupling given as $V(t) = V_0 \mathrm{sech}(t/T)\tanh(t/T)$, and called Sech-Tanh (ST) model, is also considered in paper IV in connection with the DDP method. Generally, the required form of constant detuning and a coupling that is of odd-parity makes the adiabatic coupling to be an even function of time (see Fig. 5.1),

$$\gamma(t) = \frac{\varepsilon_0 V_0 \dot{f}(t)}{2\left(\varepsilon_0^2 + V_0^2 f^2(t)\right)}. \tag{5.1}$$

Quite often, and certainly in all the exemplary pulse forms considered in Ref. [28], this adiabatic coupling is peaked in the origin, where it has the value

$$\gamma(0) = \frac{V_0 \dot{f}(0)}{2\varepsilon_0}. \tag{5.2}$$

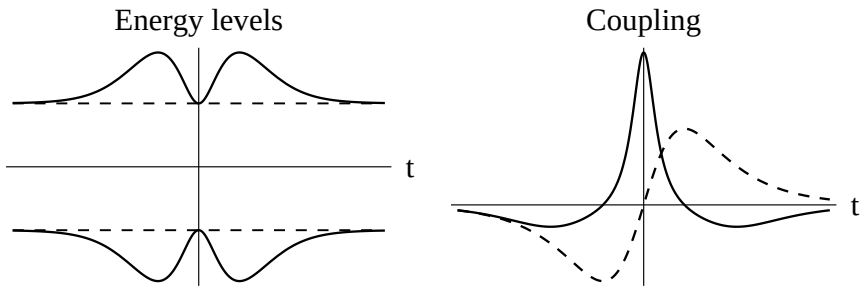

Figure 5.1: The schematics for the smooth zero-area pulse model with CPI, illustrated here with the Sech-Tanh model. The adiabatic levels and coupling are drawn with solid line and the diabatic functions are dashed.

It can be then shown, that the adiabatic coupling behaves essentially like a delta function in the strong coupling region. Firstly, from Eq. (5.2) we see, that (it is assumed that $\dot{f}(0) \neq 0$) the peak value of the function $\gamma(t)$ tends to infinity at the strong coupling limit where $V_0/\varepsilon_0 \to \infty$. Nevertheless, the time-integral of the adiabatic coupling around the peak tends to a constant value. This can be easily calculated, once we remember

the connection between the adiabatic coupling and the angle $\theta(t)$ (see Eq. (2.19)). By integrating over a symmetric region around the origin, say, from $-t_0$ to t_0, we get that

$$\begin{aligned} \frac{A_\gamma(t_0,-t_0)}{2} &\equiv \int_{-t_0}^{t_0}\gamma(s)ds \\ &= \frac{\theta(t_0)-\theta(-t_0)}{2} \\ &= \arctan\left(\frac{V_0 f(t_0)}{\varepsilon_0}\right) \\ &\to \frac{\pi}{2} \quad \text{when} \quad V_0/\varepsilon_0 \to \infty, \end{aligned} \tag{5.3}$$

because $\tan\theta(t) = V(t)/\varepsilon(t)$ and now $\theta(-t) = -\theta(t)$. In Ref. [28], t_0 was chosen to be the zero point of the adiabatic coupling $\gamma(t)$ near the origin but it can basically be any other point where $f(t_0) \neq 0$. This just changes the numerical prefactor but does not affect the argument, based on the limit in Eq. (5.3). Also, the characteristic width of the central peak of the adiabatic coupling, defined as $A_\gamma/\gamma(0)$, gets narrower and narrower as the strong coupling limit is approached. Thus, it can be concluded that around the time $t = 0$, the adiabatic coupling behaves like a delta function.

At the time of the maximum of the adiabatic coupling, $t = 0$, the splitting of the adiabatic levels is at its minimum $\Delta E(0) = E_+(0) - E_-(0) = 2\varepsilon_0$. It also varies smoothly around this point because $\dot{E}(0) = 0$. Therefore, during the interval $[-t_0, t_0]$ and in the strong coupling region, we are led to an approximation for the transition probability which is exactly analogous to conventional area-theoretic expression for the π-pulse excitation, albeit now considered in the adiabatic basis and the system being only quasiresonant. When the system starts at the ground state, this is given by

$$\begin{aligned} P &\approx \sin^2\left[\int_{-t_0}^{t_0}\gamma(s)ds\right] \\ &\to 1 \quad \text{as} \quad V_0/\varepsilon_0 \to \infty. \end{aligned} \tag{5.4}$$

It should be noted that because $\theta(-\infty) = \theta(\infty) = 0$, the total area of the nonadiabatic coupling is actually of zero area and the same area that the coupling has in the central peak is accumulated in the tails but with negative sign. Therefore, in order for the approximation (5.4) and the CPI prediction to be valid, the transitions in the tails of the pulse must be suppressed. This can be done by requiring adiabaticity in the tails, i.e., $E(t) \gg |\gamma(t)|$ for $|t| > t_0$, and leads to lower bound for the detuning, typically $\varepsilon(t) \gg 1/T$, where T is the pulse width. See Fig. 5.1.

Also of practical importance is the fact that one can consider parameter regions outside the strict limit of Eq. (5.4) and give sufficient conditions

for the required amount of excitation. Because the transition probability can be shown to scale as V_0/ε_0^2, these bounds are of the form $\varepsilon_0 < \alpha\sqrt{V_0}$, where α is a pure numerical factor.

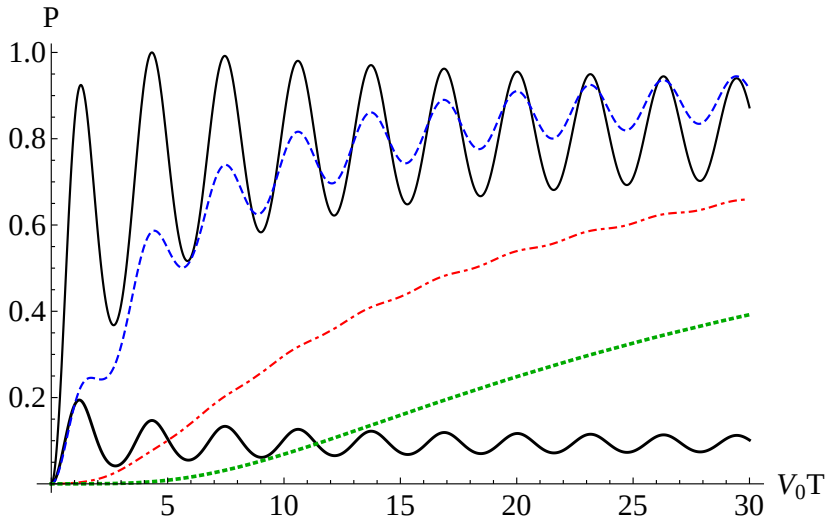

Figure 5.2: Transition probability for Sech-Tanh model obtained from numerical simulation and here plotted for few detunings as a function of the scaled coupling. The values are $\varepsilon_0 T = 0.1$ (thick black line), $\varepsilon_0 T = 0.5$ (black solid line), $\varepsilon_0 T = 1$ (blue and dashed), $\varepsilon_0 T = 2$ (red dotdashed) and $\varepsilon_0 T = 3$ (green and dotted).

As a conclusion, the described CPI effect is robust against moderate parameter variations, a feature shared with the rapid adiabatic passage. The effect in itself, however, is due to the delta function-like behavior of the adiabatic coupling and therefore highly nonadiabatic. Indeed, even the requirement of zero area diabatic coupling is strictly not required for CPI, only the rapid change of the diabatic coupling which leads to the delta peak behavior, and the effect has been demonstrated also for asymmetric pulses [87]. Zero-area pulses are, however, the most natural and, perhaps, most striking examples of this. Furthermore, the restriction to systems with zero-area coupling obtained as a consequence of the odd-parity in time of the coupling allows the study of the CPI effect in a simple manner through the transformations considered in the following section.

5.2 The effect of symmetries

Symmetry is usually defined as a transformation that maps solutions to solutions. In addition to the consideration of such transformations of independent and dependent variables in the context of differential equations, we can also consider more general notion of symmetry, namely, those which leave some aspect of the dynamics invariant. In this thesis, the relevant aspect would be the final transition probability P. It is clear that scaling of time or time translation are symmetries for time-dependent systems usually only in this more general sense. For TLS, many other symmetry properties can be considered. For example, it is well-known, that the transition probability is independent of the sign of the detuning and Rabi frequency or general phase transformation or time reversal [58]. In the following we study some of these transformations.

For example, the sign change in the diabatic energy levels $\varepsilon(t) \hookrightarrow -\varepsilon(t)$, corresponds to a change in the labeling of the basis states, $C_1 \leftrightarrow C_2$. This is obtained by the basis transformation $\tilde{\psi}(t) = A_1\psi(t)$ with $A_1 = \sigma_x$. Indeed, the corresponding similarity transform on the Hamiltonian matrix is $\tilde{H}(t) = \sigma_x H(t)\sigma_x^{-1}$, or equivalently,

$$\begin{pmatrix} -\varepsilon(t) & V(t) \\ V(t) & +\varepsilon(t) \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \varepsilon(t) & V(t) \\ V(t) & -\varepsilon(t) \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{5.5}$$

and a solution of the Schrödinger Eq. (2.5) with $H(t)$ is mapped to a solution of the Eq. (2.5) with $\tilde{H}(t)$. If the external field is in resonance, $\varepsilon(t) \equiv 0$, Eq. (2.5) does not change in this transformation and a solution ψ_1 is mapped into another solution of the same equation, $\psi_2 = \sigma_x\psi_1$.

Another interesting transformation is given by $A_2 = i\sigma_y$. Its inverse is $A_2^{-1} = -i\sigma_y$ and its effect on the Hamiltonian is given by

$$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} \varepsilon(t) & V(t) \\ V(t) & -\varepsilon(t) \end{pmatrix} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = -H(t), \tag{5.6}$$

so it reverses the sign of both the diabatic energies and the coupling. If we also reverse the direction of time, $s = -t$, (2.5) yields

$$-i\frac{\mathrm{d}}{\mathrm{d}s}\tilde{\psi}(-s) = -H(-s)\tilde{\psi}(-s), \tag{5.7}$$

where $\tilde{\psi}(t) = i\sigma_y\psi(t)$. The minus sign cancels on both sides and again if $\psi(t)$ is the solution of equation (2.5) with $H(t)$, then $\tilde{\tilde{\psi}}(t) \equiv \tilde{\psi}(-t) =$

$i\sigma_y\psi(-t)$ is the solution of that equation with $\tilde{H}(t) \equiv H(-t)$. In particular, if all the terms in the Hamiltonian are even functions of time, $H(-t) = H(t)$ and the combination of A_2 and $t \hookrightarrow -t$ is again the symmetry of the TLS Schrödinger equation in the ordinary sense. The transformation can also be written as $A_2 = e^{i\pi\sigma y/2}$ and one should note its relation to the conventional time-reversal operation of the spin-1/2 quanta given by $T = A_2K$, where K is the complex conjugation operation [88].

Combining the operations A_1 and A_2 gives $A_1A_2 = -\sigma_z$. The resulting transformation is its own inverse and the minus sign in front of σ_z cancels out when performing the similarity transformation to the Hamiltonian. Therefore, the sign can be left out and we define $A_3 = \sigma_z$. The effect of this is then, from the Eqs. (5.5) and (5.6) above,

$$\begin{pmatrix} \varepsilon(t) & -V(t) \\ -V(t) & -\varepsilon(t) \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \varepsilon(t) & V(t) \\ V(t) & -\varepsilon(t) \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (5.8)$$

namely, reversing only the sign of the diabatic coupling. The corresponding effect on the state vector is to induce an additional phase difference of π between the basis components, $\tilde{\psi} = \left(\tilde{C}_1,\, \tilde{C}_2\right)^T = \left(C_1,\, e^{i\pi}C_2\right)$.

It is easier to study the effect of these transformations to the dynamics of the system with the help of the propagators and Eq. (2.5). If the Hamiltonian is transformed as $\tilde{H}(t) = AH(t)A^{-1}$, the propagator transforms in the same way: $\tilde{U}(t) = AU(t, t_0)A^{-1}$.

5.3 Two-level phase-jump models

Even though the transition probability does not depend on the sign of the coupling, as stated, the effect of changing the sign in the middle of the evolution has quite surprising consequences generally. We approach this subject as follows. We start with some reference model with symmetric coupling function between the diabatic states and consider a symmetric time domain around the origin. We then obtain a variant model by performing the operation A_3 in the middle point of the evolution at time $t = 0$. This changes the sign of the coupling and makes it a zero-area coupling. The operation corresponds to a instantaneous jump in the phase of the field vector from $\phi = 0$ to $\phi = \pi$, which can be easily visualized in the Bloch sphere picture.

We then study the dynamics of this variant model and compare it to the reference model. It was shown in Ref. [58] that if the Hamiltonian

is completely antisymmetric in time, its final evolution is just identity. Therefore, we restrict also the diabatic energy levels of the reference model to be symmetric in time, and these are of course not altered when operated with A_3[a]. Unlike in earlier studies, for example the pioneering work [28], the energy levels are not considered to be constant. These considerations are collected in the following formulas

$$\varepsilon_{ref}(-t) = \varepsilon_{ref}(t) \tag{5.9}$$
$$V_{ref}(-t) = V_{ref}(t). \tag{5.10}$$

With the reference model given, we can write its zero-area variant with the phase-jump coupling as

$$\tilde{\varepsilon}(t) = \varepsilon_{ref}(t) \tag{5.11}$$
$$\tilde{V}(t) = (2h(-t) - 1)\, V_{ref}(t), \tag{5.12}$$

where $h(x)$ is the step function having the value zero for negative and unity for positive arguments. The zero-area model Hamiltonian is also denoted in the following by $\tilde{H}(t)$, while the non-tilde quantities refer to the reference model. With the above definition, the Hamiltonian of the variant model then coincides with the reference Hamiltonian for negative times and therefore the propagator from $t_0 = -\infty$ to $t = 0$ is the same for both models. In the following, we therefore split the total propagator into two parts,

$$S(t) = U(t, 0)U(0, -t), \tag{5.13}$$

where $t \geq 0$ and study its connection to the propagator of the variant model,

$$\tilde{S}(t) = \tilde{U}(t, 0)\tilde{U}(0, -t) \tag{5.14}$$
$$= \tilde{U}(t, 0)U(0, -t). \tag{5.15}$$

Because the operation $\sigma_z M \sigma_z$ simply changes the sign of the off-diagonal components of any 2×2 matrix M, the connection between the reference and zero-area Hamiltonians at positive times is simply given by

$$\tilde{H}_D(t) = \sigma_z H_D(t) \sigma_z, \quad t \geq 0 \tag{5.16}$$

[a]In principle, any TLS Hamiltonian with definite-parity model functions can be put into this form by transforming the diabatic basis either to adiabatic or to the first superadiabatic basis as the starting point.

and it follows from (2.5) that the similar equation holds for the propagators

$$\tilde{U}_D(t,0) = \sigma_z U_D(t,0)\sigma_z, \quad t \geq 0. \tag{5.17}$$

This just means that if the total evolution for the reference model is given in the diabatic basis by equation (5.13), then we simply have

$$\tilde{S}_D(t) = \sigma_z U_D(t,0)\sigma_z U_D(0,-t). \tag{5.18}$$

For later purposes, it should be also noted that any propagator that is a pure phase evolution,

$$U_\varphi = \begin{pmatrix} e^{i\varphi} & 0 \\ 0 & e^{-i\varphi} \end{pmatrix}, \tag{5.19}$$

commutes with this transformation and is therefore invariant $U_\varphi = \sigma_z U_\varphi \sigma_z$.

Although the nonadiabatic coupling plays no role in the Rabi model, it can be used to demonstrate the effect of the phase jump to the dynamics more generally. We assume that initially $C_1(-t) = 0$. Because $U(0,-t) = U^\dagger(-t,0)$ and from Eqs. (2.32) and (2.33) we have $u_1(-t) = u_1^*(t)$ and $u_2(-t) = u_2^*(t)$, and we firstly get for the original Rabi model without a phase jump

$$\begin{aligned} P_D &= |u_1(t)u_2^*(t) - u_1^*(t)u_2(t)|^2 \\ &= 4\left[\mathrm{Im}(u_1(t)u_2^*(t))\right]^2, \end{aligned} \tag{5.20}$$

while for the variant model with phase jump

$$\begin{aligned} \tilde{P}_D &= |u_1(t)u_2^*(t) + u_1^*(t)u_2(t)|^2 \\ &= 4\left[\mathrm{Re}(u_1(t)u_2^*(t))\right]^2. \end{aligned} \tag{5.21}$$

This can be also considered with the general formula (2.36) for the transition probability for the Rabi model. In that case the role of the evolution in the negative times is to provide the initial conditions to the time $t = 0$ and then $\tilde{P}(t)$ is obtained by applying Eq. (2.36).

5.4 Propagators in different bases

We saw above that the phase-jump phenomena is dealt mathematically in a simple way in the diabatic basis. For what follows, it is often convenient to give the propagators of the reference models also in the adiabatic basis, so

before discussing the phase-jump dynamics in detail in these bases, we need the general connection of the propagators given in diabatic and adiabatic bases. If we assume that the Eq. (2.4) is given in the diabatic basis to begin with, then by using Eq. (2.17), it reads in the adiabatic basis

$$\psi_A(t) = R(t)U_D(t,t_0)R^\dagger(t_0)\psi_A(t_0), \tag{5.22}$$

and this leads to the connection

$$U_A(t,t_0) = R(t)U_D(t,t_0)R^\dagger(t_0), \tag{5.23}$$

which is not generally a similarity transformation because the change of basis matrices R are evaluated at different times.

Now, if the propagators of the reference model are given in the adiabatic basis, and we consider infinite initial and final times, the Eq. (5.18) reads

$$\tilde{S}_D = \sigma_z R^\dagger(\infty)S_{A,+}R(0)\sigma_z R^\dagger(0)S_{A,-}R(-\infty), \tag{5.24}$$

where $S_{A,-} = U_A(0,-\infty)$ and $S_{A,+} = U_A(+\infty,0)$. Because the diabatic and adiabatic bases coincide in the initial and final times (in the models we are interested here, there is not even swapping of the labels), this can be excluded from the consideration. Also the first factor in the right-hand side, σ_z, does not change the population and can be left out, so that

$$\tilde{S}_D = S_{A,+}R(0)\sigma_z R^\dagger(0)S_{A,-}. \tag{5.25}$$

If this is applied to the parabolic model in the independent crossing approximation, the propagators of the reference model $S_{A,\pm}$ are indeed given in the adiabatic basis and are composed of LZ propagator and a dynamical phase evolution (see Eqs. (3.9) and (3.11)). The transition probability for the phase-jump variant model is

$$\begin{aligned}\tilde{P} &= \{(2R^2-1)\sin[\theta(0)] \\ &\quad +2\sqrt{1-R^2}R\cos[\theta(0)]\cos[\varphi_{dyn}+\phi_S]\}^2,\end{aligned} \tag{5.26}$$

where $\theta(0) = \arctan\left(-\frac{V_0}{c}\right)$, so that

$$\sin[\theta(0)] = \frac{V_0}{\sqrt{c^2+V_0^2}}, \qquad \cos[\theta(0)] = \frac{-c}{\sqrt{c^2+V_0^2}}. \tag{5.27}$$

When $|c| \gg V_0$, the first term in the transition probability (5.26) vanishes and $\tilde{P}$ is the same as for the original parabolic model but with a shift of $\pi/2$ in the interference pattern (the oscillatory part of the transition probability). In any case, the behavior of the final population of the variant model is generally more complex, see Fig. 5.3.

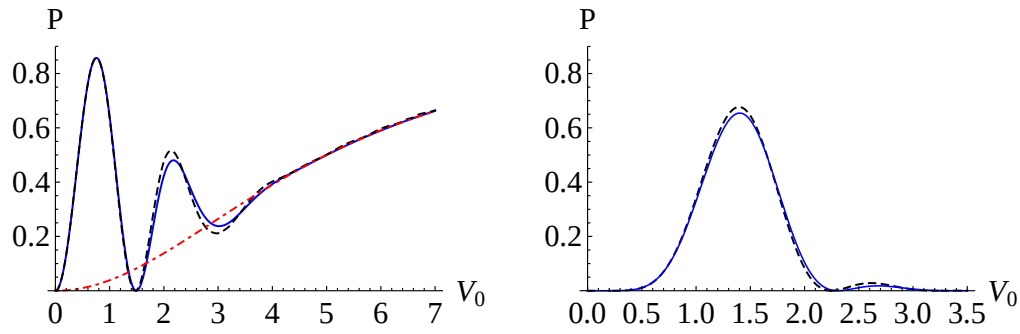

Figure 5.3: An example of the effect of a phase jump on the final transition probability for the parabolic model. On the left is the transition probability $\tilde{P}$ of the variant model, while on the right is the corresponding reference model plot. The black dashed line is the numerical solution and blue solid line is the independent crossing approximation for each case. The red dot-dashed line is the approximative formula (5.31) The parameters are chosen as $\varepsilon_0 = 1$ and $c = 5$.

5.5 Universal formula

An examination of Eq. (5.25) reveals that when there is no population transfer between the adiabatic states in the reference model, the scattering matrix for the variant model can be given by $\tilde{S}_D = R(0)\sigma_z R^\dagger(0)$.

$$R(0)\sigma_z R^\dagger(0) = \begin{pmatrix} \cos(\theta(0)) & \sin(\theta(0)) \\ \sin(\theta(0)) & -\cos(\theta(0)) \end{pmatrix}, \tag{5.28}$$

The matrix σ_z in the middle, which is due to the phase-jump, is of crucial importance, since otherwise this too would only amount to identity. Instead, now the transition probability $\tilde{P}$ in this region is given by

$$\tilde{P}_0 = \sin^2[\theta(0)] \tag{5.29}$$

$$= \frac{V^2(0)}{V^2(0)+\varepsilon^2(0)}, \tag{5.30}$$

or more generally, by the same function, but with the angle evaluated at the moment of the phase jump, which can be different from $t = 0$. It should be noted that this formula exhibits a certain universality. According to it, the final population does not depend on a particular model but only on the

value at a single time point, namely, at the time of the phase jump. Of course, the parameter region where this approximation is valid may depend on the model. As discussed above, Eq. (5.30) is valid when the reference model exhibits adiabatic behaviour. For parabolic and superparabolic models this is the region of large V_0 and this prediction is demonstrated in Figs. 5.3 and 5.4. Also, it can be noted, that the formula tends monotonously to the value one as $(V(0)/\varepsilon(0))^2$ increases and it gives the value of one half always at $|\varepsilon(0)| = V(0)$.

For the parabolic case we have

$$\tilde{P}_0 = \frac{V_0^2}{V_0^2 + c^2}, \tag{5.31}$$

which assigns the same value for the double-crossing and tunnelling cases with the same value of $|c|$.

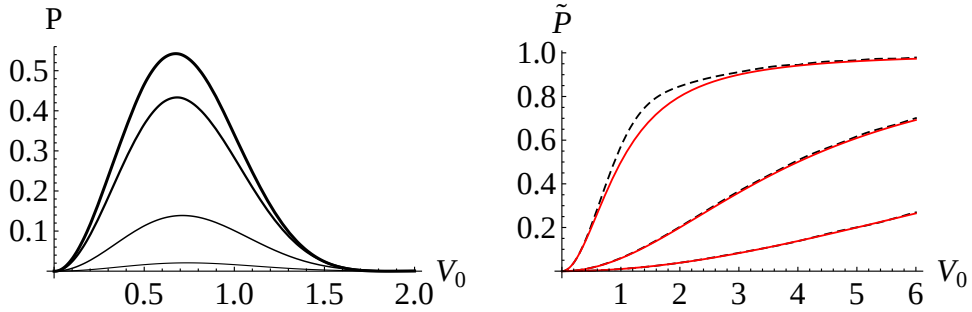

Figure 5.4: The effect of a phase jump on the tunnelling probability. On left is the transition probability P of the reference parabolic model in the tunnelling case, from uppermost to lowermost curve: $c = 0$, $c = -0.1$, $c = -0.5$ and $c = -1$. On right: The transition probability $\tilde{P}$ of the parabolic phase-jump model in the tunnelling case. The black dashed line is the exact value, the red solid line is the Eq. (5.31). The curves correspond, from top to bottom $c = -1$, $c = -4$ and $c = -10$. In all of the plots we have $\varepsilon_0 = 1$. The phase jump strongly enhances tunnelling.

This reveals a seemingly paradoxical situation: the CPI effect of the ZPA phase-jump model is of non-adiabatic origin but it shows most clearly in the adiabatic region of the original model.

5.6 Zero-area models and DDP theory

Although the CPI effect under study here is of highly nonadiabatic nature, it is interesting to consider the application of DDP approximation to these models. For example, defining the variant model with the phase-jump to each reference model, one does not alter the eigenenergies but only the adiabatic coupling, which depends on the derivatives of the model functions. Here we, however, consider only ST model where the diabatic coupling changes smoothly and find an example of the complex-zero structure for the eigenenergies of a zero-area model. There are infinite number of zero points for the ST model, and they are given by ($\tau \equiv t/T$)

$$\tau_c^k = \pm\frac{1}{2}\text{arcosh}\left(2X_\pm - 1\right) + i\pi k, \tag{5.32}$$

where k is an integer and

$$X_\pm = -\frac{1}{2}\left(V_0/\varepsilon_0\right)^2 \pm \frac{1}{2}\sqrt{\left(V_0/\varepsilon_0\right)^4 + 4\left(V_0/\varepsilon_0\right)^2}. \tag{5.33}$$

The weight factors are again simply $\Gamma = \pm 1$. The behavior of the zeros are most easily understood from the Fig. 5.5. Instead of drawing away from the real axis as the diabatic coupling parameter V_0 is increased, as happens for example in LZ model, the nearest complex crossing point of ST model actually approaches it.

Taking into account only the zero point nearest to the real axis, we get an approximation for the transition probability as is illustrated in Fig. 5.6. This is approximated by the formula

$$P \approx \exp\left[-\pi\varepsilon_0 T \text{Im}\left(\text{arcosh}(2X_+ - 1)\right)/2\right]. \tag{5.34}$$

These are found to be in excellent agreement with the numerical simulations in the region we are most interested in, namely in the region where the transition probability no longer oscillates with the parameters but the population transfer is robust (see Sec. 5.1).

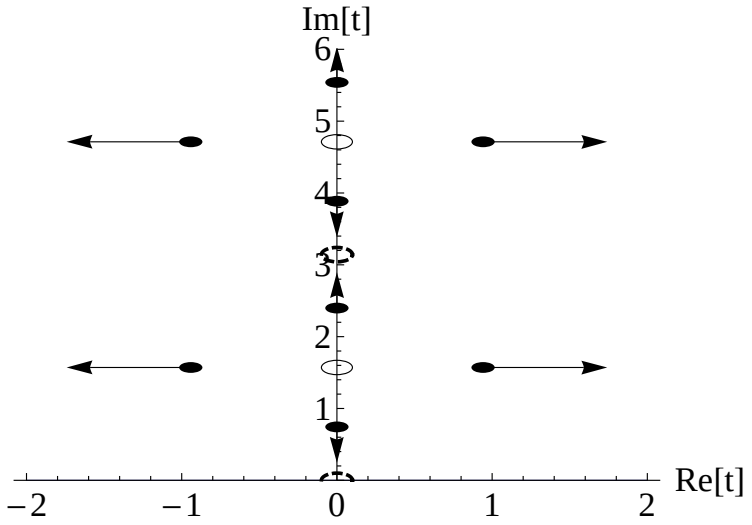

Figure 5.5: The complex crossing point structure of the ST model. Here is showing few of the nearest zero points as black dots with the parameters chosen to be $V_0/\varepsilon_0 = 0.8$. Also their behavior as V_0/ε_0 increases is shown with arrows. The initial and final positions (corresponding to the values $V_0/\varepsilon_0 = 0$ and $V_0/\varepsilon_0 = \infty$) are indicated by solid and dashed circles, respectively.

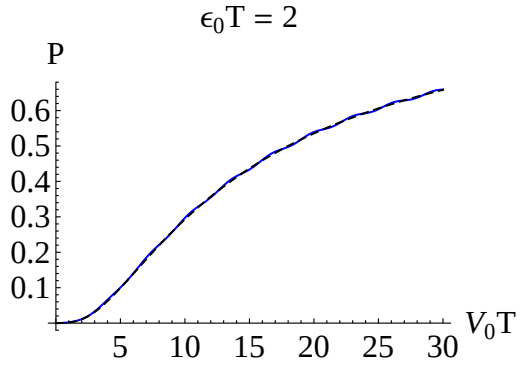

Figure 5.6: The nearest zero-point DDP approximation (black dashed line) is plotted with the exact transition probability (blue solid line) for the ST model with $\varepsilon_0 T = 2$.

Chapter 6

Conclusion

In this Thesis, we have studied simple models of time-dependent coherent dynamics in two-level quantum systems. An overarching topic has been the interplay between the non-adiabatic transitions and the way the adiabatic limit is approached in these systems.

Another one of the main themes has been obtaining flexible and robust means for transferring population between two states of a qubit. In paper **I**, we studied the case of a level-glancing. In addition of corresponding to an important special case in the curve-crossing problems historically, it offers interesting prospects for coherent excitation. The main motivation behind introducing the superparabolic models was to obtain a way to overcome the poor efficiency of the transitions in the parabolic case ($P_{\max} \approx 1/2$). It was indeed shown to be possible to reach a complete population inversion with higher superparabolic models. At the same time we have explored the applicability of different approximative methods, in particular the Dykhne-Davis-Pechukas (DDP) theory and further confirmed the idea that taking into account all of the complex crossing points, one can improve the quality of the approximation even in highly non-adiabatic regions.

At the same time we became aware of the Zhu-Nakamura theory, that originated from the partial solution of the parabolic model. Based on the complicated expressions for the Stokes constants of the parabolic model, it was modified by Zhu and Nakamura into a theory which involved only elementary functions and could be seen as a counterbalance to the more mathematically involved techniques and theories such as phase-integral approach or DDP theory. What is won in simplicity may, however, be lost in elegance. In any case, the final judgement on any theory resides on its usefulness. In paper **II**, we applied the Zhu-Nakamura theory to the superparabolic models and level-glancing phenomenon but found it lacking,

despite the supposed general applicability of the theory.

The idea of paper **III** was to take an alternative viewpoint on the general time-dependent two-level problem. The definition of the non-adiabatic coupling directed towards an interesting geometrical framework in which to study the problem. This framework makes all of the differential geometric results of plane curves available to be used in the study of the quantum mechanical problem. This theory was indeed used to find interesting effects on the adiabatic dynamics of various systems. Many possibilities await in the future to expand this connection further.

In papers **IV** and **V** we considered a relatively newly-found, and also surprising, population inversion phenomenon related to zero-area pulses. We expanded the previous results to a more general time-dependent setting and paid attention more to the adiabatic parameter region of the reference model. We highlighted also the universal character of the phenomenon.

Bibliography

[1] M. Planck, Ann. Phys. **4**, 553 (1901).

[2] A. Einstein, Ann. Phys. **17**, 132 (1905).

[3] N. Bohr, Philos. Mag. **26**, 1 (1913).

[4] B. W. Shore *Manipulating Quantum Structures Using Laser Pulses*, (Cambridge University Press, Cambridge, 2011).

[5] A. Bohm, A. Mostafazadeh, H. Koizumi, Q. Niu and J. Zwanziger *The Geometric Phase in Quantum Systems*, (Springer-Verlag, Berlin Heidelberg, 2003).

[6] V. M. Akulin *Dynamics of Complex Quantum Systems* (Springer-Verlag, Berlin Heidelberg, 2006).

[7] S. Stenholm and K.-A. Suominen *Quantum Approach to Informatics*, (Wiley, New York, 2005).

[8] M. Born and V. Fock, Zeit. f. Phys. **51**, 165 (1928).

[9] L. D. Landau, Phys. Z. Sowjet Union **2**, 46 (1932).

[10] C. Zener, Proc. R. Soc. London, A **137**, 696 (1932).

[11] E. C. G. Stückelberg, Helv. Phys. Acta **5**, 370 (1932).

[12] E. Majorana, Nuovo Cimento **9**, 43 (1932).

[13] N. V. Vitanov and K.-A. Suominen, Phys. Rev. A **59**, 4580 (1999).

[14] G. Hagedorn, Comm. Math. Phys. **136**, 433 (1991).

[15] A. Joye and C.-E. Pfister, Phys. Lett. A **169**, 62 (1992).

[16] B. T. Torosov and N. V. Vitanov, Phys. Rev. A **84**, 063411 (2011).

[17] N. Rosen and C. Zener, Phys. Rev. **40**, 502 (1932).

[18] Yu. N. Demkov and M. Kunike, Vestn. Leningr. Univ. Fis. Khim. **16**, 39 (1969).

[19] A. Ronveaux, *Heun's Differential Equation*, (Oxford University Press, New York, 1995).

[20] C. Zhu and H. Nakamura, J. Math. Phys. **33**, 2697 (1992).

[21] C. Zhu, Y. Teranishi and H. Nakamura, Adv. Chem. Phys. **117**, 127 (2001).

[22] H. Nakamura *Nonadiabatic Transition: Concepts, Basic Theories and Applications, 2nd ed.* (World Scientific, Singapore, 2012).

[23] A. M. Dykhne, Sov. Phys. JETP **11**, 411 (1960); **14**, 941 (1962).

[24] J. P. Davis and P. Pechukas, J. Chem. Phys. **64**, 3129 (1976).

[25] A. Joye, H. Kunz and Ch.-Ed. Pfister, Ann. Phys. **208**, 299 (1991).

[26] A. Joye, G. Mileti and Ch.-Ed. Pfister, Phys. Rev. A, **44**, 4280 (1991).

[27] K.-A. Suominen, Ph.D. thesis, University of Helsinki, Finland, 1992.

[28] G. S. Vasilev and N. V. Vitanov, Phys. Rev. A **73**, 023416 (2006).

[29] N. V. Vitanov, New J. Phys. **9**, 58 (2007).

[30] V. M. Akulin and W. P. Schleich, Phys. Rev. A **46**, 4110 (1992).

[31] Y. Avishai and Y. B. Band, Phys. Rev. A **90**, 032116 (2014).

[32] G. Dridi and S. Guérin, J. Phys. A: Math. Theor. **45**, 185303 (2012).

[33] M. V. Berry, Ann. N. Y. Acad. Sci. **755**, 303 (1995).

[34] M. V. Berry, J. Phys. A: Math. Theor. **42**, 365303 (2009).

[35] Xi Chen, I. Lizuain, A. Ruschhaupt, D. Guéry-Odelin and J. G. Muga, Phys. Rev. Lett. **105**, 123003 (2010).

[36] D. Daems, A. Ruschhaupt, D. Sugny and S. Guérin, Phys. Rev. Lett. **111**, 050404 (2013).

[37] R. Feynman, F. Vernon and R. Hellwarth, J. App. Phys. **28**, 49 (1957).

[38] A. Gray, E. Abbena and S. Salamon, *Modern Differential Geometry of Curves and Surfaces with Mathematica, 3rd ed.*, (Chapman and Hall/CRC, Boca Raton, FL, 1997).

[39] L. Allen and J. H. Eberly *Optical Resonance and Two-Level Atoms*, (Wiley, New York, 1975).

[40] I. I. Rabi, Phys. Rev. **51**, 652 (1937).

[41] F. W. J. Olver, D. W. Lozier, R. F. Boisvert, and C. W. Clark, *NIST Handbook of Mathematical Functions*, (Cambridge University Press, Cambridge, 2010).

[42] K.-A. Suominen and B. M. Garraway, Phys. Rev. A **45**, 374 (1992).

[43] F. T. Hioe and C. E. Carroll, Phys. Rev. A **32**, 1541 (1985).

[44] G. S. Vasilev and N. V. Vitanov, Phys. Rev. A **70**, 053407 (2004).

[45] E. E. Nikitin, Opt. and Spectr. **13**, 431 (1962).

[46] Yu. N. Demkov, Sov. Phys. JETP **18**, 138 (1964).

[47] A. Bambini and P. R. Berman, Phys. Rev. A **23**, 2496 (1981).

[48] E. J. Robinson, Phys. Rev. A **24**, 2239 (1981).

[49] M. V. Berry, Proc. R. Soc. **329**, 45 (1984).

[50] A. P. Kazantsev, G. I. Surdutovich and V. P. Yakovlev, *Mechanical Action of Light on Atoms*, (World Scientific, Singapore, 1990).

[51] A. M. Ishkhanyan, Opt. Comm. **176**, 155 (2000).

[52] E. Shimshoni and Y. Gefen, Ann. Phys. **210**, 16 (1991).

[53] K.-A. Suominen, Optics Comm. **93**, 126 (1992).

[54] M. S. Child, *Molecular Collision Theory*, (Academic Press, London, 1974).

[55] Bo Y. Chang, S. Shin, J. Santamaria, and I. R. Sola, J. Phys. Chem. A **116**, 2691 (2012).

[56] J.-N. Fuchs, L.-K. Lim and G. Montambaux, Phys. Rev. A **86**, 063613 (2012).

[57] S. L. McCall and E. L. Hahn, Phys. Rev. Lett. **18**, 908 (1967); Phys. Rev. **183**, 457 (1969).

[58] N. V. Vitanov and P. L. Knight, Opt. Comm. **121**, 31 (1995).

[59] A. P. Kazantsev, G. I. Surdutovich and V. P. Yakovlev, *Mechanical Action of Light on Atoms*, (World Scientific, Singapore, 1990).

[60] M. V. Berry, J. Phys. A: Math. Gen. **17**, 1225 (1984).

[61] T. Kato, Journ. Phys. Soc. Jap. **5**, 435 (1950).

[62] J. P. Boyd, Acta Appl. Math. **56**, 1 (1999).

[63] W. Magnus, Comm. Pure Appl. Math. VII, 649 (1954).

[64] P. Pechukas and J. C. Light, J. Chem. Phys. **44**, 3897 (1966).

[65] S. Blanes, F. Casas, J. A. Oteo and J. Ros, Phys. Rep. **470**, 151 (2009).

[66] S. Teufel, *Adiabatic Perturbation Theory in Quantum Dynamics*, (Springer-Verlag, Berlin Heidelberg, 2003).

[67] Y. N. Demkov, V. N. Ostrovskii and E. A. Solov'ev, Phys. Rev. A **18**, 2089 (1978).

[68] M. V. Fedoryuk, *Asymptotic Analysis: Linear Ordinary Differential Equations*, (Springer-Verlag, Berlin Heidelberg, 1993).

[69] G. G. Stokes, Trans. Cambridge Philos. Soc. **10**, 105 (1864).

[70] K. O. Friedrichs, Bull. Amer. Math. Soc. **61**, 485 (1955).

[71] N. Fröman and P.O. Fröman, *Physical Problems Solved by the Phase-Integral Method*, (Cambridge University Press, Cambridge, 2002).

[72] F. L. Hinton, J. Math. Phys. **20**, 2036 (1979).

[73] Y. Sibuya, *Global Theory of a Second-Order Linear Ordinary Differential Equation With a Polynomial Coefficient*, (North-Holland, Amsterdam, 1975).

[74] C. Zhu and H. Nakamura, J. Chem. Phys. **97** (3), 1892 (1992).

[75] V. I. Osherov and V. G. Ushakov, J. Phys. A: Math. Theor. **43**, 145203 (2010).

[76] K. Drese and M. Holthaus, Eur. Phys. J. D **3**, 73 (1998).

[77] S. Guérin, S. Thomas and H. R. Jauslin, Phys. Rev. A **65**, 023409 (2002).

[78] T. F. George and Y.-W. Lin, J. Chem. Phys. **60**, 2340 (1974).

[79] E. E. Nikitin, Annu. Rev. Phys. Chem. **50**, 1 (1999).

[80] T. Frankel, *The Geometry of Physics, 2nd ed.*, (Cambridge University Press, Cambridge, 2004).

[81] D. Chruściński and A. Jamiolkowski, *Geometric Phases in Classical and Quantum Mechanics* (Boston: Birkäuser, 2004).

[82] A. G. Rojo and A. M. Bloch, Am. J. Phys. **78**, 1014 (2010).

[83] M. V. Berry and J. M. Robbins, Proc. R. Soc. A **442**, 641 (1993).

[84] M. V. Berry, Proc. R. Soc. London A **430**, 405 (1990).

[85] M. Spivak, *A Comprehensive Introduction to Differential Geometry, Vol. II, 3rd ed.*, (Publish of Perish, Inc., Houston, 1999).

[86] K. Noba and Y. Kayanuma, Phys. Rev. A **64**, 013413 (2001).

[87] G. S. Vasilev, Ph.D. thesis, University of Sofia, 2008.

[88] F. Haake, *Quantum Signature of Chaos*, (Springer, Berlin, 1991).

Annales Universitatis Turkuensis

Turun yliopisto
University of Turku

Painosalama Oy, Turku, Finland 2017

ISBN 978-951-29-6854-1 (PRINT)
ISBN 978-951-29-6855-8 (PDF)
ISSN 0082-7002 (Print) | ISSN 2343-3175 (Online)