Coherent control of quantum systems with pulsed fields

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Dedicated to

My Inspiration - Lora
My Family
And to the people who believe that this thesis will be ever written
Abstract

Many branches of contemporary physics require atoms or molecules prepared in specified quantum states—not only for traditional studies of state-to-state collision dynamics, isotope separation, or laser-controlled chemical reactions, but also in more recently developing research areas of atom optics and quantum information. Of greatest interest is the fraction of all atoms or molecules in a specific state, a time-varying probability here termed the population $P(t)$. Schemes for transferring population selectively, such as excitation with frequency-swept pulses and stimulated Raman adiabatic passage (STIRAP), have opened new opportunities for coherent control of atomic and molecular processes. With the growing interest in quantum information, there is also concern with creating and controlling specified coherent superpositions of quantum states. These more general properties of an ensemble of atoms or molecules are embodied in the time-varying state vector $\Psi(t)$.

This thesis describe the basic principles underlying a variety of two and three state techniques that can be used to control state vectors and, in particular, to transfer population, selectively, between quantum states of atoms or molecules.
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Chapter 1

Introduction

The problem of manipulation of two and three quantum state system plays a central role in quantum physics. First of all, this problem is interesting by itself both physically and mathematically: physically, because the two state and the three state quantum system are the simplest nontrivial systems with discrete energy states in quantum mechanics; mathematically, because the equation for the two states and three state poses interesting mathematical challenges for the two state case some are exactly soluble, for the three state case some are exactly solvable, while other are solvable with some assumptions and approximations. Furthermore, already in the two-state case, important nonclassical phenomena occur, for instance, the famous Rabi oscillations, which often serve as a test for quantum behaviour, and also provide a powerful tool for coherent control of quantum dynamics, e.g. by \( \pi \) pulses. Finally, in almost all cases (except for a few exactly soluble), the behaviour of a multistate quantum system can only be understood by reduction to one or more effective two and three state systems, e.g., by adiabatic elimination of weakly coupled states or by using some intrinsic symmetries. This thesis is organized as follows: in Chapter 1 a brief summary of the historical background of the subsequent discussions of adiabatic-transfer schemes is given. In Chapter 2 the general mathematical principles needed to describe coherent excitation and adiabatic time evolution of quantum systems are developed. In Chapter 3 the main two-state adiabatic techniques are presented. In Chapter 4 Morris-Shore transformation is introduced and its extension to multilevel ladders is investigated in Chapter 8. In Chapters 5, 6 and 7 the three state adiabatic techniques are presented such as Stimulated Raman Adiabatic Passage (STIRAP), Stimulated Raman adiabatic passage into continuum.
and Stark-shift-chirped rapid-adiabatic-passage technique among three states. In Chapter 9 counterintuitive transitions between crossing energy levels is present. In Chapter 10 an alternative and powerful transformation (Householder reflections) to Morris-Shore transformation is described and an example of how useful this transformation could be is given in case of three state loop system. In the last Chapter 11 the conclusions are made.

The population transfer techniques described in this thesis have in common the need for coherent laser radiation. To emphasize the qualitative importance of coherence in the radiation field, we first summarize some basic results obtainable with incoherent light, such as that from filtered atomic vapor lamps or from broadband lasers with poor coherence properties.

1.1 Incoherent Population Transfer Schemes

1.1.1 Incoherent Excitation of Two-State Systems

One of the simplest theoretical descriptions of near-resonant excitation of a two-state atom or molecule by incoherent radiation is credited to Einstein [1], who first postulated that the rate of change in an atomic population within a blackbody cavity is proportional to radiation energy density; the Einstein $B$ coefficient quantifies this proportionality. The resulting rate equations include not only transitions induced by any experimentally controlled radiation field, but also the possibility of spontaneous emission of radiation, as quantified by the Einstein $A$ coefficient ($1/A$ is the spontaneous emission lifetime). If the atoms are initially (at time $t \to -\infty$) unexcited, if the radiation is sufficiently intense that spontaneous emission has a negligible effect on the population (the saturated regime), and if the excited level has the same degeneracy as the initial level, then the excited-state population at time $t$ is

$$P_e(t) = \frac{1}{2} \left[ 1 - e^{-BF(t)} \right],$$

where $F(t) = \int_{-\infty}^{t} I(t')dt'$ is the pulsed radiation fluence (energy per unit area) up to time $t$, $I(t)$ being the time-varying laser intensity (power per unit area). As this expression shows, when the pulse fluence increases, the excited-state population approaches monotonically the saturation value of 50%, which is the best transfer efficiency one can achieve with incoherent light. Of course, once the radiation ceases,
the atom must return to lower-lying levels by spontaneously emitting radiation, and eventually no excitation will remain.

1.1.2 Optical Pumping

Although spontaneous emission hinders direct creation of excitation, it can be used to advantage. Consider the excitation linkage shown in Fig. 1.1: an initially populated state $\psi_1$, resonantly excited to state $\psi_2$, from which spontaneous emission occurs, not only returning to state $\psi_1$ but possibly also to some third state $\psi_3$ whose energy lies far from resonance with the initial state or which is prevented, by selection rules based on polarization of the light, from being excited by the intense radiation. Every time the atom is excited from state $\psi_1$ to state $\psi_2$ by absorbing a photon there is a chance that spontaneous emission will carry the population to state $\psi_3$, after which the atom will be immune to further action by the radiation. The resulting population transfer, optical pumping, will eventually place the entire population into state $\psi_3$.

The simplicity of optical pumping, which requires only a single light source (not necessarily a laser), has made it a widely used method for preparing atoms or molecules in a well-defined ground or metastable state. Its main limitation is the lack of selectivity: Because the population arrives in the target level by spontaneous emission, it will simultaneously arrive in all levels into which the excited state can decay. Therefore, the pumping procedure will generally populate a statistical mixture of possible final states, not a single state. The distribution of final populations is determined by the relative decay rates that link each final state with the excited state. For vibrational transitions, these rates are proportional to Franck-Condon factors; because the latter rarely exceed 10%, the selectivity is correspondingly low.

1.1.3 Stimulated Emission Pumping

Optical pumping uses only a single light source, acting on the pump transition. The overall transfer, however, involves two photons: absorption of a pump photon from the imposed light source and spontaneous emission of a Stokes photon. The names pump and Stokes serve notice that we are dealing with a two-photon Raman process. It is natural to consider a Raman-type process in which both fields are externally
1.1. Incoherent Population Transfer Schemes

Figure 1.1: (Color online) (a) Linkage diagram for optical pumping. A pump field (not necessarily a laser) excites state $\psi_2$, which spontaneously decays back to state $\psi_1$, to state $\psi_3$, or possibly to some other states. (b) Linkage diagram for stimulated emission pumping. A pump field populates state $\psi_2$, and a subsequent Stokes (or dump) field populates state $\psi_3$.

supplied (a stimulated Raman process), so that the final step proceeds to a selected final state rather than to a statistical distribution.

One variant of the suggested two-photon process of population transfer, stimulated emission pumping (SEP) [2, 3], uses a pump field to place a population from the initial state $\psi_1$ into the excited state $\psi_2$, followed some time later by a Stokes (or dump) field that transfers the population into the desired final state $\psi_3$ (hence RAP the names pump and dump), as depicted by the 3-type linkage in Figure 1b. If the intensity of the pump laser is sufficiently strong to saturate the $\psi_1 \leftrightarrow \psi_2$ transition, then, as suggested by the rate equations, the pump step can transfer at most 50% of the population from state $\psi_1$ to state $\psi_2$. If the Stokes laser is also sufficiently strong to saturate its transition, then half the population in state $\psi_2$ will be further transferred to the target state $\psi_3$. Hence, at most one quarter of the population is transferred to the target state, while one half of the population remains in the initial state. The remaining quarter is distributed statistically according to the branching of spontaneous emission from state $\psi_2$. The SEP efficiency can be improved slightly if the pump and Stokes pulses are applied simultaneously, rather than successively. If they are sufficiently strong to saturate the transitions, thereby equalizing the populations, then one third of the population can be dispatched to
Because of its simplicity, the SEP technique has enjoyed widespread application in collision dynamics and spectroscopy [4], [5]. Its main limitations are low efficiency and low selectivity. Typically, a transfer efficiency of 10% is rarely exceeded, but this is quite adequate for many spectroscopic studies.

1.2 Resonant Coherent Excitation: Rabi Oscillations

The response of a quantum system to coherent (laser) radiation differs in significant and qualitative ways from the response of the same system to light from a lamp, even a very monochromatic lamp. Whereas the sudden application of incoherent radiation to an atom or molecule typically results in a monotonic approach to some equilibrium excitation, the sudden application of steady laser radiation typically produces oscillatory populations. These differences are most clearly seen in the study of two-state systems.

1.2.1 Two-State Systems

When coherent radiation is resonant (the carrier frequency equal to the Bohr frequency) and steady, the excitation oscillates sinusoidally (a behavior known as Rabi oscillations),

\[
P_e(t) = \frac{1}{2} (1 - \cos (\Omega t)),
\]

(1.2)

The frequency of population oscillation \(\Omega\) is known as the Rabi frequency; it will be associated below with the strength of the interaction. When the radiation varies in amplitude, the cosine argument is replaced by the so-called pulse area \(A(t)\),

\[
\Omega t \rightarrow A(t) = \int_{-\infty}^{t} \Omega(t')dt',
\]

(1.3)

Unlike the monotonic behavior for incoherent excitation, here the excited-state population oscillates between 0 and 1, depending on the value of \(A(t)\). For pulse areas equal to odd multiples of \(\pi\) (odd-\(\pi\) pulses), a complete population transfer to the excited state takes place, whereas for pulse areas equal to even multiples of \(\pi\) (even-\(\pi\) pulses), the system returns to the initial state.
In practice, the sample of atoms or molecules consists of an ensemble, often with a distribution of velocities. Atoms moving in the direction of a travelling wave experience a Doppler shift, so that their excitation is not exactly resonant; their population oscillations are more rapid and have smaller peak values than those of resonant atoms. Atoms moving transversely to a laser beam will experience a pulse area dependent on the duration of their transit time across the beam. These velocity-dependent interactions and the presence of fluctuations in the laser intensity require an averaging over excitation probabilities. The result is an effective excitation probability that has less pronounced oscillations; in extreme cases the averaging can bring the excitation probability to 0.5, the same as with incoherent excitation.

1.2.2 Three-State Systems

Rabi cycling is not confined to two-state systems: It can be found in multi-state systems too. One example is a coherently driven three-state system subjected to the same pulse sequence as in SEP: the pump pulse first, followed after its completion (without overlap) by the Stokes pulse. Then the excitation can still be considered as a two-step process, but the probabilities for each step are different from those in SEP. In the case of exact single-photon resonances, the transition probabilities $P_{12}$ from state $\psi_1$ to state $\psi_2$ and $P_{23}$ from state $\psi_2$ to state $\psi_3$ are

$$P_{12} = \frac{1}{2} \left( 1 - \cos(A_P) \right), \quad P_{23} = \frac{1}{2} \left( 1 - \cos(A_S) \right),$$

(1.4)

where $A_P$ and $A_S$ are the pump and Stokes pulse areas. If the system is initially in state $\psi_1$, then the population of state $\psi_3$ after the excitation is the product of the two probabilities,

$$P_{13} = \frac{1}{4} \left( 1 - \cos(A_P) \right) \left( 1 - \cos(A_S) \right).$$

(1.5)

Hence, for suitably chosen pulse areas (both equal to odd multiples of $\pi$) there is complete population transfer from state $\psi_1$ to state $\psi_3$. However, the transfer efficiency depends strongly on the pulse areas, and it can even vanish (when $A_P$ or $A_S$ are even multiples of $\pi$).

When the pump and Stokes pulses have the same time dependence, the interaction dynamics can no longer be separated into two consecutive, independent
two-state transitions. However, an exact solution can still be derived. If the system is initially in state $\psi_1$, and the two lasers are each resonantly tuned, then the population of state $\psi_3$ at the end of the excitation is

$$P_{13} = \frac{A_P A_S}{A^2} \left(1 - \cos \left(\frac{A}{2}\right)\right),$$  \hspace{1cm} (1.6)$$

where $A = \sqrt{A_P^2 + A_S^2}$. Here again the transfer efficiency depends on the pulse areas: Complete population transfer from state $\psi_1$ to state $\psi_3$ occurs when $A = 2(2k + 1)\pi$ ($k = 0, 1, 2, \ldots$) and $A_P = A_S$, whereas complete population return to the initial state $\psi_1$ takes place when $A = 4k\pi$.

As for two-state Rabi oscillations, the presence of a distribution of velocities or intensity fluctuations will tend to average out the oscillations and to lower the transfer efficiency. Moreover, because the population passes through the intermediate state $\psi_2$, inevitable population losses will take place by spontaneous emission unless the excitation time is much shorter than the lifetime of $\psi_2$.

The Rabi cycling is but one of the ways in which coherent laser pulses can induce population changes. Another class of change, adiabatic evolution, which can occur when the Hamiltonian changes slowly. The chapter three describes the basic principles of adiabatic population transfer by using a level crossing, and chapter five, six and seven describes adiabatic population transfer by sequential laser pulses.
Chapter 2

Two-state system in an external pulsed field

The present chapter introduce the basic quantum theory of Light-atom interaction for two state atom (e.g two state system), as governed by the time dependent Schrödinger equation. Light with circular and linear polarization is investigated. The Rotating-wave approximation is derived and the concept of diabatic and adiabatic basis is present.

2.1 The Two-state Schrödinger equation

The Schrödinger picture of quantum dynamics describes probability distribution for atomic states. It does so by means of probability amplitudes, whose absolute squares provide the desired probabilities. This chapter concerns not primarily electron density distributions within atoms, but rather excitation from one stationary state to another. These states, when no radiation is present, the atom has sharply defined energy. Further they are usually chosen as the basis states and are labelled by the value of the excitation energy and by any other convinient, mutually compatible labels or, more simply, they may just be assigned indices 1, 2, . . . within a suitable catalog. We require probability amplitudes of these states.

For describing the quantum-mechanical principles of a system we construct a multidimensional abstract vector space – the Hilbert space $\mathcal{H}$. We can introduce a complete set of orthogonal vectors of unit length to serve as a basis for $\mathcal{H}$. Each vector of this basis corresponds to a possible allowed physical state of the system.
2.1. The Two-state Schrödinger equation

and the Hilbert space has as many dimensions as there are distinct quantum states in our catalogue. Even for a finite-dimensional space there are an infinite number of ways to choose the basis vectors $\psi_1, \psi_2, \ldots$. Each choice of basis is termed a \textit{representation}. Typically we choose basis vectors to be eigenstates of some operator and we shall find it most convenient to adopt an \textit{energy representation}, in which $\psi_n$ corresponds to a stationary state of the system where no external field is present. In this representation the label $n$ identifies a stationary energy value. The description of the internal excitation of a quantum system in a \textit{pure state}, is embodied in a \textit{state vector} $\Psi(t) \in \mathcal{H}$ and we can express it as a time-varying superposition,

$$
\Psi(t) = \sum_n C_n(t) \exp\{-i\zeta_n(t)\} \psi_n, \quad (2.1)
$$

where the phase $\zeta_n(t)$ is chosen \textit{a priori} for mathematical convenience, and the complex valued function of time $C_n(t)$ is a \textit{probability amplitude}, whose absolute square is the probability $P_n(t)$ that the atom will be found in state $\psi_n$ during a measurement

$$
P_n(t) = |C_n(t)|^2 = |(\psi_n, \Psi(t))|^2. \quad (2.2)
$$

If the quantum system is closed, then the sum of all probability amplitudes does not change with time, but remains unity,

$$
\sum_n P_n(t) = 1. \quad (2.3)
$$

Probability conservation (2.3) amounts to the statement that the state vector maintains constant (unit) norm at all time,

$$
(\Psi, \Psi) = 1. \quad (2.4)
$$

We chose the basis states to be stationary and this means that they are eigenstates of $\mathcal{H}^0$ and satisfy the \textit{time-independent Schrödinger equation}

$$
\mathcal{H}^0 \psi_i = E_i^0 \psi_i, \quad (2.5)
$$

where $\mathcal{H}^0$ is a time-independent Hamiltonian operator, which governs the evolution of the system when no external field applied. In terms of the laser field interactions this assumption suggests that if the system is initialized in a stationary state it will remain in it, so long as no external force intervenes.
Once we introduce a laser field to interact with the quantum system, the state vector varies, governed by the \textit{time-dependent Schrödinger equation} (in units $\hbar = 1$),

\[ i \frac{d}{dt} \Psi(t) = H(t)\Psi(t), \quad (2.6) \]

where $H(t)$ is the Hamiltonian operator, which represents the total energy of the system – the sum of kinetic, potential and interaction energies. When the external field depends upon time (as they do when the interaction begins and ends at finite times or is periodic), the elements of the matrix $H(t)$ depend explicitly upon time either.

Equation (2.6) underlies all nonrelativistic descriptions of microscopic temporal behaviour. It is the basis for the quantum-mechanical description of excitation. In particular, it provides the foundation of all discussions of coherent excitation and defines the dynamical behaviour of a quantum system.

The definition of a state vector $\Psi(t)$ in energy representation (2.1) has some flexibility in choosing the phases $\zeta_n(t)$ . Their choice, for a given representation, establishes a \textit{picture}. The simplest, and most obvious choice, $\zeta_n \equiv 0$ , defines the \textit{Schrödinger picture}.

\subsection{2.1.1 The Two–State Schrödinger Atom}

The idealized notion of two-state system provides the simplest application of time-dependent Schrödinger equation. By definition, such system can exist in two, and only two, possible states of motion – a ground state $\psi_1$ and an excited state $\psi_2$.

The Hilbert space for this system is 2-dimensional and the space vector is expressed as

\[ \Psi(t) = C_1(t) \exp\{-i\zeta_1(t)\} \psi_1 + C_2(t) \exp\{-i\zeta_2(t)\} \psi_2, \quad (2.7) \]

where the complex-valued expansion coefficient $C_i(t)$ is the projection of the state vector $\Psi(t)$ onto the fixed basis vector $\psi_i$.

Let us assume the case of no external forces acting upon the system and substitute the state vector (2.7) into the Schrödinger equation(in units $\hbar = 1$)

\[ i \frac{d}{dt} \Psi(t) = E_1^0 e^{-i\zeta_1(t)} C_1(t) \psi_1 + E_2^0 e^{-i\zeta_2(t)} C_2(t) \psi_2. \]

Taking into account that the basis states are stationary we multiply this equation sequentially with $\psi_1$ and $\psi_2$ from the left. As a result we obtain a set of two
2.1. The Two-state Schrödinger equation

independent first-order linear differential equations for the probability amplitudes

\[ i\dot{C}_n(t) = (E_0^n - \dot{\zeta}_n(t))C_n(t), \quad n = 1, 2. \]  

(2.8)

The solution is a probability amplitude with time evolution only in its phase,

\[ C_n(t) = C_n(0) \exp\left\{-i(E_0^n - \dot{\zeta}_n(t))t/\right\}, \]  

(2.9)

and so the probabilities remain fixed at their initial values

\[ P_n(t) = |C_n(0)|^2 = P_n(0). \]  

(2.10)

This constancy implies the meaning of a stationary state.

If the system interacts with a laser field, its Hamiltonian operator \( H(t) \) from

the time-dependent Schrödinger equation (2.6), can be expressed as a sum of the

time-independent Hamiltonian \( H^0 \) and another operator \( V(t) \), representing the

perturbative time-dependent interaction with the pulsed field

\[ H(t) = H^0 + V(t). \]  

(2.11)

We assume that \( H(t) \) is hermitian, which provides real the eigenvalues and hence real excitation energies. This, together with (2.11), suggests that the interaction Hamiltonian operator \( V(t) \) is also hermitian, i.e. its matrix elements satisfy

\[ V_{ij} = V_{ji}^*. \]  

(2.12)

The time-dependent Schrödinger equation for the state vector

\[ i\frac{d}{dt} \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} E_0^1 - \dot{\zeta}_1(t) + V_{11}(t) & V_{12}(t)e^{-i\zeta_2(t)+i\zeta_1(t)} \\ V_{21}(t)e^{-i\zeta_1(t)+i\zeta_2(t)} & E_0^2 - \dot{\zeta}_2(t) + V_{22}(t) \end{bmatrix} \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} \]  

(2.13)

is transformed in a set of two coupled first order differential equations for the probability amplitudes \( C_n(t) \). Written in a vector–matrix form this reads

\[ i\frac{d}{dt} \mathbf{C}(t) = H(t)\mathbf{C}(t), \]  

(2.14)

where \( \mathbf{C}(t) = [C_1(t), C_2(t)]^T \).

The definition of the two-state problem is to determine the probabilities at \( t \to \infty \), \( |C_m(\infty)|^2 \), \( m = 1, 2 \), if we know their initial values (at \( t \to -\infty \)). We usually solve (2.13) with initial conditions

\[ C_1(-\infty) = 1, \quad C_2(-\infty) = 0, \]  

(2.15)
which physically means that in the beginning of the evolution the system was in state $\psi_1$. Equation (2.13), together with initial conditions (2.15), completes the mathematical description of the two-state atom. The Schrödinger picture suggests that all phases in the expression for the state vector (2.7) are fixed at zero and

$$\Psi(t) = \sum_{n=1}^{2} C_n(t) \psi_n.$$  

(2.16)

The equations for the probability amplitudes obtain the form

$$i \frac{d}{dt} \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \begin{bmatrix} E_0^1 + V_{11}(t) & V_{12}(t) \\ V_{21}(t) & E_0^2 + V_{22}(t) \end{bmatrix} \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix}.$$  

(2.17)

Although, it may look easier to solve this set of equations, compared to the set involving time-dependent phases (2.13), in many cases this assumption proves wrong. The freedom of choosing the phases $\zeta_n(t)$ arbitrary, without changing the solutions for the probability amplitudes (up to an unimportant phase), often gives us the advantage to solve the set (2.13) analytically.

### 2.1.2 Light–Atom Interaction

For radiation within the optical region of the spectrum, wavelengths are much larger than the atomic dimensions and we can assume that the interaction is that between a spatially uniform electric field and an atomic dipole moment. The interaction energy is

$$V(t) = -\mathbf{d} \cdot \mathbf{E}(t),$$  

(2.18)

where $\mathbf{d}$ is the atomic dipole transition moment operator and $\mathbf{E}(t)$ is the electric field operator evaluated at the center of mass of the atom. For electric dipole induced transitions amongst bound atomic states of an isolated atom the matrix representation of $V(t)$ usually has no diagonal elements. If the external field is static any diagonal elements, $V_{nn}$, would produce an energy shift in the undisturbed energies of the atom. With a simple phase transformation of the kind

$$\tilde{C}_n(t) = C_n(t) \exp\{-iV_{nn}t\},$$  

(2.19)

this energy shift can be incorporated in the definition of the probability amplitudes. This is identical to fixing the diagonal elements of $V(t)$ at zero. Therefore, we shall
2.1. The Two-state Schrödinger equation

assume that the only nonvanishing two-state elements of the interaction Hamiltonian are those that connect state $\psi_1$ to state $\psi_2$.

In the simplest examples the electric field $E(t)$ has the form of a periodic variation at a carrier frequency (the optical frequency $\omega$) and a more slowly varying envelope $E(t)$

$$E(t) = eE|E(t)|\cos(\omega t + \phi) + \exp\{i\omega t + i\phi\},$$  \hspace{1cm} (2.20)

where $e$ is a unit vector defining the direction of the electric field vector, i.e. the polarization direction, and $\phi$ is the phase of the amplitude $E(t)$, i.e. the phase of the laser wave.

We need to determine the matrix element of the dipole transition moment between basis states 1 and 2, which is the component of the vector operator $d$ along the direction of the electric field. The quantitative description of the atomic properties enters the theory through the matrix elements

$$(\psi_n, d \cdot e \psi_m) \equiv d_{nm} \cdot e.$$  \hspace{1cm} (2.21)

Using these definitions and approximations I can write the nonvanishing matrix elements of the interaction as

$$V_{21}(t) = -d_{21} \cdot e\frac{1}{2}|E(t)|\Re[\exp\{i\omega t + i\phi\}] = V_{12}^*(t).$$  \hspace{1cm} (2.22)

2.1.3 Light with Circular Polarization

The treatment of the interaction between an atom and circularly polarized light involves complex unit vectors. For complex-valued vectors $e$, say the vector appropriate to right-circular polarization $e = (e_x - ie_y)/\sqrt{2}$, the matrix element becomes

$$V_{21}(t) = -d_{21} \cdot e\frac{1}{2}|E(t)|\exp\{-i\omega t - i\phi\}$$

$$-\frac{1}{2}(\psi_2, (d_x + id_y) \psi_1)\frac{|E(t)|}{\sqrt{2}}\exp\{i\omega t + i\phi\},$$  \hspace{1cm} (2.23)

The replacement $id_y \rightarrow -id_y$ gives the matrix elements for left-circular polarization. Angular momentum selection rules ordinarily permit only one of the operators $d_x + id_y$ or $d_x - id_y$ to have non-zero matrix elements between any two states, so that one of the contributions to $V_{21}(t)$ vanishes. Expression (2.23) shows that for light with circular polarization the interaction element of the Hamiltonian $V_{21}(t)$ is
2.1. The Two-state Schrödinger equation

complex valued – it is proportional to either \( \exp\{+i\omega t\} \) or \( \exp\{-i\omega t\} \). We see that

\[
V_{21}(t) = \begin{cases} 
\frac{i}{2}\Omega(t) \exp\{i\omega t + i\phi\}, & \text{for circular polarization,} \\
\frac{i}{2}\Omega(t) \exp\{-i\omega t - i\phi\}, & \text{for circular polarization,}
\end{cases}
\]  

(2.24)

where \( \Omega(t) \) is real-valued quantity, with dimension of angular frequency. This frequency is known as the Rabi frequency. Together with the Bohr frequency \( \omega_0 \) and the interaction frequency \( \omega \), the Rabi frequency provides one of the three characteristic time scales for the coherent atomic excitation, and it parameterizes the interaction strength between the atom and the external field. For the expression above the Rabi frequency is evaluated as

\[
|\Omega(t)| = |d_{21} \cdot e| |E(t)|.
\]

(2.25)

So, the elements of the interaction Hamiltonian are

\[
V_{11}(t) = V_{22}(t) = 0, \\
V_{21}(t) = V_{12}^*(t) = \frac{1}{2}\Omega(t) \exp\{-i\omega t - i\phi\}
\]

(2.26a)

and we substitute them in the time-dependent Schrödinger equation (in units of \( \hbar = 1 \))

\[
i \frac{d}{dt}C_1(t) = (E^0_1 - \dot{\zeta}_1(t))C_1(t) + \frac{1}{2}\Omega(t)e^{i(\omega t + \phi)}e^{-i\zeta_2(t)}e^{i\zeta_1(t)}C_2(t) \]  

(2.27a)

\[
i \frac{d}{dt}C_2(t) = \frac{1}{2}\Omega(t)e^{-i(\omega t + \phi)}e^{-i\zeta_1(t)}e^{i\zeta_2(t)}C_1(t) + (E^0_2 - \dot{\zeta}_2(t))C_2(t). \]  

(2.27b)

From this expression we can see that by choosing the arbitrary phase functions \( \zeta_n(t) \) appropriately we can simplify these equations and eliminate completely the time-varying exponential factors.

Let us set

\[
\zeta_2(t) - \zeta_1(t) = \omega t + \phi
\]

(2.28)

and fix \( \dot{\zeta}_1(t) \) to be

\[
\dot{\zeta}_1(t) = E^0_1 + \frac{1}{2}\Delta(t),
\]

(2.29)

which is the Dirac picture. It is here that we have introduced the detuning \( \Delta(t) \)

\[
\Delta(t) = \omega_0 - \omega,
\]

(2.30)
2.1. The Two-state Schrödinger equation

which is the difference between the Bohr (or transition) frequency $\omega_0$ for the atom and the frequency of the laser pulse $\omega$.

The next step is to put these phases in (2.27) and as a result we obtain

$$
\frac{id}{dt} \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \frac{1}{2} \begin{bmatrix} -\Delta(t) & \Omega(t) \\ \Omega(t) & \Delta(t) \end{bmatrix} \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix}.
$$

(2.31)

These equations govern the dynamics of a two-state system under the influence of the exponentially oscillating interaction (2.26a).

2.1.4 Light with Linear Polarization

For a linearly polarized laser wave we can choose the unit vector $e$, defining the polarization direction to be real. By introducing real unit vectors $e(x)$, $e(y)$ and $e(z)$ we can express the atomic dipole operator in Cartesian coordinates

$$
d = d_x e(x) + d_y e(y) + d_z e(z).
$$

(2.32)

The interaction takes simplest form if we choose the atomic axis $z$ to lie along the polarization direction $e = e(z)$, for then we have the expression

$$
V_{21}(t) = -\left(\psi_2, \hat{d}_z \psi_1 \right) |E(t)| \cos(\omega t + \phi).
$$

(2.33)

This expression makes it clear, that for a linear polarization of monochromatic light, $V_{21}(t)$ may be taken as real valued. We conclude that the matrix elements of the interaction operator $V(t)$ in the stationary basis are

$$
\begin{align*}
V_{11}(t) &= V_{22}(t) = 0, \quad \text{(2.34a)} \\
V_{12}(t) &= V_{21}(t) = V_{21} \cos(\omega t + \phi) \\
&= \frac{1}{2} V_{21} \left[ \exp\{i\omega t + i\phi\} + \exp\{-i\omega t - i\phi\} \right], \quad \text{(2.34b)}
\end{align*}
$$

where $V_{21}$ is real. We substitute them in Eq. (2.13) and the full Hamiltonian operator for this type of interaction in this basis has the explicit elements

$$
H(t) = \begin{bmatrix}
E_1^0 - \hat{\zeta}_1(t) & \frac{1}{2} V_{21} \left[ e^{i\omega t + i\phi} + e^{-i\omega t - i\phi} \right] e^{-i\zeta_2(t) + iG_1(t)} \\
\frac{1}{2} V_{21} \left[ e^{i\omega t + i\phi} + e^{-i\omega t - i\phi} \right] e^{i\zeta_2(t) - i\zeta_1(t)} & E_2^0 - \hat{\zeta}_2(t)
\end{bmatrix}.
$$

(2.35)
As we saw above, a suitable choice of the phases can often facilitate solution of the Schrödinger equation, so we introduce the so-called rotating-wave picture, in which the phase difference is set to

\[ \zeta_2(t) - \zeta_1(t) = \omega t + \zeta_0, \quad (2.36) \]

where \( \zeta_0 \) is independent of time. By doing so, the difference \( \zeta_2 - \zeta_1 \) incorporates the time dependence \( \pm \omega t \) and we can replace one of the two exponentials in Eq. (2.35) by unity. With the further choice (as in the case for complex-valued interactions)

\[ \dot{\zeta}_1(t) = E_1^0 + \frac{1}{2} \Delta(t), \quad (2.37a) \]
\[ \dot{\zeta}_2(t) = E_2^0 - \frac{1}{2} \Delta(t), \quad (2.37b) \]

the final form of the time-dependent Schrödinger equation, with the Hamiltonian (2.35), is

\[
i \frac{d}{dt} \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \frac{1}{2} \begin{bmatrix} -\Delta(t) & \Omega(t)[1 + e^{-2i(\omega t + \phi)}] \\ \Omega^*(t)[1 + e^{2i(\omega t + \phi)}] & \Delta(t) \end{bmatrix} \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix}. \quad (2.38)\]

The Rabi frequency \( \Omega(t) \) that appears in the Hamiltonian operator is defined as

\[ \Omega(t) = V_{21} \exp\{i\phi - i\zeta_0\}, \quad (2.39) \]

and so it may be complex-valued. This Rabi frequency is connected to the interaction Rabi frequency (2.25) through a phase transformation and for simplicity we denote them with one and the same symbol. If and only if, the excitation phase \( \phi \) remains fixed, then it is always possible to choose the arbitrary constant \( \zeta_0 \) such that \( \Omega(t) \) becomes real and positive.

In Eq. (2.38) we involved no approximations, apart form that of a two-state atom. The rotating-wave picture is particularly suited to the use of approximations that allow simple exact solutions, as we shall see next.

## 2.2 Rotating-wave approximation (RWA)

The principle concern in laser-induced excitation is with optical frequencies \( \omega \) much larger than the Rabi frequency \( \Omega \). To eliminate the uninteresting high-frequency
components that oscillate at frequency $\omega$, we average the differential equations over an optical period $\tau = 2\pi/\omega$ and obtain the cycle-averaged amplitude and derivative

$$\bar{C}_n(t) = \frac{1}{\tau} \int_t^{t+\tau} C_n(t')dt', \quad (2.40a)$$

$$\frac{d}{dt}\bar{C}_n(t) = \frac{1}{\tau} \int_t^{t+\tau} \frac{d}{dt'}C_n(t')dt'. \quad (2.40b)$$

We assume that during such an interval the function $C_n(t)$ changes very little. Under this condition we may replace the cycle average of $\exp\{2i\omega t\}C_n(t)$ by its average value, zero

$$\frac{1}{\tau} \int_t^{t+\tau} \exp\{2i\omega t'\}C_n(t')dt' \simeq \bar{C}_n(t)\frac{1}{\tau} \int_t^{t+\tau} \exp\{2i\omega t'\}dt' = 0. \quad (2.41)$$

This approximation, known in the context of the two-state atomic excitation as the rotating-wave approximation (RWA) [2,3], essentially assumes that the exponential $\exp\{2i\omega t\}$ undergoes many oscillations during the time needed for $C_n(t)$ to change appreciably. Thus, the RWA amounts to the replacement

$$\{1 + \exp\{2i\omega t\}\} \simeq 1 \quad (2.42)$$

for the time average. In this approximation the Schrödinger equation obtains the form

$$i\frac{d}{dt}\begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix} = \frac{1}{2} \begin{bmatrix} -\Delta(t) & \Omega(t) \\ \Omega^*(t) & \Delta(t) \end{bmatrix} \begin{bmatrix} C_1(t) \\ C_2(t) \end{bmatrix}, \quad (2.43)$$

where the overbar that explicitly indicates time average, is omitted, and we will simply have $C_n(t)$ instead of $\bar{C}_n(t)$. The dynamical behaviour becomes identical to that of a two-state atom subjected to a suddenly-applied steady interaction.

### 2.3 Adiabatic basis, adiabatic approximation

The Schrödinger equation (2.14) is rewritten in the so-called diabatic basis, which is the stationary basis of the system, involving the time-independent Hamiltonian $H^0$ eigenvectors $(\psi_1, \psi_2)(2.5)$. However, we have the possibility to choose any other basis, for mathematical convenience, which would simplify the expression of the Schrödinger equation. Theoretical discussion of time-evolving quantum systems is greatly facilitated by introducing instantaneous eigenstates $(\Phi_-, \Phi_+)$ of the time-varying Hamiltonian matrix

$$H(t)\Phi_i(t) = \varepsilon_i(t)\Phi_i(t), \quad (i = -, +). \quad (2.44)$$
Because the Hamiltonian changes with time, both the eigenvalues \( \varepsilon_i(t) \) and the eigenvectors, the \textit{adiabatic states} \( \Phi_i(t) \), will change with time. Knowing the explicit form of the time-dependent Hamiltonian (2.43), it is easy to find its eigenvalues
\[
\varepsilon_{\pm}(t) = \pm \frac{1}{2} \sqrt{\Omega^2(t) + \Delta^2(t)}
\]
and their difference
\[
\varepsilon(t) = \varepsilon_+(t) - \varepsilon_-(t) = \sqrt{\Omega^2(t) + \Delta^2(t)} ,
\]
which defines the energy splitting. We express the state vector \( \Psi(t) \) as a superposition of the adiabatic states
\[
\Psi(t) = A_-(t)\Phi_-(t) + A_+(t)\Phi_+(t)
\]
with coefficients \( A_-(t) \) and \( A_+(t) \). Comparing it with the expression for the state vector, written in the diabatic basis (2.7), we find that the two bases are connected through orthogonal rotating transformation
\[
\begin{bmatrix}
\Phi_-(t) \\
\Phi_+(t)
\end{bmatrix} = R^{-1}(\vartheta(t))
\begin{bmatrix}
\cos \vartheta(t) & -\sin \vartheta(t) \\
\sin \vartheta(t) & \cos \vartheta(t)
\end{bmatrix}
\begin{bmatrix}
\psi_1 \\
\psi_2
\end{bmatrix},
\]
or shortly
\[
\Phi(t) = R^{-1}(\vartheta(t))\psi ,
\]
where \( \Phi(t) = [\Phi_-(t), \Phi_+(t)]^T \) and \( \psi = [\psi_1, \psi_2]^T \). The rotating angle \( \vartheta(t) \), being a function of time, is defined as follows
\[
\tan 2\vartheta(t) = \frac{\Omega(t)}{\Delta(t)}.
\]
The connection between the superposition coefficients for the diabatic basis \( (C_1(t), C_2(t)) \) and the adiabatic basis \( (A_-(t), A_+(t)) \) is expressed in terms of \( R(\vartheta(t)) \)
\[
\begin{bmatrix}
C_1(t) \\
C_2(t)
\end{bmatrix} = R(\vartheta(t))
\begin{bmatrix}
\cos \vartheta(t) & \sin \vartheta(t) \\
-\sin \vartheta(t) & \cos \vartheta(t)
\end{bmatrix}
\begin{bmatrix}
A_-(t) \\
A_+(t)
\end{bmatrix}.
\]
Substituting the adiabatic states as a time-varying superposition (2.49) in the expression (2.44), we obtain that
\[
R^{-1}(\vartheta(t))H(t)R(\vartheta(t)) = \begin{bmatrix}
-\varepsilon & 0 \\
0 & +\varepsilon
\end{bmatrix}.
\]
Let’s rewrite the Schrödinger equation in the adiabatic basis. We use its representation in the diabatic basis (2.14) and express the diabatic amplitudes according to (2.51)

$$i \frac{d}{dt} [R(\vartheta(t))A(t)] = H(t)[R(\vartheta(t))A(t)].$$

(2.53)

After taking the time derivative, the result for the Schrödinger equation is

$$i \frac{d}{dt} A(t) = [R^{-1}(\vartheta(t))H(t)R(\vartheta(t)) - iR^{-1}(\vartheta(t))\dot{R}(\vartheta(t))]A(t),$$

(2.54)

or written in matrix form

$$i \frac{d}{dt} \begin{bmatrix} A_-(t) \\ A_+(t) \end{bmatrix} = \begin{bmatrix} -\varepsilon & -i\dot{\vartheta} \\ i\dot{\vartheta} & +\varepsilon \end{bmatrix} \begin{bmatrix} A_-(t) \\ A_+(t) \end{bmatrix}.$$

(2.55)

The adiabatic states can serve as a moving coordinate system in which to place the state vector $\Psi(t)$ as it changes under the influence of the coherent radiation pulse. Such coordinates are most useful when the elements of the Hamiltonian – the Rabi frequency and the detuning – change sufficiently slowly (i.e. adiabatically); then the state vector remains fixed in the adiabatic coordinate space. Mathematically, adiabatic evolution requires the off-diagonal elements of the Hamiltonian (2.55) to be negligible compared to the diagonal ones, or

$$|\dot{\vartheta}(t)| \ll \varepsilon(t),$$

(2.56)

which expresses the adiabatic condition. According to this condition, adiabatic evolution requires a smooth pulse, long interaction time, and large Rabi frequency and/or large detuning.

When the adiabatic condition holds, there are no transitions between the adiabatic states and their populations are conserved. That is, the state vector remains fixed in the time-varying coordinate system of adiabatic states, as the latter move with respect to the fixed basis states $\psi_1$ and $\psi_2$. In particular, if the state vector $\Psi(t)$ coincides with a single adiabatic state at some time $t$, then it will remain in that adiabatic state as long as the evolution is adiabatic; the state vector $\Psi(t)$ will adiabatically follow the state $\Phi(t)$. 


Chapter 3

Two-state adiabatic technics

In this chapter we present two schemes for complete transfer of atomic or molecular population between two bound states. The first technique is Rapid adiabatic passage (RAP), which produce frequency-swept pulses and thus induce a level crossing, which in case of adiabatic limit leads to complete population transfer. The second is the Stark-chirped rapid adiabatic passage (SCRAP). In this laser technique a delayed-pulse laser-induced Stark shift sweeps the transition frequency between two coupled states twice through resonance with the frequency of the population-transferring coupling laser. The delay of the Stark-shifting pulse with respect to the pulse of the coupling-laser Rabi frequency guarantees adiabatic passage of population at one of the two resonances while the evolution is diabatic at the other. The SCRAP method can give a population-transfer efficiency approaching unity.

3.1 Rapid Adiabatic Passage

In brief, coherent excitation of a two-state quantum system is described by the Schrödinger equation, which in the rotating-wave approximation (RWA) [2] (see also Chapter 2) reads

\[ i \frac{d}{dt} \mathbf{C}(t) = \mathbf{H}(t) \mathbf{C}(t), \]  

(3.1)

where \( \mathbf{C}(t) = [C_1(t), C_2(t)]^T \) is the column-vector with the probability amplitudes \( C_1(t) \) and \( C_2(t) \) of the two states \( \psi_1 \) and \( \psi_2 \), and \( \mathbf{H}(t) \) is the Hamiltonian, [2]

\[
\mathbf{H}(t) = \frac{1}{2} \begin{pmatrix}
0 & \Omega(t) \\
\Omega(t) & 2\Delta(t)
\end{pmatrix}.
\]  

(3.2)
In the above, $\Omega(t)$ is the Rabi frequency and $\Delta(t)$ is detuning. Now to derive the properties of Rapid adiabatic passage (RAP), we consider the adiabatic states $\Phi_{\pm}$. These states are the instantaneous eigenvectors of (9.2) (see also Chapter 2) and can be expressed as coherent superpositions of the bare states $\psi_1$ and $\psi_2$ by:

$$\Phi_+(t) = \cos \vartheta(t) \psi_1 + \sin \vartheta(t) \psi_2,$$

$$\Phi_-(t) = \sin \vartheta(t) \psi_1 - \cos \vartheta(t) \psi_2.$$  

(3.3) 

(3.4) 

with the mixing angle $\vartheta(t)$ given by

$$\tan 2\vartheta(t) = \frac{\Omega(t)}{\Delta(t)}.$$  

(3.5) 

There are two distinct types of adiabatic population changes depending on the behavior of the diabatic energies of the Hamiltonians (9.2). The no-crossing case is depicted in Fig. 3.1 (top left frame) in the particular case of constant detuning; the diabatic energies are parallel to each other. In the absence of interaction, the adiabatic energies coincide with the diabatic ones, but the (pulsed) interaction $\Omega(t)$ pushes them away from each other. As Eq. (3.3) and (3.4) show, at early and late times each adiabatic state is identified with the same diabatic state: $\Phi_-(t \to \pm\infty) = \psi_1$, $\Phi_+(t \to \pm\infty) = \psi_2$, whereas at intermediate times it is a superposition of diabatic states. Consequently, starting from the ground state $\psi_1$, the population makes a partial excursion into the excited state $\psi_2$ at intermediate times and eventually returns to $\psi_1$ in the end (bottom left frame). Hence, in the no-crossing case adiabatic evolution leads to complete population return. A rather different situation occurs when the detuning $\Delta(t)$ sweeps slowly from some very large negative value to some very large positive value or vice versa (irrespective of whether the laser frequency or the transition frequency is changed), as shown in Fig. 3.1 (top right frame). Then the angle $\vartheta(t)$ rotates clockwise from 0 to $-\pi/2$ and the adiabatic eigenstate $\Phi_-(t)$ changes from $\psi_1$ to $\psi_2$:

$$\Phi_-(\infty) = \psi_1$$

$$\Phi_-(\infty) = \psi_2$$  

(3.6) 

(3.7) 

Thus such an adiabatic change (chirp) of $\Delta(t)$ will produce complete population transfer from the initially populated state $\psi_1$ to the initially unpopulated state $\psi_2$ Fig. 3.1 (bottom right frame). The process is known as rapid adiabatic passage (RAP) [2].
3.2 Stark-shift-chirped rapid-adiabatic-passage

The essence of the Stark-chirped rapid adiabatic passage (SCRAP) [2] procedure is the well established technique of rapid adiabatic passage (RAP) [2]. This technique utilizes two sequential laser pulses. Fig. 3.2 illustrates these ideas. One of the pulses—the pump pulse—is slightly detuned off resonance with the transition frequency and moderately strong; it serves to drive the population from the ground to the excited state. The other pulse—the Stark pulse—is far off-resonant and strong; it is used merely to modify the atomic transition frequency by inducing Stark shifts in the energies of the two states. Because the Stark shifts $S_g(t)$ and $S_e(t)$ of the ground and excited states are generally different (usually $|S_g(t)| \ll |S_e(t)|$) and each of them is proportional to the intensity of the Stark pulse, the transition frequency will experience a net Stark shift $S(t) = S_e(t) - S_g(t)$ By choosing an appropriate detuning for the pump pulse it is always possible to create two diabatic level crossings in the wings of the Stark pulse: one crossing during the growth and the

Figure 3.1: (Color online) Time evolution of the energies (upper frames) and the populations (lower frames) in a two-state system. In the upper plots, the dashed lines show the unperturbed (diabatic) energies, and the solid curves show the adiabatic energies. The left-hand frames are for the no-crossing case, and the right-hand frames are for the level-crossing case.
other during the decline of the Stark pulse. For successful population transfer, the
evolution must be adiabatic at one and only one of these crossings. This asymmetry
can only occur if the pump and Stark pulses are not simultaneous: The pump pulse
must be strong at one and only one of the crossings. It proves appropriate to set the
time delay between the two pulses so that the maximum of the pump pulse occurs
at one of the crossings in order to optimize the adiabatic passage there. It is also
appropriate that the pump pulse width be smaller than both the Stark pulse width
and the delay between the pulses in order to suppress adiabatic passage at the other
crossing. In this adiabatic-diabatic scenario the system will follow the path shown
in the middle right frame in Fig. 3.2: The state vector will adiabatically follow the
lower adiabatic state through the first crossing, whereas during the second crossing
it will follow the diabatic state $\psi_2$ (rather than an adiabatic state) and remain there
until the end of the interaction. The net result is complete population transfer from
state $\psi_1$ to state $\psi_2$. It should be appreciated that the adiabatic and diabatic inter-
nals can occur in either order: The pump pulse may either precede or follow the
Stark pulse.

The SCRAP technique resembles the early experiment by Loy [6], who used adi-
abatic quasistatic pulses of about 5 ms duration to induce Stark shifts. However,
he induced two sequential population transfers per pulse—excitation for the leading
edge and deexcitation for the trailing edge of each pulse—resulting in no net popu-
lation transfer. In contrast, the time delay between the pump and Stark pulses in
SCRAP ensures that population transfer takes place at just one of the crossings,
thus leading to overall population transfer.

It should be obvious from the above description that complete population trans-
fer will only occur within finite ranges of values of the various interaction parameters.
For example, in order that there be level crossings the static detuning $\Delta_0$ must be
smaller than the maximum Stark shift $S_0$ and must have the same sign as $S_0$. Also,
the pump pulse should be strong enough to ensure adiabatic passage at one of the
crossings, but weak enough to prevent adiabatic passage at the other. For Gaus-
sian pulse shapes, $\Omega (t) = \Omega_0 \exp \left(-t^2/T_p^2\right)$ and $S (t) = S_0 \exp \left(-(t-\tau)^2/T_S^2\right)$, the
latter requirements lead to the conditions [7]

$$1 \ll \frac{(\Omega_0 T_S)^2}{\Delta_0 \tau} \ll \exp \left(8 \tau^2/T_P^2\right)$$  \hspace{1cm} (3.8)
These conditions set upper and lower limits on the peak pump Rabi frequency $\Omega_0$ and the static detuning $\Delta_0$.

The SCRAP technique benefits from the fact that strong fixed-frequency long-wavelength pulsed-laser radiation, suitable for Stark shifting the levels, is often available because it is used to generate (by frequency conversion) the visible or ultraviolet radiation needed for the pump interaction. Moreover, its pulse width is longer than the pump pulse width, which is beneficial for SCRAP.

As with simple adiabatic passage, the SCRAP technique can produce population transfer in an ensemble of atoms having a distribution of Doppler shifts. The peak value of the Stark shift sets the maximum detuning that can be accessed; in turn, this sets the range of Doppler shifts for which population transfer can be produced.

![Figure 3.2: (Color online) Time evolution of the Rabi frequencies (top frames), the level energies (middle frames), and the populations (bottom frames) in a two-state system driven by a pump pulse $\Omega_P$ and a Starkshifting pulse $\Omega_S$. (Left) Simultaneous pump and Stark pulses. (Right) Pump pulse before Stark pulse (Stark-chirped rapid adiabatic passage method).]
Chapter 4

Degenerate multistate systems, Morris-Shore transformation

In this chapter we present a transformation that in case of any RWA-degenerate two-level system, in which all couplings share the same time dependence, can reduce the system to an equivalent system comprising only independent two-state systems and uncoupled dark states. Such a transformation is known as the Morris-Shore transformation.

4.1 Hamiltonian

We assume completely coherent evolution, i.e., there are no decoherence processes during the interaction. Then the excitation dynamics is described by the Schrödinger equation, which in the rotating-wave picture and with the rotating-wave approximation (RWA) [2](see Chapter 2) takes the form of coupled ordinary differential equations for time-dependent complex-valued probability amplitudes $C_n(t)$,

$$i\frac{d}{dt}C_n(t) = \sum_m H_{nm}(t)C_m(t),$$

from which one evaluates the probability of finding the population in state $n$ at time $t$ as $P_n(t) = |C_n(t)|^2$.

The coefficient matrix $H$, obtained from the Hamiltonian matrix in RWA [2, 3], has detunings $\Delta_n = H_{nn}$ as diagonal elements and Rabi frequencies $\Omega_{nm} = 2H_{nm}$ as off-diagonal elements.
Though not explicitly shown, the matrix elements may vary with time. For the present interest, only two different detunings $\Delta_n$ occur in the Hamiltonian $H$; each may vary (independently) with time. We also assume that all the Rabi frequencies $\Omega_{nm}$ have the same time dependence, although their maximal amplitudes may differ. The special case when all nonzero elements of the Hamiltonian, Rabi frequencies and detunings, have the same time dependence, say $f(t)$, reduces to that of a constant Hamiltonian by defining a new time variable $x = \int f(t)\,dt$. Here, we do not make this latter assumption and we show that analytic solutions can be found in the more general case when the detunings vary independently of the Rabi frequencies. This includes the important special case of constant detunings and pulse-shaped Rabi frequencies.

With the assumed two distinct detunings, and suitable ordering of the basis states, the matrix $H$ has the form

$$H = \begin{bmatrix} \Delta_a I_a & V \\ V^\dagger & \Delta_b I_b \end{bmatrix}. \quad (4.2)$$

Here $I_a$ and $I_b$ are unit matrices, of dimensions $N_a$ and $N_b$, respectively, and $V$ is a $N_a \times N_b$ matrix of Rabi frequencies (all with the same time dependence). By suitable choice of overall phase for the probability amplitudes one of the two detunings can always be set to zero; this is traditionally taken to be the first of these detunings $\Delta_a$, which is associated with the initially populated state. When all transitions are resonant, as is often assumed, both detunings are zero.

### 4.2 Morris-Shore Basis

Morris and Shore [8] showed that any system that has the Hamiltonian (4.2) can be transformed, via suitable redefinition of basis states, to one involving a set of $N_<$, independent two-state systems, where $N_<$ is the lesser of $N_a$ and $N_b$, together with a set of decoupled spectator states that are unaffected by the radiation (one-state systems). That is, one is led to equations for new MS amplitudes $\tilde{C}_n(t)$,

$$\tilde{C}_n(t) = \sum_m U_{nm}(t)C_m(t), \quad (4.3)$$

of the form

$$i\frac{d}{dt}\tilde{C}_n(t) = \sum_m \tilde{H}_{nm}(t)\tilde{C}_m(t), \quad (4.4)$$
where the matrix $\tilde{H} = U H U^\dagger$ is block diagonal

$$\tilde{H} = \begin{bmatrix}
H^{(1)} & 0 & 0 & \ldots \\
0 & H^{(2)} & 0 & \ldots \\
0 & 0 & H^{(3)} & \ldots \\
\ldots & \ldots & \ldots & \ldots & \ldots 
\end{bmatrix}.$$ \hspace{1cm} (4.5)

Though not shown explicitly, the elements of $U$ and $\tilde{H}$, like those of $H$ and $H^{(m)}$, may be time dependent. Here each $H^{(m)}$ is a one- or two-dimensional matrix. The two dimensional ones (there are $N_\prec$, of these) have the form

$$H^{(m)} = \begin{bmatrix}
\Delta_a & \frac{1}{2} \Omega^{(m)} \\
\frac{1}{2} \Omega^{(m)} & \Delta_b
\end{bmatrix},$$ \hspace{1cm} (4.6)

where $\Delta_a$ and $\Delta_b$ are the detunings of the original system. The remaining matrices $H^{(m)}$ are one-dimensional (there are $N_\succ - N_\prec$ of these). Their elements are detunings, either $\Delta_a$ if $N_a > N_b$, or $\Delta_b$ if $N_b > N_a$ . These one-dimensional Hamiltonians induce only time-dependent phase factors $e^{-i\Delta_a t}$ or $e^{-i\Delta_b t}$ in the evolution of the dark-state amplitudes.

The elements of the transformation matrix $U$ are obtainable from the transformation that diagonalize the product of interaction matrices $VV^\dagger$ by means of a transformation matrix $A$, which operates in the lower-states manifold (referred to as A space),

$$AVV^\dagger A^\dagger = \text{diag},$$ \hspace{1cm} (4.7)

and the similar transformation of $V^\dagger V$ within the excited states (B space) by means of a matrix $B$,

$$BV^\dagger VB^\dagger = \text{diag}.$$ \hspace{1cm} (4.8)

In each case the diagonal elements are squares of Rabi frequencies. Given the matrices $A$ and $B$, one constructs the desired transformation of the Hamiltonian as

$$U = G \begin{bmatrix}
A & 0 \\
0 & B
\end{bmatrix} G^{-1},$$ \hspace{1cm} (4.9)

where $G$ is a permutation matrix that reorders the states into pairs. The set of nonzero eigenvalues is identical for the A and B subspaces, but if these are of different dimensions ($N_a \neq N_b$) then the larger set will include also null eigenvalues.
associated with decoupled states, also known as multilevel dark states [9,10]. For example, in the five-state $M$ system of Fig. 4.1, the dimensions of the subspace $A$ is $N_a = 3 = N_\geq$, and the diagonalization (of basis states 1, 2, and 3) produces the results

$$\sqrt{AVV^\dagger A} = \frac{1}{2} \{ |\Omega^{(1)}|, |\Omega^{(2)}|, 0 \}.$$  (4.10)

In the $B$ subspace of dimension $N_b = 2 = N_\leq$, and involving basis states 4 and 5, the null eigenvalue is missing,

$$\sqrt{BV^\dagger VB} = \frac{1}{2} \{ |\Omega^{(1)}|, |\Omega^{(2)}| \}.$$  (4.11)

The phases of the eigenvalues (the Rabi frequencies $\Omega^{(m)}$) are obtained only with the evaluation of $\tilde{H} = UHU^\dagger$.

With appropriate reorganization of the MS states, $\tilde{C}_n^{(m)} \equiv \tilde{C}_{2m+n-2}$, one has the equation

$$i \frac{d}{dt} \begin{bmatrix} \tilde{C}_1^{(m)} \\ \tilde{C}_2^{(m)} \end{bmatrix} = \begin{bmatrix} \Delta_a & \frac{1}{2} \Omega^{(m)} \\ \frac{1}{2} \Omega^{(m)} & \Delta_b \end{bmatrix} \begin{bmatrix} \tilde{C}_1^{(m)} \\ \tilde{C}_2^{(m)} \end{bmatrix}.$$  (4.12)

The detunings in this last formula are unchanged from the original problem. The Rabi frequency $\Omega^{(m)}$ for the $m$th two-state system is obtained from square roots of the eigenvalues of the matrix $VV^\dagger$ or $V^\dagger V$, as explained above. Because, by assumption, all of the original Rabi frequencies share a common time dependence, the eigenvalue frequencies $\Omega^{(m)}$ share this same time dependence.

Although the original Rabi frequencies may have very simple symmetries, involving repetition of common values (they may be proportional to Clebsch-Gordon coefficients, for example), the eigenvalue Rabi frequencies $\Omega^{(m)}$ of the two-state systems are generally not degenerate: they are all different.

### 4.3 Applications to exactly soluble models

The Morris-Shore transformation is quite general (given the constraint of only two distinct detunings). It can be used, for example, with various “bent” linkages ($\Lambda, V, M, W$) [12], with various many-to-one connections ($\Lambda$, the tripod, . . . ) [13], as well as with complicated hyperfine interactions [14]. It can also be used with a
4.3. Applications to exactly soluble models

Figure 4.1: (Color online) Frame (a): the linkage pattern of the five-state $M$ system. The states with $M = -2, 0, 2$ ($\psi_{-2}$, $\psi_0$, and $\psi_2$) form the ground-state manifold, whereas the states with $M = -1, 1$ ($\psi_{-1}$ and $\psi_1$) form the excited-state manifold. The coupling pulse is elliptically polarized and the relative coupling strengths, i.e., the Clebsch-Gordon coefficients, are denoted by $\xi^{M}_{Ma}$. The pulse is detuned by $\Delta$ from exact resonance. Frame (b): the MS transformation casts this system into a set of two two-state systems and a decoupled state. The driven two-state systems have Rabi frequencies $\Omega^{(m)}$.

resonant $N$-state ladder of excitation: alternating states of the chain are placed into the $A$ and $B$ set.
Chapter 5

Stimulated Raman Adiabatic Passage in Three-State System

In this chapter we discuss Stimulated Raman adiabatic passage (STIRAP), which is a simple, robust, and efficient technique for complete population transfer (CPT) in three-state quantum systems [10]. In this technique, the population is transferred adiabatically in a Raman transition from an initially populated state $\psi_1$ via an intermediate state $\psi_2$ to a target state $\psi_3$ by two pulsed fields, pump and Stokes, whose frequencies are maintained on the two-photon resonance between states $\psi_1$ and $\psi_3$. If the pulses are ordered counterintuitively, the Stokes before the pump, then the dark state is associated with state $\psi_1$ initially and state $\psi_3$ in the end, thus providing an adiabatic route from $\psi_1$ to $\psi_3$. A unique and remarkable feature of STIRAP is that during the transfer the population remains trapped in a dark state, which is a time-dependent coherent superposition of states $\psi_1$ and $\psi_3$ only and does not involve the intermediate state $\psi_2$. State $\psi_2$ therefore remains unpopulated during the transfer, and its properties, including possible population decay, are largely irrelevant for STIRAP.

5.1 Basic three-state STIRAP: Theory

5.1.1 STIRAP

When the three-state linkage forms a lambda pattern (see Fig. 1.1b) one has a typical stimulated-Raman excitation scheme. The field acting on the initial state
ψ₁ is termed the *pump* field, and the interaction leading to the final (target) state ψ₃ is termed the *Stokes*.

It is intuitively evident that population transfer between states ψ₁ and ψ₃ can take place, as in SEP, when the pump pulse precedes the Stokes pulse. Simultaneous and steady pulses can also produce complete population transfer, if the pulse areas are carefully chosen. What may not be obvious at first is that even more satisfactory population transfer can be produced if the Stokes pulse occurs first – the pulses then arrive in a “counterintuitive” ordering. This is the basis for a process now called stimulated Raman adiabatic passage (STIRAP) [10, 16, 17].

The STIRAP technique uses the coherence of two pulsed laser fields to achieve a (nearly) complete population transfer from an initially populated state ψ₁ to a target state ψ₃ via an intermediate state ψ₂ (see Fig. 1.1b). If a two-photon resonance between ψ₁ and ψ₃ is maintained, if there is sufficient overlap of the two pulses and if the pulses are sufficiently strong that the time evolution is adiabatic, then (almost) complete population transfer occurs between states ψ₁ and ψ₃. Furthermore, there is almost no population in the (usually decaying) intermediate state ψ₂ at any time. The following sections offer explanations for this remarkable result.

**Basic equations and definitions**

The mathematical description of STIRAP derives from the Schrödinger equation (in units \(\hbar = 1\))

\[
\frac{d}{dt} C(t) = H(t) C(t),
\]

with \(C(t)\) a three component column vector. Initially the population resides entirely in state ψ₁, meaning \(C(-\infty) = [1, 0, 0]^T\). The objective is to transfer population into state ψ₃, meaning a final condition \(C(+\infty) = [0, 0, 1]^T\).

With the rotating wave approximation, the Hamiltonian \(H(t)\) for purely coherent excitation has the form

\[
H(t) = \begin{bmatrix}
0 & \frac{1}{2}\Omega_p(t) & 0 \\
\frac{1}{2}\Omega_p(t) & \Delta_p & \frac{1}{2}\Omega_s(t) \\
0 & \frac{1}{2}\Omega_s(t) & \Delta_p - \Delta_s
\end{bmatrix}.
\]

Here \(\Omega_p(t)\) and \(\Omega_s(t)\) are the (real-valued) Rabi frequencies of the pump and Stokes pulses, respectively,

\[
\Omega_p(t) = d_{12}\mathcal{E}_p(t), \quad \Omega_s(t) = d_{23}\mathcal{E}_s(t).
\]
The diagonal elements of this matrix involve the single-photon detunings of the pump and Stokes lasers from their respective transitions,

\[ \Delta_p = E_2 - E_1 - \omega_p, \quad \Delta_s = E_2 - E_3 - \omega_s. \]  

(5.3)

An essential condition for STIRAP is that there be two-photon resonance between states \( \psi_1 \) and \( \psi_3 \), meaning \( \Delta_p = \Delta_s \equiv \Delta \), or

\[ \Delta_p - \Delta_s = 0. \]  

(5.4)

The single-photon detuning \( \Delta \) has relatively little effect on STIRAP.

Although the definitions of Eq. (5.3) pertain to excitation in the absence of any incoherent processes, it is easy to include the possibility of loss from state \( \psi_2 \) at a rate \( \Gamma \) by making the replacement \( E_2 \to E_2 - \frac{i}{2} \Gamma \). In this way it is possible to model the effect of spontaneous emission out of state \( \psi_2 \) into states other than \( \psi_1 \) or \( \psi_2 \). As long as the excitation is adiabatic, the presence of a complex-valued detuning has no effect on the STIRAP process, because population never is found in state \( \psi_2 \). However, as the detuning and the loss rate increase, adiabaticity deteriorates, which eventually reduces the transfer efficiency.

In practice, a part of the spontaneous emission acts to re-populate states \( \psi_1 \) and \( \psi_2 \). Such effects cannot be treated within the Schrödinger equation; they require a density matrix treatment.

**Adiabatic states**

The population transfer mechanism in STIRAP is most easily understood in a Hilbert space whose coordinate basis vectors are instantaneous eigenstates of the time-varying Hamiltonian (i.e. a basis of adiabatic states, see Chapter 2 and Chapter 3). When the two-photon resonance condition (5.4) is fulfilled, the eigenvalues of \( H(t) \), which represent the energies of the adiabatic states, read

\[ \varepsilon_+(t) = \frac{1}{2} \left[ \Delta + \sqrt{\Delta^2 + \Omega^2(t)} \right] = \frac{1}{2} \Omega(t) \cot \varphi(t), \]  

(5.5a)

\[ \varepsilon_0(t) = 0, \]  

(5.5b)

\[ \varepsilon_-(t) = \frac{1}{2} \left[ \Delta - \sqrt{\Delta^2 + \Omega^2(t)} \right] = -\frac{1}{2} \Omega(t) \tan \varphi(t). \]  

(5.5c)

The presence of a null eigenvalue follows from the choice of energy zero point [and the phases \( \zeta_n(t) \)], which here reckons all energies as excitation from the initial state \( \psi_1 \).
The corresponding eigenstates $\Phi_+(t), \Phi_0(t),$ and $\Phi_-(t)$ of $H(t)$ are connected to the bare (diabatic) states $\psi_1, \psi_2$ and $\psi_3$ (which are the eigenstates of the unperturbed Hamiltonian) by the relations

$$\Phi_+(t) = \psi_1 \sin \vartheta(t) \sin \varphi(t) + \psi_2 \cos \varphi(t) + \psi_3 \cos \vartheta(t) \sin \varphi(t),$$  \hspace{1cm} (5.6a)

$$\Phi_0(t) = \psi_1 \cos \vartheta(t) - \psi_3 \sin \vartheta(t),$$ \hspace{1cm} (5.6b)

$$\Phi_-(t) = \psi_1 \sin \vartheta(t) \cos \varphi(t) - \psi_2 \sin \varphi(t) + \psi_3 \cos \vartheta(t) \cos \varphi(t),$$ \hspace{1cm} (5.6c)

where the time-dependent mixing angles $\vartheta(t)$ and $\varphi(t)$ are defined as:

$$\tan \vartheta(t) = \frac{\Omega_p(t)}{\Omega_s(t)}, \quad \tan 2\varphi(t) = \frac{\Omega(t)}{\Delta},$$ \hspace{1cm} (5.7)

with $\Omega(t)$ the rms field

$$\Omega(t) = \sqrt{\Omega_p^2(t) + \Omega_s^2(t)}. \hspace{1cm} (5.8)$$

The adiabatic state $\Phi_0(t)$ associated with the null eigenvalue has particular importance: it has no component of the excited state $\psi_2$. The latter state can undergo spontaneous emission back to state $\psi_1$, state $\psi_3$ (in the $\Lambda$-configuration), and in most cases it can also decay to other states. By avoiding the possibility of such loss, the state $\Phi_0(t)$ acts to trap population; it is known as a trapped state [18–22].

**Adiabatic basis**

We introduce the diabatic or adiabatic bases by writing one of the two expansions

$$\Psi(t) = \sum_n \psi_n C_n(t) \exp[-i\zeta_n(t)] = \sum_k \Phi_k(t) B_k(t) \exp[-i\chi_k(t)]. \hspace{1cm} (5.9)$$

According to Eqs. (5.6) the probability amplitudes of the adiabatic states $B(t) = [B_+(t), B_0(t), B_-(t)]^T$ are connected to the diabatic-state (or bare-state) amplitudes $C(t)$ by the orthogonal transformation

$$C(t) = R(t)B(t), \hspace{1cm} (5.10)$$

where the rotation matrix $R(t)$ is given by

$$R(t) = \begin{bmatrix} \sin \vartheta \sin \varphi & \cos \vartheta & \sin \vartheta \cos \varphi \\ \\
\cos \varphi & 0 & -\sin \varphi \\
\cos \vartheta \sin \varphi & -\sin \vartheta & \cos \vartheta \cos \varphi \end{bmatrix}. \hspace{1cm} (5.11)$$
The Schrödinger equation in the adiabatic representation is obtained from Eqs. (6.3), (5.10) and (8.4) and is given by

$$\frac{d}{dt} \mathbf{B}(t) = -iH_a(t)\mathbf{B}(t)$$  \hspace{1cm} (5.12)

with

$$H_a = \begin{bmatrix} \frac{1}{2}\Omega \cot \varphi & i\dot{\varphi} \sin \varphi & i\dot{\varphi} \\ -i\dot{\varphi} \sin \varphi & 0 & -i\dot{\varphi} \cos \varphi \\ -i\dot{\phi} & i\dot{\varphi} \cos \varphi & -\frac{1}{2}\Omega \tan \varphi \end{bmatrix}$$  \hspace{1cm} (5.13)

where an overdot means a time derivative.

The STIRAP mechanism

STIRAP is based on tying the state vector $\Psi(t)$ to the zero-eigenvalue adiabatic state $\Phi_0(t)$, which is a coherent superposition of the initial state $\psi_1$ and the final state $\psi_3$ only. For the counterintuitive pulse ordering the relations $\Omega_p(t)/\Omega_s(t) \rightarrow -\infty$ 0 and $\Omega_p(t)/\Omega_s(t) \rightarrow +\infty$ apply; hence as time progresses from $-\infty$ to $+\infty$, the mixing angle $\vartheta(t)$ rises from 0 to $\pi/2$. Consequently, the adiabatic state $\Phi_0(t)$ evolves from the bare state $\psi_1$ initially to a superposition of states $\psi_1$ and $\psi_3$ at intermediate times and finally to the target state $\psi_3$ at the end of the interaction; thus, state $\Phi_0(t)$ links adiabatically the initial state $\psi_1$ to the target state $\psi_3$. Since the Hamiltonian is explicitly time dependent, the derivative terms in Eq. (5.13) (the nonadiabatic couplings) are nonzero and consequently, diabatic transitions between the adiabatic states will occur. The goal is to reduce the diabatic transition rates to negligibly small values, i.e. to ensure adiabatic evolution. Then the system can be forced to stay in the trapped state at all times, a complete population transfer from $\psi_1$ to $\psi_3$ will be achieved, as shown in Fig. 5.1. Moreover, because the intermediate state $\psi_2$ does not participate in the trapped state $\Phi_0$, it does not participate in the population transfer either and remains unpopulated throughout the interaction. Hence, as long as the excitation is adiabatic, its properties, such as radiative decay, do not influence STIRAP. From another viewpoint, when the Stokes pulse is stronger (in the beginning) the population is predominantly in state $\psi_1$, and when the pump pulse is stronger (in the end) the population is predominantly in state $\psi_3$; thus the intermediate state is always weekly coupled to the more populated state, which provides another explanation why this state is bypassed by STIRAP during the transfer. An intuitive vector picture of the STIRAP process is shown in Fig. 5.2.
A five-stage description of STIRAP

The STIRAP process can be viewed as comprising five stages, each defined by the relative strengths of the two fields (Fig. 5.1). For each stage, coherence is essential.

- **Phase 1:** Only the Stokes pulse is present; its intensity increases steadily. The pump laser does not act yet, i.e. the population in state $\psi_1$ does not feel any coupling yet, the mixing angle remains zero, and the state vector remains parallel to state $\psi_1$. The Stokes pulse prepares for the lossless transfer process in the sense that it provides the Autler-Townes splitting of levels, needed in phase 2. This phase is therefore the *Stokes-induced Autler-Townes-phase*. Its purpose is to line up the state vector $\Psi$ with the state $\Phi_0$, i.e. $|\langle \Psi | \Phi_0 \rangle| = 1$.

- **Phase 2:** The Stokes pulse has (nearly) reached the maximum intensity, but the pump pulse is still weak. The state vector deviates only by a very small angle from state $\psi_1$. One might ask: why is the pump laser radiation not absorbed?
5.1. Basic three-state STIRAP: Theory

Figure 5.2: Vector picture of STIRAP. $\psi_1, \psi_2,$ and $\psi_3$ are bare atomic eigenstates or diabatic states. $\Phi_0, \Phi_+,$ and $\Phi_-$ are the adiabatic dressed states. The trapped state $\Phi_0$ is rotated from $\psi_1$ to $\psi_3$. Under adiabatic conditions, the state vector $\Psi$ follows the evolution of $\Phi_0$.

Here the Autler-Townes effect leads to a cancellation of the transition rate from the ground state to the two Autler-Townes levels. This is the same mechanism that leads to EIT. The effect of the Stokes-induced Autler-Townes splitting is very obvious here. This phase is therefore the *Stokes-induced-EIT-phase*.

- **Phase 3:** The Stokes pulse decreases and the pump pulse increases. Now the essential part of the population dynamics starts. The pump pulse couples state $\psi_1$ strongly to the other levels. The mixing angle increases and the state vector departs from the $\psi_1$ direction. State $\psi_2$ remains unpopulated. This phase is the *adiabatic passage (AP) phase*, with Stokes and pump acting on equal footing, because it is the ratio of these two Rabi frequencies which determines the dynamics.

- **Phase 4:** The population is now almost completely deposited into state $\psi_3$, but the Stokes pulse is still not zero. Why is there no loss due to optical pumping out of state $\psi_3$ by the Stokes field? The answer is that the pump field protects the population in state $\psi_3$ by inducing Autler-Townes splitting and interference (coupling of states $\psi_1$ and $\psi_2$). This is the *pump-induced-EIT-phase*. 

• *Phase 5:* The Stokes pulse intensity is zero and the pump-induced Autler-Townes splitting must be reduced to zero. This phase is the *pump-induced Autler-Townes phase.*

We emphasize that the phenomena of Autler-Townes splitting, EIT, and adiabatic passage all depend on the coherence of the radiation. Phase fluctuations would cause the state vector to “jiggle around”, thereby causing strong non-adiabatic coupling.
Chapter 6

Stimulated Raman adiabatic passage into continuum

In this chapter we propose a technique which produces nearly complete ionization of the population of a discrete state coupled to a continuum by a two-photon transition via a lossy intermediate state whose lifetime is much shorter than the interaction duration. We show that using counterintuitively ordered pulses, as in stimulated Raman adiabatic passage STIRAP (see chapter 5), wherein the pulse coupling the intermediate state to the continuum precedes and partly overlaps the pulse coupling the initial and intermediate states, greatly increases the ionization signal and strongly reduces the population loss due to spontaneous emission through the lossy state. For strong spontaneous emission from that state, however, the ionization is never complete because the dark state required for STIRAP does not exist. We demonstrate that this drawback can be eliminated almost completely by creating a laser-induced continuum structure LICS by embedding a third discrete state into the continuum with a third control laser. This LICS introduces some coherence into the continuum, which enables a STIRAP-like population transfer into the continuum. A highly accurate analytic description is developed and numerical results are presented for Gaussian pulse shapes.

6.1 STIRAP into continuum

We first consider TPI of an atom, initially in state $\psi_1$, coupled to the ionization continuum via state $\psi_2$, as illustrated in Fig. 6.1. The transition 1-2 is driven by a pump laser pulse with Rabi frequency $\Omega(t)$ and detuning $\Delta$, and state $\psi_2$ is connected to the continuum by a second laser pulse with a time-dependent rate $\Gamma_i(t)$. State $\psi_2$ can decay irreversibly via spontaneous emission (or other mechanisms) to other states with a constant rate $\Gamma$; we shall refer to the respective signal as the fluorescence signal,

$$F = \int_{-\infty}^{\infty} \Gamma P_2(t)dt.$$  \hfill (6.1)

The ionization signal is

$$I = 1 - P_1(\infty) - P_2(\infty) - F,$$  \hfill (6.2)

where $P_n(t)$ are the populations of the discrete states ($n = 1, 2$). Our objective is to set up the laser pulses such that the ionization signal $I$ is maximized, while the fluorescence signal $F$ is minimal.

We wish to design a recipe to maximize ionization when the loss rate $\Gamma$ is large compared to the interaction duration $T$. In other words, we wish to ionize the atom, without exciting it, despite being on resonance with state $\psi_2$. This objective reminds one of STIRAP. The significant difference here is that state $\psi_3$ is replaced by a continuum.

The equation that describes the dynamics of the system (in units $\hbar = 1$) is the Schrödinger equation,

$$i \frac{d}{dt} C(t) = H(t)C(t).$$  \hfill (6.3)

Here $C(t) = [C_1(t), C_2(t)]^T$ is the column-vector with the probability amplitudes $C_1(t)$ and $C_2(t)$ of states $\psi_1$ and $\psi_2$, and $H(t)$ is the Hamiltonian, obtained by adiabatic elimination of the continuum states and within the rotating-wave approximation (RWA) [24],

$$H(t) = \frac{1}{2} \begin{bmatrix} 0 & \Omega(t) \\ \Omega(t) & 2\Delta + 2S(t) - i\Gamma_1(t) - i\Gamma \end{bmatrix},$$  \hfill (6.4)

where $S = S_2 - S_1$ is the difference between the Stark shifts of states $\psi_1$ and $\psi_2$, produced by virtual excitation to other atomic states.
6.1. STIRAP into continuum

Figure 6.1: (Color online) TPI scheme. An initially populated discrete state $\psi_1$ is coupled to another discrete state $\psi_2$ by a resonant, or nearly resonant, pump laser field. State $\psi_2$ is coupled to the ionization continuum by a second, ionizing laser pulse. State $\psi_2$ can decay irreversibly to other states.

We are interested in situations when the ionization signal $I$ is large, i.e. in the non-perturbative regime. This implies large peak Rabi frequency $\Omega(t)$ and large ionization rate $\Gamma_i(t)$. Because we also assume that the loss rate $\Gamma$ is fixed and large, $\Gamma \gg 1/T$, state $\psi_2$ is subjected to strong population decay, due to both spontaneous emission and ionization. This implies that it receives very little transient population and can therefore be eliminated adiabatically. Hence we find after simple algebra

$$P_1(t) \approx \exp \left[ - \int_{-\infty}^{t'} \frac{\Omega(t')^2 [\Gamma_i(t') + \Gamma]}{[\Gamma_i(t') + \Gamma]^2 + 4 [\Delta + S(t')]^2} dt' \right], \quad (6.5a)$$

$$P_2(t) \approx \frac{\Omega(t)^2}{[\Gamma_i(t) + \Gamma]^2 + 4 [\Delta + S(t)]^2} P_1(t). \quad (6.5b)$$

Now we use these formulas to examine the possibilities of how to minimize fluorescence $F$, i.e. $P_2(t)$, and simultaneously maximize ionization $I$.

The first choice is to use a large detuning $\Delta$. Indeed, this will reduce the population of state $\psi_2$, because $P_2(t) \sim \Delta^{-2}$ for large $\Delta$ [see Eq. (6.5b)]; however, this decrease will be accompanied by an increase in the population of state $\psi_1$, see Eq. (6.5a). In result, the increase in the ionization will be little, if any. A similar con-
clusion applies to the Stark shift $S(t)$, which can be induced by the ionizing laser, or, if needed, by an additional far-off-resonance laser, as in SCRAP technique [31].

A straightforward alternative is to increase the magnitude of the ionizing pulse $\Gamma_i(t)$ alone. Then the population (6.5b) of state $\psi_2$ decreases as $\Gamma_i^{-2}$, as vs $\Delta$; however, the increase in the population (6.5a) of state $\psi_1$ is smaller vs $\Gamma_i$ than vs $\Delta$. In result, the ionization signal will increase more markedly when increasing $\Gamma_i$.

Figure 6.2: Contour plots of the ionization signal $I$ as a function of the delay of the ionizing pulse $\tau_i$ and the pump detuning $\Delta = 0$. The pulses have Gaussian shapes, Eqs. (7.10). The decay rate from state $\psi_2$ is $\Gamma = 100/T$, the peak ionization rate is $\Gamma_{i0} = 50/T$, the peak Rabi frequency is $\Omega_0 = 50/T$, and the Stark shift is $S = 0$.

A closer inspection of Eqs. (6.5) suggests that one can decrease $P_2(t)$, without increasing $P_1(t)$ (implying thence a net increase of the ionization $I$), by delaying the pump pulse $\Omega(t)$ with respect to the ionizing pulse $\Gamma_i(t)$. Indeed, it is obvious that the pump pulse $\Omega(t)$ must not arrive before the ionizing pulse $\Gamma(t)$, because then the fluorescence will deplete the population even before ionization has the chance to begin; mathematically, this implies large values for the fractions in Eqs. (6.5), with resulting small population of state $\psi_1$ and large fluorescence signal $F$. In contrast, if the pump pulse $\Omega(t)$ arrives simultaneously, or after the ionizing pulse $\Gamma_i(t)$, with some overlap, then fluorescence can only begin simultaneously with ionization. Moreover, if during the ionization the ratio $\Omega(t)/\Gamma_i(t)$ is very small, while the ratio $\Omega(t)^2/\Gamma_i(t)$ is moderately large compared to $1/T$, then both $P_1(t)$ and
$P_2(t)$ will remain small, as easily seen from Eqs. (6.5) when $\Delta = S = 0$. Therefore, our objective of producing ionization without excitation requires that during the population depletion we have

$$\Omega(t)^2 T \gtrsim [\Gamma_1(t) + \Gamma] \gg \Omega(t). \quad (6.6)$$

These conditions require large pulse areas over the interaction duration,

$$A_\Omega = \int_{-\infty}^{\infty} \Omega(t) dt \gg 1, \quad (6.7a)$$
$$A_{\Gamma_i} = \int_{-\infty}^{\infty} \Gamma_i(t) dt \gg 1. \quad (6.7b)$$

Conditions (6.6) suggest that the pump pulse Rabi frequency $\Omega(t)$ should be small in comparison with the ionizing rate $\Gamma_i(t)$. This can be naturally achieved, indeed, if the pump pulse is delayed to, but overlapped with, the ionizing pulse. Then ionization will occur during the rising edge of the pump pulse.

![Contour plots of the ionization signal $I$ as a function of the delay of the ionizing pulse $\tau_i$ and the peak ionization rate $\Gamma_0$. The pulses have Gaussian shapes, Eqs. (7.10). The pump detuning is $\Delta = 0$, the decay rate from state $\psi_2$ is $\Gamma = 100/T$, the peak Rabi frequency is $\Omega_0 = 50/T$, and the Stark shift is $S = 0$.](image)

These conclusions are illustrated in Figs. 6.2 and 6.3 where the ionization signal is plotted as a function of, respectively, the ionizing pulse delay and the pump pulse detuning $\Delta$, and the ionizing pulse delay and the ionizing pulse intensity. These
6.2. STIRAP into LICS

Figure 6.4: (Color online) The scheme for ionization by LICS-STIRAP, which extends the scheme in Fig. 6.1. The additional discrete state $\psi_c$ is embedded into the continuum by a control laser field, which creates a LICS in the continuum.

Figures clearly demonstrate that the counterintuitive pulse order – ionizing pulse before pump pulse – is favorable for ionization. Figure 6.2 demonstrates also that the detuning $\Delta$ is of little help in respect to ionization, as predicted by Eqs. (6.5a) and (6.5b).

As follows from the above analysis, counterintuitive pulse order increases ionization and suppresses excitation. However, very strong ionizing laser is needed to ensure the conditions (6.6). In the following section we shall show that a LICS in the continuum can help ionization and make this process very similar to STIRAP because of the creation of a quasi-dark state between state $\psi_1$ and the LICS, with ensuing nearly complete ionization with moderate laser resources.
6.2 STIRAP into LICS

6.2.1 The system

Let us assume now that, in addition to the scheme in Fig. 6.1, an additional laser pulse couples a third discrete state \( \psi_c \) with the continuum, as shown in Fig. 6.4. The dynamics of the system is again described by Eq. (6.3), with \( \mathbf{C}(t) = [C_1(t), C_2(t), C_c(t)]^T \). The Hamiltonian after adiabatic elimination of the continuum states and within the RWA reads

\[
H = \frac{1}{2} \begin{pmatrix}
0 & \Omega & 0 \\
\Omega & 2\Delta + 2S_2 - i\Gamma_i - i\Gamma_c - (q + i)\sqrt{\Gamma_i\Gamma_c} & 0 \\
0 & -(q + i)\sqrt{\Gamma_i\Gamma_c} & 2\delta + 2S_3 - i\Gamma_c
\end{pmatrix},
\]

(6.8)

where explicit time dependences are omitted for brevity.

The constant \( q \), called the Fano parameter [32], is an important feature of LICS. It is responsible for the asymmetric dependence of the ionization signal on the two-photon detuning in LICS [24], and it plays an important role in the context of population transfer via continuum too [23]. The quantities \( \Gamma_2 = \sum_{\alpha} \Gamma_{2\alpha}^\alpha \) and \( \Gamma_c = \sum_{\alpha} \Gamma_{c\alpha}^\alpha \) (\( \alpha = p, i, c \)) are the total ionization rates of states \( \psi_2 \) and \( \psi_c \), respectively, which are given by sums of ionization rates induced by the pump (p), ionization (i) and control (c) pulses, whereas \( S_2 = \sum_{\alpha} S_{2\alpha}^\alpha \) and \( S_c = \sum_{\alpha} S_{c\alpha}^\alpha \) are the corresponding dynamic Stark shifts of states \( \psi_2 \) and \( \psi_c \). The ionization widths and the Stark shifts are proportional to the pulse intensities \( I_p(t), I_i(t) \) and \( I_c(t) \), \( \Gamma_{n0}\alpha(t) = \Gamma_{n0}\alpha I_{\alpha}(t) \), \( S_{n\alpha}(t) = S_{n\alpha0}\alpha I_{\alpha}(t) \), where the parameters \( \Gamma_{n0}\alpha \) and \( S_{n\alpha0}\alpha \) depend on the particular atomic states and the laser frequencies.

For simplicity, we will assume that the ionization of state \( \psi_2 \) occurs due to the action of the ionizing laser \( I_i \) only: \( \Gamma_2 = \Gamma_{2i}^2 \); this condition can be satisfied by selecting appropriate atomic levels and laser frequencies such that the pump and control lasers do not cause direct ionization from state \( \psi_2 \). We will also assume that the ionization rate of state \( \psi_c \) is induced by the control laser \( I_c \) only: \( \Gamma_c = \Gamma_{ci}^c \). Given the preceding assumption for \( \Gamma_2 \) it is clear that the ionizing laser \( I_i \) will ionize also state \( \psi_c \) (\( \Gamma_{ci}^c \neq 0 \)). However, because from state \( \psi_c \) the ionizing laser points deeply into the continuum this ionization rate is small; moreover, as state \( \psi_c \) remains largely unpopulated, this ionization channel (which is actually favorable for our goal of maximizing ionization) does not alter the dynamics markedly.
6.2. STIRAP into LICS

In addition, we also neglect the Stark shifts, \( S_2 = S_3 = 0 \); these are important in population transfer via continuum [23], but do not have much effect here.

The signal due to the irreversible losses from state \( \psi_2 \) is given by Eq. (6.1), and the ionization signal by

\[
I = 1 - P_1(\infty) - P_2(\infty) - P_c(\infty) - F. \tag{6.9}
\]

The optimal pulse order of the three pulsed fields is determined by the objective to maximize ionization. We have already come to the conclusion that the pump and ionizing pulses must arrive in a counterintuitive order: ionizing pulse before pump. The optimal timing of the control pulse, which creates LICS and enables STIRAP-like population transfer into the continuum, can be deduced from the following arguments.

Because the objective is ionization, we must avoid population transfer via the continuum into state \( \psi_c \), which will occur if the control pulse precedes the ionizing pulse [23]; the control should therefore be applied after the ionizing pulse. The timing of the control pulse with respect to the pump pulse is not so significant but these pulses should not be separated too much because it is obvious that, for LICS to have any effect, the control pulse must overlap significantly with the pump and ionizing pulses. We therefore conclude that for maximal ionization, the pulses should be applied in the order \textit{ionizing-control-pump}, with a sufficient overlap between them. We shall therefore assume this pulse ordering in the analytical description in the next section, which will be confirmed as optimal also by numerical simulations in Sec. 6.3.

6.2.2 Analytical description

Our analysis is based on the assumption that the population dynamics takes place mainly during the time interval when \( \Omega \ll \sqrt{\Gamma_i \Gamma_c} \), i.e. during the rising edge of the pump pulse (which is the last to arrive). This assumption derives from our interest in the regime of large ionization, which requires strong laser fields and considerable population depletion of the bound states.

It is appropriate to describe the evolution of the system in the basis of the instantaneous eigenstates of the Hamiltonian (6.8). Because this Hamiltonian is non-Hermitian its eigenvalues \( \varepsilon_\alpha(t) \) are complex valued, and the right eigenvectors \( \varphi_\alpha(t) \)
differ from Hermitian conjugates of the left eigenvectors \([33]\). The right eigenvectors, and the eigenvalues, are defined by the equations \((\alpha = +, 0, -)\)

\[ H(t)\varphi_\alpha(t) = \varepsilon_\alpha(t)\varphi_\alpha(t), \quad (6.10) \]

where \(\varphi_\alpha(t) = [f_{1\alpha}(t), f_{2\alpha}(t), f_{3\alpha}(t)]^T\) is a column vector.

Using such states we expand the state vector as

\[ \Psi(t) = b_+(t)\varphi_+(t) + b_0(t)\varphi_0(t) + b_-(t)\varphi_-(t). \quad (6.11) \]

The probability amplitudes in the original diabatic basis and the adiabatic basis are related through the transformation

\[ c(t) = R(t)b(t), \quad (6.12) \]

where the column vector \(b(t) = [b_+(t), b_0(t), b_-(t)]^T\) comprises the probability amplitudes of the adiabatic states. The columns of \(R\) are the components of \(\varphi_\alpha(t)\), \((R(t))_{n\alpha} = f_{n\alpha}(t)\) with \(n = 1, 2, 3\) and \(\alpha = +, 0, -\).

The Schrödinger equation for the vector \(b\) reads

\[ i\frac{d}{dt}b(t) = H^{ad}(t)b(t), \quad (6.13) \]

where \(H^{ad}(t) = H^a(t) + H^{na}(t)\), with an adiabatic diagonal Hamiltonian

\[ H^a(t) = R^{-1}(t)H(t)R(t) = \begin{bmatrix} \varepsilon_+(t) & 0 & 0 \\ 0 & \varepsilon_0(t) & 0 \\ 0 & 0 & \varepsilon_-(t) \end{bmatrix}, \quad (6.14) \]

and a nonadiabatic coupling

\[ H^{na}(t) = -iR^{-1}(t)\frac{d}{dt}R(t). \quad (6.15) \]

If the time evolution is slow we can neglect the nonadiabatic coupling (9.15); then Eq. (6.13) is easily solved,

\[ b_\alpha(t) = b_\alpha(-\infty)\exp\left[-i\int_{-\infty}^{t} \varepsilon_\alpha(t')dt'\right] \quad (\alpha = +, 0, -). \quad (6.16) \]

Our major approximation is based on the assumption that the population dynamics takes place mainly during time interval when \(\Omega \ll \sqrt{\Gamma_i\Gamma_c}\). In this case we
can approximate the eigenvalues and the eigenvectors by assuming that \( \Omega \) is a small parameter \cite{33}. After simple algebra we obtain

\[
\varepsilon_+ = \frac{1}{2} \left[ \tilde{\Delta} + \tilde{\delta} + \eta \right] + \frac{\Omega^2 \eta + \tilde{\Delta} - \tilde{\delta}}{4 \eta \eta + \tilde{\Delta} + \tilde{\delta}}, \tag{6.17a}
\]

\[
\varepsilon_0 = \frac{\Omega^2 \eta}{\tilde{\Gamma}^2 - 4 \Delta \delta}, \tag{6.17b}
\]

\[
\varepsilon_- = \frac{1}{2} \left[ \tilde{\Delta} + \tilde{\delta} - \eta \right] - \frac{\Omega^2 \eta - \tilde{\Delta} + \tilde{\delta}}{4 \eta \eta - \tilde{\Delta} - \tilde{\delta}}, \tag{6.17c}
\]

where

\[
\tilde{\Delta} = \Delta - \frac{i \Gamma_i + \Gamma}{2}, \tag{6.18a}
\]

\[
\tilde{\delta} = \delta - \frac{i \Gamma_c}{2}, \tag{6.18b}
\]

\[
\tilde{\Gamma} = -(q + i) \sqrt{\Gamma_i \Gamma_c}, \tag{6.18c}
\]

\[
\eta = \sqrt{\left[ \Delta - \delta - \frac{i (\Gamma_i + \Gamma - \Gamma_c)}{2} \right]^2 + (q + i)^2 \Gamma_i \Gamma_c}. \tag{6.18d}
\]

The corresponding eigenvectors are

\[
\varphi_+(t) = \left[ \frac{\Omega \eta + \tilde{\Delta} - \tilde{\delta}}{\Gamma \eta + \Delta + \delta} \sin \xi, \cos \xi, \sin \xi \right]^T, \tag{6.19a}
\]

\[
\varphi_0(t) = \left[ 1 - \frac{\Omega^2 (\tilde{\Gamma}^2 + 4 \tilde{\delta}^2)}{2 (\tilde{\Gamma}^2 - 4 \Delta \delta)^2} - \frac{2 \tilde{\delta} \Omega}{\tilde{\Gamma}^2 - 4 \Delta \delta} - \frac{\Omega \tilde{\Gamma}}{\tilde{\Gamma}^2 - 4 \Delta \delta} \right]^T, \tag{6.19b}
\]

\[
\varphi_-(t) = \left[ \frac{\Omega \eta - \tilde{\Delta} + \tilde{\delta}}{\tilde{\Gamma} \eta - \Delta - \delta} \cos \xi, -\sin \xi, \cos \xi \right]^T, \tag{6.19c}
\]

where the complex-valued angle \( \xi \) is defined as

\[
\tan 2 \xi = \frac{\tilde{\Gamma}}{\Delta - \delta}. \tag{6.20}
\]

Because the pulses are applied in the sequence ionizing-control-pump and the population is initially in state \( \psi_1 \), the initial adiabatic-state amplitudes are \( b_0(-\infty) = 1, b_\pm(-\infty) = 0 \). In the adiabatic limit the population \( P_0(t) = |b_0(t)|^2 \) of state \( \varphi_0(t) \) evolves as

\[
P_0(t) = \exp \left[ -i \tilde{\delta}(t) \int_{-\infty}^{t} \frac{\Omega^2(t')}{\tilde{\Gamma}^2(t') - 4 \tilde{\Delta}(t') \tilde{\delta}(t')} dt' \right]^2. \tag{6.21}
\]
The populations of the original states are

\[
P_1(t) = \left| 1 - \frac{\Omega^2(t)\Gamma^2(t) + 4\delta^2(t)}{2\Gamma^2(t) - 4\Delta(t)\delta(t)} \right|^2 P_0(t),
\]

(6.22a)

\[
P_2(t) = \left| \frac{2\Omega(t)\delta(t)}{\Gamma^2(t) - 4\Delta(t)\delta(t)} \right|^2 P_0(t),
\]

(6.22b)

\[
P_c(t) = \left| \frac{\Omega(t)\Gamma(t)}{\Gamma^2(t) - 4\Delta(t)\delta(t)} \right|^2 P_0(t).
\]

(6.22c)

The fluorescence signal is calculated from Eq. (6.1) and (6.22b), and then the ionization signal from Eq. (6.9).

In the following section we will use these formulas to examine how to minimize the fluorescence \( F \), i.e. \( P_2(t) \), and simultaneously to maximize the ionization \( I \).

### 6.3 Numerical Examples

We compare the analytical results derived in the preceding section with numerical simulations for the fluorescence signal of Eq. (6.1), the ionization signal of Eq. (6.9), and the populations of states \( \psi_1, \psi_2 \) and \( \psi_c \), derived from numerical integration of Eq. (6.3), with the Hamiltonian (6.8). We assume Gaussian pulse shapes,

\[
\Omega(t) = \Omega_0 e^{-\frac{(t-\tau)^2}{T^2}},
\]

(6.23a)

\[
\Gamma_i(t) = \Gamma_{i0} e^{-\frac{(t-\tau_i)^2}{T_i^2}},
\]

(6.23b)

\[
\Gamma_c(t) = \Gamma_{c0} e^{-\frac{(t-\tau_c)^2}{T_c^2}}.
\]

(6.23c)

We use the pump pulse duration \( T \) as a time unit and \( 1/T \) as a frequency unit, and choose the center of the pump pulse to define the zero reference point of time, \( \tau = 0 \). All remaining parameters are variable: the peak pump Rabi frequency \( \Omega_0 \), the peak ionization rates \( \Gamma_{i0} \) and \( \Gamma_{c0} \), the centers of the ionizing and control pulses \( \tau_i \) and \( \tau_c \), their widths \( T_i \) and \( T_c \), the detunings \( \Delta \) and \( \delta \). The Stark shifts are assumed zero because, as we have verified, they do not affect significantly the ionization signal. For the Fano parameter we have chosen three values: \( q = 1 \), \( q = 3 \), \( q = 6 \), which are close to the experimental values for LICS in sodium \( (q = 3.7) \) [34], helium \( (q = 0.73) \) [36], and hydrogen atoms \( (q = -5.9) \) [35], for electric-field mixing in rubidium \( (q = 3.3) \) [37], and for configuration mixing in potassium \( (q = 1) \) [38], in rubidium \( (q = 0.1 - 0.3) \) [39], and in cesium \( (q \approx 0.43) \) [39].
Figure 6.5: Contour plots of the ionization signal as a function of the control pulse center $\tau_c$ and the control ionization rate $\Gamma_{c0}$. The $\psi_2$ loss rate is $\Gamma = 1/T$ (top frames), $\Gamma = 10/T$ (middle frames), or $\Gamma = 100/T$ (bottom frames). The Fano parameter is $q = 1$ (left frames), $q = 3$ (middle frames), or $q = 6$ (right frames). The other parameters are $T_i = T_c = T$, $\Gamma_i = 50/T$, $\Omega_0 = 50/T$, $\tau_i = -T$, $\delta = 10/T$, $\Delta = 0$. The number $I_{\max}$ atop each frame indicates the respective maximal ionization signal. Without the control field $I_{\max}$ is 0.978, 0.822, and 0.317 for $\Gamma = 1$, 10, and 100, respectively.

Figure 6.5 shows contour plots of the ionization signal as a function of the center of the control pulse $\tau_c$ and the peak control ionization rate $\Gamma_{c0}$ for different values of the Fano parameter $q$ and the irreversible loss rate $\Gamma$ from state $\psi_2$. Larger Fano parameters are clearly favourable for ionization but improvement is seen for $q = 1$ too. In principle a lower Fano parameter could be compensated by stronger ionizing and control fields. For $\Gamma_{c0} = 0$ (near the horizontal axis in each frame), the plain STIRAP into continuum, discussed in Sec. 6.1, occurs. The bottom frames
Figure 6.6: Contour plots of the ionization signal as a function of the control laser detuning $\delta$ and the peak control ionization rate $\Gamma_{c0}$. The $\psi_2$ loss rate is $\Gamma = 1/T$ (top frames), $\Gamma = 10/T$ (middle frames), or $\Gamma = 100/T$ (bottom frames). The Fano parameter is $q = 1$ (left frames), $q = 3$ (middle frames), or $q = 6$ (right frames). The other parameters are $T_i = T_c = T$, $\Gamma_{i0} = 50/T$, $\Omega_0 = 50/T$, $\tau_i = -T$, $\tau_c = -0.5T$, $\Delta = 0$. The number $I_{\text{max}}$ atop each frame indicates the respective maximal ionization signal. Without the control field $I_{\text{max}}$ is 0.978, 0.822, and 0.317 for $\Gamma = 1$, 10, and 100, respectively.

Determine that for strong loss ($\Gamma T \gg 1$) the LICS-STIRAP improves ionization dramatically, for example, from 0.317 without the control field to 0.875 with it. We have verified that for larger laser intensities, a nearly complete ionization can be achieved.

Figure 6.6 shows contour plots of the ionization signal as a function of the control laser detuning $\delta$ and the control peak ionization rate $\Gamma_{c0}$. Again, the presence of the control laser pulse, and the ensuing LICS, are essential in achieving high ionization
signal, even for strong loss rate form state $\psi_2$. The asymmetry of the ionization signal vs the detuning is typical for the Fano LICS profile.

![Graph showing ionization and fluorescence signals vs the center $\tau_i$ of the ionizing laser pulse.](image)

Figure 6.7: (Color online) Ionization $I$ and florescence $F$ signals vs the center $\tau_i$ of the ionizing laser pulse. The $\psi_2$ loss rate is $\Gamma = 10/T$ (top frames) or $\Gamma = 100/T$ (bottom frames). The pulse widths are $T_i = T_c = T$ (left frames) or $T_i = T_c = 3T$ (right frames). Other parameters are $q = 3$, $\Gamma_{i0} = \Gamma_{c0} = 50/T$, $\Omega_0 = 50/T$, $\tau_c = -0.5T$, $\Delta = \delta = 10/T$. The solid curves show the analytical approximation, Eqs. (6.1), (6.9), and (6.22), the dots show the numerical results.

In Fig. 6.7, we display the fluorescence and ionization signals vs the timing of the ionizing pulse, for different values of the irreversible loss rate $\Gamma$ and different widths of the control and ionizing pulses. The figure demonstrates that efficient ionization requires a counterintuitive pulse ordering, with the ionizing laser applied before the pump laser ($\tau_i < 0$, with optimum about $\tau_i = -T$). It also shows that an increase of the pulse widths (right frames) leads to broadening of the ionization profile but does not affect appreciably the maximal ionization signal. The figure evidences an excellent agreement between the analytical theory and the numerical simulations. This agreement indicates that indeed, the ionization dynamics occurs during the rising edge of the pump pulse, when the ionizing and control pulses are already present. The manner in which the pulses terminate is not important, as evident
when comparing the left frames (where the pump pulse starts and terminates later) and the right frames (where the pump pulse starts later but terminates earlier because its width is shorter than the others). This is one of the main differences between conventional STIRAP between discrete levels [10] and LICS-STIRAP proposed here. In conventional STIRAP both the initial and final times of the pulses are important (the pump must start and terminate last). In LICS-STIRAP the initial times are important, but the final times are not, because there is no population left in the discrete states.

Figure 6.8: (Color online) The ionization and fluorescence signals vs the center $\tau_c$ of the control laser pulse. The loss rate from state $\psi_2$ is $\Gamma = 100/T$ and the pulse widths are $T_i = T_c = T$. The other parameters are $q = 3$, $\Gamma_{i0} = \Gamma_{c0} = 50/T$, $\Omega_0 = 50/T$, $\tau_i = -T$, $\Delta = \delta = 10/T$. The solid curves show the analytical results: Eqs. (6.1), (6.9), and (6.22). The dots indicate the numerical results.

Figure 6.8 shows the fluorescence and ionization signals vs the timing of the control pulse. The figure demonstrates that the best timing between the ionizing and pump pulses is at $\tau_c \sim \tau_i/2$, as used in other figures. However, the technique is relatively robust against the control timing and moderate deviations from this prescription do not affect the ionization efficiency very much. The background signal appearing for large deviations of $\tau_c$ from this region is produced by c-STIRAP. It serves as a reference for the influence of LICS on STIRAP, significant in this case, once again. This figure reveals another excellent agreement between analytical
6.3. Numerical Examples

theory and numerical simulations.

Figure 6.9: (Color online) Ionization signal vs the $\psi_2$ irreversible loss rate $\Gamma$ for three different techniques. TPI: coincident pulses ($\tau_i = \tau = 0$), no control pulse ($\Gamma_{c0} = 0$); c-STIRAP: counterintuitively delayed pulses ($\tau_i = -T$, $\tau = 0$), no control pulse ($\Gamma_{c0} = 0$); LICS-STIRAP: counterintuitively delayed pulses ($\tau_i = -T$, $\tau = 0$), with control pulse ($\Gamma_{c0} = 50/T$, $\tau_c = -0.5T$). The other parameters are $T_i = T_c = T$, $q = 3$, $\Gamma_{i0} = 50/T$, $\Omega_0 = 50/T$, $\Delta = \delta = 10/T$. The solid curves show the analytical results, Eqs. (6.1), (6.9), and (6.22). The dots display numerical results.

Figure 6.9 shows the ionization signal as a function of the irreversible loss rate $\Gamma$ from state $\psi_2$. The three curves show how the ionization efficiency decreases with $\Gamma$ for TPI, c-STIRAP (no control laser and LICS), and LICS-STIRAP. The c-STIRAP efficiency is clearly superior to TPI, and LICS-STIRAP adds further considerable improvement over c-STIRAP. Note the horizontal logarithmic scale in $\Gamma$. Remarkably, LICS-STIRAP maintains high ionization efficiency even when the intermediate state $\psi_2$ can decay hundreds of times during the interaction. Again, the figure reveals an excellent agreement between the analytical theory and the numerical simulations.

Figure 6.10 shows the ionization signal vs the Fano parameter $q$ and the peak control ionization rate. For moderate values of $q$ ($1 \lesssim q \lesssim 10$) nearly complete ionization is achieved for sufficiently strong control pulses. When $q$ is too small LICS is not sufficiently strong to simulate the presence of a bound state and to create a quasi-dark state. When $q$ is too large, a very large atomic coherence is created.
Figure 6.10: Contour plot of the ionization signal as a function of the Fano parameter $q$ and the peak control ionization rate $\Gamma_{c0}$. The other parameters are $T_i = T_c = T$, $\Gamma_{i0} = 50/T$, $\Omega_0 = 50/T$, $\Gamma = 100/T$, $\tau_i = -T$, $\tau_c = -0.5T$, $\delta = 10/T$, $\Delta = 0$.

through the continuum, so that state $\psi_c$ is directly involved in the dynamics, with some atomic population transfered to this state.
Chapter 7

Stark-shift-chirped
rapid-adiabatic-passage technique
among three states

In this chapter we show that the technique of Stark-chirped rapid adiabatic passage (SCRAP), hitherto used for complete population transfer between two quantum states (see chapter 3), offers a simple and robust method for complete population transfer amongst three states in atoms and molecules. In this case SCRAP uses three laser pulses: a strong far-off-resonant pulse modifies the transition frequencies by inducing dynamic Stark shifts and thereby creating time-dependent level crossings amongst the three diabatic states, while near-resonant and moderately strong pump and Stokes pulses, appropriately offset in time, drive the population between the initial and final states via adiabatic passage. The population transfer efficiency is robust to variations in the intensities of the lasers, as long as these intensities are sufficiently large to enforce adiabatic evolution. With suitable pulse timings the population in the possibly decaying intermediate state can be minimized, as with stimulated Raman adiabatic passage (STIRAP) (see chapter 7). This technique applies to one-photon as well as multiphoton transitions and it is also applicable to media exhibiting inhomogeneous broadening; these features represent clear advantages over STIRAP by overcoming the inevitable dynamical Stark shifts that accompany multiphoton transitions as well as unwanted detunings, e.g., induced by Doppler shifts.

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7.1 Three-state SCRAP

7.1.1 Sequential double-SCRAP

The most obvious extension of SCRAP to three states is by two consecutive SCRAPs: first from state 1 to state 2 and then from state 2 to state 3. Such a procedure corresponds to the sequence of transitions,

\[ \Psi(-\infty) = \psi_1 \xrightarrow{\text{SCRAP}_1} \psi_2 \xrightarrow{\text{SCRAP}_2} \psi_3 = \Psi(\infty). \]  

(7.1)

The disadvantage of this scenario is that state 2 receives the entire population between the two steps. Hence to avoid appreciable population loss by spontaneous emission from state 2, both SCRAP processes must be completed in a time shorter than the lifetime of state 2.

We will show in the following section that alternative pulse sequences, resulting in a genuine three-state SCRAP process, do not suffer from this limitation. In this process all three states are coupled during the population transfer, which offers considerably more flexibility than two sequential SCRAP processes. As with elementary two-state SCRAP, we need a diabatic-adiabatic evolution scenario for population transfer.

7.1.2 The three-state Hamiltonian

The RWA Hamiltonian of the laser-excited three-state system is expressible as

\[ H(t) = \hbar \begin{bmatrix} 0 & \frac{1}{2} \Omega_p(t) & 0 \\ \frac{1}{2} \Omega_p(t) & \Delta_2 + S_{21}(t) - \frac{1}{2} i \Gamma & \frac{1}{2} \Omega_s(t) \\ 0 & \frac{1}{2} \Omega_s(t) & \Delta_3 + S_{31}(t) \end{bmatrix}, \]  

(7.2)

where \( \Omega_p(t) \) and \( \Omega_s(t) \) are Rabi frequencies associated with the pump and Stokes fields, respectively. The imaginary term \(-\frac{1}{2} i \Gamma\) in the Hamiltonian (7.2) describes possible population loss from state 2 out of the system (due to spontaneous emission, ionization, etc.) at a rate \( \Gamma \).
The constants $\Delta_2$ and $\Delta_3$ represent the static detunings, which for one-photon transitions are given by

$$\hbar \Delta_2 = E_2 - E_1 - \hbar \omega_p,$$

$$\hbar \Delta_3 = E_3 - E_1 - \hbar \omega_p + \hbar \omega_s.$$  

The detuning shifts

$$S_{mn}(t) = S_m(t) - S_n(t),$$

are the differences between the Stark shifts $S_m(t)$ and $S_n(t)$ of states $m$ and $n$ $(m, n = 1, 2, 3)$. Usually, the Stark shifts of the excited states are much greater than those of the ground and metastable states; hence we assume that

$$|S_2(t)| \gg |S_1(t)|, |S_3(t)|.$$  

For simplicity, we neglect at the moment the Stark shifts of states 1 and 3; hence $S_{21}(t) \approx S_2(t)$ and $S_{31}(t) \approx 0$. We shall discuss the effect of the Stark shifts $S_1(t)$ and $S_3(t)$ in Sec. 7.3.

Underlying this assertion is the expectation that there are no near resonances of single-photon transitions that contribute to the Stark shifts. Should such resonances be present, as they have been in some instances [10], the shifts can become significant, but this is not the general case. Usually it is possible to have strong interaction on one-photon transitions without strong Stark shifts (as the latter are effects of higher order in the laser electric field).

Without loss of generality we shall assume that the Stark shift $S_2(t)$ is negative,

$$S_2(t) = -S(t) < 0.$$  

Hence the Hamiltonian (7.2) reads

$$H(t) = \hbar \begin{bmatrix}
0 & \frac{1}{2} \Omega_p(t) & 0 \\
\frac{1}{2} \Omega_p(t) & \Delta_2 + S_2(t) - \frac{1}{2} i \Gamma & \frac{1}{2} \Omega_s(t) \\
0 & \frac{1}{2} \Omega_s(t) & \Delta_3
\end{bmatrix}.$$  

The eigenvalues $\hbar \varepsilon_n(t)$ of the Hamiltonian (8.9) are roots of a cubic equation and are too cumbersome to be presented here. The corresponding eigenstates (for $k = 1, 2, 3$) can be written as

$$\Phi_k(t) = \frac{1}{N_k(t)} \begin{bmatrix}
[\varepsilon_k(t) - \Delta_3] \Omega_p(t) \\
2 \varepsilon_k(t) [\varepsilon_k(t) - \Delta_3] \\
\varepsilon_k(t) \Omega_s(t)
\end{bmatrix}.$$  

(7.9)
where $N_k(t)$ is a normalization factor. For specific results in simulations we shall assume Gaussian shapes for all pulses, and will take the pump and Stokes Rabi frequencies to have identical peak values $\Omega_0$,

$$\Omega_p(t) = \Omega_0 e^{-(t-\tau_p)^2/T_p^2}, \quad \Omega_s(t) = \Omega_0 e^{-(t-\tau_s)^2/T_s^2}, \quad S(t) = S_0 e^{-t^2/T^2}. \quad (7.10a)$$

The center of the Stark pulse defines the time $t = 0$. Relative to this, the pump and Stokes pulses peak at times $\tau_p$ and $\tau_s$, respectively. In our numerical simulations we take the pump and Stokes durations equal, $T_p = T_s$, and use $T_p$ as the unit of time and $1/T_p$ as the unit of frequency. We assume that the Stark pulse has twice this duration, $T = 2T_p$, following an earlier conclusion for simple SCRAP that the Stark pulse should be longer than the driving pulse [42,53,54].

Our analysis will follow three steps: first, we shall identify the conditions for the appearance of level crossings; second, we shall identify the timings of the pulses so that an adiabatic path linking states 1 and 3 is created; third, we shall find the conditions under which the unwanted population of the intermediate state 2 is minimized.

### 7.1.3 Eigenenergies and conditions for diabatic level crossings

The first crucial condition for designing an adiabatic path between states 1 and 3 is to create a set of level crossings of the diabatic energies of the three states. Because we neglect their Stark shifts the energies of states 1 and 3 are constant, cf. Eq. (8.9). These states can be linked adiabatically only if the varying energy of state 2, forced by the Stark shift $S_2(t)$, crosses both the energies of 1 and 3. For such level crossings to occur, as can be seen from Eq. (8.9) and condition (7.7), we must have

$$S_0 > \Delta_2 > 0, \quad (7.11a)$$

$$S_0 > \Delta_2 - \Delta_3 > 0. \quad (7.11b)$$

Condition (7.11a) ensures that the diabatic energies of states 1 and 2 cross, whereas condition (7.11b) ensures the crossing of the energies of states 2 and 3. If these
conditions are satisfied, then there are four level crossings. For Gaussian pulses (7.10) the energies of states 1 and 2 cross at times $t_{12}^\pm = \pm t_{12}$, and those of states 2 and 3 cross at times $t_{23}^\pm = \pm t_{23}$, with

\begin{align}
  t_{12} &= T \sqrt{\ln(S_0/\Delta_2)}, \quad (7.12a) \\
  t_{23} &= T \sqrt{\ln[S_0/(\Delta_2 - \Delta_3)]}. \quad (7.12b)
\end{align}

We can therefore move the crossing points along the time axis by varying the laser carrier frequencies (entering through $\Delta_2$ and $\Delta_3$) and the peak Stark shift $S_0$.

It follows from Eqs. (7.12) that $t_{12} > t_{23}$ for

\begin{equation}
  0 > \Delta_3 > \Delta_2 - S_0, \quad (7.13a)
\end{equation}

and $t_{23} > t_{12}$ for

\begin{equation}
  \Delta_2 > \Delta_3 > 0. \quad (7.13b)
\end{equation}

We shall see below that these two cases (7.13a) and (7.13b) lead to significant differences.

### 7.1.4 Pulse timings and connectivity between states 1 and 3

We assume that conditions (7.11) are satisfied, i.e the energy of state 2 crosses the (parallel) energies of states 1 and 3. Given these crossings, the connectivity between states 1 and 3 depends upon the timings of the pump, Stokes and Stark pulses. It is obvious that these three pulses cannot have the same time dependence because then symmetry will prevent complete adiabatic passage, as for two-state SCRAP [53,54]. Hence there must be some delays between the three pulses; however, the optimal choice of these delays is not immediately obvious. We consider three timings of the pump and Stokes pulses.

**Intuitively ordered pump and Stokes pulses (pump-Stark-Stokes)**

Figure 7.1 displays the time evolutions of the three pulse envelopes and the adiabatic eigenergies for situations wherein the pump and Stokes pulses are well separated from each other but they each overlap a longer Stark pulse. Reading the figures from left to right we follow a description of intuitive pulse ordering (i.e. pump
Figure 7.1: (color online) Time evolutions of the pump, Stokes and Stark pulse envelopes (upper frames), the diabatic (dotted) and adiabatic (solid) energies of the Hamiltonian (8.9) (in units $\hbar$). The diabatic and adiabatic energies are plotted in two cases: middle frame: for detunings satisfying condition (7.13a), with $\Delta_3 = -\Delta_2/2$; lower frame: for detunings satisfying condition (7.13b), with $\Delta_3 = \Delta_2/2$. Arrows started from the left show time evolution of the energies for intuitively ordered pulses (pump-Stark-Stokes). Arrows started from the right show time evolution for counterintuitively ordered pulses (Stokes-Stark-pump). The other parameters are $S_0 = 2.5\Delta_2$, $\Omega_0 = \Delta_2$, $\tau_p = \tau_s = -2T_p$, $T = 2T_p$, $T_s = T_p$.

For intuitive pulse ordering (pump-Stark-Stokes) both cases (7.13a) and (7.13b) permit adiabatic paths connecting states 1 and 3. For the middle frame, case (7.13a),
this path first goes adiabatically from state 1 to state 2 through the crossing at \( t_{12} \). It then follows state 2 on to an adiabatic crossing with state 3 at \( t_{23}^+ \) to end finally in state 3. The early crossing at \( t_{23}^- \) and the late crossing at \( t_{12}^+ \) are irrelevant because there is no field coupling the states whose energies cross. Similar conclusions apply for the display of the lower frame, case (7.13b): the adiabatic path from state 1 to 3 has an analogous structure, proceeding from state 1 to 2 to 3.

In both cases (7.13a) and (7.13b), the adiabatic path from 1 to 3 coincides with the intermediate state 2 during the middle part of the process. Thus state 2 receives almost the entire population for some time. Hence the pump-Stark-Stokes pulse ordering represents a more compact version, with a single Stark pulse, of sequential-double-SCRAP, but it is still vulnerable to decay from state 2.

**Counterintuitively ordered pump and Stokes pulses (Stokes-Stark-pump)**

By reading Fig. 7.1 from right to left, one can understand the time evolution when the pulse order is counterintuitive (Stokes-Stark-pump). In the absence of the Stark pulse, and with appropriate overlap of Stokes and pump pulses together with two-photon resonance, this would be an example of the STIRAP process; it would produce complete population transfer. However, in the present circumstances, with dynamic Stark shifts, this pulse ordering is inappropriate because in both cases (7.13a) and (7.13b) the initial state 1 connects to state 2 as the final state, not to the desired target state 3. The reason is evident: population changes occur only during the pump pulse. Even with a smaller delay between the pump and Stokes (i.e. for larger overlap) than the one shown in Fig. 7.1, the desired population transfer fails.

**Coincident pump and Stokes pulses (pump/Stokes-Stark or Stark-pump/Stokes)**

When the pump and Stokes pulses act simultaneously but precede or follow the Stark pulse, as shown in Fig. 7.2, the two cases (7.13a) and (7.13b) produce different population evolutions.

Figure 7.2, read from left to right, shows the evolution when simultaneous pump and Stokes pulses occur before the Stark pulse. For the bottom frame, case (7.13b), state 1 connects finally to state 2 because the 2-3 crossing \( t_{23}^- \) occurs before the 1-2 crossing \( t_{12}^+ \); the later crossings \( t_{12}^- \) and \( t_{23}^+ \) are irrelevant because there are no coupling
fields at those times. However, for case (7.13a), displayed in the middle frame, the
1-2 crossing $t_{12}^-$ is before the 2-3 crossing $t_{23}^-$ and thus state 1 connects finally to
state 3. Moreover, as evident from Fig. 7.2, this adiabatic path coincides only
for an instant with state 2, which therefore receives at most only a small transient
population during the population transfer from 1 to 3. This important feature,
which is very reminiscent of STIRAP, will be discussed in more detail below.

Figure 7.2: (color online) As in Fig. 7.1 but for coincident pump and Stokes pulses.
Arrows from left to right show evolution when pump and Stokes pulses precede the
Stark pulse; arrows from the right show evolution when the Stark pulse occurs first.

Figure 7.2, read from right to left, shows the evolution when simultaneous pump
and Stokes pulses occur after the Stark pulse. This situation leads to similar conclu-
sions as those just mentioned, with the difference that it is now case (7.13b) (bottom
frame) which leads to adiabatic connection from state 1 to state 3, whereas for case
(7.13a) state 1 connects to state 2.


7.1. Three-state SCRAP

Discussion

The several illustrations discussed above are representative of many specific simulations; the qualitative picture of curve crossings and population transfers is unchanged by small variations of the pulse timings and the other parameters. From examining these figures we can identify the conditions (of pulse timings and static detunings), for which a true three-state SCRAP process can occur, i.e. a process which involves all three states and cannot be interpreted as two sequential two-state SCRAP processes. In each case there is an adiabatic path between states 1 and 3 – adiabatic-transfer (AT) state, which involves only a small contribution from the (lossy) state 2. This process can occur when

Case I  the detunings satisfy condition (7.13a) and the pump and Stokes pulses both arrive during the rising of the Stark pulse, or alternatively,

Case II  the detunings satisfy condition (7.13b) and the pump and Stokes pulses both arrive during the falling of the Stark pulse.

Hence for fixed detunings, unlike two-state SCRAP, in three-state SCRAP the application of the driving pulses (pump and Stokes) before or after the Stark pulse leads to different results.

Successful population transfer requires appropriate settings for the interaction parameters: the timing of the pump and Stokes pulses relative to each other and to the Stark pulse, the settings of the static detunings (adjusted through the carrier frequencies of pump and Stokes pulses), and the strengths of the peak Rabi frequencies and the peak Stark shift. The following sections discuss the choice of these parameters, with figures that illustrate their relationship to needed adiabatic-diabatic crossing scenarios. We also discuss the conditions which minimize the transient population of state 2 and the ensuing population losses.

7.1.5  Adiabatic and diabatic conditions

The three-state SCRAP, like the original two-state SCRAP, uses a diabatic-adiabatic population transfer scenario: the path between the initial state 1 and the target final state 3 requires that certain crossings have to be passed adiabatically, others
7.1. Three-state SCRAP

diabatically; hence we shall impose conditions for diabatic or adiabatic evolution as
appropriate at each crossing.

We derive the adiabatic and diabatic conditions from the Landau-Zener formula [45],

$$P = 1 - \exp\left(-\frac{\pi \Omega^2(t_c)}{2|\Delta(t_c)|}\right), \quad (7.14)$$

for the probability of a transition between two diabatic states, whose energies cross
at time $t_c$. Here $\Omega(t)$ is the coupling between them, and $\dot{\Delta}(t)$ is the detuning slope,
both of which are evaluated at time $t_c$.

For Case I, when the detunings satisfy condition (7.13a) and the pump and
Stokes pulses precede the Stark pulse, three-state SCRAP requires adiabatic evo-
lution during the crossings at $t_{12}^-$ and $t_{23}^-$, i.e., transition probability $P > 1 - \nu$, and
diabatic evolution during the crossings at $t_{12}^+$ and $t_{23}^+$, i.e., transition probability
$P < \nu$, where $\nu$ is a small positive number measuring the deviation from perfect
adiabatic transfer. Hence the adiabatic conditions at $t_{12}^-$ and $t_{23}^-$, giving lower limits
on $\Omega_0$, read

$$\frac{(\Omega_0 T)^2 \exp\left[-2(t_{12}^- + \tau_p)^2/T_p^2\right]}{2\Delta_2 t_{12}^-} > \frac{2}{\pi} \ln \frac{1}{\nu}, \quad (7.15a)$$

$$\frac{(\Omega_0 T)^2 \exp\left[-2(t_{23}^- + \tau_s)^2/T_s^2\right]}{2(\Delta_2 - \Delta_3)t_{23}^-} > \frac{2}{\pi} \ln \frac{1}{\nu}, \quad (7.15b)$$

where $t_{12}$ and $t_{23}$ are given by Eqs. (7.12). The diabatic conditions at $t_{12}^+$ and $t_{23}^+$,
giving upper limits on $\Omega_0$, are

$$\frac{(\Omega_0 T)^2 \exp\left[-2(t_{12}^+ - \tau_p)^2/T_p^2\right]}{2\Delta_2 t_{12}^+} < \frac{2}{\pi} \ln \frac{1}{1 - \nu}, \quad (7.16a)$$

$$\frac{(\Omega_0 T)^2 \exp\left[-2(t_{23}^+ - \tau_s)^2/T_s^2\right]}{2(\Delta_2 - \Delta_3)t_{23}^+} < \frac{2}{\pi} \ln \frac{1}{1 - \nu}. \quad (7.16b)$$

Similar conditions can be derived for Case II, when the detunings satisfy condi-
tion (7.13b) and the pump and Stokes pulses follow the Stark pulse, with appropriate
redefinition of diabatic and adiabatic crossings.

7.1.6 Minimization of the transient population of state 2

Figure 7.3 provides examples of the effects of slight alteration of the pump-Stokes
pulse timings for Case I, when the detunings satisfy condition (7.13a) and the pump
and Stokes pulses both precede the Stark pulse. As seen in the middle frames, and
Figure 7.3: (color online) Time evolutions of the pulses (upper frames), the diabatic (dotted) and adiabatic (solid) energies of the Hamiltonian (8.9) (in units $\hbar$, middle frames), and the populations of the diabatic states (lower frames). Three different timings of the pump and Stokes pulses, both preceding the Stark pulse, are shown: left frames: $\tau_p = t_{12}; \tau_s = t_{23}$; middle frames: $\tau_s = \tau_p = (t_{12} + t_{23})/2$; right frames: $\tau_p = t_{23}; \tau_s = t_{12}$. The other parameters are $\Delta_3 = -\Delta_2/2$, $S_0 = 2.5\Delta_2$, $\Omega_0 = 2\Delta_2$, $T = 2T_p$, $T_s = T_p$. The thick curves in the energy (middle) frames show the AT state, which connects states 1 and 3. The populations (lower frames) are calculated in the adiabatic limit as the squared components of the AT state.

as follows from Eqs. (7.12), the crossing between states 1 and 2 at time $t_{12}$ occurs before the crossing between states 2 and 3 at $t_{23}$. One may naively expect that the best timing is to apply the pump pulse at the crossing $t_{12}$ and the Stokes pulse at the crossing $t_{23}$. However, as the figure demonstrates, this choice is not the optimal one, if we wish to minimize the transient population of the lossy state 2. Indeed, for such an “intuitive” timing (left frames) state 2 receives more population than in the other two cases, of coincident pulses (middle frames) and “counterintuitive” timing (right frames). In fact, it is the “counterintuitive” timing, when the pump pulse is applied at the crossing $t_{23}$ and the Stokes pulse at the crossing $t_{12}$, which produces
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minimum transient population of state 2.

The explanation of this important result can be found in the behaviour of the
eigenenergies in a simple two-state system under the action of a coupling field: the
interaction $\Omega(t)$ always induces repulsion between the energies since the splitting
between them is $\sqrt{\Omega^2(t) + \Delta^2(t)}$. In our three-state system, the pump pulse causes
repulsion between the energies of states 1 and 2 (the top two energies in Fig. 7.3,
middle frames) and barely influences the energy of state 3. Hence, if the pump
pulse is strong enough (which is required for adiabaticity) and the Stokes is weak
or absent, the energy of the intermediate adiabatic state $\Phi_2(t)$ (which is the AT
state) can approach the lowest adiabatic energy of state $\Phi_3(t)$ (creating an avoided
crossing), which will increase the probability for nonadiabatic transitions from state
$\Phi_2(t)$ to $\Phi_3(t)$. Likewise, the Stokes pulse applied at the crossing $t_{23}$ causes repulsion
between the energies of states 2 and 3 and does not affect markedly the energy of
state 1. Consequently, the energy of the AT state $\Phi_2(t)$ can approach the energy
of the upper adiabatic state $\Phi_1(t)$ with ensuing nonadiabatic losses. Nonadiabatic
transitions in these two regions produce non-negligible transient population of state
2 (lower left frame).

This picture is altered significantly when the pump and Stokes pulses exchange
their positions, when the Stokes arrives slightly before its crossing at $t_{12}$, whereas
the pump pulse arrives somewhat after its crossing at $t_{12}$. For example, the right
frames in Fig. 7.3 display such a case: the pump pulse is applied at the Stokes’s
crossing $t_{23}$ and the Stokes pulse is applied at the pump’s crossing $t_{12}$. Then around
$t_{12}$ the pump field is still large enough to open up the crossing between states 1
and 2 and make it adiabatic, while at the same time the Stokes pulse is strong
enough to push the energy of the adiabatic state $\Phi_3(t)$ away, so that no avoided
crossing between $\Phi_2(t)$ and $\Phi_3(t)$ is formed. Similarly, around the second crossing
at time $t_{23}$ the Stokes pulse opens up the crossing of states 2 and 3 and makes it
adiabatic, whereas the action of the pump pulse pushes the uppermost energy of
state $\Phi_1(t)$ away and prevents an avoided crossing between $\Phi_1(t)$ and $\Phi_2(t)$. As a
result, a smooth transfer of population from state 1 to state 3 occurs, with very
small transient population in the decaying state 2.

One can estimate the conditions that minimize the population of state 2 by
analyzing the components of the AT state $\Phi_2(t)$, which connects states 1 and 3, and
corresponds to the middle eigenenergy in Fig. 7.3. The condition $P_2 \ll P_1 + P_3$ translates into [cf. Eq. (7.9)]

$$\frac{P_1(t) + P_3(t)}{P_2(t)} = \frac{\Omega_p^2(t)}{4\varepsilon_2^2(t)} + \frac{\Omega_s^2(t)}{4[\varepsilon_2(t) - \Delta_3]^2} \ll 1. \quad (7.17)$$

Near the crossings $t_{12}$ and $t_{23}$ we have $\varepsilon_2(t) \sim \Delta_3/2$ and thence in the range $(t_{12}^- , t_{23}^-)$ we should have

$$\frac{P_1(t) + P_3(t)}{P_2(t)} \approx \frac{\Omega_p^2(t) + \Omega_s^2(t)}{\Delta_3^2} \ll 1. \quad (7.18)$$

The conclusions derived for the considered arrangement of detunings and pulse timing in this section (Case I) extend readily to the alternative arrangement (Case II), when the detunings satisfy condition (7.13b) and the pump and Stokes pulses both follow the Stark pulse. By careful examination of the eigenenergies one can derive similar conclusions regarding the pulse timing: for the minimization of $P_2(t)$ the pump pulse has to be applied at the Stokes’s crossing $t_{23}^+$ and the Stokes pulse at the pump’s crossing $t_{12}^+$. Here again, the Stokes pulse has to precede the pump pulse because $t_{12}^+ < t_{23}^+$. For the sake of brevity, we shall consider below only Case I.

The fact that the transient population $P_2(t)$ of state 2 is minimized when the Stokes pulse precedes the pump pulse is reminiscent of STIRAP; however, the reason is quite different, as discussed above. Further discussion and comparison of three-state SCRAP and STIRAP is presented in Sec. 7.3.

### 7.2 Properties of three-state SCRAP

#### 7.2.1 Sensitivity to pulse timings

Figure 7.4 shows contour plots of the final target-state population $P_3$ as a function of the Stokes position $\tau_s$ and the pump position $\tau_p$. The upper frame presents results in the absence of loss, while the lower frame is with loss from state 2.

In the upper frame we see two regions having high transfer probability. The region on the left corresponds to pump and Stokes pulses both applied during the rising of the Stark pulse (three-state SCRAP, Case I), whereas the region on the right corresponds to the pulse ordering pump-Stark-Stokes (sequential double-SCRAP). In the absence of losses these two regions have almost equal shapes and areas. The adiabatic conditions (7.15), marked by arrows, describe very accurately the high-
Figure 7.4: Contour plots of the final target-state population $P_3$ as a function of the timings of the pump and Stokes pulses, $\tau_p$ and $\tau_s$. *Upper frame:* no decay from state 2, $\Gamma = 0$; *lower frame:* decay from state 2 with rate $\Gamma = 1/T_p$. The diagonal line marks the locus of coincident pulses; counterintuitive pulse orderings are to the left of this line. The arrows alongside the axes indicate the parameter ranges where, according to Eqs. (7.15), the probability should exceed 0.9. The other parameters are $\Delta_2 = 100/T_p$, $\Delta_3 = -50/T_p$, $S_0 = 300/T_p$, $\Omega_0 = 50/T_p$, $T = 2T_p$, $T_s = T_p$.

The lower frame of this figure shows the effect of irreversible loss from state 2 out of the system. Comparison of the upper and lower frames shows the difference between three-state SCRAP and sequential double-SCRAP. The region of high probability associated with sequential double-SCRAP disappears in the presence of losses, because the population transfer proceeds through the lossy intermediate state 2. The region on the left, which is associated with three-state SCRAP, is changed less dramatically. The transfer efficiency in the part below the diagonal line, corresponding to the intuitive pulse order pump-Stokes, decreases; however, the transfer efficiency in the part above the diagonal line, corresponding to the counterintuitive pulse order Stokes-pump, is barely changed. The reason is that, as shown in Fig. 7.4.
To conclude, the three-state SCRAP can transfer population from state 1 to state 3 without placing sizeable transient population into state 2, a feature reminiscent of STIRAP. This suggests that three-state SCRAP can be implemented even on time scales comparable to the lifetime of state 2. However, SCRAP is not as perfect as STIRAP because some population, albeit small, does visit state 2, whereas in STIRAP this state remains completely unpopulated in the adiabatic limit. Hence some population will be lost in three-state SCRAP if the lifetime of state 2 is shorter than the pulse durations.

### 7.2.2 Sensitivity to detunings

Figure 7.5 shows contour plots of the final-state population $P_3$ as a function of the detunings $\Delta_2$ and $\Delta_3$. Detunings can arise both from fluctuations in the laser frequencies as well as from variations in the transition frequency by inhomogeneous broadenings, e.g. Doppler-shifts. The pump and Stokes pulses appear in counter-intuitive ordering (Stokes-pump), during the rising of the Stark pulse (Case I). In the upper frame there is no loss from state 2, while in the lower frame there is irreversible loss. In both cases high population transfer efficiency is localized in one distinct triangular region, corresponding to three-state SCRAP. The analytic conditions, depicted by lines, describe very well the high-efficiency region. In the presence of loss from state 2 this region shrinks, but it is still possible to achieve good population transfer for smaller $\Delta_3$ because, as follows from condition (7.18), the transient population of the lossy state 2 is smaller for smaller $\Delta_3$. Near two-photon resonance ($\Delta_3 = 0$) one finds a vertical band of high transfer efficiency, resilient to losses, which is identified with STIRAP.

### 7.2.3 Sensitivity to Rabi frequency

Figure 7.6 shows the final target-state population $P_3$ versus the peak Rabi frequencies $\Omega_0$ for several values of the loss rate from state 2 (denoted by numbers on the curves). The detunings and the pulse timings are chosen to satisfy the conditions for Case I of three-state SCRAP, when the detunings satisfy condition (7.13a) and
Figure 7.5: Contour plots of the final target-state population $P_3$ as a function of the static detunings $\Delta_2$ and $\Delta_3$. Upper frame: no decay from state 2, $\Gamma = 0$; lower frame: decay from state 2 with rate $\Gamma = 1/T_p$. The pulses are ordered counterintuitively, with $\tau_p = -T_p$, $\tau_s = -2T_p$. The other parameters are $\Omega_0 = 50/T_p$, $S_0 = 200/T_p$, $T = 2T_p$, $T_s = T_p$. The solid lines show the bounds of Eqs. (7.13). The dashed lines show the bounds of Eqs. (7.15).

the pump and Stokes pulses are applied during the rising of the Stark pulse. The pump and Stokes pulses appear in counterintuitive ordering (Stokes-pump). For sufficiently large Rabi frequency the population transfer efficiency approaches unity for any value of the loss rate; for larger $\Gamma$ larger $\Omega_0$ is required. The adiabatic conditions (7.15) are seen to predict very well the high-efficiency region in the lossless case ($\Gamma = 0$). From this value on, the population transfer is very robust to variations of the Rabi frequency, as indicative of three-state SCRAP. The stability of the population transfer efficiency versus variations in the Rabi frequency is particularly
Figure 7.6: (color online) Final target-state population $P_3$ as a function of the peak Rabi frequency $\Omega_0$. The numbers on the curves denote the rate of population loss from state 2 (in units $1/T_p$). The other parameters are $S_0 = 200/T_p$, $\Delta_2 = 100/T_p$, $\Delta_3 = -50/T_p$, $\tau_p = -T_p$, $\tau_s = -2T_p$, $T = 2T_p$, $T_s = T_p$. The arrows show the adiabatic conditions (7.15a) and (7.15b) for $\nu = 0.1$. The diabatic conditions (7.16) require $\Omega_0 T_p < 1.5 \times 10^5$ and cannot be seen here.

important for experimental implementations when both intensity fluctuations and averaging over the spatial intensity distribution of the driving radiation fields have to be considered.

7.3 Two-photon transitions: STIRAP, STIHRAP and SCRAP

So far we have assumed that the Stark shifts of levels 1 and 3 are negligible compared to the Stark shift of state 2. We have also assumed that the pump and Stark pulses cause no Stark shifts at all, which is a relevant assumption for single-photon transitions only. In this section we will explore the effects of Stark shifts caused by the pump pulse as will occur for a two-photon transition. To be specific, we shall consider the hyper-Raman process wherein states 1 and 2 are coupled by a two-photon transition. In this case both the pump-induced Stark shifts $S_{21}^p(t)$ and $S_{31}^p(t)$ and the pump Rabi frequency $\Omega_p(t)$ are proportional to the pump laser intensity.
7.3. Two-photon transitions: STIRAP, STIHRAP and SCRAP

7.3.1 SCRAP vs STIRAP

Laser-induced Stark shifts are recognized as the main obstacle for using STIRAP with two-photon and multiphoton transitions. These shifts, induced by the pump or/stokes lasers, change the energy diagram qualitatively by destroying the two-photon resonance and inducing time-dependent two-photon detuning. Such a detuning, if caused by imperfect laser frequency tuning, can in principle be overcome by increasing the laser intensities. The pump- or stokes-induced Stark shifts, however, are tied to the corresponding Rabi frequency, which cannot be increased independently. Because these Stark shifts are usually comparable to or larger than the respective Rabi frequency, they can prevent the population transfer.

Figure 7.7: (color online) Final target-state population $P_3$ vs the peak Rabi frequency $\Omega_0$ for STIRAP ($S_0 = 0, \Delta_2 = \Delta_3 = 0$) and three-state SCRAP ($S_0 = 200/T_p, \Delta_2 = 50/T_p, \Delta_3 = -25/T_p$). Three cases of different pump-induced Stark shift $S_{31}(t) = \sigma \Omega_p(t)$ of state 3 with respect to state 1 are shown with $\sigma = 0$, 1 and 2. For all cases the other interaction parameters are $\tau_p = -T_p$, $\tau_s = -2T_p$, $T = 2T_p$, $T_s = T_p$, $\Gamma = 0$.

Figure 7.7 demonstrates these features. Here plots of the final target-state population $P_3$ are shown as a function of the peak Rabi frequency $\Omega_0$ for three choices of the Stark shift $S_{31}$ caused by the pump pulse, which destroys the two-photon resonance. The Stark shift $S_{21}$ is less significant and it is taken to be zero. Figure 7.7 shows that for single-photon transitions ($S_{31} = 0$) STIRAP is superior as it requires far less intensity. However, for SCRAP the pump-induced Stark shift changes only slightly the transfer efficiency as long as it is smaller than the main Stark shift,
induced by the Stark pulse. In contrast, for STIRAP the pump-induced Stark shifts are detrimental and ruin the population transfer. Figure 7.7 therefore reveals a crucial advantage of SCRAP over STIRAP: SCRAP can be used with multiphoton transitions, despite the induced additional Stark shifts. The reason is that the pump-induced Stark shifts, as long as they are small compared to those produced by the Stark pulse, modify only slightly the energy diagram in SCRAP and do not change it qualitatively; hence the population transfer is not affected significantly. Moreover, the Stark-induced Stark shifts can always be increased independently to diminish the effect of the pump-induced Stark shifts.

### 7.3.2 SCRAP vs STIHRAP

It has been suggested [46] that the detrimental effects of dynamic Stark shifts in STIRAP can be compensated to some extent by a suitable choice of static detunings, via STIHRAP (stimulated hyper-Raman adiabatic passage). Indeed, successful coherent population transfer via STIHRAP has been demonstrated experimentally in [47]. That work has achieved a transfer efficiency of about 50% because of averaging over the spatial profile of the pump laser. The experiments [47] have shown that practical applications of STIHRAP are difficult because the optimal static detunings are very sensitive to the intensity of the pump laser: power variations across the pump-laser beam are detrimental and have to be avoided in order to achieve uniform excitation across the molecular beam. Therefore, to minimize intensity variations in the interaction region it is necessary to work with laser beam diameters substantially larger than the diameter of the molecular beam, which implies that high pulse energies are necessary to saturate the two-photon transition.

Figure 7.8 shows the final target-state population $P_3$ as a function of the detunings $\Delta_2$ and $\Delta_3$ for the cases of SCRAP (upper frame) and STIHRAP (lower frame). Figure 7.9 shows the same plots in the case when state 2 decays out of the system: this figure provides the opportunity to identify the ranges of detunings where the lossy intermediate state 2 gets little transient population and high transfer efficiency persists. Both Figs. 7.8 and 7.9 show that high transfer efficiency can be achieved by both SCRAP and STIHRAP. Comparison of the upper and lower frames in Figs. 7.8 and 7.9 suggests that SCRAP is more robust than STIHRAP against parameter variations in the presence of unwanted Stark shifts, because of the level-crossing
nature of the transition mechanism. This advantage of SCRAP over STIHRAP is very pronounced in the absence of losses (Fig. 7.8), whereas with losses the two techniques tend to deliver similar results.

Figure 7.8: Contour plots of the final target-state population $P_3$ as a function of the detunings $\Delta_2$ and $\Delta_3$ in the absence of decay from state 2, $\Gamma = 0$. The pulses are ordered counterintuitively, with $\tau_p = -T_p$, $\tau_s = -2T_p$. The other parameters are $\Omega_0 = 50/T_p$, $T = 2T_p$, $T_s = T_p$. Upper frame: $S_0 = 200/T_p$ (SCRAP); lower frame: $S_0 = 0$ (STIHRAP).
Figure 7.9: The same as Fig. 7.8, but for decaying state 2, with loss rate $\Gamma = 1/T$. 
Chapter 8

Extension of the Morris-Shore transformation to multilevel ladders

In this chapter we describe situations in which chains of $N$ degenerate quantum energy levels, coupled by time-dependent external fields, can be replaced by independent sets of chains of length $N$, $N-1$, $\ldots$, 2 and sets of uncoupled single states. The transformation is a generalization of the two-level Morris-Shore transformation (see chapter 5). We illustrate the procedure with examples of three-level chains.


8.1 The quasi-two-level case

The two-level MS transformation is readily extended to multiple degenerate levels $a - b - c - d - \cdots$ when two conditions are fulfilled: (i) all couplings share the same time dependence (in particular, all couplings may be constant), and (ii) the two-photon resonances $a - c - \cdots$ and $b - d - \cdots$ are fulfilled (in particular, all fields may be on resonance with the respective transition frequency). This can be achieved by formally combining the RWA-degenerate sets $a, c, \ldots$ into one larger set of RWA-degenerate states, and the sets $b, d, \ldots$ into another larger set of RWA-degenerate states. Then one can carry out the MS factorization on the new degenerate two-
level system, as displayed in Fig. 8.1. Then the MS states in the lower set will be superpositions of $a, c, \ldots$ states, whereas the MS states in the upper set will be superpositions of $b, d, \ldots$ states.

Figure 8.1: (Color online) The reducible multilevel Morris-Shore transformation in a multistate system consisting of $N$ coupled sets of degenerate levels when the two-photon resonances $a - c - \cdots$ and $b - d - \cdots$ are fulfilled (top). All interactions have the same time dependence $f(t)$. We first formally combine the RWA-degenerate sets $a, c, \ldots$ into one larger (“lower”) set of RWA-degenerate states, and the sets $b, d, \ldots$ into another larger (“upper”) set of RWA-degenerate states (middle). Then the new degenerate two-level system is decomposed into a set of independent nondegenerate two-state systems and a set of uncoupled (dark) states (bottom).

When the above conditions (i) or (ii) are not met, then we cannot reduce the multilevel case to a two-level one. Nevertheless, it may still be possible to replace the complicated linkages by simple sets of independent ladders. The next section presents a truly multilevel extension of the MS transformation that produces this reduction.
8.2 The three-level Morris-Shore transformation

8.2.1 The RWA Hamiltonian

We consider excitation by a set of coherent laser pulses of a multilevel system for which the generalized RWA is applicable. The excitation dynamics is governed by the time-dependent Schrödinger equation for the coupled probability amplitudes $C_n(t)$. In matrix form it reads

$$i \frac{d}{dt} C(t) = H(t)C(t). \quad (8.1)$$

The elements of the RWA Hamiltonian matrix $H(t)$ (in units of $\hbar$) are detunings (on the diagonal) and time-dependent Rabi frequencies times $1/2$. For simplicity we shall, in the following, omit explicit time arguments.

Let us specialize this equation to a three-level system, wherein there are $N_k$ degenerate sublevels of level $k$, where $k$ runs over indices $a$, $b$ and $c$. For definiteness we assume that these degenerate levels form a ladder, i.e. $E_a < E_b < E_c$. Figure 8.2 shows a possible linkage pattern amongst the quantum states: those of level $a$ link only to those of level $b$, as do those of level $c$; we assume there are no direct linkages between the $a$ states and the $c$ states. These assumptions allow us to present the RWA Hamiltonian in the block-matrix form

$$H = \begin{bmatrix}
O & V_1 & O \\
V_1^\dagger & D_b & V_2 \\
O & V_2^\dagger & D_c
\end{bmatrix}. \quad (8.2)$$

Here the matrix $O$ in the upper left corner is a $N_a$-dimensional square null matrix, where the null off-diagonal elements reflect the absence of radiative couplings amongst the $a$ sublevels, while the null diagonal elements originate with our (conventional) choice of RWA phases. The null matrices in the upper right and lower left corners indicate the absence of direct linkages between the $a$ states and the $c$ states. The square matrices $D_b$ and $D_c$ are scalar multiples of unit matrices of dimensions $N_b$ and $N_c$, respectively, $D_b = \Delta_b 1_{N_b}$ and $D_c = \Delta_c 1_{N_c}$. The scalars $\Delta_b$ and $\Delta_c$ are, respectively, the usual one- and two-photon detunings associated with the RWA. Although not shown explicitly, the interactions $V_1$ and $V_2$ may depend upon time. However, the elements of each matrix must share a common time dependence, say $f_1(t)$ for $V_1$ and $f_2(t)$ for $V_2$. 
8.2. The three-level Morris-Shore transformation

8.2.2 The MS transformation

We wish to transform the original Hamiltonian (8.2) to a form in which the radiative couplings occur only in single unlinked chains, of length 2 or 3. That is, we seek a transformed MS basis, linked to the original basis by the transformation (9.11), and a corresponding transformed MS Hamiltonian, which must appear in the block form

$$H^{MS} = SHS^\dagger = \begin{pmatrix} O & M_1 & O \\ M_1^\dagger & D_b & M_2 \\ O & M_2^\dagger & D_c \end{pmatrix},$$

(8.3)

where $M_1$ and $M_2$ are diagonal matrices supplemented by null columns or rows.

The transformation must only combine sublevels within a given level. Therefore
8.2. The three-level Morris-Shore transformation

it must have the form

\[ S = \begin{bmatrix} S_a & 0 & 0 \\ 0 & S_b & 0 \\ 0 & 0 & S_c \end{bmatrix}, \]  

(8.4)

where \( S_a, S_b \) and \( S_c \) are constant square unitary matrices of dimensions \( N_a, N_b, \) and \( N_c, \) respectively. With this transformation the block elements of the transformed Hamiltonian (8.3) read

\[ M_1 = S_a V_1 S_a^\dagger, \]  

(8.5a)

\[ M_2 = S_b V_2 S_b^\dagger. \]  

(8.5b)

The matrices \( M_1 \) and \( M_2 \) may have null rows or columns; these correspond to dark states. The desired decomposition of \( H \) into a set of independent two- or three-state systems requires that, after removing the null rows or columns, \( M_1 \) and \( M_2 \) reduce (possibly after an appropriate relabeling) to diagonal matrices. It follows from Eqs. (8.5) that the following matrices are diagonal:

\[ S_a V_1 V_1^\dagger S_a^\dagger = M_1 M_1^\dagger = \text{diag}, \]  

(8.6a)

\[ S_b V_1 V_1^\dagger S_b^\dagger = M_1 M_1^\dagger = \text{diag}, \]  

(8.6b)

\[ S_b V_2 V_2^\dagger S_b^\dagger = M_2 M_2^\dagger = \text{diag}, \]  

(8.6c)

\[ S_c V_2 V_2^\dagger S_c^\dagger = M_2 M_2^\dagger = \text{diag}. \]  

(8.6d)

Hence \( S_a \) and \( S_c \) are defined by the condition that they diagonalize \( V_1 V_1^\dagger \) and \( V_2 V_2^\dagger, \) respectively. The matrix \( S_b \) must, by definition, diagonalize both matrices \( W_1 \) and \( W_2, \) where

\[ W_1 = V_1 V_1^\dagger, \quad W_2 = V_2 V_2^\dagger. \]  

(8.7)

This can only occur if these two products commute,

\[ [W_1, W_2] = 0. \]  

(8.8)

Hence \( W_1 \) and \( W_2 \) must have the same set of eigenvectors. This set, when normalized, forms the transformation matrix \( S_b \) for the \( b \)-state manifold. We shall assume hereafter that Eq. (8.8) is satisfied; we will discuss the implications of this assumption in Sec. 8.2.4.
It is easy to show that the eigenvalues of $V_1 V_1^\dagger$ and $V_2 V_2^\dagger$ are all non-negative, and hence they can be written as squares of real numbers, $\left[ \lambda_1^{(n)} \right]^2$ and $\left[ \lambda_2^{(n)} \right]^2$, respectively. The matrices $W_1$ and $W_2$ have the same eigenvalues, except for additional (or missing) zero eigenvalues.

In the MS basis, the description of the dynamics comprises sets of independent ladders, of length no greater than $N = 3$. The three-state systems, expressing the linkages $a \leftrightarrow b \leftrightarrow c$, are governed by Hamiltonian matrices of the form

$$H_{abc}^{(n)} = \begin{bmatrix} 0 & \lambda_1^{(n)} & 0 \\ \lambda_1^{(n)} & \Delta_b & \lambda_2^{(n)} \\ 0 & \lambda_2^{(n)} & \Delta_c \end{bmatrix}.$$  \hspace{1cm} (8.9)

Two-state systems $a \leftrightarrow b$, if present, are governed by the Hamiltonians

$$H_{ab}^{(n)} = \begin{bmatrix} 0 & \lambda_1^{(n)} \\ \lambda_1^{(n)} & \Delta_b \end{bmatrix},$$  \hspace{1cm} (8.10)

while two-state linkages $b \leftrightarrow c$ are governed by the Hamiltonians

$$H_{bc}^{(n)} = \begin{bmatrix} \Delta_b & \lambda_2^{(n)} \\ \lambda_2^{(n)} & \Delta_c \end{bmatrix}.$$  \hspace{1cm} (8.11)

Finally, there may be single unlinked states, in any of the three levels; these can be regarded as being governed by one-dimensional matrices (scalars) $H_a^{(n)} = 0$ or $H_b^{(n)} = \Delta_b$ or $H_c^{(n)} = \Delta_c$.

In general, if the number of states in each initial manifold is different, we denote the minimum and maximum degeneracies by $N_{\min} \equiv \min \{N_a, N_b, N_c\}$, $N_{\max} \equiv \max \{N_a, N_b, N_c\}$, and the intermediate number by $N_{\text{mid}}$. We can then identify the following possibilities:

- if $N_{\min} = N_b$ then in the MS basis there will be $N_b$ three-state systems, $N_a - N_b$ dark states in the $a$ set of states, and $N_c - N_b$ dark states in the $c$ set;

- if $N_{\min} = N_a$ or $N_c$ then in the MS basis there will be $N_{\min}$ three-state systems, $N_{\text{mid}} - N_{\min}$ two-state systems composed of states of the sets with $N_{\text{mid}}$ and $N_{\max}$, and $N_{\max} - N_{\text{mid}}$ dark states composed of states of the set with $N_{\max}$.

Figure 8.2 shows an example in which the MS transformation reduces a general linkage pattern involving ten states to a pair of dark states, a single two-state linkage,
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and a pair of three-state linkages. The time dependencies $f_1(t)$ and $f_2(t)$ of the lower and upper transitions are arbitrary. In particular, the $f_2(t)$ interaction may precede the $f_1(t)$ interaction, as is the case of the STIRAP process [10].

8.2.3 Special case: single intermediate state

The commutation condition (8.8) is fulfilled automatically in the special case of a single, nondegenerate intermediate state, $N_b = 1$, because then the matrices $W_1^\dagger$ and $W_2$ reduce to scalars. Then, regardless of the degeneracies $N_a$ and $N_c$ of states $a$ and $c$, the three-level MS transformation always produces a nondegenerate three-state system comprising a bright state from the $a$ level, a bright state from the $c$ level, and the intermediate state. In addition, there will be $N_a - 1$ uncoupled states in the $a$ level and $N_c - 1$ uncoupled states in the $c$ level. Hence for a single intermediate state the MS transformation is always possible. Figure 8.3 depicts an example of such a linkage pattern and the result of a MS transformation.

![Diagram of Morris-Shore transformation for a single nondegenerate intermediate state](image)

Figure 8.3: (Color online) The Morris-Shore transformation for a single nondegenerate intermediate state: the MS decomposition produces a nondegenerate three-state system and two sets of uncoupled (dark) states in the $a$ and $c$ sets of states.
8.2.4 Consequences of the interaction commutation

We now turn to the implications of the commutation relation (8.8). This condition limits the generality of the MS transformation for three sets of degenerate states. We here pose the question: given the interaction $V_1$, what is the most general form of the interaction $V_2$, for which the three-level MS transformation applies?

The Frobenius problem

The required commutation relation (8.8) is equivalent to solving a matrix equation of the form

$$AX = XA$$  \hspace{1cm} (8.12)

for the matrix $X$, given that $A$ and $X$ are both square Hermitian matrices of the same dimension $N_b$. This is known as the Frobenius problem [48]. Because $A$ and $X$ commute, they have the same set of eigenvectors $\gamma_n$,

$$A\gamma_n = \alpha_n \gamma_n; \quad (8.13a)$$
$$X\gamma_n = \xi_n \gamma_n; \quad (8.13b)$$

and they are diagonalized by the same unitary matrix $G$, composed of these eigenvectors,

$$GAG^\dagger = A_0 = \text{diag}\{\alpha_1, \alpha_2, \ldots, \alpha_{N_b}\}; \quad (8.14a)$$
$$GXG^\dagger = X_0 = \text{diag}\{\xi_1, \xi_2, \ldots, \xi_{N_b}\}. \quad (8.14b)$$

Hence,

$$X = G^\dagger X_0 G. \quad (8.15)$$

We can view these results as follows. Given any Hermitian matrix $A$, we can find the transformation matrix $G$ which diagonalizes it. Then the most general form of the matrix $X$ is the construction of Eq. (8.15), where the real diagonal matrix $X_0$ is arbitrary. Therefore, if $A$ and $X$ are $N_b$-dimensional then the matrix $X$ is parametrized by $N_b$ parameters: the diagonal elements of $X_0$.

Alternatively, we can express the matrix $X$ as a power series in $A$. The Cayley-Hamilton theorem [48] implies that only $N_b - 1$ of these powers, e.g. $A^0, A^1, \ldots, A^{N_b-1}$, are linearly independent. Then the expansion reads

$$X = \sum_{n=0}^{N_b-1} x_n A^n, \quad (8.16)$$
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where the $N_b$ coefficients $x_n$ are arbitrary. Because $X$ is Hermitian, these numbers must be real.

Hence either of the two alternative solutions of the Frobenius problem (8.12) – either Eq. (8.15) or Eq. (8.16) – involve $N_b$ arbitrary real parameters.

**Implications for linkages**

We now apply these results to the MS transformation. We know that any given interaction $V_1$ determines the transformation matrix $S_b$ through Eq. (8.6b). It follows that the interaction $V_2$ must satisfy

$$W_2 = S_b^\dagger W_0 S_b,$$

with $W_2 = V_2 V_2^\dagger$, where $W_0$ is an arbitrary $N_b$-dimensional real diagonal matrix. Equation (8.16) implies that the most general representation of $W_2$, for which the commutation relation (8.8) is satisfied and hence there exists MS transformation, has the form

$$W_2 = \sum_{n=0}^{N_a-1} w_n W_n \tag{8.18}$$

where the $N_b$ arbitrary real coefficients $w_n$ determine the degrees of freedom for $W_2$.

**8.2.5 Example: $J = 3/2 \leftrightarrow J = 1/2 \leftrightarrow J = 1/2$ ladder**

**The system and the couplings**

We here illustrate the rather formal results with a specific example. We consider a three-level ladder whose degeneracy stems from angular momentum. Specifically we consider the sequence $J = 3/2 \leftrightarrow J = 1/2 \leftrightarrow J = 1/2$; hence the magnetic sublevels form a degenerate three-level system with $N_a = 4$, $N_b = N_c = 2$. Taking into account the Clebsch-Gordan coefficients [49] we find

$$V_1(t) = \frac{f_1(t)}{\sqrt{6}} \begin{bmatrix} r_1\sqrt{3} & 0 \\ -p_1\sqrt{2} & r_1 \\ l_1 & -p_1\sqrt{2} \\ 0 & l_1\sqrt{3} \end{bmatrix}, \tag{8.19a}$$

$$V_2(t) = \frac{f_2(t)}{\sqrt{3}} \begin{bmatrix} -p_2 & -r_2\sqrt{2} \\ l_2\sqrt{2} & p_2 \end{bmatrix}, \tag{8.19b}$$
where \( f_1(t) \) and \( f_2(t) \) define the (generally different) time envelopes of the pulsed interactions in the lower and upper transitions, respectively; \( r_n, p_n, l_n \) are related to the amplitudes (with the respective phases) of the right-circular (\( \sigma^+ \)), linear (\( \pi \)), and left-circular (\( \sigma^- \)) polarizations for the lower (\( n = 1 \)) or upper (\( n = 2 \)) transition.

### The MS states

The MS states in the \( a \) manifold are defined as the eigenstates of the matrix \( V_1 V_1^\dagger \) [see Eq. (8.6a)],

\[
V_1 V_1^\dagger = \frac{f_1^2(t)}{6} \begin{bmatrix}
3|r_1|^2 & -\sqrt{6}p_1^* r_1 & \sqrt{3}l_1^* r_1 & 0 \\
-\sqrt{6}p_1 r_1^* & 2|p_1|^2 + |r_1|^2 & -\sqrt{2}(p_1 l_1^* + p_1^* r_1) & \sqrt{3}l_1^* r_1 \\
\sqrt{3}l_1 r_1^* & -\sqrt{2}(p_1^* l_1 + p_1 r_1^*) & |l_1|^2 + 2|p_1|^2 & -\sqrt{6}p_1 l_1^* \\
0 & l_1 r_1^* \sqrt{3} & -\sqrt{6}p_1^* l_1 & 3|l_1|^2
\end{bmatrix}.
\] (8.20)

Two of these eigenstates are dark, with zero eigenvalues, whereas the other two are bright, with eigenvalues \((\lambda_{1}^{(1)})^2\) and \((\lambda_{1}^{(2)})^2\); the explicit forms of these eigenstates are too cumbersome to be presented here.

The MS states in the \( c \) manifold are defined as the eigenstates of the matrix \( V_2 V_2^\dagger \) [see Eq. (8.6d)],

\[
V_2 V_2^\dagger = \frac{f_2^2(t)}{3} \begin{bmatrix}
|p_2|^2 - 2r_2^2 l_2 & 2\sqrt{2}i\text{Im}(p_2^* r_2) \\
2\sqrt{2}i\text{Im}(p_2^* l_2) & |p_2|^2 - 2r_2 l_2^*
\end{bmatrix}.
\] (8.21)

They have eigenvalues \((\lambda_{2}^{(1)})^2\) and \((\lambda_{2}^{(2)})^2\). Explicitly, the \( \lambda \)'s are given by

\[
\lambda_{1}^{(1,2)} = \frac{f_1(t)}{\sqrt{6}} \eta_1 [2(1 + \xi_1)] \mp \sqrt{\epsilon_1^2 + 2\xi_1 \left[ 1 + \sqrt{1 - \epsilon_1^2 \cos \alpha_1} \right]}^{1/2}, \tag{8.22a}
\]

\[
\lambda_{2}^{(1,2)} = \frac{f_2(t)}{\sqrt{3}} \eta_2 [1 + \xi_2] \mp \sqrt{\epsilon_2^2 + 2\xi_2 \left[ 1 + \sqrt{1 - \epsilon_2^2 \cos \alpha_2} \right]}^{1/2}, \tag{8.22b}
\]
with \((n = 1, 2)\)

\[
\begin{align*}
\varepsilon_n &= \frac{|l_n|^2 - |r_n|^2}{\eta_n^2}, \\
\xi_n &= \frac{|p_n|^2}{\eta_n^2}, \\
\eta_n &= \sqrt{|l_n|^2 + |r_n|^2}, \\
\alpha_n &= \arg l_n^* r_n^* p_n^2.
\end{align*}
\]

(8.23a) \(\text{---} \)

The MS states in the intermediate level \(b\) are the common eigenstates of the matrices \(W_1 = V_1 V_1^\dagger\) and \(W_2 = V_2 V_2^\dagger\) [see Eqs. (8.6b) and (8.6c)], i.e.,

\[
W_1 = \begin{bmatrix}
3 |r_1|^2 + 2 |p_1|^2 + |l_1|^2 & -\sqrt{2} (p_1^* r_1 + p_1 l_1^*) \\
-\sqrt{2} (p_1^* l_1 + p_1^* r_1) & |r_1|^2 + 2 |p_1|^2 + 3 |l_1|^2
\end{bmatrix} \frac{f_2^2(t)}{6},
\]

(8.24a) \(\text{---} \)

\[
W_2 = \begin{bmatrix}
|p_2|^2 + 2 |r_2|^2 & -\sqrt{2} (p_2^* l_2 + p_2 r_2^*) \\
-\sqrt{2} (p_2^* r_2 + p_2^* l_2) & |p_2|^2 + 2 |l_2|^2
\end{bmatrix} \frac{f_2^3(t)}{3}.
\]

(8.24b) \(\text{---} \)

If \(W_1\) and \(W_2\) do not commute, then the eigenstates of \(W_1\) will differ from the eigenstates of \(W_2\) and there will be no MS factorization. In other words, the two-state MS transformation, when applied to the lower transition \(a - b\), will produce MS states in the \(b\) level (defined as the eigenstates of \(W_1\)), which will differ from the MS states in this same \(b\) level produced by two-state MS transformation in the upper transition \(b - c\) (defined as the eigenstates of \(W_2\)). Three-state MS transformation will only occur if these two sets of \(b\) states are the same, a necessary and sufficient condition for which is the commutation of \(W_1\) and \(W_2\).

**Commutation implications**

The commutation relation (8.8) leads to the equations

\[
\text{Im} \left[ (l_1^* p_1 + r_1^* p_1^*) (l_2 p_2^* + p_2 r_2^*) \right] = 0,
\]

(8.25a) \(\text{---} \)

\[
(l_1^* p_1 + r_1^* p_1) (|r_2|^2 - |l_2|^2) = (|r_1|^2 - |l_1|^2) (l_2 p_2^* + p_2 r_2^*).
\]

(8.25b) \(\text{---} \)

Obviously, if all interactions are real, the first condition (8.25a) is satisfied automatically.

In the general case of complex interactions, one can solve this system of equations, for example, by considering two cases: when \(|r_1| \neq |l_1|\) and \(|r_1| = |l_1|\).
(i) For $|r_1| \neq |l_1|$, it is readily seen, by replacing the term $(l_2p_2^* + p_2r_2^*)$ from Eq. (8.25b) into Eq. (8.25a), that Eq. (8.25a) is satisfied identically; hence condition (8.8) requires only one condition to be fulfilled: Eq. (8.25b). The latter condition can be solved, for example, for $p_2$,

$$p_2 = \frac{l_2(l_1^*p_1 + r_1p_1^*) - r_2(l_1p_1^* + r_1^*p_1)}{|l_1|^2 - |r_1|^2}. \tag{8.26}$$

Condition (8.26) restricts the amplitude of the linearly polarized field for the upper transition to be a function of the arbitrary amplitudes of the other fields. Because $p_2$ is complex-valued, condition (8.26) represents, in fact, two conditions: for the modulus and the phase of $p_2$.

(ii) For $|r_1| = |l_1|$, there are obviously two solutions. The first of these is $|r_2| = |l_2|$; then Eq. (8.25a) is also required because it is not satisfied automatically. The second solution is $l_1p_1^* + r_1^*p_1 = 0$; it fixes one of the phases of the lower-transition fields (e.g., $2 \arg p_1 = \pi - \arg l_1 + \arg r_1$).

With either of these choices (i) or (ii) for the fields it is possible to reduce the original linkage pattern to a pair of three-state ladders and two uncoupled dark states, as shown in Fig. 8.4.

One special example for conditions (8.25) is when the left- and right-polarized fields for the lower transition have the same intensity and the same phase ($r_1 = l_1$), and the linearly-polarized field is shifted in phase by $\pi/2$ with respect to them; then $l_1p_1^* + r_1^*p_1 = 0$. No restrictions are imposed on the couplings of the upper transition in this case.

In another simple example, the left- and right-polarized fields for the lower transition have the same intensity ($|r_1| = |l_1|$) and the same applies for the upper transition ($|r_2| = |l_2|$), and all interactions are real.
Figure 8.4: (Color online) The MS transformation for the three-level ladder $J = 3/2 \leftrightarrow J = 1/2 \leftrightarrow J = 1/2$: the MS decomposition produces two independent nondegenerate three-state systems and two uncoupled (dark) states in the $J = 3/2$ set.

The MS picture

If the commutation relation (8.8) is satisfied then the Hamiltonian in the MS basis reads

$$
H^{MS} = \begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_1^{(1)} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \lambda_1^{(2)} & 0 & 0 & 0 \\
0 & \lambda_1^{(1)} & 0 & \Delta_b & 0 & \lambda_2^{(1)} & 0 & 0 \\
0 & 0 & \lambda_1^{(2)} & 0 & \Delta_b & 0 & \lambda_2^{(2)} & 0 \\
0 & 0 & 0 & \lambda_2^{(1)} & 0 & \Delta_c & 0 & 0 \\
0 & 0 & 0 & 0 & \lambda_2^{(2)} & 0 & \Delta_c & 0
\end{bmatrix}.
$$

(8.27)

By rearranging the states, it is readily seen that there are two independent three-state systems driven by Hamiltonians of the form (8.9) ($n = 1, 2$), with MS couplings $\lambda_1^{(n)}$ and $\lambda_2^{(n)}$ given by Eqs. (8.22).
8.3 Extension to $N$ levels

The results for the three-level MS transformation are readily extended to $N$ degenerate levels. For each transition $n$ ($n = 1, 2, \ldots, N - 1$), described by an interaction matrix $V_n$, time envelope $f_n(t)$ of all fields in this transition, and common detuning $\Delta_n$, we form the matrices $W_n = V_n V_n^\dagger$. The $N$-level MS transformation exists if

$$[W_1, W_2] = O,$$  \hfill (8.28a)
$$[W_2, W_3] = O,$$  \hfill (8.28b)
$$\cdots$$
$$[W_{N-2}, W_{N-1}] = O.$$  \hfill (8.28c)

The relations (8.28) imply that the interactions for any two adjacent transitions $n$ and $n + 1$ must be such that, after the MS transformation, the resulting MS states of the common level of these two transitions are the same for the lower and upper transitions; mathematically this is ensured by the commutation of $W_n$ and $W_{n+1}$.

If conditions (8.28) are satisfied, the MS transformation will produce sets of independent nondegenerate $N$-state systems, $(N - 1)$-state systems, and so on, and a number of uncoupled states, depending on the particular system.
Chapter 9

Counterintuitive transitions between crossing energy levels

In this chapter we calculate analytically the probabilities for intuitive and counterintuitive transitions in a three-state system, in which two parallel energies are crossed by a third, tilted energy. The state with the tilted energy is coupled to the other two states in a chainwise linkage pattern Fig. 9.1 with constant couplings of finite duration. The famous Landau-Zener (LZ) model [44,45] is used as a tool for estimating the transition probability between the states. The purpose is not just to show that the probability for a counterintuitive transition is nonzero but rather to derive accurate analytical estimates for it. Our approach involves transformation to the adiabatic basis where the evolution is represented as a sequence of instantaneous two-state LZ transitions at each crossing and adiabatic evolution elsewhere. This approach allows us to derive the transition probabilities between each pair of diabatic states, including the probability for the counterintuitive transition. The probability for a counterintuitive transition is found to increase with the square of the coupling and decrease with the squares of the interaction duration, the energy splitting between the parallel energies, and the tilt chirp rate. Physical examples of this model can be found in coherent atomic excitation and optical shielding in cold atomic collisions.

The results of this chapter are published at: A. A. Rangelov, J. Piilo, and N. V. Vitanov "Counterintuitive transitions between crossing energy levels" Phys. Rev. A 72, 053404 (2005).
9.1 Definition of the problem

9.1.1 The system

The probability amplitudes of the three-state system \( C(t) = [C_1(t), C_2(t), C_3(t)]^T \) with the energies shown in Fig. 9.1 satisfy the Schrödinger equation \((\hbar = 1)_1 \)

\[
i\dot{C}(t) = H(t)C(t),
\]

where the overdot denotes \( d/dt \). The Hamiltonian in the usual rotating-wave approximation is given by \([2]\)

\[
H(t) = \begin{bmatrix}
-\delta & \Omega_{12} & 0 \\
\Omega_{12} & \beta t & \Omega_{23} \\
0 & \Omega_{23} & \delta
\end{bmatrix}.
\]

As the Hamiltonian (9.2) shows, there is no direct coupling between states \( \psi_1 \) and \( \psi_3 \) but each of them is coupled to state \( \psi_2 \). Without loss of generality the constant couplings \( \Omega_{12} \) and \( \Omega_{23} \) will be assumed real and positive. Both couplings are supposed to have the same finite duration, being turned on at time \( t_i \) and turned off at time \( t_f \). In the original DO model the couplings last from \(-\infty\) to \(+\infty\). Furthermore, the
9.1. Definition of the problem

energy splitting parameter $\delta$ and the slope $\beta$ of the energy of state $\psi_2$ are assumed positive too,

$$\delta > 0, \quad \beta > 0. \quad (9.3)$$

Given these assumptions, the crossing between the diabatic energies of states $\psi_1$ and $\psi_2$, occuring at time $t_-= -\tau$ precedes the crossing between states $\psi_2$ and $\psi_3$, occurring at time $t_+ = \tau$, where

$$\tau = \frac{\delta}{\beta}. \quad (9.4)$$

Therefore, the transition $\psi_1 \rightarrow \psi_3$ is intuitive, while the opposite transition $\psi_3 \rightarrow \psi_1$ is counterintuitive. In the adiabatic limit, the transition probability from $\psi_1$ to $\psi_3$ is $P_{1 \rightarrow 3} = 1$, whereas that from $\psi_3$ to $\psi_1$ is $P_{3 \rightarrow 1} = 0$.

9.1.2 The Demkov-Osherov model

In the DO model the transition probabilities $P_{m \rightarrow n}$ from state $\psi_m$ at $t \rightarrow -\infty$ to state $\psi_n$ at $t \rightarrow +\infty$ are given exactly by products of two-state single-crossing LZ probabilities, as follows

$$
egin{align*}
P_{1 \rightarrow 1} &= p_-, & P_{1 \rightarrow 2} &= q_- p_+, & P_{1 \rightarrow 3} &= q_- q_+,
P_{2 \rightarrow 1} &= q_-, & P_{2 \rightarrow 2} &= p_- p_+, & P_{2 \rightarrow 3} &= p_- q_+,
P_{3 \rightarrow 1} &= 0, & P_{3 \rightarrow 2} &= q_+, & P_{3 \rightarrow 3} &= p_+,
\end{align*}
$$

(9.5)

where

$$p_\pm = e^{-2\pi \alpha_\pm^2}, \quad q_\pm = 1 - p_\pm, \quad (9.6)$$

i.e. $q_\pm$ is the transition probability and $p_\pm$ is the probability of no transition at the crossing $t_\pm$, with

$$\alpha_- = \Omega_{12}/\beta_1^{1/2}, \quad \alpha_+ = \Omega_{23}/\beta_1^{1/2}. \quad (9.7)$$

These simple results coincide with what would be expected naively, by treating the crossings independently, no matter how close they are to each other, and multiplying LZ probabilities. In particular, if the system is initially in state $\psi_3$, the transition probability to state $\psi_1$ is exactly zero at $t \rightarrow +\infty$, $P_{3 \rightarrow 1} = 0$, which means that the counterintuitive transition $\psi_3 \rightarrow \psi_1$ is forbidden. This zero probability is rather unexpected because state $\psi_1$ acquires some nonzero population during the interaction. However, it vanishes at $t \rightarrow +\infty$ for any set of parameters, irrespective of whether the interaction is adiabatic or not. This property is unique for the DO
model and it depends crucially on any of its features: infinite coupling durations, constant couplings, constant energies of states \( \psi_1 \) and \( \psi_3 \) and linear energy of state \( \psi_2 \). The goal of the present paper is to estimate the probability for counterintuitive transitions in the case of finite coupling duration.

9.2 Transition matrix

9.2.1 Eigenvalues and eigenstates

We need the eigenvalues and the eigenstates (the adiabatic states) of \( H(t) \). The eigenvalues read [2]

\[
\begin{align*}
\lambda_1 &= -\frac{1}{3}a + \frac{2}{3}s \cos \frac{1}{3}\theta, \\
\lambda_2 &= -\frac{1}{3}a - \frac{2}{3}s \cos \frac{1}{3}(\theta + \pi), \\
\lambda_3 &= -\frac{1}{3}a - \frac{2}{3}s \cos \frac{1}{3}(\theta - \pi),
\end{align*}
\]

where

\[
\begin{align*}
a &= -\beta t, \\
b &= -(\delta^2 + \Omega_{12}^2 + \Omega_{23}^2), \\
c &= \delta(\Omega_{12}^2 - \Omega_{23}^2 + \delta \beta t), \\
s &= \sqrt{a^2 - 3b}, \\
cos \theta &= -\frac{2a^3 - 9ab + 27c}{2s^3}.
\end{align*}
\]

The eigenstates are given by \( \varphi_k = [f_{1k}, f_{2k}, f_{3k}]^T \), with

\[
\begin{align*}
f_{1k} &= \frac{1}{N_k} \Omega_{12} (\lambda_k - \delta), \\
f_{2k} &= \frac{1}{N_k} (\lambda_k^2 - \delta^2), \\
f_{3k} &= \frac{1}{N_k} \Omega_{23} (\lambda_k + \delta),
\end{align*}
\]

where \( N_k \) are normalization factors \((k = 1, 2, 3)\). The asymptotic behaviors at large times of the eigenvalues and the eigenstates are presented in Appendix A.
9.2.2 Adiabatic basis

The transformation linking the diabatic amplitudes \( C(t) \) and the adiabatic amplitudes \( A(t) \) is given by

\[
C(t) = F(t)A(t),
\]

(9.11)

where \( A(t) = [A_1(t), A_2(t), A_3(t)]^T \) and \( F(t) \) is an orthogonal rotation matrix \( [F^{-1}(t) = F^T(t)] \) whose columns are the eigenvectors (9.10),

\[
F(t) = \begin{bmatrix}
    f_{11}(t) & f_{12}(t) & f_{13}(t) \\
    f_{21}(t) & f_{22}(t) & f_{23}(t) \\
    f_{31}(t) & f_{32}(t) & f_{33}(t)
\end{bmatrix}
\]

(9.12)

The Schrödinger equation in the adiabatic basis reads

\[
i\dot{A}(t) = H_A(t)A(t),
\]

(9.13)

with \( H_A(t) = F^T(t)H(t)F(t) - iF^T(t)\dot{F}(t) \), or

\[
H_A(t) = \begin{bmatrix}
    \lambda_1 & -i\nu_{12} & -i\nu_{13} \\
    -i\nu_{21} & \lambda_2 & -i\nu_{23} \\
    -i\nu_{31} & -i\nu_{32} & \lambda_3
\end{bmatrix},
\]

(9.14)

where the nonadiabatic coupling between the adiabatic states \( \varphi_k(t) \) and \( \varphi_l(t) \) is

\[
\nu_{kl}(t) = \langle \varphi_k(t) | \dot{\varphi}_l(t) \rangle = -\nu_{lk}(t)
\]

(9.15)

We use the fact that the transition times in the adiabatic basis are shorter than in the diabatic basis [50]. This is so because while the asymptotic behaviors of the adiabatic energies at large times (A.0.2) are approximately the same as the asymptotics of the diabatic energies, the couplings \( \nu_{kl} \) in the adiabatic basis (9.15) vanish as \( t^{-2} \) [see Eqs. (A.0.2)], in contrast to the constant couplings \( \Omega_{12} \) and \( \Omega_{23} \) in the diabatic basis. The difference in the transition times is illustrated in Fig. 9.2, where the oscillations in the populations of the adiabatic states vanish much faster.

9.2.3 Evolution matrix in the adiabatic basis

Our method is based on two simplifying assumptions. First, we assume that appreciable transitions take place only between neighboring adiabatic states, \( \varphi_1(t) \leftrightarrow \)
Figure 9.2: (Color online) Time evolutions of the populations of the diabatic and adiabatic states for the original DO model \((t_i = -\infty)\). The system starts in state \(\psi_1\). The interaction parameters are \(\Omega_{12} = \Omega_{23} = \beta^{1/2}\), \(\delta = \beta^{1/2}\).

\(\varphi_2(t)\) and \(\varphi_3(t)\) ↔ \(\varphi_3(t)\), but not between states \(\varphi_1(t)\) and \(\varphi_3(t)\), because the energies of the latter pair are split by the largest gap. Second, we assume that the nonadiabatic transitions occur instantly at the corresponding avoided crossings and the evolution is adiabatic elsewhere. This allows us to obtain the propagator in the adiabatic basis by multiplying five simple transition matrices describing LZ transitions or adiabatic evolution.

The adiabatic evolution matrix \(U^A(t_f, t_i)\) is most conveniently determined in the adiabatic interaction representation, where the diagonal elements of \(H^A(t)\) are nullified. The transformation reads

\[
A(t) = M(t)B(t),
\]

where

\[
M(t, t_0) = \begin{bmatrix}
e^{-i\Lambda_1(t, t_0)} & 0 & 0 \\
0 & e^{-i\Lambda_2(t, t_0)} & 0 \\
0 & 0 & e^{-i\Lambda_3(t, t_0)}
\end{bmatrix},
\]

\[\Lambda_k(t, t_0) = \int_{t_0}^{t} \lambda_k(t') dt',\]

\[\Lambda_{kl}(t, t_0) \equiv \Lambda_k(t, t_0) - \Lambda_l(t, t_0),\]
9.2. Transition matrix

and $t_0$ is an arbitrary fixed time. The Schrödinger equation in this basis reads

$$i \dot{\mathbf{B}}(t) = H_B(t) \mathbf{B}(t),$$

with

$$H_B(t) = -i \begin{bmatrix}
0 & \nu_{12} e^{i\Lambda_{12}(t,t_0)} & \nu_{13} e^{i\Lambda_{13}(t,t_0)} \\
\nu_{21} e^{i\Lambda_{21}(t,t_0)} & 0 & \nu_{23} e^{i\Lambda_{23}(t,t_0)} \\
\nu_{31} e^{i\Lambda_{31}(t,t_0)} & \nu_{32} e^{i\Lambda_{32}(t,t_0)} & 0
\end{bmatrix}. \quad (9.20)$$

In this basis, the evolution matrix for adiabatic evolution is given by the identity matrix.

The LZ transitions at the crossings at $\pm \tau$ are described by the transition matrices

$$U_{LZ}(-\tau) = \begin{bmatrix}
1 & 0 & 0 \\
0 & \sqrt{q_-} e^{-i\phi_-} & -\sqrt{p_-} \\
0 & \sqrt{p_-} & \sqrt{q_-} e^{i\phi_-}
\end{bmatrix}, \quad (9.21a)$$

$$U_{LZ}(\tau) = \begin{bmatrix}
\sqrt{q_+} e^{-i\phi_+} & -\sqrt{p_+} & 0 \\
\sqrt{p_+} & \sqrt{q_+} e^{i\phi_+} & 0 \\
0 & 0 & 1
\end{bmatrix}, \quad (9.21b)$$

where $p_{\pm}$ and $q_{\pm}$ are given by Eqs. (9.6) and

$$\phi_{\pm} = \arg \Gamma(1 - i\alpha_{\pm}^2) + \frac{\pi}{4} + \alpha_{\pm}^2 \left( \ln \alpha_{\pm}^2 - 1 \right), \quad (9.22)$$

with $\alpha_{\pm}$ given by Eqs. (9.7). The LZ phases $\phi_{\pm}$ do not depend on time, unlike the dynamical phases (9.18a).

The propagator in the adiabatic basis reads

$$U^A(t_f, t_i) = M(t_f, \tau) U_{LZ}(\tau) M(\tau, -\tau) U_{LZ}(-\tau) M(-\tau, t_i),$$

$$M(t, \tau) = \begin{bmatrix}
1 & \nu_{12} e^{i\Lambda_{12}(t,t_\tau)} & \nu_{13} e^{i\Lambda_{13}(t,t_\tau)} \\
\nu_{21} e^{i\Lambda_{21}(t,t_\tau)} & 0 & \nu_{23} e^{i\Lambda_{23}(t,t_\tau)} \\
\nu_{31} e^{i\Lambda_{31}(t,t_\tau)} & \nu_{32} e^{i\Lambda_{32}(t,t_\tau)} & 0
\end{bmatrix}. \quad (9.23)$$
or explicitly

\[
\begin{align*}
    U_{11}(t_f, t_i) &= \sqrt{q} e^{-i\phi - i\Lambda_1(t_f, t_i)} \\
    U_{12}(t_f, t_i) &= -\sqrt{p} e^{-i\phi - i\Lambda_1(t_f, t_i) - i\Lambda_2(t_f, t_i)} \\
    U_{13}(t_f, t_i) &= \sqrt{p} e^{-i\Lambda_1(t_f, t_i) - i\Lambda_2(t_f, t_i) - i\Lambda_3(-t_f, t_i)} \\
    U_{21}(t_f, t_i) &= \sqrt{p} e^{-i\Lambda_1(t_f, t_i) - i\Lambda_2(t_f, t_i)} \\
    U_{22}(t_f, t_i) &= \sqrt{q} e^{-i\phi - i\Lambda_1(t_f, t_i)} \\
    U_{23}(t_f, t_i) &= -\sqrt{p} e^{-i\Lambda_2(t_f, t_i) - i\Lambda_3(t_f, t_i)} \\
    U_{31}(t_f, t_i) &= 0 \\
    U_{32}(t_f, t_i) &= \sqrt{q} e^{i\phi - i\Lambda_3(t_f, t_i)} \\
    U_{33}(t_f, t_i) &= \sqrt{p} e^{i\Lambda_3(t_f, t_i)} \\
\end{align*}
\]

(9.23a)

In the special case when \( t_i = -T \), \( t_f = T \) and \( \Omega_{12} = \Omega_{23} \equiv \Omega \), many expressions simplify, as shown in Appendix A.1. Then \( \alpha_+ = \alpha_- \equiv \alpha \), \( p_+ = p_- \equiv p \), \( q_+ = q_- \equiv q = 1 - p \), and Eq. (9.23) reduces to

\[
U^A(T, -T) = \begin{bmatrix}
    \sqrt{q} e^{-i\phi - i\Lambda_1(T, -T)} & -\sqrt{p} q e^{-i\phi - i\Lambda_2(T, T)} & 0 \\
    \sqrt{p} e^{i\Lambda_3(T, -T) - i\Lambda_2(T, T)} & q & -\sqrt{p} q e^{i\phi + i\Lambda_1(T, -T)} \\
    0 & \sqrt{p} e^{i\Lambda_2(T, -T) - i\Lambda_3(T, T)} & \sqrt{q} e^{i\phi + i\Lambda_1(T, -T)}
\end{bmatrix}.
\]

(9.24)

### 9.2.4 Evolution matrix in the diabatic basis

The propagator in the diabatic basis can be obtained by using the transformation (9.11); it reads

\[
U(t_f, t_i) = F(t_f) U^A(t_f, t_i) F^T(t_i).
\]

(9.25)

We shall use this relation to derive the transition probabilities in the finite and original DO models below.
9.3 Transition Probabilities in the finite Demkov-Osherov model

9.3.1 The propagator

In order to obtain simpler formulas for the probabilities we assume that \( t_i = -T \), \( t_f = T \), although our approach is not limited to these restrictions. The transition probability from state \( \psi_m \) to \( \psi_n \) is given by \( P_{m \rightarrow n} = |U_{nm}(T, -T)|^2 \), where

\[
U_{nm}(T, -T) = \sum_{k,l=1}^{3} f_{nk}(T)U_{kl}^A(T, -T)f_{ml}(-T).
\] (9.26)

Using this relation one can calculate the transition probability between any two states of the system. We pay special attention to the probability for counterintuitive transitions \( P_{3 \rightarrow 1} \), which is zero in the original DO model.

9.3.2 Counterintuitive transition

In the special case of equal couplings, \( \Omega_{12} = \Omega_{23} \equiv \Omega \), we find from Eqs. (9.24), (9.26) and (A.1.6) that the transition probability \( P_{3 \rightarrow 1} = |U_{13}(T, -T)|^2 \) reads

\[
P_{3 \rightarrow 1} = |pf_{11}^2 + qf_{12}^2 - 2\sqrt{pq}f_{11}f_{12}\cos[\Lambda_{12}(T, \tau) + \phi]$
\[
+2\sqrt{pq}f_{12}f_{13}\cos[\Lambda_2(T, \tau) - \Lambda_3(T, -\tau)]$
\[
+2\sqrt{pq}f_{11}f_{13}\cos[\Lambda_1(T, -T) + \phi]|^2.
\] (9.27)

It can be written as

\[
P_{3 \rightarrow 1} = \overline{P}_{3 \rightarrow 1} + \widetilde{P}_{3 \rightarrow 1},
\] (9.28)

where \( \overline{P}_{3 \rightarrow 1} \) is the average probability and \( \widetilde{P}_{3 \rightarrow 1} \) is the oscillating part. By using the asymptotic expansions (A.0.3) for \( f_{mn} \) in Appendix A and keeping the leading terms in the expansion over \( 1/T \) we find

\[
\overline{P}_{3 \rightarrow 1} = (pf_{11}^2 + qf_{12}^2)^2 + 2(qf_{11}^2 + pf_{12}^2)f_{13}^2 + 2pqf_{11}f_{12}^2
\]
\[
\sim \frac{\Omega^2(\Omega^2p + 4\delta^2q)}{2\delta^2\beta^2T^2} + \frac{\Omega^2(\Omega^4p - 8\delta^4q)}{2\delta^3\beta^3T^3} + \ldots,
\] (9.29a)
9.3. Transition Probabilities in the finite Demkov-Osherov model

\[ \overline{P_{3\to1}} \sim \frac{\Omega^2}{\beta^2T^2} \left\{ 4q \cos^2[\Lambda_1(T, -T) + \phi] \right. \\
+ \frac{p\Omega^2}{\delta^2} \cos^2 [\Lambda_2(T, \tau) - \Lambda_3(T, -\tau)] \\
- \frac{4\sqrt{pq}\Omega}{\delta} \cos[\Lambda_1(T, -T) + \phi] \\
\times \cos [\Lambda_2(T, \tau) - \Lambda_3(T, -\tau)] \right\} + \ldots \quad (9.30) \]

For unequal couplings \((\Omega_{12} \neq \Omega_{23})\), the expansion over \(1/T\) of the average probability reads

\[ \overline{P_{3\to1}} \sim \frac{\Omega_{12}^2\Omega_{23}^2(p_- + p_+)}{4\delta^2\beta^2T^2} + \frac{\Omega_{12}^2\Omega_{23}^2(p_- + 2\delta q_+ + \Omega_{23}^2 q_-)}{4\delta^3\beta^3T^3} + \ldots \quad (9.31) \]

The part \(\overline{P_{3\to1}}\) is too cumbersome to be presented here.

In the near-adiabatic regime \((\alpha \gg 1, p \ll 1, q \approx 1, \text{and} \ \phi \ll 1)\), we find from Eq. (9.27) that

\[ P_{3\to1} \sim \frac{4\Omega^2}{\beta^2T^2} \cos^2[\Lambda_1(T, -T) + \phi]. \quad (9.32) \]

In the weak-coupling limit \((\alpha \ll 1, p \approx 1, q \ll 1, \text{and} \ \phi \approx \pi/4)\), we find from Eq. (9.27) that

\[ P_{3\to1} \sim \frac{\Omega^4}{\delta^2\beta^2T^2} \cos^2 [\Lambda_2(T, \tau) - \Lambda_3(T, -\tau)]. \quad (9.33) \]

Figure 9.3 shows the counterintuitive transition probability \(P_{3\to1}\) against the coupling duration \(T\). The probability decreases in an oscillatory manner, as predicted by our results. The analytical approximation (9.27) describes very accurately both the phase and the amplitude of the oscillations. The approximation (9.29) describes very accurately also the average probability \(\overline{P_{3\to1}}\).

Fig. 9.4 displays the counterintuitive transition probability \(P_{3\to1}\) as a function of the energy separation parameter \(\delta\). As with \(T\), the probability decreases in an oscillatory manner. The analytical approximations are seen again to describe the probability very accurately.

9.3.3 Other transition probabilities

By using Eq. (9.26) we can find all transition probabilities \(P_{m\to n} = |U_{nm}(T, -T)|^2\) \((m, n = 1, 2, 3)\). For the sake of simplicity we assume again that \(t_i = -T, t_f = T\)
9.3. Transition Probabilities in the finite Demkov-Osherov model

Figure 9.3: (Color online) Probability for counterintuitive transition $P_{3 \rightarrow 1}$ plotted against the coupling duration $T$ for interaction parameters $\Omega_{12} = \Omega_{23} = \beta^{\frac{1}{2}}$, $\delta = \beta^{\frac{1}{2}}$. The full line shows numerical results, the thin dashed curve the analytical approximation (9.27) and the thick dashed curve the average probability (9.29).

and $\Omega_{12} = \Omega_{23} \equiv \Omega$, although our approach applies to the general non-symmetric case as well. Using Eq. (9.24) we find the average probabilities expanded to the lowest order of $1/T$,

$$
\overline{P}_{1 \rightarrow 1} \sim p + \frac{\Omega^2}{\beta^2 T^2} [x^2(q^2 - 2p) + 1 - 2p - p^2],
$$

(9.34a)

$$
\overline{P}_{1 \rightarrow 2} \sim pq + \frac{\Omega^2}{\beta^2 T^2} (x^2 q^2 + 1 - 6p + 7p^2),
$$

(9.34b)

$$
\overline{P}_{1 \rightarrow 3} \sim q^2 + \frac{2\Omega^2}{\beta^2 T^2} [x^2(p - q^2) + 3pq - q],
$$

(9.34c)

$$
\overline{P}_{2 \rightarrow 1} \sim q + \frac{\Omega^2}{\beta^2 T^2} (p^2 + 4p - 3 - x^2 q^2),
$$

(9.34d)

$$
\overline{P}_{2 \rightarrow 2} \sim p^2 + \frac{2\Omega^2}{\beta^2 T^2} (1 + p - 4 p^2),
$$

(9.34e)

$$
\overline{P}_{2 \rightarrow 3} \sim pq + \frac{\Omega^2}{\beta^2 T^2} (x^2 q^2 + 1 - 6p + 7p^2),
$$

(9.34f)

$$
\overline{P}_{3 \rightarrow 1} \sim \frac{2\Omega^2}{\beta^2 T^2} (x^2 p + q),
$$

(9.34g)

$$
\overline{P}_{3 \rightarrow 2} \sim q + \frac{\Omega^2}{\beta^2 T^2} (p^2 + 4p - 3 - x^2 q^2),
$$

(9.34h)

$$
\overline{P}_{3 \rightarrow 3} \sim p + \frac{\Omega^2}{\beta^2 T^2} [x^2(q^2 - 2p) + 1 - 2p - p^2],
$$

(9.34i)


Figure 9.4: (Color online) Probability for counterintuitive transition $P_{3\rightarrow1}$ plotted against the energy splitting parameter $\delta$. The other interaction parameters are $\Omega_{12} = \Omega_{23} = \beta^{\frac{1}{2}}$, $T = 5\beta^{\frac{1}{2}}$. The full line shows numerical results, the thin dashed curve the analytical approximation (9.27) and the thick dashed curve the average probability (9.29).

where $\kappa^2 = \Omega^2/4\delta^2$. All these probabilities have the correct DO limits (9.5) for $T \rightarrow \infty$. Note that $P_{1\rightarrow1} \sim P_{3\rightarrow3}$, $P_{1\rightarrow2} \sim P_{2\rightarrow3}$, and $P_{2\rightarrow1} \sim P_{3\rightarrow2}$.

9.4 Time evolution in the original Demkov-Osherov model

In the original DO model the time-dependent transition probability from state $\psi_m$ to $\psi_n$ is given by $P_{m\rightarrow n}(t) = |U_{nm}(t, -\infty)|^2$. We find from Eq. (9.25) for $t_i = -\infty$, $t_f = t$ that

$$U_{nm}(t, -\infty) = \sum_{k,l=1}^{3} f_{nk}(t) U_{kl}^A(t, -\infty) f_{ml}(-\infty), \quad (9.35)$$

and we take into account that

$$F(-\infty) = \begin{bmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}. \quad (9.36)$$
9.4. Time evolution in the original Demkov-Osherov model

9.4.1 Counterintuitive transition

By using Eq. (9.35) we find that the probability of counterintuitive transition $P_{3 \rightarrow 1}$ after the crossings reads

$$P_{3 \rightarrow 1}(t) = |\sqrt{q_+}f_{11}(t) + \sqrt{p_+}f_{12}(t)e^{i(A_{12}(t,\tau)+\phi_+)}|^2$$

(9.37a)

$$= P_{3 \rightarrow 1}(t) + \tilde{P}_{3 \rightarrow 1}(t)$$

(9.37b)

where

$$P_{3 \rightarrow 1}(t) = q_+f_{11}^2 + p_+f_{12}^2,$$

(9.38a)

$$\sim \frac{\Omega_{12}^2 (4\delta^2 q_+ + \Omega_{23}^2 p_+)}{4\delta^2 \beta^2 t^2},$$

(9.38b)

$$\tilde{P}_{3 \rightarrow 1}(t) = 2\sqrt{p_+}q_+ f_{11}f_{12} \cos[A_{12}(t,\tau) + \phi_+],$$

(9.39a)

$$\sim -\frac{\Omega_{12}^2 \Omega_{23}}{\delta \beta^2 t^2} \sqrt{p_+ q_+} \cos[A_{12}(t,\tau) + \phi_+].$$

(9.39b)

Figure 9.5 shows the time evolution of the probability for counterintuitive transition $P_{3 \rightarrow 1}$ for three values of the couplings $\Omega_{12} = \Omega_{23} \equiv \Omega$. For these values of $\Omega$ there are almost no oscillations visible, because $p_+ \ll 1$ in Eq. (9.39b). The probability $P_{3 \rightarrow 1}(t)$ decreases with time, as predicted by Eq. (9.38), and vanishes for large times towards the DO result $P_{3 \rightarrow 1}(\infty) = 0$. As predicted, the transition probability $P_{3 \rightarrow 1}(t)$ increases with the couplings. The analytical approximation (9.38) describes very accurately the average probability $\overline{P}_{3 \rightarrow 1}(t)$.

9.4.2 Other transition probabilities

By using Eq. (9.35) and the large-$t$ asymptotic expansions in Appendix A, we find the leading terms of all average transition probabilities $\overline{P}_{m \rightarrow n}(t)$ after the crossings.
9.5 Experimental implementations

for equal couplings ($\Omega_{12} = \Omega_{23} \equiv \Omega$),

\begin{align*}
P_{1\to1}(t) & \sim p + \frac{\Omega^2}{\beta^2 t^2} \left[ \kappa^2 (q^2 - \frac{p}{\Omega}) - \frac{p^2}{\Omega^2} \right], \\
P_{1\to2}(t) & \sim \frac{pq}{\beta^2 t^2} (1 - 3pq), \\
P_{1\to3}(t) & \sim q^2 + \frac{\Omega^2}{\beta^2 t^2} \left[ q (p - q) + \kappa^2 (p - q^2) \right], \\
P_{2\to1}(t) & \sim q + \frac{\Omega^2}{\beta^2 t^2} \left( p^2 - q - \kappa^2 q^2 \right), \\
P_{2\to2}(t) & \sim p^2 + \frac{\Omega^2}{\beta^2 t^2} (1 - 3p^2), \\
P_{2\to3}(t) & \sim pq + \frac{\Omega^2}{\beta^2 t^2} \left[ p(p - q) + \kappa^2 q^2 \right], \\
P_{3\to1}(t) & \sim \frac{\Omega^2}{\beta^2 t^2} \left( \kappa^2 p + q \right), \\
P_{3\to2}(t) & \sim q + \frac{\Omega^2}{\beta^2 t^2} (p - 2q), \\
P_{3\to3}(t) & \sim p + \frac{\Omega^2}{\beta^2 t^2} \left( q - p - \kappa^2 p \right),
\end{align*}

where, as before, $\kappa^2 = \frac{\Omega^2}{4\beta^2}$. All these probabilities have the correct DO limits (9.5) for $t \to \infty$. It is interesting to note that the counterintuitive-transition probability in the original DO model (9.40g) is one-half of the one in the finite DO model (9.34g).

9.5 Experimental implementations

This three-state DO model discussed here can be realized in several physical systems. One example is when a chirped laser pulse couples an initially populated state to a manifold of two levels simultaneously [78], the energy diagram for which is identical to the one in Fig. 9.1, with state $\psi_2$ being the initial state. Adiabatic evolution can produce in this system a very selective excitation even if the Fourier bandwidth of the laser pulse is larger than the level spacing within the manifold. Indeed, for red-to-blue chirp ($\beta > 0$) the system will follow from left to right the lowest adiabatic energy, which links the initial state $\psi_2$ to the lowest diabatic (unperturbed) state $\psi_1$ of the manifold. In contrast, for blue-to-red chirp ($\beta < 0$) the system would follow (from right to left in Fig. 9.1) the highest adiabatic energy, linking state $\psi_2$ to the highest diabatic state $\psi_3$. Therefore, the chirp sign alone determines if
9.5. Experimental implementations

Figure 9.5: (Color online) Time evolution of the probability for counterintuitive transition $P_{3 \to 1}$ in the original DO model ($t_i = -\infty$) for $\delta = \beta^{1/2}$ and three values of the couplings, $\Omega_{12} = \Omega_{23} = \beta^{1/2}$, $3\beta^{1/2}$, and $10\beta^{1/2}$ (denoted near the respective curves). The solid curves show numerical results and the dots show the analytical approximation (9.38) for the average probability.

The population is directed towards the lowest or the highest state of the manifold. This excitation scheme has been demonstrated experimentally by Warren and co-workers [52] on the $3s-3p$ transition in sodium. Red-to-blue chirped picosecond pulses populated predominantly the lower fine-structure level $3p^2P_{1/2}$, while blue-to-red chirped pulses placed the population onto the upper fine-structure level $3p^2P_{3/2}$. Counterintuitive transitions can be demonstrated in this system by using the same setup as described above, but starting in one of the fine-structure levels.

Another example of the model discussed here is Stark-chirped rapid adiabatic passage (SCRAP) [53–55] where level crossings are created by inducing ac Stark shifts of the energy levels by a strong off-resonant laser pulse. A level diagram similar to the one in Fig. 9.1 is found in the three-state version of SCRAP [55].

It is also worth noting a similarity between the finite DO model presented here and multiple-ground-state models of optical shielding of cold collisions in magneto-optical atom traps [56–60]. Optical shielding techniques were originally developed to prevent laser cooled atoms from escaping the trap by making the collisions between the atoms elastic [57]. The experiments show that the shielding process saturates, in
contrast to the expected complete shielding, when the intensity of the shielding field is increased [57]. The reason for the saturation is still an open problem and may have a connection to the counterintuitive transitions in the corresponding multiple-ground-state level scheme of the quasimolecule, which in its simple form resembles the present model.
Chapter 10

Population trapping in three-state quantum loops revealed by Householder reflections

In chapter 4 and 8 we show how a MS and extend MS transformation can reduce the many state quantum system to an effective two and three state systems. Unfortunately for a loop systems MS transformation do not hold, but luckily an alternative transformation exist- Householder reflection. In this chapter we show that in a three-state loop linkage, a Hilbert-space Householder reflection breaks the loop and presents the linkage as a single chain. With certain conditions on the interaction parameters, this chain can break into a simple two-state system and an additional spectator state (dark state). Alternatively, a two-photon resonance condition in this Householder-basis chain can be enforced, which heralds the existence of another spectator state. These spectator states generalize the usual dark state to include contributions from all three bare basis states and disclose hidden population trapping effects, and hence hidden constants of motion. Insofar as a spectator state simplifies the overall dynamics, its existence facilitates the derivation of analytic solutions and the design of recipes for quantum state engineering in the loop system. Moreover, it is shown that a suitable sequence of Householder transformations can cast an arbitrary $N$-dimensional hermitian Hamiltonian into a tridiagonal form. The implication is that a general $N$-state system, with arbitrary linkage patterns where each state connects to any other state, can be reduced to an equivalent chainwise-connected system, with nearest-neighbor interactions only,
with ensuing possibilities for discovering hidden multidimensional spectator states and constants of motion.


10.1 Introduction

Descriptions of optical excitation of few-state quantum systems traditionally make use of the rotating-wave approximation (RWA), in which the Hilbert-space unit vectors (the bare quantum states) rotate with angular velocities that are fixed at various laser carrier frequencies, and the Hamiltonian, with the neglect of rapidly varying terms, becomes a matrix of slowly varying Rabi frequencies and detunings [2,3]. For three states the usual electric-dipole selection rules of optical transitions produce a simple chain of inter-state linkages, depicted as either a ladder, a lambda or a vee.

For some time it has been known that, either by means of a rotation of the arbitrary quantization axis for defining magnetic sublevels, or by more general reorganization of the Hilbert-state basis states (a Morris-Shore transformation [8]), such patterns can be presented as a set of independent two-state excitations (bright states) together with spectator states that are unaffected by the specific radiation (dark states or spectator states).

The presence of a third interaction, linking the two states that terminate the three-state chain, turns the linkage pattern into a loop, see Fig. 10.1. Such interaction would violate the usual selection rules for electric-dipole radiation (which connects only states of opposite parity), but is possible for a variety of other interactions, such as occur with two-photon optical transitions or microwave transitions between hyperfine states. To avoid the presence of rapidly varying exponential phases in the RWA Hamiltonian, such a link should occur with carrier frequency suitably chosen.

Within the RWA there is no longer a distinction of the original bare-state energies; all that matters is the detunings, i.e. differences between a Bohr frequency and the associated laser-field carrier frequency. Nonetheless, it is traditional, when
10.1. Introduction

Figure 10.1: (Color online) RWA linkage pattern for a loop, showing linkages: states 1 and 2 by Rabi frequency $\Omega_P$, states 2 and 3 by $\Omega_S$ and states 1 and 3 by $\Omega_C$. The energy levels are shown with an ordering appropriate to state $\psi_1$ as ground state and state $\psi_2$ as excited state, but the symmetry of the loop linkage allows initial population in any state.

depicting the linkage pattern of laser-induced interactions, to place representations of the states in a vertical direction ranked according to the original bare-state energies, and to consider excitation in which the initial population resides entirely in a ground state. Such display convention is particularly useful in emphasizing the difference between low-energy stable or metastable states, unable to radioactively decay, and excited states, from which spontaneous emission is possible – visible as fluorescence.

The three-state loop is the simplest example of discrete quantum states that can exhibit nontrivial probability-amplitude interferences, and hence it has attracted continuing interest [61–71].

With the loop pattern it is not immediately obvious that any simple restructuring of the Hilbert-space coordinates will produce a single unit vector that is immune to the effects of any interaction – a spectator state. For example, the loop system does not satisfy an essential condition for the MS transformation [8], namely that the quantum states be classified in two sets, with transitions only between the sets, not within them.

A special case of the three-state loop was considered by Carroll and Hioe [63]. They presented analytical solutions for the probability amplitudes when three resonant laser pulses of different shapes were present and two of the couplings where
real, while the third was purely imaginary. For this special case, the underlying SU(2) symmetry allows the three-state loop to be reduced to an effective two-state system.

Another fully resonant three-state loop was examined by Unanyan et al. [67]. In that work a pulsed quasistatic magnetic field supplemented the two optical pulses of a lambda linkage used for stimulated Raman adiabatic passage (STIRAP) [10]. This additional field provided a supplement to the usual adiabatic constraints and allowed a reduction of diabatic loss, thereby improving the usual adiabatic constraints on achieving complete population transfer.

The three-state loop was examined also by Fleischhauer et al. [68]. They showed that when each link was resonant, the dark state of STIRAP [10] could be modified to a higher-order trapping state, becoming an approximate constant of motion even for small pulse areas. This state adiabatically rotates, in Hilbert space, from the initial to the target state. This adiabatic motion leads to efficient population transfer, though at the expense of placing some population into the decaying atomic state.

Recently a three-state loop was shown to occur in physical processes where the free-space symmetry is broken, as it is in chiral systems [69, 70]. Such quantum systems occur in left- and right-handed chiral molecules [69], or in “artificial atoms”. Loop linkages amongst discrete quantum states can also occur in superconducting quantum circuits [70], and in modelling entangled atoms coupled through an optical cavity [71].

We here consider loops that have less stringent constraints on the frequencies, although some do exist. We shall show in the following that it is possible, under appropriate conditions (including three-photon resonance), to break the loop into a chain. A further transformation of the basis states can then convert the linkage pattern into a pair of coupled states and a spectator state. Alternatively, if the population resides initially in the middle state of the chain, the system has the dynamics of the vee linkage.

The required initial transformation, converting the loop into a simple chain, is taken to be a Householder reflection (HR) of the Hamiltonian matrix [72]. Such matrix manipulations, commonplace in works dealing with linear algebra [73], have recently been applied to quantum-state manipulations [13, 74–76].
produces an upper-diagonal (or lower-diagonal) matrix. When acting upon a unitary matrix, such a sequence produces a diagonal matrix, with phase factors on the diagonal. This property has been used for decomposition, and therefore synthesis, of arbitrary preselected propagators in multistate systems [13,74–76]. We show here that, when utilized for a change of basis in Hilbert space, a suitable HR (or a sequence of HRs) can cast a (hermitian) Hamiltonian into a tridiagonal form. This tridiagonalization implies the replacement of a general linkage pattern (for example, each state interacting with any other state) with an effective chainwise-connected system where only nearest-neighbour interactions are present. We here apply this tridiagonalization to the simplest nontrivial multistate system – a three-state loop system – and demonstrate its potential applications, with examples ranging from effective chain breaking and novel spectator states to hidden two-photon resonances.

10.2 The loop RWA Hamiltonian

We consider three fields, labelled pump ($P$), Stokes ($S$), and control ($C$),

\[ E_k(t) = \mathbf{e}_k \mathcal{E}_k(t) \cos(\omega_k t + \phi_k), \quad (k = P, S, C). \]

(10.1)

The three carrier frequencies $\omega_k$ can be chosen arbitrarily, so long as they fulfill the three-photon resonance condition (Fig. 10.1)

\[ \omega_C - \omega_P + \omega_S = 0. \]

(10.2)

This constraint is necessary for the application of the rotating-wave approximation (RWA) [2,3]. However, at the outset we impose no constraints on the single-photon detunings,

\[ \hbar \Delta_P \equiv E_2 - E_1 - \hbar \omega_P, \quad \hbar \Delta_S \equiv E_2 - E_3 - \hbar \omega_S. \]

(10.3)

We introduce probability amplitudes $C_n(t)$ in the usual rotating Hilbert-space coordinates $\psi_n(t)$,

\[ \Psi(t) = \exp(-i\zeta_0 t) \left[ C_1(t)\psi_1 + C_2(t)\psi_2(t) + C_3(t)\psi_3(t) \right], \]

(10.4)

where the rotations originate with field carrier frequencies, $\psi_2(t) \equiv \exp(-i\omega_P t)\psi_2$ and $\psi_3(t) \equiv \exp(-i\omega_C t)\psi_3$. From the time-dependent Schrödinger equation we obtain three coupled equations

\[ i \frac{d}{dt} \mathbf{C}(t) = \mathbf{H}(t) \mathbf{C}(t), \]

(10.5)
where $C(t) \equiv [C_1(t), C_2(t), C_3(t)]^T$ is a three-component column vector of probability amplitudes and $\hbar H(t)$ is the slowly varying RWA Hamiltonian. We take the overall phase factor $\zeta_0$ to nullify the first diagonal element of the RWA Hamiltonian matrix; it then has the structure

$$
H(t) = \frac{1}{2} \begin{bmatrix}
0 & \Omega_P(t)e^{i\phi_P} & \Omega_C(t) \\
\Omega_P(t)e^{-i\phi_P} & 2\Delta_2 & \Omega_S(t)e^{i\phi_S} \\
\Omega_C(t) & \Omega_S(t)e^{-i\phi_S} & 2\Delta_3
\end{bmatrix},
$$

where the interactions are parameterized by slowly varying real-valued Rabi frequencies $\Omega_k(t)$, for $k = P, S, C$. For simplicity and without loss of generality the $C$ field is assumed real ($\phi_C = 0$); then $\phi_P$ and $\phi_S$ represent the phase differences between the $P$ and $S$ fields, respectively, and the $C$ field. The cumulative detunings are

$$
\Delta_2 = \Delta_P, \quad \Delta_3 = \Delta_P - \Delta_S.
$$

### 10.3 The Householder reflection

We seek a unitary transformation of the Hilbert-space basis states that will first replace the loop with a three-state chain. As we will show, the desired result can be produced by a Householder reflection acting upon the RWA Hamiltonian [74].

An $N$-dimensional Householder reflection is defined as the operator

$$
R = I - 2|v\rangle \langle v|,
$$

where $I$ is the identity operator and $|v\rangle$ is an $N$-dimensional normalized complex column vector. The Householder operator $R$ is Hermitian and unitary, $R = R^{-1} = R^\dagger$, hence $R$ is involutary, $R^2 = I$. The transformation is a reflection, so $\det R = -1$. If the vector $|v\rangle$ is real, the Householder reflection has a simple geometric interpretation: it is a reflection with respect to an $(N-1)$-dimensional plane normal to the vector $|v\rangle$.

The Householder reflection, acting upon an arbitrary $N$-dimensional matrix, uses $N - 1$ operations to produce an upper or lower triangular matrix. This behavior makes the Householder reflection a powerful tool for many applications in classical data analysis, e.g., in solving systems of linear algebraic equations, finding eigenvalues of high-dimensional matrices, least-squares optimization, QR decomposition,
etc. [73]. For us, the reflection serves to transform the Hamiltonian from a full matrix to one that lacks one interaction – it breaks the loop into a chain.

The three-state system offers three basis vectors with which to define a Householder reflection. Because of the symmetry of the loop system it is only necessary to consider one of these; the effect of others can be examined by a permutation of state labels. We shall take state $\psi_1$ as a fixed coordinate, within the plane of the reflection, and introduce an alteration of the Hilbert subspace spanned by the remaining unit vectors $\psi_2(t)$ and $\psi_3(t)$. Figure 10.2 illustrates the connection of the reflection with the basis states, and the possible choices of initial state.

![Figure 10.2: (Color online) The Householder reflection leaves state $\psi_1$ unchanged. Initial population might be (a) in this state, or (b) in one of the altered states. Relative energies of the original bare states are not relevant, only the couplings.](image)

With this choice the Householder vector reads

$$|v\rangle = \begin{bmatrix} 0, \sin(\theta/2)e^{-i\phi_P}, \cos(\theta/2) \end{bmatrix}^T,$$

and the matrix representation of the Householder reflection is

$$R = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & e^{-i\phi_P} \sin \theta \\ 0 & e^{i\phi_P} \sin \theta & -\cos \theta \end{bmatrix}. \quad (10.10)$$

The angle $\theta$, defined by the equation

$$\tan \theta \equiv \frac{\Omega_C}{\Omega_P}, \quad (10.11)$$

is twice the angle from the mirror normal to state $\psi_2$ (i.e. the twist of the mirror about the $\psi_1$ axis). Hereafter we omit explicit mention of time dependences; all
Rabi frequencies are to be considered slowly varying in time, as is the Householder reflection $R$ and the angle $\theta$.

The connection between the probability amplitudes $\tilde{C}$ in the Householder basis and the amplitudes $C$ in the original (bare) basis is

$$\tilde{C} = RC.$$ (10.12)

The transformed equation of motion reads

$$\frac{d}{dt} \tilde{C} = -i\tilde{H}\tilde{C},$$ (10.13)

where the Householder Hamiltonian is $\tilde{H} = RHR - iR\dot{R}$, with an overdot denoting a time derivative. Explicitly,

$$\tilde{H} = \frac{1}{2} \begin{bmatrix} 0 & \tilde{\Omega}_P & 0 \\ \tilde{\Omega}_P & 2\Delta_2 & \tilde{\Omega}_S - 2ie^{-i\phi_p}\dot{\theta} \\ 0 & \tilde{\Omega}_S + 2ie^{i\phi_p}\dot{\theta} & 2\Delta_3 \end{bmatrix},$$ (10.14)

with effective detunings

$$\Delta_2 = \frac{\Delta_3\Omega_C^2 + \Delta_2\Omega_P^2 + \Omega_P\Omega_C\Omega_S \cos (\phi_P + \phi_S)}{\Omega^2},$$ (10.15a)

$$\Delta_3 = \frac{\Delta_2\Omega_C^2 + \Delta_3\Omega_P^2 - \Omega_P\Omega_C\Omega_S \cos (\phi_P + \phi_S)}{\Omega^2},$$ (10.15b)

and effective couplings

$$\tilde{\Omega}_P = e^{i\phi_p}\Omega,$$ (10.16a)

$$\tilde{\Omega}_S = \frac{1}{\Omega^2} \left[ 2e^{-i\phi_P} (\Delta_2 - \Delta_3) \Omega_P\Omega_C \\ + \left(e^{-2i(\phi_P + \phi_S)}\Omega_C^2 - \Omega_P^2\right) e^{i\phi_S}\Omega_S \right],$$ (10.16b)

with $\Omega \equiv \sqrt{\Omega_P^2 + \Omega_C^2}$. All of these elements acquire time dependence from the pulses, though that is not shown explicitly.

The Hamiltonian in the Householder basis is that of a simple chain, $\psi_1 \leftrightarrow \tilde{\psi}_2 \leftrightarrow \tilde{\psi}_3$. By design the Householder reflection places the original two interactions of state $\psi_1$ into a single effective interaction with a new superposition state $\tilde{\psi}_2$. This state, in turn, has an interaction with the other terminal state of the chain $\tilde{\psi}_3$, also a superposition state. The new Householder states $\tilde{\psi}_n$ are superpositions of the original basis states $\psi_n$,

$$\tilde{\psi}_1 = \psi_1,$$ (10.17a)

$$\tilde{\psi}_2 = \cos \theta \psi_2 + e^{-i\phi_P} \sin \theta \psi_3,$$ (10.17b)

$$\tilde{\psi}_3 = e^{i\phi_P} \sin \theta \psi_2 - \cos \theta \psi_3.$$ (10.17c)
When the initial population resides entirely in state $\psi_1$, this chain is equivalent to a lambda or ladder system. When the initial population occurs in state $\tilde{\psi}_2$ it is a generalization of the vee linkage. The chain Hamiltonian (10.14) in the Householder representation is conceptually simpler than the original loop Hamiltonian (10.6) for it allows only for nearest-neighbour interactions; the resulting chain linkage is easier to understand and treat analytically by a variety of exact or approximate approaches. The inherent interference in the loop system is now imprinted onto the Householder transformation and is absent in the Householder chain. Moreover, this transformation allows one to use the considerable literature available on chainwise-connected three-state systems.

10.4 Special cases

In the remainder of this paper we consider special cases of the Householder Hamiltonian, obtained when we constrain the various pulse parameters, which lead to simplification of the resulting Hamiltonian matrix. Two simplifications are particularly interesting: (i) breaking the three-state Householder chain $\psi_1 \leftrightarrow \tilde{\psi}_2 \leftrightarrow \tilde{\psi}_3$ into a two-state system and a spectator state, and (ii) two-photon resonance in the Householder basis. We shall identify conditions, and deduce implications, for these important special cases.

10.4.1 Effective two-state system and spectator state

Under appropriate conditions the three-state Householder chain $\psi_1 \leftrightarrow \tilde{\psi}_2 \leftrightarrow \tilde{\psi}_3$ breaks into two coupled states and a spectator state. This occurs whenever one of the Householder linkages vanishes. The vanishing of $\tilde{\Omega}_P$ requires that both $\Omega_P$ and $\Omega_C$ vanish, which is trivial and uninteresting. We hence assume the null linkage to be the coupling between states $\tilde{\psi}_2$ and $\tilde{\psi}_3$,

$$\tilde{\Omega}_S + 2ie^{-i\phi_P}\dot{\theta} = 0.$$ (10.18)

Under this condition state $\tilde{\psi}_3$, Eq. (10.17c), decouples from the other two states and becomes a spectator state: its population is trapped, within a subspace of the full Hilbert space. The population distribution between states $\psi_2$ and $\psi_3$ may change, but in a manner that conserves the population of the spectator state (10.17c).
10.4. Special cases

Conditions for chain breaking

One possible solution to Eq. (10.18) reads

\[ \Delta_2 = \Delta_3, \quad \phi_P = -\phi_S - \frac{\pi}{2}, \quad \Omega_S = -2\dot{\theta}. \] (10.19a, b, c)

The latter condition imposes a strict constraint on the pulse shape. Given \( \Omega_P \) and \( \Omega_C \), which determine \( \dot{\theta} \) through Eq. (10.11), condition (10.19c) determines both the shape and the magnitude of \( \Omega_S \).

Another possible solution to Eq. (10.18) emerges when the \( P \) and \( C \) pulses have the same time dependence, say \( f(t) \), \( \Omega_P(t) = \Omega_{P0} f(t) \), \( \Omega_C(t) = \Omega_{C0} f(t) \), while the \( S \) pulse could differ, \( \Omega_S(t) = \Omega_{S0} g(t) \). Then \( \dot{\theta} = 0 \) and condition (10.18) becomes \( \tilde{\Omega}_S = 0 \). This condition can be satisfied in several ways, cf. Eq. (10.16b). A simple realization for that condition occurs with the choice

\[ \Delta_2 = \Delta_3, \quad \phi_P = -\phi_S, \quad \Omega_C = \Omega_P. \] (10.20a, b, c)

Then \( \theta = \pi/4 \) and the spectator state reads

\[ \tilde{\psi}_3 = \frac{1}{\sqrt{2}} \left( e^{-i\phi_S} \psi_2 - \psi_3 \right). \] (10.21)

Analytical three-state solutions

The dynamics of the two coupled Householder states \( \psi_1 \) and \( \tilde{\psi}_2 \), coupled by the interaction \( \tilde{\Omega}_P \), offer other interesting possibilities. For the two-state system \( \psi_1 \leftrightarrow \tilde{\psi}_2 \), analytic solutions may be possible; these are known for many examples of pulse and detuning time dependences. Hence, by writing down the propagator in the Householder basis for a known two-state analytical solution, and by using the transformation back to the original basis by the Householder reflection \( R(t) \), one can write down a number of analytic solutions for the three-state loop system. These would generalize the similar analytical solutions for a \( \Lambda \) system [77].
Population initially in state $\psi_1$

If only state $\psi_1$ is initially populated then the dynamics remains confined within the effective two-state system $\psi_1 \leftrightarrow \tilde{\psi}_2$. In this two-state system we can enforce complete population return to state $\psi_1$, complete population inversion to state $\tilde{\psi}_2$ or create a superposition of states $\psi_1$ and $\tilde{\psi}_2$.

Complete population transfer from state $\psi_1$ to the Householder state $\tilde{\psi}_2$ can be produced by a resonant $\pi$-pulse [2], by adiabatic level-crossing adiabatic passage [78], or by a variety of novel more sophisticated techniques [31, 79–81]. Viewed in the original basis, the system ends up in a superposition of $\psi_2$ and $\psi_3$,

$$\cos \theta \psi_2 + e^{-i\phi_P} \sin \theta \psi_3,$$

(10.22)

with the angle $\theta$ given by (10.11); thus the superposition is fully controlled by the ratio of $\Omega_C$ and $\Omega_P$ and has a relative phase $\phi_P$.

A predetermined superposition of states $\psi_1$ and $\tilde{\psi}_2$ can be created by resonant fractional-$\pi$ pulses, or by modifications of adiabatic-passage techniques, for example, half-SCRAP [42] and two-state STIRAP [82]. Such techniques allow, for instance, the creation of an arbitrary predetermined maximally coherent superposition of the three states $\psi_1$, $\psi_2$, and $\psi_3$. For example, one can create a maximally coherent superposition using fractional-$\pi$ pulses that obey conditions (10.20) and which are resonant in the Householder basis ($\Delta_2(t) = \Delta_3(t) = -\Omega_S(t)/2$). Such an example is demonstrated in Fig. 10.3. For example, as illustrated in Fig. 10.4, one can use fractional-$\pi$ pulses to create an equal superposition of states $\psi_1$, $\psi_2$ and $\psi_3$.

Population initially in state $\psi_2$

Let us assume now that it is state $\psi_2$ that is populated initially. (The symmetric case of state $\psi_3$ initially populated is just a matter of relabelling the states.) If the $C$ pulse precedes the $P$ pulse, then we are in the dark state (10.17c) and this is a situation similar to STIRAP, then there will occur complete population transfer to state $\psi_3$. The resonant case of this process was discussed and explained earlier [67,68]. If we are in state $\psi_2$ and we apply the pulse in the intuitive order (the $P$ pulse precedes the $C$ pulse), then we are in the bright state and depending on the pulses we can have complete population transfer to state $\psi_1$, or end up in a superposition of states $\psi_1$, $\psi_2$ and $\psi_3$. 
Figure 10.3: (Color online) Creation of an equal superposition of states $\psi_1$, $\psi_2$ and $\psi_3$ for Gaussian pulses: $\Omega_P(t) = \Omega_{P0} e^{-t^2/T^2}$, $\Omega_C(t) = \Omega_{C0} e^{-t^2/T^2}$, $\Delta_2(t) = \Delta_3(t) = -\Omega_S(t)/2$, $\Omega_S(t) = \Omega_{S0} e^{-(t-\tau)^2/T^2}$, with the following parameters $\Omega_{P0} = \Omega_{C0} = 0.76/T$, $\Omega_{S0} = 1/T$, $\tau = 0.5T$.

Figure 10.4: (Color online) Creation of an equal superposition of states $\psi_1$, $\psi_2$ and $\psi_3$ for Gaussian pulses: $\Omega_P(t) = \Omega_0 e^{-(t+\tau)^2/T^2} + \Omega_0 \cos \alpha e^{-(t-\tau)^2/T^2}$, $\Omega_C(t) = \Omega_0 \sin \alpha e^{-(t-\tau)^2/T^2}$, $\Delta_2(t) = \Delta_3(t) = 0$, $\Omega_S(t) = -2\dot{\theta}$, with the following parameters $\alpha = \pi/4$, $\Omega_0 = 0.567/T$, $\tau = 0.5T$. 

10.4. Special cases

10.4.2 Effective two-photon resonance

We assume now that the $P$ and $C$ pulses have the same time dependence and consider a resonance condition between states $\psi_1$ and $\tilde{\psi}_3$,

$$\tilde{\Delta}_3 = 0. \quad (10.23)$$

The resulting Householder Hamiltonian is exactly that of the lambda linkage on two-photon resonance used for STIRAP [10]. The traditional dark state of the STIRAP process appears here as

$$\Phi_D = \cos \varphi \psi_1 - \sin \varphi \tilde{\psi}_3 = \cos \varphi \psi_1 - e^{i\varphi P} \sin \varphi \sin \theta \psi_2 + \sin \varphi \cos \theta \psi_3, \quad (10.24)$$

where $\tan \varphi = \tilde{\Omega}_P / \tilde{\Omega}_S$. The state $\Phi_D$ is a spectator (or population-trapping) state because it is not affected by the specified radiation, but it has components of all three of the original basis states. One can use this new kind of spectator state, with the traditional STIRAP pulse sequence of $\tilde{\Omega}_S$ preceding $\tilde{\Omega}_P$, to move the initial population from state $\psi_1$ to a superposition of state $\tilde{\psi}_2$ and state $\tilde{\psi}_3$. The superposition is controlled by the ratio of $\Omega_C$ and $\Omega_P$ and has the phase $\varphi_P$.

Condition (10.23) can always be satisfied for an appropriate choice of the (time-dependent) detuning $\Delta_2(t)$ [or $\Delta_3(t)$]. However, the specific time dependence, although possible in principle, might be complicated and difficult to produce experimentally. Condition (10.23) can be satisfied with constant detunings when the $P$ and $C$ pulses share the same time dependence: $\Omega_P(t) = \Omega_P f(t)$ and $\Omega_C(t) = \Omega_C f(t)$. Then the mixing angle $\theta$ is constant [see Eq. (10.11)] and $\dot{\theta} = 0$. Two options provide the needed pulses:

(i) The conditions

$$\phi_P + \phi_S = \pi/2, \quad \Delta_3 = -\Delta_2 \frac{\Omega_C^2}{\Omega_P^2} \quad (10.25a)$$

hold. Then the $S$ field can be arbitrary and both detunings $\Delta_2$ and $\Delta_3$ can be constant.

(ii) The $S$ field is constant. Then condition (10.23) can be fulfilled for constant detunings that obey the relation

$$\Delta_3 = -\Delta_2 \frac{\Omega_C^2}{\Omega_P^2} + \frac{\Omega_C}{\Omega_P} \Omega_S \cos(\phi_P + \phi_S). \quad (10.26)$$
Therefore, the usual two-photon resonance condition, necessary for the emergence of a spectator (dark) state in the original basis, is replaced by a condition for the two-photon detuning $\Delta_3$: either (i) Eq. (10.25b), for arbitrary $S$ field but with the phase relation (10.25a), or (ii) Eq. (10.26), for constant $S$ field.

If we now start initially in state $\psi_1$ and apply the $S$ pulse before the $P$ pulse, then the following superposition is formed

$$-ie^{-i\phi_S} \sin \theta \psi_2 + \cos \theta \psi_3. \quad (10.27)$$

The superposition characteristics are fixed by the $S$-field phase and the angle $\theta$ defined by Eq. (10.11). Figure 10.5 illustrates how, starting in state $\psi_1$ and applying the $S$ pulse before the $P$ pulse we obtain an equal superposition of $\psi_2$ and $\psi_3$.

![Figure 10.5: (Color online) Creation of an equal superposition of states $\psi_2$ and $\psi_3$, with the following couplings and detunings: $\Omega_P(t) = \Omega_0 \cos \theta e^{-(t-\tau)^2/T^2}$, $\Omega_C(t) = \Omega_0 \sin \theta e^{-(t-\tau)^2/T^2}$, $\Omega_S(t) = \Omega_0 e^{-(t+\tau)^2/T^2}$, $\Delta_2(t) = \Delta_3(t) = 0$, where the parameters are $\theta = \pi/4$, $\Omega_0 = 30/T$, $\tau = 0.5T$.](image-url)

### 10.5 Reduction of $N$-dimensional quantum systems to chains

The Householder transformation introduced here for a three-state loop system is readily extended to a general $N$-state quantum system with arbitrary linkages, even
in the most general case when each state connects to any other state. A suitable sequence of at most \( N - 2 \) Householder transformations can cast the Hamiltonian, which is a hermitian matrix, into a \textit{tridiagonal} form. In this sequence the Householder vector for the \( n \)th reflection is chosen as

\[
|v_n\rangle = \frac{|x_n\rangle - |x_n\rangle |e_{n+1}\rangle}{||x_n\rangle - |x_n\rangle |e_{n+1}\rangle||},
\]

where \( |e_{n+1}\rangle \) is a unit vector that defines the \((n + 1)\)-st axis, i.e. its components are zero except a unity at the \((n + 1)\)st place, Here \(|x_n\rangle\) is the \(n\)th column vector of the transformed Hamiltonian after the \(n\)th step.

The tridiagonalization of the Hamiltonian implies that in the Householder basis, each of the new basis states is connected only to its nearest neighbor states, thus forming a \textit{chainwise} linkage pattern. The chain is conceptually simpler, and analytically easier, to treat, with a variety of exact and approximate approaches available in the literature.
Chapter 11

Conclusions

This thesis investigated the problem of manipulation of two and three quantum state systems.

This problem of two and three state quantum systems is interesting by itself both physically and mathematically: physically, because the two state and the three state quantum system are the simplest nontrivial systems with discrete energy states in quantum mechanics; mathematically, because the equation for the two states and three state poses interesting mathematical challenges for the two state case some are exactly solvable, for the three state case some are exactly solvable, while other are solvable with some assumptions and approximations. Furthermore, already in the two-state case, important nonclassical phenomena occur, for instance, the famous Rabi oscillations, which often serve as a test for quantum behaviour, and also provide a powerful tool for coherent control of quantum dynamics, e.g. by $\pi$ pulses. Finally, in almost all cases (except for a few exactly soluble), the behaviour of a multistate quantum system can only be understood by reduction to one or more effective two and three state systems, e.g., by adiabatic elimination of weakly coupled states or by using some intrinsic symmetries.

The structure of this thesis was organized as follows: In Chapter 1 a brief summary of the historical background of the subsequent discussions of adiabatic-transfer schemes was given. In Chapter 2 the general mathematical principles needed to describe coherent excitation and adiabatic time evolution of quantum systems was developed. In Chapter 3 the main two-state adiabatic technics were presented. In Chapter 4 Morris-Shore transformation was introduced and its extension to multi-level ladders was investigated in Chapter 8. In Chapters 5, 6 and 7 the three state
adiabatic techniques were presented such as Stimulated Raman Adiabatic Passage (STIRAP), Stimulated Raman adiabatic passage into continuum and Stark-shift-chirped rapid-adiabatic-passage technique among three states. In Chapter 9 counterintuitive transitions between crossing energy levels was present. In Chapter 10 an alternative and powerful transformation (Householder reflections) to Morris-Shore transformation was described and an example of how useful this transformation could be was given with three state loop system.
Appendix A

Asymptotics of the eigenvalues and the eigenstates

Here we present the asymptotics of the eigenvalues (9.8) at large positive time \( t > 0 \), i.e. for \( \beta t \gg \delta \) and \( \beta t \gg \Omega \). Then \( a = -\beta t \), \( b = -(\delta^2 + \Omega_{12}^2 + \Omega_{23}^2) \), \( c = \delta^2 \beta t [1 + (\Omega_{12}^2 - \Omega_{23}^2)/ (\delta \beta t)] \), and

\[
\begin{align*}
    s &\sim \beta t + \frac{3 (\delta^2 + \Omega_{12}^2 + \Omega_{23}^2)}{2 \beta t}, \quad (A.0.1a) \\
    \cos \theta &\sim 1 - \frac{27 \delta^2}{2 \beta^2 t^2}, \quad (A.0.1b) \\
    \theta &\sim \frac{3 \sqrt{3} \delta}{\beta t}. \quad (A.0.1c)
\end{align*}
\]

The eigenvalues have the asymptotics

\[
\begin{align*}
    \lambda_1 &\sim \beta t + \frac{\Omega_{12}^2 + \Omega_{23}^2}{\beta t}, \quad (A.0.2a) \\
    \lambda_2 &\sim \delta - \frac{\Omega_{23}^2}{\beta t}, \quad (A.0.2b) \\
    \lambda_3 &\sim -\delta - \frac{\Omega_{12}^2}{\beta t}. \quad (A.0.2c)
\end{align*}
\]

Hence we find from Eqs. (9.10) that

\[
\begin{align*}
    \phi_1 &\sim \left[ \frac{\Omega_{12}}{\beta t}, 1 - \frac{\Omega_{12}^2 + \Omega_{23}^2}{2 \beta^2 t^2}, \frac{\Omega_{23}}{\beta t} \right]^T, \quad (A.0.3a) \\
    \phi_2 &\sim \left[ -\frac{\Omega_{12} \Omega_{23}}{2 \delta \beta t}, -\frac{\Omega_{23}}{\beta t}, 1 - \frac{\Omega_{23}^2 (\Omega_{12}^2 + 4 \delta^2)}{8 \delta^2 \beta^2 t^2} \right]^T, \quad (A.0.3b) \\
    \phi_3 &\sim \left[ -1 + \frac{\Omega_{12}^2 (\Omega_{23}^2 + 4 \delta^2)}{8 \delta^2 \beta^2 t^2}, \frac{\Omega_{12}}{\beta t}, -\frac{\Omega_{12} \Omega_{23}}{\beta t} \right]^T. \quad (A.0.3c)
\end{align*}
\]
A.1 Symmetries of the eigenvalues and the eigenstates

The eigenvalues and the eigenstates simplify when \( t_i = -T, \ t_f = T \) and \( \Omega_{12} = \Omega_{23} \equiv \Omega \). Then \( \alpha_+ = \alpha_- \equiv \alpha, \ p_+ = p_- \equiv p, \ q_+ = q_- \equiv q = 1 - p, \ a(T) = -\beta T, \ b(T) = -\delta^2 - 2\Omega^2, \ c(T) = \delta^2 \beta T, \) and

\[
\begin{align*}
s(T) &= \sqrt{\beta^2 T^2 + 3\delta^2 + 6\Omega^2}, \quad \text{(A.1.4a)} \\
\cos \theta(T) &= \frac{\beta T}{s^3}(\beta^2 T^2 - 9\delta^2 + 9\Omega^2). \quad \text{(A.1.4b)}
\end{align*}
\]

Hence \( \theta(-T) = \pi - \theta(T) \) and therefore \( \lambda_1(-T) = -\lambda_3(T), \ \lambda_2(-T) = -\lambda_2(T), \ \lambda_3(-T) = -\lambda_1(T), \) and

\[
\begin{align*}
\Lambda_2(-\tau,-T) &= \Lambda_2(\tau,T) = -\Lambda_2(T,\tau), \quad \text{(A.1.5a)} \\
\Lambda_2(T,-T) &= \Lambda_2(\tau,-\tau) = 0, \quad \text{(A.1.5b)} \\
\Lambda_1(-\tau,-T) &= \Lambda_3(\tau,T) = -\Lambda_3(T,\tau), \quad \text{(A.1.5c)} \\
\Lambda_3(-\tau,-T) &= \Lambda_1(\tau,T) = -\Lambda_1(T,\tau). \quad \text{(A.1.5d)}
\end{align*}
\]

The transformation matrix at \( -T \) is given by

\[
F(-T) = \begin{bmatrix}
-f_{33}(T) & -f_{32}(T) & -f_{31}(T) \\
f_{23}(T) & f_{22}(T) & f_{21}(T) \\
-f_{13}(T) & -f_{12}(T) & -f_{11}(T)
\end{bmatrix} \quad \text{(A.1.6)}
\]

With these relations taken into account the propagator (9.23) reduces to Eq. (9.24).
Bibliography


Publication of the author used for the dissertation


Participated Internationals conferences, schools and workshops

B1  2003 July, 35th Meeting of the European Group for Atomic Systems (EGAS 35), Brussels, Belgium. (poster contribution)


B3  2006 July, 20th International Conference on Atomic Physics, ICAP Innsbruck, Austria. (poster contribution)

B4  2006 July, Atomic, Molecular, and Optical (AMO) International summer school, Innsbruck, Austria.

B5  2007 June, Central European Workshop on Quantum Optics, Palermo, Italy. (oral contribution)
B6 2007 September, EMALI school ”Basic concepts and physical systems: paving the ground”  Kaiserslautern, Germany.

B7 2007 October, annual meeting of EMALI, Heraklion, Greece. (oral contribution)