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Control of quantum dynamics by laser pulses: Adiabatic Floquet theory

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We present in a self-contained way a set of theoretical tools that allow us to analyze the quantum dynamics of atoms and molecules driven by laser pulses and to determine pulse designs that lead to specific effects. In particular, we discuss processes to control the internal excitation of states, like electronic states or vibrational and rotational states of molecules. We describe the Floquet formalism, and we show how it can be used to establish the relation between the semiclassical model and a quantized representation that allows us to describe explicitly the exchange of photons. We also describe an approach to perturbation theory that is based on applying unitary transformations that reduce the size of the coupling terms. The main ideas of adiabatic dynamics, combined with the Floquet approach, are also discussed. We describe how the possible transfers of population by adiabatic passage are determined by the topology of the eigenenergy surfaces defined by varying the parameters of the pulses. Finally, we describe a more elaborate application of the method to state selectivity by bichromatic pulses in two- and three-level systems.

Keywords: Adiabatic dynamics, Floquet dressed states, quantum KAM theory, effective Hamiltonians, coherent control, molecular processes.

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I. INTRODUCTION

The development of laser sources yielding pulses of high intensity and short duration has opened up possibilities to manipulate atoms and molecules with high precision. The aim of this article is to present in a self-contained way a set of theoretical tools that allow to analyze the quantum dynamics of atoms or molecules driven by laser pulses, and to determine pulse designs that lead to specific effects. In particular we will discuss processes to control the internal excitation of states, like electronic states or vibrational and rotational states of molecules. Many of the tools apply indifferently to atoms or molecules; often we will use one or the other term interchangeably. The idea is to design the characteristics of the laser pulse in such a way that if initially the molecule is in a given state, at the end of the pulse the population will be completely transferred to a selected target state. The parameters of a single pulse that can be designed are the peak intensity, the shape of the pulse envelope, the carrier frequency and the chirp, which is a slow variation of the carrier frequency during the pulse. Furthermore one can use sequences of two or several pulses of different characteristics, acting simultaneously or with a well-defined delay. An important condition for the successful implementation of a control process is that it should be robust with respect to variations or imprecisions in the values of the parameters. For instance, the usual resonant π -pulse technique is not robust for a complete transfer, since it is achieved only for precise values of the total pulse area that interacts with the molecule, which is very difficult to fix in an experimental setup. A different type of techniques that yields much more robust results is based on adiabatic passage. The analysis that we present here yields an explanation of the principles on which this robustness is based.

The models for the control processes start with the Schrödinger equation for the molecule in interaction with a laser field that is either treated as a classical or as a quantized electromagnetic field. In Section II we describe the Floquet formalism, and show how it can be used to establish the relation between the semi-classical model and a quantized representation that allows to describe explicitly the exchange of photons. The molecule in interaction with the photon field is described by a time independent Floquet Hamiltonian, which is essentially equivalent to the time dependent semi-classical Hamiltonian. The analysis of the effect of the coupling with the field can thus be done by methods of stationary perturbation theory, instead of the time-dependent one used in the semi-classical description. In Section III we describe an approach to perturbation theory that is based on applying unitary transformations that simplify the problem. The method is an iterative construction of unitary transformations that reduce the size of the coupling terms. This procedure allows to detect in a simple way dynamical or field induced resonances, i.e. resonances that appear only beyond a threshold of the field amplitudes. If resonances are present, the simple perturbative approach is not enough to capture the relevant effects. It can be however improved by performing a different kind of unitary transformations, that are non-perturbative and are specifically adapted to the relevant resonances. This can be interpreted as a generalization of rotating wave transformations to strong coupling regimes. The method of iterative unitary transformations can furthermore be adapted to the construction of effective models by partitioning of degrees of freedom. The idea is to simplify the problem by determining the most relevant subspace in Hilbert space and to construct a simplified Hamiltonian in which the coupling with the complement subspace is reduced by suitably chosen unitary transformations.

In Section IV we describe the main ideas of adiabatic dynamics and combine it with the Floquet approach. The essential idea is that if some parameters like the pulse envelope or the frequency vary sufficiently slowly compared with the other characteristic times of the system, the time evolution will follow instantaneous eigenstates of the Floquet Hamiltonian. The analysis of adiabatic dynamics is thus reduced to the determination of eigenvalues and eigenvectors of Floquet Hamiltonians, as a function of the parameters of the pulse. In Section V we describe how the possible transfers of population by adiabatic passage are determined by the topology of the eigenenergy surfaces defined by varying the parameters of the pulses. The topology is in turn determined by resonances and quasi-resonances. This topological aspect is the basis of the robustness of the adiabatic transfer. An important conclusion of this analysis is that in the adiabatic regime the final result of the process is determined almost exclusively by the resonances of the Floquet Hamiltonian. The perturbative corrections lead only to small deformations of the path in Hilbert space that is followed while the pulse is in interaction, but they do not change the target state that is reached at the end.

The different aspects of this approach are illustrated with some simple examples in the corresponding sections. In Section VI we describe a more elaborate application of the method to state selectivity by bichromatic pulses in two and three level systems. The appendices contain some mathematical complements.

II. FLOQUET THEORY

We will discuss the Floquet approach from two different points of view. In the first one, discussed in section II A, the Floquet formalism is just a mathematically convenient tool that allows to transform the Schrödinger equation with a time-dependent Hamiltonian into an equivalent equation with a time-independent Hamiltonian. This new equation is defined on an enlarged Hilbert space. The time dependence has been substituted by the introduction

of one auxiliary dynamical variable for each laser frequency. The second point of view, described in Section II B, consists of constructing the Floquet representation starting from a model in which both the molecule and the field are quantized.

The initial photon state can be a number state (with a not well defined phase) or a linear combination of number states, for instance a coherent state. We formulate the construction of coherent states in the Floquet theory and show that choosing one as the initial photon state allows to recover the usual semi-classical time dependent Schrödinger equation, with a classical field of a well defined phase (see Section II C).

This Floquet approach provides a physical interpretation of the dynamics in terms of photons in interaction with the molecule, which is in close analogy to the theory of dressed states in a cavity (see Section II D).

The formalism is developed for the case of an interacting field of a single frequency. It can be easily extended to the multifrequency case as shown in Section II E.

A. Floquet formalism from the semi-classical point of view

In the semi-classical model the molecule is treated quantum mechanically whereas the field is represented classically. The field is an externally given function of time F that is not affected by any feedback from the interaction with the molecule. We consider the simplest case of a dipole coupling. The formalism is easily extended to other types of couplings. The time dependence of the periodic Hamiltonian is introduced through the time evolution of the initial phase: $F = F(\theta + \omega t) = \mathcal{E} \cos(\theta + \omega t)$ [1–6], where \mathcal{E} is the amplitude of the electric field and ω its frequency. The semiclassical Hamiltonian can be e.g. written as

$$H = H(x, \theta + \omega t) = H_0(x) - \mu(x)\mathcal{E} \cos(\theta + \omega t), \quad (1)$$

where x symbolizes the degrees of freedom of the atom or molecule, $\mu(x)$ is its dipole moment and $H_0(x)$ the Hamiltonian of the free molecule. The semi-classical Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \phi = H(x, \theta + \omega t) \phi, \quad \phi \in \mathcal{H} \quad (2)$$

is defined on a Hilbert space \mathcal{H} , which can be of infinite dimension (e.g. the space of square-integrable functions $\mathcal{H} = L_2(\mathbb{R}^n, d^n x)$, where n is the number of the degrees of freedom of the molecule) or of finite dimension (e.g. in N -level models $\mathcal{H} = \mathbb{C}^N$). The initial phase θ appears as a parameter. One can think of Eq. (2) as a family of equations parametrized by the angle θ . We denote the corresponding family of propagators by $U(t, t_0; \theta)$, which describe the time evolution of arbitrary initial conditions $\phi(t_0)$:

$$\phi(t) = U(t, t_0; \theta)\phi(t_0), \quad (3)$$

and satisfy

$$i\hbar \frac{\partial}{\partial t} U(t, t_0; \theta) = H(\theta + \omega t) U(t, t_0; \theta), \quad U(t, t; \theta) = \mathbb{1}_{\mathcal{H}}. \quad (4)$$

The Floquet Hamiltonian K , also called quasienergy operator, is constructed as follows: We define an enlarged Hilbert space

$$\mathcal{K} := \mathcal{H} \otimes \mathcal{L}, \quad (5)$$

where $\mathcal{L} := L_2(\mathbb{S}^1, d\theta/2\pi)$ denotes the space of square integrable functions on the circle \mathbb{S}^1 of length 2π , with a scalar product

$$\langle \xi_1 | \xi_2 \rangle_{\mathcal{L}} := \int_{\mathbb{S}^1} \frac{d\theta}{2\pi} \xi_1^*(\theta) \xi_2(\theta). \quad (6)$$

This space is generated by the orthonormal basis $\{e^{ik\theta}\}$, $k \in \mathbb{Z}$ (i.e. all integers). On the enlarged Hilbert space \mathcal{K} the Floquet Hamiltonian is defined as

$$K = -i\hbar\omega \frac{\partial}{\partial \theta} + H(\theta). \quad (7)$$

In this expression $H(\theta)$ is just the semiclassical Hamiltonian (1) but with the phase $\theta + \omega t$ taken at the (fixed) initial value θ corresponding to $t = 0$. The usefulness of the Floquet Hamiltonian comes from the fact that it is

time independent and that the dynamics it defines on \mathcal{K} is essentially equivalent with the one of (2). This can be formulated as follows. The Floquet Hamiltonian K defines a time evolution in \mathcal{K} through the equation

$$i\hbar\frac{\partial}{\partial t}\psi = K\psi, \quad \psi \in \mathcal{K} = \mathcal{H} \otimes \mathcal{L}. \quad (8)$$

This time evolution can be expressed in terms of a propagator $U_K(t, t_0)$ characterized by

$$i\hbar\frac{\partial}{\partial t}U_K(t, t_0) = KU_K(t, t_0), \quad U_K(t, t) = \mathbb{1}_{\mathcal{K}}, \quad (9)$$

i.e. $\psi(t) = U_K(t, t_0)\psi(t_0)$, (where $\mathbb{1}_{\mathcal{K}}$ is the identity operator in \mathcal{K}). Since K is time independent, the propagator can be written as

$$U_K(t, t_0, \theta) = U_K(t - t_0, \theta) = e^{-iK(t-t_0)/\hbar}. \quad (10)$$

In order to establish a relation between U and U_K we define the following phase translation operator $\mathcal{T}_{\omega t}$ which acts on $\xi \in \mathcal{L}$, by

$$\mathcal{T}_{\omega t}\xi(\theta) = \xi(\theta + \omega t) \quad (11)$$

and can be expressed as

$$\mathcal{T}_{\omega t} = e^{\omega t \partial / \partial \theta}. \quad (12)$$

We first lift the family of operators $U(t, t_0; \theta)$ (defined on \mathcal{H}) into an operator acting on the enlarged space \mathcal{K} by treating the dependence on θ as a multiplication operator. This operator is unitary in \mathcal{K} . The relation between U and U_K can then be expressed by

$$\mathcal{T}_{-\omega t}U(t, t_0; \theta)\mathcal{T}_{\omega t_0} = U_K(t - t_0, \theta) \equiv e^{-iK(t-t_0)/\hbar} \quad (13)$$

The proof of this relation is given in Appendix VIB 3. It implies that if $\psi(t, x, \theta)$ is a solution of (8) then we can obtain a solution of (2) by $\phi(t, x) = \mathcal{T}_{\omega t}\psi(t, x, \theta) = \psi(t, x, \theta + \omega t)$.

The fact that K is time independent opens the possibility to work with eigenfunction expansions. We consider the case in which K has pure point spectrum, i.e. no continuum. This is always the case for N-level models with periodic time dependent fields. Further remarks on other cases are given in Appendix VIB 3.

First we lift the initial condition $\phi(t_0)$ for (2) to the enlarged space \mathcal{K} by taking $\phi(t_0) \otimes \mathbb{1}_{\mathcal{L}}$. This form reflects the fact that the initial condition is the same for the whole family of equations (2), i.e. it does not depend on the phase θ . With the eigenvalues and eigenvectors of

$$K\psi_{\nu} = \lambda_{\nu}\psi_{\nu}, \quad (14)$$

using the inverse of (13), the time evolution can be expressed by the eigenfunction expansion

$$\begin{aligned} \phi(t) &= U(t, t_0; \theta)\phi(t_0) \\ &= \mathcal{T}_{\omega t}e^{-iK(t-t_0)/\hbar}\mathcal{T}_{-\omega t_0}\phi(t_0) \otimes \mathbb{1}_{\mathcal{L}} \\ &= \sum_{\nu} c_{\nu}e^{-i\lambda_{\nu}(t-t_0)/\hbar}\psi_{\nu}(x, \theta + \omega t), \end{aligned} \quad (15)$$

where the coefficients c_{ν} are determined by the scalar product

$$c_{\nu} = \langle \psi_{\nu}, \phi(t_0) \otimes \mathbb{1} \rangle_{\mathcal{K}} = \langle \bar{\psi}_{\nu}, \phi(t_0) \otimes \mathbb{1} \rangle_{\mathcal{H}}, \quad (16)$$

where the subindices \mathcal{K} and \mathcal{H} specify to which space the scalar product corresponds, and $\bar{\psi}_{\nu} := \int_{\mathbb{S}^1} d\theta/2\pi \psi_{\nu}(\theta)$ is the average of $\psi_{\nu}(\theta)$ over the phase, or equivalently, its constant Fourier component.

Thus, the determination of the Floquet eigenvectors and eigenvalues allows to solve the dynamics of the semiclassical model.

The Floquet eigenlements have a periodic structure: $\psi_{\nu} \equiv \psi_{n,k} = \psi_{n,0}e^{ik\theta}$ and $\lambda_{\nu} \equiv \lambda_{n,k} = \lambda_{n,0} + k\hbar\omega$, where the index n refers to the molecule's Hilbert space \mathcal{H} (i.e. $n = 1, \dots, N$ if $\mathcal{H} = \mathbb{C}^N$), and k are all positive or negative integers. This allows to classify the Floquet eigenstates in families labeled by n . The individual members within one family are distinguished by the index k .

The eigenfunction expansion can be simplified using only one representative of each family (e.g. the one with $k = 0$):

$$\phi(t) = \sum_n \tilde{c}_n(\theta) e^{-i\lambda_{n,0}(t-t_0)/\hbar} \psi_{n,0}(x, \theta + \omega t) \quad (17)$$

with

$$\tilde{c}_n(\theta) := \langle \psi_{n,0}(\theta), \phi(t_0) \rangle_{\mathcal{H}} \quad (18)$$

The coefficients $\tilde{c}_n(\theta + \omega t)$ are functions of θ , and become thus time dependent.

B. Floquet formalism from quantized cavity dressed states

Although in the semi-classical model the only dynamical variables are those of the molecule, and that the extended Hilbert space $\mathcal{K} = \mathcal{H} \otimes \mathcal{L}$ and the Floquet Hamiltonian K can be thought as only mathematically convenient techniques to analyse the dynamics, it was clear from the first work of Shirley [1] that the enlarged Hilbert space should be related to photons. This relation was made explicit by Bialynicki-Birula [7, 8] and completed in [9]. The construction starts with a quantized photon field in a cavity of finite volume in interaction with the molecule. The limit of infinite volume with constant photon density leads to the Floquet Hamiltonian, which describes the interaction of the molecule with a quantized laser field propagating in free space. The construction presented below is taken from [9], where further details and mathematical precisions can be found.

We consider a quantized photon field in a cavity of volume V , of single frequency ω and polarized in the \vec{e} direction, described by the Hamiltonian H_L , in interaction with a molecule characterized by the Hamiltonian H_M . For simplicity we consider the simplest situation of a dipole interaction described by the Hamiltonian [10, 11]

$$H_{ML} = H_M + H_L + H_{\text{int}} \quad (19)$$

with

$$H_L = \hbar\omega a^\dagger a, \quad (20a)$$

$$H_{\text{int}} = -\mu \otimes \mathcal{E}_V (a + a^\dagger), \quad (20b)$$

and $\mu = \vec{\mu} \cdot \vec{e}$, where $\vec{\mu}$ is the dipole moment of the molecule. The mode of the laser with frequency ω is described by the number operator of a harmonic oscillator, which can be expressed in terms of the annihilation and creation operators a, a^\dagger . They act on the Fock space \mathcal{F} generated by the stationary states $|n\rangle$, $n = 0, 1, 2, \dots$ of the harmonic oscillator. The coupling constant is given by

$$\mathcal{E}_V = \sqrt{\frac{\hbar\omega}{2\varepsilon_0 V}}, \quad (21)$$

where ε_0 is the permeability of the vacuum. The states of the coupled system evolve in the Hilbert space

$$\mathcal{H}_{ML} = \mathcal{H} \otimes \mathcal{F}, \quad (22)$$

where we call \mathcal{H} the Hilbert space of the molecule and \mathcal{F} the Hilbert space of the photons.

We will establish a precise relation between dressed states in a cavity and the Floquet formalism. We show that the Floquet Hamiltonian K can be obtained exactly from the dressed Hamiltonian in a cavity in the limit of infinite cavity volume and large number of photons: K represents *the Hamiltonian of the molecule interacting in free space with a field containing a large number of photons*. We establish the physical interpretation of the operator

$$N_r = -i \frac{\partial}{\partial \theta} \quad (23)$$

in the limit of large number of photons as the *relative photon number operator*. It characterizes the relative photon number of the field with respect to the average \bar{n} . The variation of the average of N_r in the Floquet formalism gives the number of photons gained or lost (depending on the sign) by the field.

We remark that, with the cavity dressed state model (19), the field intensity does not appear explicitly. It depends on the average number of photons contained in the initial state of the field. The connection between this model and the Floquet formulation is given by the following property: Since the radiation is not confined in a cavity, but propagates and interacts with the molecule in free space, we have to take the limit

$V \rightarrow \infty$ (infinite cavity volume),
 $\bar{n} \rightarrow \infty$ (large photon number average),
 $\rho = \bar{n}/V = \text{const}$ (constant photon density).

In this limit, the Hamiltonian H_{ML} is identical, up to an additive constant, to the Floquet Hamiltonian K

$$H_{\text{ML}} - \hbar\omega\bar{n} \longrightarrow -i\hbar\omega\frac{\partial}{\partial\theta} + H_0 - \mu\mathcal{E}\cos\theta \equiv K, \quad (24)$$

where

$$\mathcal{E} = \sqrt{\frac{2\rho\hbar\omega}{\varepsilon_0}}. \quad (25)$$

To show this relation, we use the phase representation of H_{LM} , as formulated by Bialynicki-Birula [7, 8, 12, 13]. We construct an isomorphism between the Fock space and the space $\mathcal{L}_{\bar{n},\theta}$ defined as a subspace of $\mathcal{L} = L_2(\mathbb{S}^1, \frac{d\theta}{2\pi})$, generated by the basis functions $\{|e^{ik\theta}\rangle; -\bar{n} \leq k < +\infty\}$:

$$|n\rangle \in \mathcal{F} \quad \longleftrightarrow \quad |e^{ik\theta}\rangle \in \mathcal{L}_{\bar{n},\theta} \text{ with } \bar{n} + k = n, \quad \text{i.e. } k \in [-\bar{n}, \infty). \quad (26)$$

In the limit $\bar{n} \rightarrow \infty$ we obtain the whole space

$$\mathcal{L}_{\bar{n},\theta} \xrightarrow{\bar{n} \rightarrow \infty} \mathcal{L}, \quad \text{and} \quad \mathcal{H}_{\text{LM}} \xrightarrow{\bar{n} \rightarrow \infty} \mathcal{K} = \mathcal{H} \otimes \mathcal{L}. \quad (27)$$

By this isomorphism, the creation, annihilation and photon number operators (a^\dagger , a and N) have a corresponding representation acting on $\mathcal{L}_{\bar{n},\theta}$, which we denote respectively $a_{\bar{n},\theta}^\dagger$, $a_{\bar{n},\theta}$ and $N_{\bar{n},\theta}$:

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle \quad \longleftrightarrow \quad a_{\bar{n},\theta}^\dagger = \sqrt{\bar{n} - i\frac{\partial}{\partial\theta}} e^{i\theta} P_{\bar{n}}, \quad (28a)$$

$$a |n\rangle = \sqrt{n} |n-1\rangle \quad \longleftrightarrow \quad a_{\bar{n},\theta} = e^{-i\theta} \sqrt{\bar{n} - i\frac{\partial}{\partial\theta}} P_{\bar{n}}, \quad (28b)$$

$$N |n\rangle = a^\dagger a |n\rangle = n |n\rangle \quad \longleftrightarrow \quad N_{\bar{n},\theta} = \left(\bar{n} - i\frac{\partial}{\partial\theta}\right) P_{\bar{n}}, \quad (28c)$$

where $P_{\bar{n}} = \sum_{k=-\bar{n}}^{\infty} |e^{ik\theta}\rangle \langle e^{ik\theta}|$ is the projector on $\mathcal{L}_{\bar{n},\theta}$. The operator in the coupling term becomes

$$a_{\bar{n},\theta} + a_{\bar{n},\theta}^\dagger = P_{\bar{n}} \left(e^{-i\theta} \sqrt{\bar{n} - i\frac{\partial}{\partial\theta}} + \sqrt{\bar{n} - i\frac{\partial}{\partial\theta}} e^{i\theta} \right) P_{\bar{n}}, \quad (29)$$

and the Hamiltonian reads

$$H_{\text{LM}}^{(\bar{n})} = H_0(x) \otimes P_{\bar{n}} + \mathbb{1}_{\mathcal{H}} \otimes \hbar\omega N_{\bar{n},\theta} - \mu(x) \otimes \mathcal{E}_V \left(a_{\bar{n},\theta} + a_{\bar{n},\theta}^\dagger \right). \quad (30)$$

We remark that this is an exact correspondence, which is just a precise expression of Dirac's transformation formalism of quantum mechanics [14, 15]. The explicit writing of the projector $P_{\bar{n}}$ in (28) is motivated by the fact that in this way the operators $H_0(x) \otimes P_{\bar{n}}$, $N_{\bar{n},\theta}$, $a_{\bar{n},\theta}$, $a_{\bar{n},\theta}^\dagger$ and $H_{\text{LM}}^{(\bar{n})}$ are also well defined in the total space $\mathcal{L} = L_2(\mathbb{S}^1, d\theta/2\pi)$, and the discussion of the limit $\bar{n} \rightarrow \infty$ becomes conceptually clearer.

In [7, 8] the formal hypothesis

$$-i\frac{\partial}{\partial\theta} \ll \bar{n} \quad (31)$$

is invoked to approximate

$$\sqrt{\bar{n} - i\frac{\partial}{\partial\theta}} = \sqrt{\bar{n}} \sqrt{1 - \frac{i}{\bar{n}} \frac{\partial}{\partial\theta}} = \sqrt{\bar{n}} + \mathcal{O}\left(\frac{1}{\sqrt{\bar{n}}}\right),$$

which leads to

$$(a_{\bar{n},\theta} + a_{\bar{n},\theta}^\dagger)/\sqrt{\bar{n}} \xrightarrow{\bar{n} \rightarrow \infty} (e^{-i\theta} + e^{i\theta}) = 2 \cos \theta. \quad (32)$$

In the limit $V \rightarrow \infty$, $\bar{n} \rightarrow \infty$, keeping the photon density $\rho = \bar{n}/V$ constant, we obtain the interaction term

$$\mathcal{E}_V (a_{\bar{n},\theta} + a_{\bar{n},\theta}^\dagger) \longrightarrow \sqrt{\frac{2\rho\hbar\omega}{\varepsilon_0}} \cos \theta. \quad (33)$$

Introducing the laser intensity per unit surface I

$$I = \frac{1}{2}\varepsilon_0 c \mathcal{E}^2 = \hbar\omega\Phi_{\text{ph}} \quad (34)$$

with the photon velocity c , the field amplitude \mathcal{E} and the photon flow $\Phi_{\text{ph}} = \bar{n}c/V$, allows to identify the interaction constant of equation (33) with \mathcal{E} of Eq. (24) as $\mathcal{E} = \sqrt{2\rho\hbar\omega/\varepsilon_0}$. We obtain thus the Floquet Hamiltonian K of equation (24).

The formal hypothesis (31) must be interpreted in relation with the functions on which $-i\partial/\partial\theta$ acts. The statement is that if all the states $\{|e^{ik\theta}\rangle\}$ that are relevant in the dynamics are such that $|k| \ll \bar{n}$, i.e. if only few photons are exchanged between light and matter compared to the average photon number \bar{n} contained in the laser field, then *the coupled Hamiltonian $H_{\text{LM}}^{(\bar{n})}$ can be identified with the Floquet Hamiltonian K .*

One can give a more precise formulation of this construction, based on the dynamics of the coupled system. Since $H_{\text{LM}}^{(\bar{n})}$ and K are both well defined on $\mathcal{H} \otimes \mathcal{L}$, we can compare the time evolutions generated by the two Hamiltonians of any initial state $\psi_0 \in \mathcal{H} \otimes \mathcal{L}$: *For N -level models ($\mathcal{H} = \mathbb{C}^N$), given any initial state $\psi_0 \in \mathcal{H} \otimes \mathcal{L}$, the limit of the cavity dressed state dynamics is identical to the Floquet dynamics:*

$$\lim_{\substack{V, \bar{n} \rightarrow \infty \\ V/\bar{n} = \rho}} e^{-i(H_{\text{LM}}^{(\bar{n})}/\hbar - \bar{n}\omega)t} \psi_0 = e^{-iKt/\hbar} \psi_0. \quad (35)$$

The proof of this statement is given in [9].

C. Connection with the semiclassical formulation: interaction representation and coherent states

From the formulation of the Floquet formalism given above, we can establish the precise connection between the dynamics in the enlarged space \mathcal{K} defined by the Floquet Hamiltonian K , and the one defined by the semiclassical Hamiltonian in \mathcal{H} with a classical description of the electric field:

The Schrödinger equation of the Floquet Hamiltonian in \mathcal{K} , where θ is a dynamical variable, is equivalent, in an interaction representation, to the semiclassical Schrödinger equation in \mathcal{H} , where θ is considered as a parameter corresponding to the fixed initial phase. The dynamics of the two models are identical if the initial photon state in the Floquet model is a coherent state.

1. Interaction representation

The Schrödinger equation of the Floquet Hamiltonian in \mathcal{K}

$$i\hbar \frac{\partial}{\partial t} \psi(t) = K \psi(t) \quad (36)$$

can be expressed equivalently in an interaction representation defined by the unitary transformation

$$\phi(t) = U_{0r}^\dagger(t) \psi(t), \quad (37)$$

where

$$U_{0r}(t) = e^{-\omega t \partial/\partial \theta} \equiv \mathcal{T}_{-\omega t} \quad (38)$$

is the free photon field propagator, which is just the translation operator (12) used in the Floquet construction of Section II A. Using equation (13), we obtain

$$\begin{aligned} \phi(t) &= \mathcal{T}_{\omega t} \psi(t) = \mathcal{T}_{\omega t} U_K(t - t_0, \theta) \mathcal{T}_{-\omega t_0} \phi(t_0) \\ &= U(t, t_0; \theta) \phi(t_0), \end{aligned}$$

and the evolution equation in this representation becomes

$$i\hbar \frac{\partial}{\partial t} \phi(t) = H(\theta + \omega t) \phi(t), \quad (39)$$

where we have still $\phi(t) \in \mathcal{K}$, i.e. $H(\theta + \omega t)$ is still interpreted as an operator acting on the enlarged Hilbert space \mathcal{K} , which with respect to the variable θ is a multiplication operator.

Although this equation looks formally like the semiclassical Schrödinger equation (2), we emphasize that it is still different since it is defined in the enlarged Hilbert space \mathcal{K} and the phase θ does not have a definite value, since it is a dynamical variable on the same footing as x . In order to recover the semiclassical equation from (39) we have to reduce it to an equation defined in the Hilbert space \mathcal{H} . From a mathematical point of view, this can be done by fixing a particular value of θ , as we did in Section II A. Physically this can be achieved, as we show in the following, by choosing the initial condition of the photon field as a coherent state.

2. Coherent states

The coherent states of the photon field can be defined as the eigenvectors of the annihilation operator

$$a |\alpha\rangle = \alpha |\alpha\rangle, \quad \alpha = |\alpha| e^{-i\theta_0}. \quad (40)$$

In the usual Fock number state representation they are given, up to a phase factor, by

$$|\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle. \quad (41)$$

In the phase representation they can be written as

$$\begin{aligned} \Phi_{\theta_0}^{(\bar{n})}(\theta) &= e^{i\zeta} e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} e^{i(n-\bar{n})\theta} \\ &= e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{|\alpha|^n}{\sqrt{n!}} e^{i(n-\bar{n})(\theta-\theta_0)} \end{aligned} \quad (42)$$

(where ζ is an arbitrary constant phase that we have chosen as $\zeta = \bar{n}\theta_0$). In order to obtain the representation of coherent states in Floquet theory we have to take $|\alpha| = \sqrt{\bar{n}}$, since the average photon number in a coherent state is given by $|\alpha|^2$, and then apply the limit $\bar{n} \rightarrow \infty$. In Appendix B we show that in this limit the coherent states are represented by a generalized function $\Phi_{\theta_0}(\theta)$, which is real, and depends on $\theta - \theta_0$, where $\theta_0 \in \mathbb{S}^1$ is a fixed angle, and

$$(\Phi_{\theta_0}(\theta))^2 = 2\pi\delta(\theta - \theta_0). \quad (43)$$

3. Expectation values for general initial states of the photon field

For a general initial condition of the photon field $\xi(\theta) \in \mathcal{L}$, we first remark that the evolution of the initial condition (that we take here at $t = t_0 = 0$) $\phi(x) \otimes \xi(\theta)$ can be obtained from the one of the initial condition $\phi(x) \otimes 1$ (where the constant function $1 \equiv e^{i(k=0)\theta}$ is the relative number state of zero photons):

$$\begin{aligned} U_K(t, \theta) (\phi(x) \otimes \xi(\theta)) &= \mathcal{T}_{-\omega t} U(t, 0; \theta) (\phi(x) \otimes \xi(\theta)) \\ &= \xi(\theta - \omega t) U(t, 0; \theta - \omega t) (\phi(x) \otimes 1) \\ &= \xi(\theta - \omega t) U_K(t, \theta) (\phi(x) \otimes 1) \end{aligned} \quad (44)$$

(since $U(t, 0; \theta)$ is a multiplication operator with respect to θ).

As a consequence, for any observable $M(\theta) : \mathcal{K} \rightarrow \mathcal{K}$ that with respect to θ is a multiplication operator, using Eq. (13), we can write the expectation value as

$$\begin{aligned} \langle M \rangle(t) &:= \langle \phi \otimes \xi | U_K^\dagger(t, \theta) M(\theta) U_K(t, \theta) | \phi \otimes \xi \rangle_{\mathcal{K}} \\ &= \int_0^{2\pi} \frac{d\theta}{2\pi} |\xi(\theta)|^2 \langle \phi | U^\dagger(t, 0; \theta) M(\theta + \omega t) U(t, 0; \theta) | \phi \rangle_{\mathcal{H}} \\ &= \int_0^{2\pi} \frac{d\theta}{2\pi} |\xi(\theta)|^2 \langle \phi(t; \theta) | M(\theta + \omega t) | \phi(t; \theta) \rangle_{\mathcal{H}}, \end{aligned} \quad (45)$$

where we denote by $\phi(t; \theta) \equiv U(t, 0; \theta)\phi$ the semiclassical evolution with initial phase θ of the initial condition $\phi \in \mathcal{H}$. In particular, for an observable A of the molecule (i.e. $A \otimes \mathbb{1}_{\mathcal{L}}$) we have

$$\langle A \rangle(t) = \int_0^{2\pi} \frac{d\theta}{2\pi} |\xi(\theta)|^2 \langle \phi(t; \theta) | A | \phi(t; \theta) \rangle_{\mathcal{H}}. \quad (46)$$

4. Expectation values on coherent states; relation with the semi-classical model

We have stated that we can recover the evolution of the semi-classical model from the Floquet evolution in the interaction representation by taking initial states in which the photon field is in a coherent state. This can be formulated more precisely by the following statements:

If we take an initial condition of the form $\psi(t=0) = \phi(x) \otimes \Phi_{\theta_0}(\theta)$, then

- i) If $A : \mathcal{H} \rightarrow \mathcal{H}$ is an observable of the molecule, then according to Eqs. (46) and (43)

$$\langle A \rangle(t) = \langle \phi(t; \theta_0) | A | \phi(t; \theta_0) \rangle_{\mathcal{H}}. \quad (47)$$

The last expression is the expectation value calculated with the semiclassical model with initial phase θ_0 . We conclude thus that, *if one considers only observables of the molecule, the Floquet evolution with a coherent state in the initial condition is equivalent to the semiclassical model.*

We remark that a somewhat related construction, linking the evolution from cavity dressed states directly to the semi-classical model (i.e. without the intermediate level of Floquet states as we do here) was established in [16].

- ii) More generally, if $M(\theta) : \mathcal{K} \rightarrow \mathcal{K}$ is an observable that with respect to θ is a multiplication operator, continuous in θ , then taking for θ a particular value θ_0 defines a family of operators $M(\theta_0) : \mathcal{H} \rightarrow \mathcal{H}$, parametrized by θ_0 . Then, according to Eqs. (45) and (43)

$$\langle M \rangle(t) = \langle \phi(t; \theta_0) | M(\theta_0 + \omega t) | \phi(t; \theta_0) \rangle_{\mathcal{H}}. \quad (48)$$

It was remarked in References [1, 7] that in the semiclassical model, if the initial phase θ_0 is not known, one can take a statistical average over the initial phases, with uniform distribution:

$$\overline{A}_{\text{sc}}(t) := \int_0^{2\pi} \frac{d\theta_0}{2\pi} \langle \phi(t; \theta_0) | A | \phi(t; \theta_0) \rangle_{\mathcal{H}}. \quad (49)$$

From the discussion above, this coincides with the expectation value $\langle A \rangle(t)$ calculated with the evolution in the Floquet picture of an initial condition of the photon field that is a photon number eigenstate $e^{ik\theta}$ (with arbitrary k), that is $\langle A \rangle(t) = \int_0^{2\pi} \frac{d\theta_0}{2\pi} \langle \phi(t; \theta_0) | A | \phi(t; \theta_0) \rangle_{\mathcal{H}}$ according to Eq. (46). We have seen on the other hand that the semiclassical evolution with an initial phase θ_0 corresponds, in the Floquet picture, to a coherent state initial condition for the photon field.

This property is quite remarkable: *In the large photon number regime the coherent quantum average on a number state gives the same result as the incoherent statistical average over coherent states.*

D. Emission and absorption of photons in Floquet theory

1. Exchanges of photons in Floquet theory

In Floquet theory the exchange of photons can be analyzed from the temporal variation of the relative photon number. In experiments, one measures for instance the difference in intensity of the laser pulse before and after the interaction with the molecules. Denoting the initial condition (at $t = t_0 = 0$) by $\phi(x) \otimes \xi(\theta)$, we describe the exchange of photons by

$$\delta \langle N \rangle(t) := \left\langle \phi \otimes \xi \left| U_K^\dagger(t) \left(-i \frac{\partial}{\partial \theta} \right) U_K(t) \right| \phi \otimes \xi \right\rangle_{\mathcal{K}} - \left\langle \phi \otimes \xi \left| -i \frac{\partial}{\partial \theta} \right| \phi \otimes \xi \right\rangle_{\mathcal{K}} \quad (50)$$

and we show below that

$$\delta \langle N \rangle(t) = \int_0^{2\pi} \frac{d\theta}{2\pi \hbar \omega} |\xi(\theta)|^2 \left[\langle \phi | H(\theta) | \phi \rangle_{\mathcal{H}} - \langle \phi(t; \theta) | H(\theta + \omega t) | \phi(t; \theta) \rangle_{\mathcal{H}} \right]. \quad (51)$$

In particular, if the photon field is initially in a photon number eigenstate $|e^{ik\theta}\rangle$,

$$\delta\langle N\rangle(t) = \int_0^{2\pi} \frac{d\theta}{2\pi\hbar\omega} \left[\langle \phi | H(\theta) | \phi \rangle_{\mathcal{H}} - \langle \phi(t; \theta) | H(\theta + \omega t) | \phi(t; \theta) \rangle_{\mathcal{H}} \right]. \quad (52)$$

We remark that $\delta\langle N\rangle(t)$ is independent of the particular k we take, in accordance with the interpretation as relative photon number.

If the photon field is initially in a coherent state $\Phi_{\theta_0}(\theta) = (2\pi)^{1/2}\delta_{1/2}(\theta - \theta_0)$, then

$$\delta\langle N\rangle_{\text{cs}}(t) = \frac{1}{\hbar\omega} \left[\langle \phi | H(\theta_0) | \phi \rangle_{\mathcal{H}} - \langle \phi(t; \theta_0) | H(\theta_0 + \omega t) | \phi(t; \theta_0) \rangle_{\mathcal{H}} \right]. \quad (53)$$

Again, if the precise initial phase θ_0 of the coherent state is not known, one can take the (incoherent) statistical average over all phases θ_0 :

$$\begin{aligned} \overline{\delta\langle N\rangle_{\text{cs}}}(t) &= \int_0^{2\pi} \frac{d\theta_0}{2\pi} \delta\langle N\rangle_{\text{cs}}(t) \\ &= \int_0^{2\pi} \frac{d\theta_0}{2\pi\hbar\omega} \left[\langle \phi | H(\theta_0) | \phi \rangle_{\mathcal{H}} - \langle \phi(t; \theta_0) | H(\theta_0 + \omega t) | \phi(t; \theta_0) \rangle_{\mathcal{H}} \right]. \end{aligned} \quad (54)$$

This incoherent statistical average over the phases also gives exactly the same result as the coherent average (52) in a photon number state.

We can obtain these relations as follows: Using the definition of the quasi-energy operator (7), we can express $\delta\langle N\rangle(t)$ in terms of quantities that do not involve the derivative $-i\partial/\partial\theta$:

$$\begin{aligned} \delta\langle N\rangle(t) &= \left\langle \phi \otimes \xi \left| U_K^\dagger(t) \frac{K}{\hbar\omega} U_K(t) \right| \phi \otimes \xi \right\rangle_{\mathcal{K}} \\ &\quad - \left\langle \phi \otimes \xi \left| U_K^\dagger(t) \frac{H(\theta)}{\hbar\omega} U_K(t) \right| \phi \otimes \xi \right\rangle_{\mathcal{K}} - \left\langle \phi \otimes \xi \left| -i\frac{\partial}{\partial\theta} \right| \phi \otimes \xi \right\rangle_{\mathcal{K}}. \end{aligned} \quad (55)$$

Using the fact that $[K, U_K] = 0$, $U_K^\dagger U_K = \mathbb{1}$ and equation (7), we can write

$$\delta\langle N\rangle(t) = \left\langle \phi \otimes \xi \left| \frac{H(\theta)}{\hbar\omega} \right| \phi \otimes \xi \right\rangle_{\mathcal{K}} - \left\langle \phi \otimes \xi \left| U_K^\dagger(t) \frac{H(\theta)}{\hbar\omega} U_K(t) \right| \phi \otimes \xi \right\rangle_{\mathcal{K}}, \quad (56)$$

and since

$$\begin{aligned} U_K^\dagger(t, \theta) H(\theta) U_K(t, \theta) &= U^\dagger(t, 0; \theta) \mathcal{T}_{\omega t} H(\theta) \mathcal{T}_{-\omega t} U(t, 0; \theta) \\ &= U^\dagger(t, 0; \theta) H(\theta + \omega t) U(t, 0; \theta), \end{aligned} \quad (57)$$

we obtain equation (51).

We can also get more precise information on the probability $P(L, t)$ that L photons are exchanged: If at time $t = 0$ the photon field is in a photon number eigenstate $e^{ik\theta}$ and $\psi(t = 0) = \psi_0 = \phi \otimes e^{ik\theta}$, then the probability that a measurement performed at time t yields that L photons have been exchanged, is given by

$$\begin{aligned} P(L, t) &= \left\langle U_K(t)\psi_0 \left| \left[\mathbb{1}_{\mathcal{H}} \otimes |e^{i(L+k)\theta}\rangle\langle e^{i(L+k)\theta}| \right] \right| U_K(t)\psi_0 \right\rangle_{\mathcal{K}} \\ &= \sum_n \left| \left\langle \phi_n \otimes e^{i(k+L)\theta} \left| U_K(t) \left(\phi \otimes e^{ik\theta} \right) \right\rangle_{\mathcal{K}} \right|^2, \end{aligned} \quad (58)$$

where $\{\phi_n\}$ is an arbitrary basis of \mathcal{H} .

2. Invariance with respect to the choice of the origin of the relative photon number

Due to the relative character of the number operator $-i\partial/\partial\theta$, all the physical predictions of the Floquet model must be invariant with respect to a global translation of the relative photon numbers. We show that this is indeed the case for the properties discussed above.

The probability $P(L, t)$ is independent of the particular initial photon number state chosen, i.e. it is independent of k since:

$$U_K(t) \left(\phi \otimes e^{ik\theta} \right) = U(t, 0; \theta - \omega t) \left(\phi \otimes e^{ik(\theta - \omega t)} \right) \quad (59)$$

and thus

$$P(L, t) = \sum_n \left| \left\langle \phi_n \otimes e^{iL\theta} \mid U_K(t) (\phi \otimes 1) \right\rangle_{\mathcal{K}} \right|^2. \quad (60)$$

For the average number of exchanged photons $\delta \langle N \rangle(t)$ it is straightforward to verify that one obtains the same result for the choice of any initial condition of the photon field of the form

$$\xi = \sum_k c_k e^{i(k+m)\theta}, \quad \text{with arbitrary translation } m. \quad (61)$$

3. Number of exchanged photons in adiabatic passage with photons in coherent states

In adiabatic passage processes with pulsed lasers, as we will discuss in the forthcoming sections, one often encounters the following particular situation: If the initial condition of the photon field were a number state, i.e.

$$\psi_i = \phi_i(x) \otimes e^{ik\theta}, \quad (62)$$

then at the end of the pulse, the final state would be

$$\psi_f = \phi_f(x) \otimes e^{i(k-m)\theta}, \quad (63)$$

i.e. the photon field would be again in a well-defined number state, and one can state that m photons had been adsorbed, since according to Eq. (60) $P(L, t_f) = \delta_{L, -m}$. Since k is the relative number of photons, if these relations are satisfied for one choice of the initial k they are also satisfied for all other choices of $k \in \mathbb{Z}$. However, in the actual experimental realizations the initial states of the photon field are coherent states instead of number states. The coherent states can be considered as a coherent superposition of number states of the form

$$\Phi = \sum_k c_k e^{ik\theta}, \quad \text{with } \sum_k |c_k|^2 = 1. \quad (64)$$

In the preceding sections we have taken the limit $\bar{n} \rightarrow \infty$ in which the coherent states become a $\delta_{1/2}(\theta - \theta_0)$ function. For the discussion of the exchanged photons we consider a large but finite \bar{n} , such that the coherent state is represented by a sharply peaked function that can be written as a superposition (64). Under this condition, the relations (62),(63) imply that the initial condition

$$\psi^{(i)} = \phi_i(x) \otimes \xi^{(i)}, \quad \text{with } \xi^{(i)} = \sum_k c_k e^{ik\theta}, \quad (65)$$

evolves at the end of the pulse to

$$\psi^{(f)} = \phi_f(x) \otimes \sum_k c_k e^{i(k-m)\theta} = \phi_f(x) \otimes e^{-im\theta} \xi^{(i)}(\theta). \quad (66)$$

Our aim here is to give a precise meaning to the statement that, also in this process involving coherent states, m photons have been absorbed: The probability to observe $\bar{n} + k$ photons at the initial time t_i is

$$P^{(i)}(\bar{n} + k) = |c_k|^2 \quad (67)$$

and at the end of the pulse

$$P^{(f)}(\bar{n} + k) = |c_{k+m}|^2 = P^{(i)}(\bar{n} + k + m), \quad (68)$$

which implies $P^{(f)}(\bar{n} + k - m) = P^{(i)}(\bar{n} + k)$, i.e. the probability to measure $\bar{n} + k - m$ photons at the end is equal to the probability to measure $\bar{n} + k$ at the beginning of the pulse.

In terms of averages and moments of photon numbers one can make the following statement: Eqs. (65)(66) imply that the photon expectation number changes by $-m$

$$\delta\langle N \rangle = \langle \psi^{(f)} | -i \frac{\partial}{\partial \theta} | \psi^{(f)} \rangle - \langle \psi^{(i)} | -i \frac{\partial}{\partial \theta} | \psi^{(i)} \rangle = -m \quad (69)$$

and the second moment of the relative number of photons at the end of the process is equal to the one at the beginning:

$$\langle \psi^{(f)} | \left(-i \frac{\partial}{\partial \theta} \right)^2 | \psi^{(f)} \rangle = \langle \psi^{(i)} | \left(-i \frac{\partial}{\partial \theta} \right)^2 | \psi^{(i)} \rangle. \quad (70)$$

E. Floquet representation with two or more lasers

The treatment described in the preceding sections can be easily generalized to the case in which two (or several) lasers of frequencies $\omega_j, j = 1 \dots d$ act on the molecule. We introduce the notation $\underline{\omega} = (\omega_1, \dots, \omega_d)$, and $\underline{\theta} = (\theta_1, \dots, \theta_d)$ which represents the phases at time $t = 0$ of the d lasers. The semiclassical Schrödinger equation reads

$$i\hbar \frac{\partial \phi}{\partial t} = H(x, \underline{\theta} + \underline{\omega}t) \phi \quad (71)$$

with, for example in a dipole coupling model with two lasers,

$$H(x, \underline{\theta} + \underline{\omega}t) = H_0(x) - \mu(x) \mathcal{E}_1 \cos(\theta_1 + \omega_1 t) - \mu(x) \mathcal{E}_2 \cos(\theta_2 + \omega_2 t), \quad (72)$$

where x symbolizes the degrees of freedom of the molecule, $\mu(x)$ is its dipole moment, $\mathcal{E}_1, \mathcal{E}_2$ the respective amplitudes of the two lasers and $H_0(x)$ the Hamiltonian of the free molecule. The corresponding Floquet Hamiltonian is defined as [5, 6, 17–20]

$$K = -i\hbar \underline{\omega} \cdot \frac{\partial}{\partial \underline{\theta}} + H(x, \underline{\theta}), \quad (73a)$$

$$= -i\hbar \sum_{j=1}^d \omega_j \frac{\partial}{\partial \theta_j} - \mu(x) \mathcal{E}_1 \cos \theta_1 - \mu(x) \mathcal{E}_2 \cos \theta_2, \quad (73b)$$

and acts on the enlarged Hilbert space

$$\mathcal{K} = \mathcal{H} \otimes \underbrace{\mathcal{L} \otimes \dots \otimes \mathcal{L}}_{d \text{ products}}, \quad (74)$$

where $\mathcal{L} := L_2(\mathbb{S}^1, d\theta_j/2\pi)$ denotes the space of square integrable functions on the circle \mathbb{S}^1 of length 2π . The tensor product $\mathcal{L} \otimes \dots \otimes \mathcal{L}$ is equivalent to $\mathcal{L}_2(\mathbf{T}^d, d\underline{\theta}/2\pi)$, i.e. the square integrable functions on the unit torus \mathbf{T}^d . The relations we have described for the single laser case extend in most practical cases to the d -laser case just by adapting the notation.

III. EFFECTIVE HAMILTONIAN – DYNAMICAL RESONANCES

Since in the Floquet representation the Hamiltonian K defined on the enlarged Hilbert space \mathcal{K} is time independent, the analysis of the effect of perturbations, like e.g. transition probabilities can be done by stationary perturbation theory, instead of the usual time-dependent one. Here we will present a formulation of stationary perturbation theory based on the iteration of unitary transformations (called contact transformations or KAM transformations) constructed such that the form of the Hamiltonian gets simplified. It is referred to as the KAM technique. The results are not very different from the ones of Rayleigh-Schrödinger perturbation theory, but conceptually and in terms of speed of convergence they have some advantages.

We first formulate this KAM technique in a general setting (see Section III A). Next, in Section III B, we apply it to the case of an interaction of high frequency with respect to the energy differences of the free system and show its connection with the standard Born Oppenheimer approximation.

Resonant effects that prevent convergence of the perturbation theory and that appear as small denominators will be treated specifically by rotating wave transformations (RWT) in Section III C.

Combining the KAM techniques with the RWT will allow to construct effective Hamiltonians in a systematic way and to estimate the order of the neglected terms (see Section IIID). We show that the KAM technique allows to partition at a desired order operators in orthogonal Hilbert subspaces. We adapt this partitioning technique to treat Floquet Hamiltonians. Its connection with the standard adiabatic elimination is shown at a second order approximation.

In Section IIIE this partitioning technique is illustrated for two-photon processes in atoms. It is next applied in Section IIIF to construct an effective Hamiltonian relevant for the rotational excitation in diatomic molecules.

A. Perturbation theory formulated as an iteration of unitary transformations – nonresonant case: KAM techniques

1. Iterative perturbation algorithm

We start with an unperturbed Hamiltonian

$$K_0 = -i\hbar\omega \frac{\partial}{\partial\theta} + H_0, \quad (75)$$

where H_0 is a θ -independent Hamiltonian that represents the free molecule. The coupling with the field is represented by a perturbation $\varepsilon V_1(\theta)$:

$$K = K_0 + \varepsilon V_1(\theta). \quad (76)$$

The purpose of ε is only to keep track of the different orders, and at the end we can set $\varepsilon = 1$. The method is defined quite generally, independently of the particular form of K_0 and V_1 . We assume that $V_1(\theta)$ is a bounded operator. The idea is to construct a unitary transformation $e^{\varepsilon W_1(\theta)}$, with $W_1^\dagger = -W_1$ such that

$$e^{-\varepsilon W_1} K e^{\varepsilon W_1} = K_0 + \varepsilon D_1 + \varepsilon^2 V_2 =: K_2, \quad (77)$$

where D_1 is a θ -independent operator satisfying $[K_0, D_1] = 0$. Thus the perturbation will be reduced from order ε to order ε^2 . Once this is achieved, the approximation of order ε of the eigenvalues and the eigenvectors is obtained from $K_0 + \varepsilon D_1$, i.e. neglecting $\varepsilon^2 V_2$. The eigenvectors of $K_0 + \varepsilon D_1$ are the same as those of K_0 , since the two operators commute. If the eigenvalues $\lambda_{m,k}^{(0)}$ of K_0 are nondegenerate, and we denote $D_1 = \text{diag}\{d_m\}$, then the perturbed eigenvalues of first order (i.e. neglecting corrections of second order) are

$$\lambda_{m,k}^{(1)} = \lambda_{m,k}^{(0)} + d_m, \quad (78)$$

and the corresponding eigenvectors are

$$|\psi_{m,k}^{(1)}\rangle = e^{\varepsilon W_1} |\psi_{m,k}^{(0)}\rangle \quad (79)$$

with $|\psi_{m,k}^{(0)}\rangle = |e_m \otimes e^{ik\theta}\rangle$, where $\{|e_m\rangle\}$ is the eigenbasis of H_0 in \mathcal{H} .

If some eigenvalues of K_0 are degenerate, the addition of D_1 can lift the degeneracy.

Since the transformed Hamiltonian K_2 is of the same general form as the one we started with (76), this procedure can be iterated. The order of the perturbation can thus be reduced successively from ε to ε^2 , to ε^4 , ... After N iterations the remaining perturbation is of order $\varepsilon^{2^N} = \varepsilon^{e^{N \ln 2}}$, i.e. we have a superexponential decrease. This type of iterative algorithms are therefore called superconvergent. We call this procedure a quantum KAM algorithm, since it is the quantum analogue of the Kolmogorov-Arnold-Moser (KAM) transformations developed in classical mechanics [21–25] [26, 27]. This procedure is also known as the van Vleck perturbation theory [28]. The transformations $e^{\varepsilon W_1}$ are called *contact transformations*, or *KAM transformations*. One step of the algorithm is roughly equivalent to first order perturbation theory. The idea is that instead of performing a perturbation calculation of high order, one can perform several times a calculation of first order. The acceleration of convergence can be explained by the fact that at each step of the iteration one develops around a different effective nonperturbed Hamiltonian, that contains already the corrections found in the previous iterations.

We remark that D_N , the diagonal part obtained after N iterations, is a function of ε that is not a polynomial, since as we will see below the construction involves rational functions and exponentials. However, if one expands D^N as a power series in ε up to a certain order (smaller than ε^{2^N}), the result must coincide with the Rayleigh-Schrödinger power series of that order, since the coefficients of this expansion are unique (even in the case when the series is only asymptotic, i.e. non convergent). In practice, performing one or two iterations gives already the main information of the processes we will study.

2. Construction of the contact transformations

We discuss now how one can construct the transformation for one step in the iterative algorithm. An equation to determine D_1 and W_1 can be obtained expanding eq. (77) in powers of ε and requiring that the θ -dependent terms of order ε cancel out. This leads to the two equations

$$[K_0, W_1] + V_1 - D_1 = 0, \quad (80a)$$

$$[K_0, D_1] = 0. \quad (80b)$$

The solution of this equations can be given using the eigenvalues and eigenvectors of K_0 which we will denote by λ_ν^0 and $|\nu, j\rangle$ [we represent the indices m, k of (78) and (79) by a single index ν that labels the different eigenvalues, and j distinguishes different basis vectors corresponding to a degenerate eigenvalue]. We define a projection operator Π_{K_0} that extracts from the perturbation V_1 the diagonal component with respect to the eigenbasis of K_0 :

$$\Pi_{K_0} V_1 = \sum_{\nu, j, j'} |\nu, j\rangle \langle \nu, j| V_1 |\nu, j'\rangle \langle \nu, j'|. \quad (81)$$

With this notation a solution of (80) can be written as

$$D_1 = \Pi_{K_0} V_1 = \text{diagonal part of } V_1, \quad (82a)$$

$$W_1 = - \sum_{\nu, j, j', \nu' \neq \nu} \frac{|\nu, j\rangle \langle \nu, j| V_1 |\nu', j'\rangle \langle \nu', j'|}{\lambda_\nu^0 - \lambda_{\nu'}^0}. \quad (82b)$$

The solution W_1 is not unique, since if A is any operator such that $[K_0, A] = 0$ then $W_1 + A$ is also a solution. The solution (82a) is singled out as the unique solution with zero diagonal blocks, $\Pi_{K_0} W_1 = 0$ [29].

There are two ways to proceed, depending on what we do with the diagonal part $\Pi_{K_0} V_1$ of the perturbation. It can be added to the unperturbed Hamiltonian either after or before the transformation.

(i) In the first case we take K_0 as the unperturbed Hamiltonian and the perturbation V_1 has a non-zero projection $\Pi_{K_0} V_1$, which leads to a term $D_1 = \Pi_{K_0} V_1$ in the solution (82a). In this case the second order perturbation that remains at the end of the transformation takes the form

$$\begin{aligned} \varepsilon^2 V_2 = & \frac{\varepsilon^2}{2} [V_1, W_1] + \frac{\varepsilon^3}{3} [[V_1, W_1], W_1] + \dots + \varepsilon^M \frac{(M-1)}{M!} \underbrace{[\dots [[V_1, W_1], W_1], \dots]}_{M-1 \text{ commutators}} + \dots \\ & + \frac{\varepsilon^2}{2!} [D_1, W_1] + \frac{\varepsilon^3}{3!} [[D_1, W_1], W_1] + \dots + \frac{\varepsilon^M}{M!} \underbrace{[\dots [D_1, W_1], W_1], \dots]}_{M-1 \text{ commutators}} + \dots \end{aligned} \quad (83)$$

We remark that defining an operator $L_{W_1} : V \mapsto L_{W_1}(V) := [V, W_1]$, the transformation (77) can be expressed as

$$e^{-\varepsilon W_1} K e^{\varepsilon W_1} = e^{L_{W_1}}(K) = \sum_{M=0}^{\infty} \varepsilon^M \frac{1}{M!} (L_{W_1})^M(K) \quad (84)$$

and the above expression (83) can be written as

$$\varepsilon^2 V_2 = \sum_{M=2}^{\infty} \varepsilon^M \frac{(M-1)}{M!} (L_{W_1})^{(M-1)}(V_1) + \sum_{M=2}^{\infty} \varepsilon^M \frac{1}{M!} (L_{W_1})^{(M-1)}(D_1), \quad (85a)$$

$$= \sum_{M=2}^{\infty} \varepsilon^M \frac{1}{M!} (L_{W_1})^{(M-1)}((M-1)V_1 + D_1). \quad (85b)$$

(ii) The second possibility is to define a new unperturbed Hamiltonian \tilde{K}_0^D in which the projection $\Pi_{K_0} V_1$ of the perturbation is already absorbed :

$$\tilde{K}_0^D = K_0 + \Pi_{K_0} V_1. \quad (86)$$

The remaining perturbation $V_1 - \Pi_{K_0} V_1$ has zero projection and thus there is no supplementary \tilde{D}_1 to be added. In this case the second order perturbation that remains at the end of the transformation takes the somewhat simpler form

$$\varepsilon^2 V_2 = \frac{\varepsilon^2}{2} [V_1, W_1] + \frac{\varepsilon^3}{3} [[V_1, W_1], W_1] + \dots + \varepsilon^M \frac{(M-1)}{M!} \underbrace{[\dots [[V_1, W_1], W_1], \dots]}_{M-1 \text{ commutators}} + \dots \quad (87)$$

Both alternatives can be useful; depending on the particular problem one of them can be more convenient than the other one. As we will see in Section III D, the second version is particularly adapted to the construction of effective Hamiltonians by the partitioning technique.

3. Interpretation as an averaging procedure

The perturbation theory outlined above can be interpreted as an averaging procedure [21–25, 29]: The projector can be expressed as

$$D_1 = \Pi_{K_0} V_1 = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau ds e^{-iK_0 s} V_1 e^{iK_0 s} \quad (88)$$

and

$$W_1 = \lim_{\tau \rightarrow \infty} \frac{-i}{\tau} \int_0^\tau ds' \int_0^{s'} ds e^{-iK_0 s} (V_1 - \Pi_{K_0} V_1) e^{iK_0 s}. \quad (89)$$

The term $e^{-iK_0 s} V_1 e^{iK_0 s}$ in (88) is equal to the inverse time evolution that the operator V_1 would have in the Heisenberg picture for the dynamics generated by K_0 . Thus, D_1 , which is the term that is added to constitute the approximate effective Hamiltonian $K_{01} := K_0 + D_1$, can be interpreted as the average of the perturbation with respect to the dynamics generated by K_0 .

Another equivalent expression is [30, 31]

$$D_1 = \Pi_{K_0} V_1 = \lim_{\beta \rightarrow 0^+} \beta \int_0^\infty ds e^{-\beta s} e^{-iK_0 s} V_1 e^{iK_0 s} \quad (90)$$

and

$$W_1 = -i \lim_{\beta \rightarrow 0^+} \beta \int_0^\infty ds' e^{-\beta s'} \int_0^{s'} ds e^{-iK_0 s} (V_1 - \Pi_{K_0} V_1) e^{iK_0 s}. \quad (91)$$

The relation between these two expressions can be thought of as two equivalent realizations of the time average

$$\text{Average}(f) = \lim_{\beta \rightarrow 0^+} \beta \int_0^\infty ds' e^{-\beta s'} f(s') = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau ds' f(s'). \quad (92)$$

A third alternative expression for W_1 is [30, 31]

$$W_1 = \lim_{\beta \rightarrow 0^+} -i \int_0^\infty ds e^{-\beta s} e^{-iK_0 s} (V_1 - \Pi_{K_0} V_1) e^{iK_0 s}. \quad (93)$$

B. High frequency perturbation theory

A variation of the procedures described above can be applied to situations in which the frequency ω of the perturbation is high with respect to the internal frequencies of the considered system [32]. We start with a Floquet Hamiltonian of the form

$$K = -i\hbar\omega \frac{\partial}{\partial \theta} + H_0(x) + V_1(x, \theta) \quad (94)$$

where x symbolizes the degrees of freedom of the molecule. Since we are interested in the limit $\hbar\omega \rightarrow \infty$, we define a small parameter $\epsilon := 1/(\hbar\omega)$ and we rewrite

$$K = \hbar\omega \hat{K} \quad (95)$$

with

$$\hat{K} = -i \frac{\partial}{\partial \theta} + \epsilon (H_0 + V_1). \quad (96)$$

The eigenvectors of K are the same ones as those for \hat{K} , and the eigenvalues just have to be multiplied by $\hbar\omega$. The difference with the preceding discussion is that here H_0 and V are both of order ϵ . Thus we take as the unperturbed Floquet Hamiltonian just

$$\hat{K}_0 := -i \frac{\partial}{\partial \theta}. \quad (97)$$

If the frequency is large compared with the frequencies of the system, there will not be any resonances. We can thus proceed with the iterative perturbative KAM algorithm by first determining a unitary transformation $e^{\epsilon W_1(x, \theta)}$, with $W_1^\dagger = -W_1$ such that

$$e^{-\epsilon W_1} \hat{K} e^{\epsilon W_1} = \hat{K}_0 + \epsilon D_1 + \epsilon^2 V_2 =: K_2, \quad (98)$$

where D_1 is a θ -independent operator such that $[\hat{K}_0, D_1] = 0$. Thus the perturbation will be reduced from order ϵ to order ϵ^2 . The generator W_1 of the contact transformation is determined by the equations

$$[K_0, W_1] + H_0 + V_1 - D_1 = 0, \quad (99a)$$

$$[K_0, D_1] = 0. \quad (99b)$$

The equation (99a) can be written as

$$-i \frac{\partial W_1}{\partial \theta} + H_0 + V_1 - D_1 = 0, \quad (100)$$

whose general solution is given by

$$W_1 = -i \int^\theta d\theta (H_0 + V_1 - D_1) + C, \quad (101)$$

where C is an arbitrary θ -independent operator acting on \mathcal{H} , which one can choose as $C = 0$. Since $W_1(x, \theta)$ is a multiplication operator acting on functions of the angle θ , it must be necessarily 2π -periodic. This condition determines D_1 uniquely in terms of the average

$$\overline{V}_1 := \int_0^{2\pi} \frac{d\theta}{2\pi} V_1(x, \theta) \quad (102)$$

as

$$D_1 = H_0 + \overline{V}_1. \quad (103)$$

Thus we obtain

$$W_1(x, \theta) = -i \int^\theta d\theta (V_1(x, \theta) - \overline{V}_1(x)). \quad (104)$$

We remark that the solution (103), (104) of Eqs. (99) can be obtained from the general equations (88), (89).

This contact transformation $e^{\epsilon W_1}$ can be interpreted, in the case where $[V_1(x, \theta), V_1(x, \theta')] = 0$, for all θ, θ' , as the unitary transformation which allows to diagonalize exactly the Hamiltonian $\hbar\omega \hat{K}_0 + V_1(x, \theta)$ with respect to θ , taking x as a parameter. We obtain $\lambda_k^{(0)} = \overline{V}_1 + k\hbar\omega$ (k positive or negative integer) for the eigenvalues associated to the eigenvectors $\chi(\theta, x) = \exp(\epsilon W_1(x, \theta) + ik\theta)$. We remark that if $\overline{V}_1 = 0$, the eigenvalues do not depend on the variable x .

Adapting the equation (85b) the remaining perturbation of order ϵ^2 can be written as

$$\epsilon^2 V_2 = \sum_{M=2}^{\infty} \epsilon^M \frac{1}{M!} (L_{W_1})^{(M-1)} ((M-1)(H_0 + V_1) + D_1) = \frac{\epsilon^2}{2!} [V_1 + \overline{V}_1 + 2H_0, W_1] + \epsilon^3 \dots, \quad (105)$$

In the particular case where $[V_1(x, \theta), V_1(x, \theta')] = 0$ Eq. (105) reduces to $\epsilon^2 V_2 = \epsilon^2 [H_0, W_1] + \epsilon^3 \dots$. We can apply a second contact transformation $e^{\epsilon^2 W_2}$ (with respect to \hat{K}_0), $W_2 = -i \int^\theta d\theta (V_2 - \overline{V}_2)$, which averages this rest (105) with respect to θ and leads to correction of order ϵ^3 . In the basis of the eigenvectors $\chi(\theta, x)$ of $\hbar\omega \hat{K}_0 + V_1(x, \theta)$, the non-diagonal terms $V_2 - \overline{V}_2$ of this remaining term (105) can be seen as the couplings between the states corresponding

to the eigenvalues $\lambda_k^{(0)}$ and the diagonal terms \overline{V}_2 will lead to geometrical phases for the dynamics (see Section IV B 1). We thus obtain the effective high frequency Hamiltonian H^{HF} (independent of θ) of order ϵ^2

$$H^{\text{HF}}(x) = H_0(x) + \overline{V}_1(x) + \overline{V}_2(x). \quad (106)$$

We remark that the standard Born-Oppenheimer approximation, allowing to separate the fast electronic motion with respect to the slow vibrational motion of the nuclei of molecules, can be thought as a high frequency perturbation theory. For the Born-Oppenheimer, we identify formally K_0 with the kinetic energy of the electrons and ϵ with the mass of the electrons. As we stated above, the approximation consists in first applying a contact transformation which diagonalizes exactly with respect to the electronic coordinates, keeping the nuclei coordinates as parameters, and next in neglecting the non-diagonal coupling between the eigenvalues (which are associated to the electronic states).

C. Nonperturbative treatment of resonances – Resonant transformations

The properties that we have stated in the last section allow us to analyze the situation in which there are resonances. The analysis of resonances involves two aspects: The first one is the determination of degenerate eigenvalues of an unperturbed Hamiltonian K_0 , and the second one the detection of terms in the perturbation V_1 that couple these degenerate modes. We show that the projectors of type Π_{K_0} can be used to detect resonant terms in the coupling operators V_1 . This is an alternative to another formulation that consists in writing down formally a Fourier series of the generator W_1 of the KAM transformation and detecting diverging terms, i.e. terms with zeros in the denominator and a finite numerator.

This leads to distinguish two types of resonances: the resonances induced by the field that occur beyond a threshold of the field, and resonances that occur for an arbitrary small value of the field. These are called respectively (i) the *dynamical resonances* (or equivalently *field induced resonances* or *nonlinear resonances*) and (ii) the *zero-field resonances*.

The zero-field resonances can be identified with respect to the system energy levels and the field frequency when the field is off. They are usually one- or two-photon resonances. The one-photon resonance is of first order with respect to the field amplitude in the sense that the degeneracy of the eigenvalues is lifted linearly with the field amplitude. The two-photon resonance is of second order since the degeneracy of the eigenvalues is lifted quadratically with the field amplitude. Multiphoton resonances (more than two-photon) are more complicated since they are generally accompanied by dynamical shifts of second order before the actual occurrence of the resonance at a higher order. They are in general dynamical.

For very small field amplitudes, the multiphoton resonances can be treated by time-dependent perturbation theory combined with the rotating wave approximation (RWA) [10]. In strong field, all types of resonances can be treated by the concept of the rotating wave transformation, combined with an additional stationary perturbation theory (such as the KAM techniques explained above). It will allow to construct an effective Hamiltonian in a subspace spanned by the resonant dressed states, degenerate at zero field.

To illustrate the effects of these two types of resonances, we consider the simplest concrete example of a two-level system driven by a strong field:

$$K = K_0 + V, \quad K_0 = -i\hbar\omega \frac{\partial}{\partial \theta} + \frac{\beta}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad V = \varepsilon \cos \theta \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad (107)$$

with ε and β real and positive.

1. Zero-field resonances

We consider the case $\beta = \omega$. There is a one photon resonance in K_0 , since its eigenvalues are $\lambda_{m,k}^0 = m\frac{\beta}{2} + k\omega$; $m \in \{-1, +1\}$, $k \in \mathbb{Z}$, and therefore $\lambda_{-1,k+1}^0 = \lambda_{+1,k}^0$, i.e. all the eigenvalues are degenerate of order two. The degeneracy eigenspaces are spanned by the vectors

$$\psi_{-1,k+1}^0 = e^{i(k+1)\theta} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{and} \quad \psi_{+1,k}^0 = e^{ik\theta} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \quad (108)$$

The projector Π_{K_0} applied on the coupling term yields

$$\Pi_{K_0} V \equiv V_{\text{resonant}} = \frac{\varepsilon}{2} \begin{pmatrix} 0 & e^{-i\theta} \\ e^{i\theta} & 0 \end{pmatrix}. \quad (109)$$

This resonant term cannot be eliminated by the KAM transformation. Instead we can treat it with a different type of transformation. We define a unitary transformation

$$R_1 = \begin{pmatrix} 1 & 0 \\ 0 & e^{i\theta} \end{pmatrix}. \quad (110)$$

As opposed to the KAM type transformation $e^{\varepsilon W}$, the transformation R_1 is not close to the identity. It is named *rotating wave transformation* (RWT) (or equivalently *resonant transformation*) in contrast with the usual RWA for which only the resonant terms are kept, and the counter-rotating terms are neglected. It is defined in such a way that

$$R_1^\dagger V_{\text{resonant}} R_1 = \frac{\varepsilon}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad (111)$$

i.e. the resonant term becomes θ -independent. Thus

$$R_1^\dagger K R_1 = -i\omega \frac{\partial}{\partial \theta} + \frac{\varepsilon}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \frac{\varepsilon}{2} \begin{pmatrix} 0 & e^{+i2\theta} \\ e^{-i2\theta} & 0 \end{pmatrix} + \frac{\omega}{2} \mathbb{1}_{\mathcal{K}}. \quad (112)$$

This Floquet Hamiltonian can be further simplified by diagonalizing the constant matrix with $T_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$:

$$K' = T_1^\dagger R_1^\dagger K R_1 T_1 = -i\omega \frac{\partial}{\partial \theta} + \frac{\varepsilon}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \frac{\varepsilon}{2} \begin{pmatrix} \cos(2\theta) & i \sin(2\theta) \\ -i \sin(2\theta) & -\cos(2\theta) \end{pmatrix} + \frac{\omega}{2} \mathbb{1}_{\mathcal{K}} \quad (113)$$

This transformed Floquet Hamiltonian can now be decomposed into a *renormalized* unperturbed part

$$K'_0(\varepsilon) = -i\omega \frac{\partial}{\partial \theta} + \frac{\varepsilon}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \frac{\omega}{2} \mathbb{1}_{\mathcal{K}} \quad (114)$$

(which is explicitly ε -dependent), and a perturbation

$$V' = \frac{\varepsilon}{2} \begin{pmatrix} \cos(2\theta) & i \sin(2\theta) \\ -i \sin(2\theta) & -\cos(2\theta) \end{pmatrix}. \quad (115)$$

In this form, the part of the perturbation that is left is not resonant anymore (for small ε), and we can apply KAM type transformations to eliminate it iteratively. This procedure is an adaptation of the technique developed by H. Eliasson to study the problem of localization in quasiperiodic potentials [33] and extended further to problems that are close to the one discussed here [34–38].

The RWA consists in neglecting V' . If we considers additionally a detuning $\Delta = \beta - \omega$, Eq. (112) becomes (before diagonalization)

$$R_1^\dagger K R_1 = -i\omega \frac{\partial}{\partial \theta} + \frac{1}{2} \begin{pmatrix} \Delta & \varepsilon \\ \varepsilon & -\Delta \end{pmatrix} + \frac{\varepsilon}{2} \begin{pmatrix} 0 & e^{+i2\theta} \\ e^{-i2\theta} & 0 \end{pmatrix} + \frac{\omega}{2} \mathbb{1}_{\mathcal{K}}. \quad (116)$$

and the effective RWA Hamiltonian reads (see e.g. [39, 40])

$$H_{\text{RWA}} = \frac{1}{2} \begin{pmatrix} \Delta & \varepsilon \\ \varepsilon & -\Delta \end{pmatrix}. \quad (117)$$

2. Dynamical resonances

As we have stated, the Floquet Hamiltonian (113) has no terms that are resonant if we take small enough ε , and the iteration of the KAM procedure converges. However, if we take ε large enough, we encounter new resonances, that are not present at zero or small fields, i.e. there are not related to degeneracies of the unperturbed eigenvalues of K_0 that lead to the zero-field resonances we have discussed in the previous subsection. These new resonances are related to degeneracies of the new effective unperturbed operator $K'_0(\varepsilon)$, which appear at some specific finite values of ε . These are the dynamical resonances.

In the present case, the first nontrivial dynamical resonance (for $\omega > 0$) appears at $\varepsilon = 2\omega = 2\beta$, since the eigenvalues of $K'_0(\varepsilon)$ are of the form $\lambda_{m,k}^{0'}(\varepsilon) = m\varepsilon/2 + k\omega$; $m \in \{-1, +1\}$, $k \in \mathbb{Z}$, and thus $\lambda_{-1,k+2}^{0'}(\varepsilon = 2\omega) = \lambda_{+1,k}^{0'}(\varepsilon = 2\omega)$,

i.e. all the eigenvalues are degenerate of order two at the resonant amplitude $\varepsilon = 2\omega$. This dynamical resonance can be interpreted as a two-photon resonance with respect to the effective Hamiltonian K'_0 , and a three-photon resonance with respect to the original Hamiltonian K_0 . The degeneracy eigenspaces are spanned by the vectors

$$\psi_{-1,k+2}^0 = e^{i(k+2)\theta} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{and} \quad \psi_{+1,k}^0 = e^{ik\theta} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \quad (118)$$

Again, we can detect the resonant terms of the perturbation V' by applying the projector $\Pi_{K'_0(\varepsilon=2\omega)}$:

$$\Pi_{K'_0(\varepsilon=2\omega)} V' \equiv V'_{resonant} = -\frac{\varepsilon}{4} \begin{pmatrix} 0 & e^{-i2\theta} \\ e^{i2\theta} & 0 \end{pmatrix}. \quad (119)$$

We notice that the eigenvalues of $K'_0(\varepsilon)$ are also degenerate at $\varepsilon = \omega$. But since there are no terms in V' with modes $e^{\pm i\theta}$, we have $\Pi_{K'_0(\varepsilon=\omega)} V' = 0$. This degeneracy does not give rise to an actual resonance. One can call it an inactive resonance. An equivalent way of stating this is that in the calculation of W for the perturbation analysis, the degeneracy of the eigenvalues leads to a zero in the denominator, but the corresponding numerator is identically zero.

As before, if we want to eliminate the perturbation by a KAM iteration for values of $\varepsilon \gtrsim 2\omega$, we first have to deal with the resonant term (119). This can be done as above by using a transformation, that is not close to the identity, of the form

$$R_2 = \begin{pmatrix} 1 & 0 \\ 0 & e^{i2\theta} \end{pmatrix}. \quad (120)$$

The transformed Floquet Hamiltonian becomes

$$R_2^\dagger K' R_2 = -i\omega \frac{\partial}{\partial \theta} + H_0'' + \frac{\varepsilon}{4} \begin{pmatrix} 2 \cos(2\theta) & e^{i4\theta} \\ e^{-i4\theta} & -2 \cos(2\theta) \end{pmatrix} + \frac{3}{2}\omega \mathbb{1}_{\mathcal{K}}, \quad (121)$$

with

$$H_0'' = \frac{\varepsilon}{2} \begin{pmatrix} (1 - 2\omega/\varepsilon) & -1/2 \\ -1/2 & -(1 - 2\omega/\varepsilon) \end{pmatrix}. \quad (122)$$

As before, the constant part H_0'' can be diagonalized by a transformation (which depends on ε , but not on θ):

$$T_2 = \frac{1}{d} \begin{pmatrix} \alpha_+ + \varepsilon/2 - \omega & \varepsilon/4 \\ -\varepsilon/4 & \alpha_+ + \varepsilon/2 - \omega \end{pmatrix}, \quad (123)$$

where $\alpha_{\pm} = \pm(\omega^2 + \varepsilon^2 5/16 - \varepsilon\omega)^{1/2}$ are the eigenvalues of H_0'' and $d = [(\alpha_+ + \varepsilon/2 - \omega)^2 + \varepsilon^2/16]^{1/2}$. The transformed Floquet Hamiltonian can thus be written as

$$\begin{aligned} K'' &= T_2^\dagger R_2^\dagger T_1^\dagger R_1^\dagger K R_1 T_1 R_2 T_2 \\ &= -i\omega \frac{\partial}{\partial \theta} + (\omega^2 + 5\varepsilon^2/16 - \varepsilon\omega)^{1/2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \frac{\varepsilon}{4} V'' + \frac{3\omega}{2} \mathbb{1}_{\mathcal{K}}, \end{aligned} \quad (124)$$

where

$$V'' = T_2^\dagger \begin{pmatrix} 2 \cos(2\theta) & e^{i4\theta} \\ e^{-i4\theta} & -2 \cos(2\theta) \end{pmatrix} T_2. \quad (125)$$

This transformed Floquet Hamiltonian is non resonant for values of ε up to a certain amplitude $\varepsilon > 2\omega$, and the KAM iteration based on Eq. (124) can be expected to converge.

D. Effective dressed Hamiltonians by partitioning of Floquet Hamiltonians

In this subsection we will combine the general ideas of the iterative perturbation algorithms by unitary transformations and of the Rotating wave transformation, to construct effective models. We first show that the preceding KAM iterative perturbation algorithms allow us to partition at a desired order operators in orthogonal Hilbert subspaces. Its relation with the standard adiabatic elimination is proved for the second order. We next apply this partitioning technique combined with RWT to construct effective dressed Hamiltonians from the Floquet Hamiltonian. This is illustrated in the next two sections III E and III F for two-photon resonant processes in atoms and molecules.

1. Partitioning: General formulation

We develop the partitioning technique with the use of the iterative KAM perturbation algorithms. We derive an effective Hamiltonian of second order. The scheme we show can be easily extended to higher orders.

We consider the dynamics of a system defined on a Hilbert space \mathcal{H} of dimension N , by a time-independent Hamiltonian H . We consider situations in which the Hilbert space can be split into two orthogonal subspaces $\mathcal{H} = \mathcal{H}^0 \oplus \mathcal{H}^1$, that are only weakly coupled by H . Introducing the projectors P^j into these subspaces, $\mathcal{H}^0 = P^0\mathcal{H}$ and $\mathcal{H}^1 = P^1\mathcal{H}$, the Hamiltonian can be separated into four parts:

$$H = H^{00} + H^{11} + H^{01} + H^{10} \quad \text{with} \quad H^{ij} := P^i H P^j, \quad H^{01} = (H^{10})^\dagger. \quad (126)$$

We can represent this partition symbolically in matrix form as

$$H = \begin{pmatrix} H^{00} & H^{01} \\ H^{10} & H^{11} \end{pmatrix}. \quad (127)$$

The idea is that the coupling $H^{01} + H^{10}$ is small with respect to the other relevant energies of $|H^{11} - H^{00}|$. We think of it as being of order ε . We introduce the notation

$$\varepsilon V_1 := H^{01} + H^{10} = \varepsilon(\tilde{H}^{01} + \tilde{H}^{10}). \quad (128)$$

where ε is a formal parameter, that is useful to keep track of the orders of the different terms, and it is meant to reflect the fact that $H^{01} + H^{10}$ is small. Once the formulas for the perturbative procedure are obtained, ε can be set equal to 1. The whole construction can be made without introducing ε . Its role is exclusively as an intuitive aid to follow the construction. We will show that the *effective Hamiltonian of second order* (connected with an initial condition in \mathcal{H}^0) reads as

$$H_{\text{eff}}^{00} = H^{00} + \frac{\varepsilon^2}{2} P^0 \left[\tilde{H}^{01} W_1^{10} + (\tilde{H}^{01} W_1^{10})^\dagger \right] P^0, \quad (129)$$

with W_1^{10} defined in Eq. (140c). In terms of the eigenvalues and eigenvectors of H^{00} restricted to the subspace $P^0\mathcal{H}$, which we denote by λ_n^{00} and $|n^{00}\rangle$, and those of H^{11} restricted to the subspace $P^1\mathcal{H}$ which we denote by λ_m^{11} and $|m^{11}\rangle$, it becomes

$$H_{\text{eff}}^{00} = H^{00} - \frac{1}{2} \sum_{n, \tilde{n}} |\tilde{n}^{00}\rangle \left[\sum_m \langle \tilde{n}^{00} | H^{01} | m^{11} \rangle \langle m^{11} | H^{10} | n^{00} \rangle \left(\frac{1}{\lambda_m^{11} - \lambda_n^{00}} + \frac{1}{\lambda_m^{11} - \lambda_{\tilde{n}}^{00}} \right) \right] \langle n^{00} |. \quad (130)$$

The goal is to find a unitary transformation S that transforms H into block-diagonal form, at least to some order of approximation:

$$S^\dagger H S = \begin{pmatrix} H^{00} + D_1^{00} & 0 \\ 0 & H^{11} + D_1^{11} \end{pmatrix}. \quad (131)$$

The idea is in general that instead of diagonalizing by perturbation methods the complete Hamiltonian, one first reduces it approximately to block-diagonal form, singling out a block $H^{00} + D_1^{00}$, of small dimension, that is the most relevant part for the dynamics of a particularly chosen initial condition. The Hamiltonian $H^{00} + D_1^{00}$ is called the *effective Hamiltonian* for the considered process. Since it is of small dimension it can often be analyzed in detail with non-perturbative methods (for example by exact diagonalization). The sub-block should contain all the states with which the initial state is mainly coupled by the dynamics. These states are called *essential states*. In other words, within each of the initial diagonal blocks the couplings can be strong, but the couplings between the blocks should be small. We assume in particular that the spectrum of H^{00} is well separated from the one of H^{11} by a minimal distance between eigenvalues denoted $\Delta\lambda_{\min}$. We require that the norm of the coupling $H^{01} + H^{10}$ between the two blocks is small with respect to $\Delta\lambda_{\min}$.

We thus construct a unitary transformation of the form $e^{\varepsilon W_1}$, with $W_1^\dagger = -W_1$ such that

$$e^{-\varepsilon W_1} (H^{00} + H^{11} + \varepsilon V_1) e^{\varepsilon W_1} = H^{00} + H^{11} + D_1 + \varepsilon^2 V_2, \quad (132)$$

where $D_1 = D_1^{00} + D_1^{11}$, with $D_1^{ii} = P^i D_1 P^i$, $i = 0, 1$, and V_2 is a remaining coupling term that is of order ε^2 . We will use the notation $D_1 =: \varepsilon \tilde{D}_1$. Expansion of the exponentials and extractions of the non block-diagonal terms leads to

the equations that D_1 and W_1 are required to fulfill:

$$[H^{00} + H^{11}, W_1] + V_1 - \tilde{D}_1 = 0, \quad (133a)$$

$$[P^0, D_1^{00}] = 0, \quad (133b)$$

$$[P^1, D_1^{11}] = 0. \quad (133c)$$

Defining

$$W_1^{ij} := P^i W_1 P^j, \quad (134)$$

and acting with the projectors P^0 and P^1 from the left and from the right in the four possible combinations, equation (133a) can be decomposed in four independent equations:

$$H^{00} W_1^{01} - W_1^{01} H^{11} + \tilde{H}^{01} = 0, \quad (135a)$$

$$H^{11} W_1^{10} - W_1^{10} H^{00} + \tilde{H}^{10} = 0, \quad (135b)$$

$$D_1^{00} = 0, \quad (135c)$$

$$D_1^{11} = 0. \quad (135d)$$

Equations (135c) (135d) are a direct consequence of the fact that $V_1 \equiv H^{01} + H^{10}$ have zero diagonal blocks and mean that $D_1 = 0$. We remark that equations (135a)-(135d) do not impose any condition on the components W_1^{00} and W_1^{11} , which can therefore be chosen arbitrarily. The choice that leads to the simplest expressions is $W_1^{00} = 0$ and $W_1^{11} = 0$. The two other components W_1^{10} , W_1^{01} are uniquely determined. In close analogy with the construction of Section III A 2, we define the projector Π by

$$\Pi V := P^0 V P^0 + P^1 V P^1. \quad (136)$$

A solution of equations (133a)(133b) is given by

$$\tilde{D}_1 = \Pi V_1 = 0 \quad (137)$$

and

$$W_1^{01} = \lim_{\tau \rightarrow \infty} \frac{-i}{\tau} \int_0^\tau ds' \int_0^{s'} ds e^{-iH^{00}s} \tilde{H}^{01} e^{iH^{11}s}, \quad (138a)$$

$$= \lim_{\beta \rightarrow 0^+} -i \int_0^\infty ds e^{-\beta s} e^{-iH^{00}s} \tilde{H}^{01} e^{iH^{11}s} \quad (138b)$$

with

$$W_1^{10} = -(W_1^{01})^\dagger. \quad (139)$$

This solution can be expressed in terms of the eigenvalues and eigenvectors of H^{00} and of H^{11} :

$$W_1 = W_1^{01} + W_1^{10}, \quad (140a)$$

$$W_1^{01} = - \sum_{n,m} \frac{|n^{00}\rangle \langle n^{00}| \tilde{H}^{01} |m^{11}\rangle \langle m^{11}|}{\lambda_n^{00} - \lambda_m^{11}}, \quad (140b)$$

$$W_1^{10} = - \sum_{n,m} \frac{|m^{11}\rangle \langle m^{11}| \tilde{H}^{10} |n^{00}\rangle \langle n^{00}|}{\lambda_m^{11} - \lambda_n^{00}}. \quad (140c)$$

Since $D_1 = 0$, we conclude that there is no contribution to the diagonal blocks in the first iteration, i.e. of first order in ε , and in analogy with Eq. (87), the remaining coupling term can be written as

$$\varepsilon^2 V_2 = \frac{\varepsilon^2}{2} [V_1, W_1] + \frac{\varepsilon^3}{3} [[V_1, W_1], W_1] + \dots + \varepsilon^M \frac{(M-1)}{M!} \underbrace{[\dots [[V_1, W_1], W_1], \dots]}_{M-1 \text{ commutators}} + \dots \quad (141)$$

We can obtain an effective Hamiltonian of second order with little supplementary effort: We first extract from the block-diagonal part of $\varepsilon^2 V_2$ the term

$$B_2 := \frac{\varepsilon^2}{2} [V_1, W_1], \quad (142)$$

which is the only one that carries the lowest power ε^2 . Since $P^1[V_1, W_1]P^0 = 0$ and $P^0[V_1, W_1]P^1 = 0$, the term of power ε^2 has no off-block-diagonal part. Thus we can write

$$e^{-\varepsilon W_1}(H^{00} + H^{11} + \varepsilon V_1)e^{\varepsilon W_1} = H^{00} + H^{11} + \frac{\varepsilon^2}{2}[V_1, W_1] + \varepsilon^3 V_3 \quad (143)$$

with

$$\varepsilon^3 V_3 = \frac{\varepsilon^3}{3}[[V_1, W_1], W_1] + \dots + \varepsilon^M \frac{(M-1)}{M!} \underbrace{[\dots[[V_1, W_1], W_1], \dots]}_{M-1 \text{ commutators}} + \dots \quad (144)$$

or, symbolically, in matrix notation

$$\begin{aligned} H_2 &= e^{-\varepsilon W_1} \begin{pmatrix} H^{00} & H^{01} \\ H^{10} & H^{11} \end{pmatrix} e^{\varepsilon W_1} \\ &= \begin{pmatrix} H^{00} + \frac{\varepsilon^2}{2} (\tilde{H}^{01} W_1^{10} - W_1^{01} \tilde{H}^{10}) & 0 \\ 0 & H^{11} + \frac{\varepsilon^2}{2} (\tilde{H}^{10} W_1^{01} - W_1^{10} \tilde{H}^{01}) \end{pmatrix} + \varepsilon^3 V_3 \\ &= \begin{pmatrix} H^{00} + \frac{\varepsilon^2}{2} [\tilde{H}^{01} W_1^{10} + (\tilde{H}^{01} W_1^{10})^\dagger] & 0 \\ 0 & H^{11} - \frac{\varepsilon^2}{2} [(W_1^{10} \tilde{H}^{01})^\dagger + W_1^{10} \tilde{H}^{01}] \end{pmatrix} + \varepsilon^3 V_3. \end{aligned} \quad (145)$$

Thus we find the effective Hamiltonian (129) that gives the eigenvectors and eigenvalues of order ε^2 (and corrections of order ε^3).

Remark. In fact we can show that while the next order correction for the eigenvectors is indeed of order ε^3 , the one for the eigenvalues is of order ε^4 . The term of order ε^3 in (144) is $[[V_1, W_1], W_1]$ which has zero block-diagonal projection, since the product of two off-block-diagonal operators is block-diagonal, and the product of an off-block-diagonal operator with a block-diagonal operator is off-block-diagonal. Symbolically we can represent this by

$$\begin{pmatrix} & \blacksquare \\ \blacksquare & \end{pmatrix} \begin{pmatrix} & \blacksquare \\ \blacksquare & \end{pmatrix} = \begin{pmatrix} \blacksquare & \\ & \blacksquare \end{pmatrix}, \quad \begin{pmatrix} \blacksquare & \\ & \blacksquare \end{pmatrix} \begin{pmatrix} & \blacksquare \\ \blacksquare & \end{pmatrix} = \begin{pmatrix} & \blacksquare \\ \blacksquare & \end{pmatrix} \quad (146)$$

and shown for arbitrary operators A and B by

$$(P^0 A P^1 + P^1 A P^0) (P^0 B P^1 + P^1 B P^0) = P^0 A P^1 B P^0 + P^1 A P^0 B P^1 \quad (147)$$

and

$$(P^0 A P^0 + P^1 A P^1) (P^0 B P^1 + P^1 B P^0) = P^0 A P^0 B P^1 + P^1 A P^1 B P^0 \quad (148)$$

The fact that the term of order ε^3 in (144) is off-block-diagonal implies that, if we perform a second unitary transformation $e^{\varepsilon^3 W_3}$, there will be no term of order ε^3 in the diagonal block projection D_3 , and thus the next order correction for the diagonal block, and therefore for eigenvalues, will be of order ε^4 (given by $\varepsilon^4[[[V_1, W_1], W_1], W_1]/8$).

2. Relation with adiabatic elimination

In the literature a different technique has been widely used to construct effective Hamiltonians, based on the partitioning technique combined with an approximation procedure known as adiabatic elimination for the time-dependent Schrödinger equation (see Ref. [39], p. 1165). In this section we show that the effective Hamiltonian constructed by adiabatic elimination can be recovered from the above construction by choosing the reference of the energy appropriately. Our stationary formulation allows moreover to estimate the order of the neglected terms, and to improve the approximation to higher orders in a systematic way.

The idea in the method of adiabatic elimination is that the time evolution of the components in \mathcal{H}^1 oscillates very rapidly with respect to the evolution of the components in \mathcal{H}^0 . This justifies the substitution of the time dependent components in \mathcal{H}^1 by some average values. This leads then to an effective Hamiltonian in \mathcal{H}^0 that takes the form [see Ref. [39], p. 1166, Eq. (18.7-7), where there is a sign misprint]

$$H_{\text{eff,ae}}^{00} = H^{00} - H^{01} (H^{11})^{-1} H^{10}. \quad (149)$$

This equation can be obtained from Eq. (129) as follows. Denoting by λ_{\max}^{00} the largest eigenvalue of H^{00} , we can write the denominator of W_1^{10} (140c) as

$$\lambda_m^{11} - \lambda_n^{00} = (\lambda_m^{11} - \lambda_{\max}^{00}) + (\lambda_{\max}^{00} - \lambda_n^{00}). \quad (150)$$

The condition that the time evolution of the components in \mathcal{H}^1 oscillate very rapidly with respect to the evolution of the components in \mathcal{H}^0 can be formulated by an inequality between the eigenvalues:

$$\lambda_{\max}^{00} - \lambda_n^{00} \ll \lambda_m^{11} - \lambda_{\max}^{00}. \quad (151)$$

Thus the expression (140c) can be approximated by

$$\begin{aligned} W_1^{10} &\approx - \sum_{n,m} \frac{|m^{11}\rangle \langle m^{11}| \tilde{H}^{10} |n^{00}\rangle \langle n^{00}|}{\lambda_m^{11} - \lambda_{\max}^{00}} = - \sum_{n,m} |m^{11}\rangle \langle m^{11}| (H^{11} - \lambda_{\max}^{00} \mathbb{1}_{11})^{-1} \tilde{H}^{10} |n^{00}\rangle \langle n^{00}| \\ &= - (H^{11} - \lambda_{\max}^{00} \mathbb{1}_{11})^{-1} \tilde{H}^{10}, \end{aligned} \quad (152)$$

which gives for the effective Hamiltonian (129):

$$H_{\text{eff}}^{00} \approx H^{00} - H^{01} (H^{11} - \lambda_{\max}^{00} \mathbb{1}_{11})^{-1} H^{10}. \quad (153)$$

Choosing the reference of energy $\lambda_{\max}^{00} = 0$ allows us to recover Eq. (149).

We remark that in the approach by adiabatic elimination a further approximation is implicitly made, since the eigenvectors (or the initial conditions) when it is applied to dynamics are not transformed with $e^{\varepsilon W_1}$. This amounts to the approximation $e^{\varepsilon W_1} = \mathbb{1} + \varepsilon W_1 + \dots \approx \mathbb{1}$. This does not produce a big difference when adiabatic elimination is applied to adiabatic processes with laser pulses, since, as we will see in Section V, the initial and final eigenvectors of the perturbed Hamiltonian coincide with those of the unperturbed one.

3. High frequency partitioning

We can adapt the method described for high frequency perturbation theory to the partitioning setup, which is another way to obtain the result of adiabatic elimination. We consider a partition represented symbolically in matrix form as

$$H = \begin{pmatrix} H^{00} - \lambda_{\max}^{00} \mathbb{1}_{00} & H^{01} \\ H^{10} & f (H^{11} - \lambda_{\max}^{00} \mathbb{1}_{11}) \end{pmatrix}, \quad (154)$$

in a regime where $f \rightarrow \infty$. Defining $\varepsilon := 1/f$, we decompose accordingly as

$$\hat{H} := H/f = \begin{pmatrix} 0 & 0 \\ 0 & \hat{H}^{11} \end{pmatrix} + \varepsilon \begin{pmatrix} \hat{H}^{00} & H^{01} \\ H^{10} & 0 \end{pmatrix} =: \hat{H}_0 + \varepsilon \hat{V}_1, \quad (155)$$

where we have simplified the notation by defining $\hat{H}^{00} := H^{00} - \lambda_{\max}^{00} \mathbb{1}_{00}$ and $\hat{H}^{11} := H^{11} - \lambda_{\max}^{00} \mathbb{1}_{11}$. We construct a unitary transformation $\exp(\varepsilon W_1)$ such that

$$e^{-\varepsilon W_1} (\hat{H}_0 + \varepsilon \hat{V}_1) e^{\varepsilon W_1} = \hat{H}_0 + \varepsilon D_1 + \varepsilon^2 V_2 \quad (156)$$

with the condition

$$[P^1, D_1] = 0, \quad (157)$$

where P^1 is the projection into the subspace corresponding to the 11-block. We remark that defining the projector into the orthogonal complement, $P^0 := \mathbb{1} - P^1$, the condition (157) implies that also $[P^0, D_1] = 0$, which leads to

$$D_1 = P^1 D_1 P^1 + P^0 D_1 P^0. \quad (158)$$

As before, the generator W_1 can be chosen such that $P^1 W_1 P^1 = 0$, $P^0 W_1 P^0 = 0$, and

$$D_1 = P^1 \hat{V}_1 P^1 + P^0 \hat{V}_1 P^0 = P^0 \hat{V}_1 P^0 = \begin{pmatrix} \hat{H}^{00} & 0 \\ 0 & 0 \end{pmatrix}. \quad (159)$$

The generator W_1 is determined by the equation

$$[\hat{H}_0, W_1] + \hat{V}_1 - D_1 = 0. \quad (160)$$

From the general procedure described in the preceding sections, $W_1 = W_1^{01} + W_1^{10}$ can be written e.g. as

$$W_1^{01} = \lim_{\beta \rightarrow 0^+} -i \int_0^\infty ds e^{-\beta s} H^{01} e^{i\hat{H}^{11}s}, \quad W_1^{10} = -(W_1^{01})^\dagger. \quad (161)$$

Alternatively we can write explicitly the equation (160), which in the present case becomes

$$\begin{aligned} 0 &= \left[\begin{pmatrix} 0 & 0 \\ 0 & \hat{H}^{11} \end{pmatrix}, \begin{pmatrix} 0 & W_1^{01} \\ W_1^{10} & 0 \end{pmatrix} \right] + \begin{pmatrix} 0 & H^{01} \\ H^{10} & 0 \end{pmatrix} \\ &= \begin{pmatrix} 0 & -W_1^{01}\hat{H}^{11} \\ \hat{H}^{11}W_1^{10} & 0 \end{pmatrix} + \begin{pmatrix} 0 & H^{01} \\ H^{10} & 0 \end{pmatrix} \end{aligned} \quad (162)$$

which leads to the solution

$$W_1^{01} = H^{01} (\hat{H}^{11})^{-1}, \quad (163a)$$

$$W_1^{10} = -(W_1^{01})^\dagger = -(\hat{H}^{11})^{-1} H^{10}, \quad (163b)$$

and thus to the remaining corrections of order ϵ^2 of the form

$$\begin{aligned} H_2 &= e^{-\epsilon W_1} \begin{pmatrix} \hat{H}^{00} & H^{01} \\ H^{10} & f\hat{H}^{11} \end{pmatrix} e^{\epsilon W_1} \\ &= \begin{pmatrix} H^{00} + \frac{\epsilon^2}{2} (H^{01}W_1^{10} - W_1^{01}H^{10}) & \frac{\epsilon^2}{2} \hat{H}^{00}W_1^{01} \\ -\frac{\epsilon^2}{2} W_1^{10}\hat{H}^{00} & H^{11} + \frac{\epsilon^2}{2} (H^{10}W_1^{01} - W_1^{10}H^{01}) \end{pmatrix} + \epsilon^3 V_3. \end{aligned} \quad (164)$$

After a second transformation of the form $\exp(\epsilon^2 W_2)$ designed to eliminate the non-block-diagonal terms of order ϵ^2 , one obtains an effective Hamiltonian of second order for the 00-block of the form

$$H_{\text{eff}}^{00} = H^{00} - \lambda_{\text{max}}^{00} \mathbb{1}_{00} - H^{01} (H^{11} - \lambda_{\text{max}}^{00} \mathbb{1}_{11})^{-1} H^{10}. \quad (165)$$

We remark that, as opposed to Eqs. (145)- (129), in this construction two unitary transformations are needed to obtain the effective eigenvectors to second order (after the first transformation, where keeping only the diagonal blocks in (164) yields the eigenvalues to second order, but not the eigenvectors).

4. Effective dressed Hamiltonians: partitioning in the enlarged space

When considering the stationary Floquet Hamiltonian $K = -i\hbar\omega \frac{\partial}{\partial \theta} + H(\theta)$, $H(\theta) = H_0 + \varepsilon V(\theta)$, describing the dynamics of a quantum (atomic or molecular) system H_0 , illuminated by a strong photon field (of one frequency), we have to extend the preceding partitioning to the enlarged space $\mathcal{K} = \mathcal{H} \otimes \mathcal{L}$. This is in practice done in two steps:

(i) First we identify a set of atomic (or molecular) essential states, connected with the initial condition, whose population will be appreciable during the dynamics. This means that these states are in multiphoton resonance (or quasi-resonance). This allows to split the Hilbert space into two orthogonal subspaces $\mathcal{H} = \mathcal{H}^0 \oplus \mathcal{H}^1$, and thus the enlarged Hilbert space also into two orthogonal subspaces

$$\mathcal{K} = (\mathcal{H}^0 \otimes \mathcal{L}) \oplus (\mathcal{H}^1 \otimes \mathcal{L}) = \mathcal{K}^0 \oplus \mathcal{K}^1. \quad (166)$$

We next partition the Floquet Hamiltonian with respect to these atomic blocks. We obtain effective Floquet Hamiltonians inside each block.

(ii) The second step is the construction of an effective dressed Hamiltonian, independent of the θ -variable, inside the block connected to the initial condition. This can be done by the KAM iterations combined by the RWT techniques to treat the resonances. The second step depends on the specific problem that is treated.

Two-photon process examples will be illustrated below.

a. Partitioning of the Floquet Hamiltonian. We formulate in a general way the first step for partitioning the Floquet Hamiltonian up to the second order. As before, the free atomic Hamiltonian is defined on a Hilbert space \mathcal{H} of dimension N . The Hamiltonian $H(\theta)$ can be separated into four parts such that the Floquet Hamiltonian can be represented symbolically in matrix form as

$$K = \begin{pmatrix} K_0^{00} + \varepsilon V^{00}(\theta) & \varepsilon V^{01}(\theta) \\ \varepsilon V^{10}(\theta) & K_0^{11} + \varepsilon V^{11}(\theta) \end{pmatrix}, \quad (167)$$

with

$$K_0^{ii} = -i\hbar\omega \frac{\partial}{\partial\theta} \otimes \mathbb{1}_{\mathcal{H}^i} + H_0^{ii}, \quad (168a)$$

$$V = V^{00} + V^{11} + V^{01} + V^{10}, \quad (168b)$$

$$H_0 = H_0^{00} + H_0^{11}. \quad (168c)$$

In the enlarged space, the splitting can be interpreted as two weakly coupled subspaces \mathcal{K}^0 and \mathcal{K}^1 .

As before, we construct a unitary transformation of the form $e^{\varepsilon W_1}$, with $W_1^\dagger = -W_1$ such that

$$e^{-\varepsilon W_1} (K_0^{00} + K_0^{11} + \varepsilon V) e^{\varepsilon W_1} = K_0^{00} + K_0^{11} + \varepsilon D_1(\theta) + \varepsilon^2 V_2(\theta), \quad (169)$$

where $D_1 = D_1^{00} + D_1^{11}$, with $D_1^{ii} = P^i D_1 P^i$, $i = 0, 1$, and giving the remaining coupling

$$\begin{aligned} \varepsilon^2 V_2 &= \frac{\varepsilon^2}{2} [V, W_1] + \frac{\varepsilon^3}{3} [[V, W_1], W_1] + \dots + \varepsilon^M \frac{(M-1)}{M!} \underbrace{[\dots [V, W_1], W_1], \dots]}_{M-1 \text{ commutators}} + \dots \\ &+ \frac{\varepsilon^2}{2!} [D_1, W_1] + \frac{\varepsilon^3}{3!} [[D_1, W_1], W_1] + \dots + \frac{\varepsilon^M}{M!} \underbrace{[\dots [D_1, W_1], W_1], \dots]}_{M-1 \text{ commutators}} + \dots \end{aligned} \quad (170)$$

Since we have here a block-diagonal perturbation, we can choose

$$D_1 = V^{00} + V^{11}, \quad (171)$$

which in this case is not necessarily zero, as opposed to Eqs (135). This leads to $W^{00} = 0 = W^{11}$. We obtain a Floquet Hamiltonian of second order, in matrix notation

$$\begin{aligned} K_2 &= e^{-\varepsilon W_1} (K_0^{00} + K_0^{11} + \varepsilon V) e^{\varepsilon W_1} \\ &= \begin{pmatrix} K^{00} + \varepsilon V^{00} + \frac{\varepsilon^2}{2} [V^{01} W_1^{10} + (V^{01} W_1^{10})^\dagger] & \frac{\varepsilon^2}{2} (V^{00} W_1^{01} - W_1^{01} V^{11}) \\ \frac{\varepsilon^2}{2} (V^{11} W_1^{10} - W_1^{10} V^{00}) & K^{11} + \varepsilon V^{11} - \frac{\varepsilon^2}{2} [(W_1^{10} V^{01})^\dagger + W_1^{10} V^{01}] \end{pmatrix} + \mathcal{O}(\varepsilon^3). \end{aligned} \quad (172)$$

We obtain the effective Floquet Hamiltonian (assuming that the initial condition is connected to the block \mathcal{K}_0) of second order:

$$K_{\text{eff}}^{00} = -i\hbar\omega \frac{\partial}{\partial\theta} \otimes \mathbb{1}_{\mathcal{H}^0} + H_0^{00} + \varepsilon V^{00} + \frac{\varepsilon^2}{2} [V^{01} W_1^{10} + (V^{01} W_1^{10})^\dagger]. \quad (173)$$

The next corrections of order ε^3 are given by $\frac{\varepsilon^3}{3} [[V_1, W_1], W_1] + \frac{\varepsilon^3}{3!} [[D_1, W_1], W_1]$. The particular case

$$V^{00} + V^{11} = 0, \quad (174)$$

leads to $D_1 = 0$, and to corrections for the eigenvalues of order ε^4 , given by $\varepsilon^4 [[V, W_1], W_1] / 8$.

b. Calculation of W_1 . It is convenient to calculate the term of order ε^2 of the effective Floquet Hamiltonian by expansion of V^{01} and W_1^{10} in Fourier series. The perturbation can be indeed written as

$$V(\theta) = \sum_{\ell} \tilde{V}_{\ell} e^{i\ell\theta}. \quad (175)$$

Writing W_1 in the basis of eigenvectors $|n, k\rangle$ of K_0 , denoting the corresponding eigenvalues $\lambda_{n,k}^0 = E_n + k\hbar\omega$ with E_n the eigenvalues of H_0 :

$$W_1 = \sum_{n,m,k,k', (m,k') \neq (n,k)} \frac{|n, k\rangle \langle n, k| V(\theta) |m, k'\rangle \langle m, k'|}{\lambda_{m,k'}^0 - \lambda_{n,k}^0}, \quad (176)$$

gives

$$\begin{aligned} W_1 &= \sum_{n,m,k,k',\ell} \frac{|n\rangle \langle n| \tilde{V}_\ell |m\rangle \langle m| \otimes [|k\rangle \langle k| e^{i\ell\theta} |k'\rangle \langle k'|]}{E_m + k'\hbar\omega - (E_n + k\hbar\omega)} \\ &= \sum_{n,m,\ell} \frac{|n\rangle \langle n| \tilde{V}_\ell |m\rangle \langle m|}{E_m - E_n - \ell\hbar\omega} \otimes e^{i\ell\theta}, \end{aligned} \quad (177)$$

since

$$\sum_k |k\rangle \langle k - \ell| = e^{+i\ell\theta}. \quad (178)$$

We can thus expand W_1 in the Fourier modes

$$W_1 = \sum_\ell \tilde{W}_{1,\ell} e^{i\ell\theta}, \quad \tilde{W}_{1,\ell} = \sum_{n,m} \frac{|n\rangle \langle n| \tilde{V}_\ell |m\rangle \langle m|}{E_m - E_n - \ell\hbar\omega}. \quad (179)$$

Defining $W_1^{ij} := P^i W_1 P^j$, and choosing $W_1^{00} = 0$ and $W_1^{11} = 0$, we obtain as before, in terms of the eigenvalues and eigenvectors (in the enlarged space) of K^{00} and of K^{11} :

$$W_1 = W_1^{01} + W_1^{10}, \quad (180a)$$

$$W_1^{01} = \sum_\ell \tilde{W}_{1,\ell}^{01} e^{i\ell\theta}, \quad \tilde{W}_{1,\ell}^{01} = \sum_{n,m} \frac{|n^{00}\rangle \langle n^{00}| \tilde{V}_\ell^{01} |m^{11}\rangle \langle m^{11}|}{E_m^{11} - E_n^{00} - \ell\hbar\omega}, \quad (180b)$$

$$W_1^{10} = \sum_\ell \tilde{W}_{1,\ell}^{10} e^{i\ell\theta}, \quad \tilde{W}_{1,\ell}^{10} = \sum_{n,m} \frac{|m^{11}\rangle \langle m^{11}| \tilde{V}_\ell^{10} |n^{00}\rangle \langle n^{00}|}{E_n^{00} - E_m^{11} - \ell\hbar\omega} \quad (180c)$$

with

$$\tilde{V}_\ell^{10} = \left(\tilde{V}_{-\ell}^{01}\right)^\dagger, \quad \tilde{W}_{1,\ell}^{10} = -\left(\tilde{W}_{1,-\ell}^{01}\right)^\dagger. \quad (181)$$

We remark that the denominators of W_1 allow to detect resonant states of the subspace \mathcal{H}^1 that should be thus included in the subspace \mathcal{H}^0 in the partitioning.

Using a perturbation satisfying $\tilde{V}_{-\ell} = \tilde{V}_\ell$ (such as perturbation proportional to $\cos\theta$), we obtain for the second order effective Floquet Hamiltonian

$$\begin{aligned} K_{\text{eff}}^{00} &= -i\hbar\omega \frac{\partial}{\partial\theta} \otimes \mathbb{1}_{\mathcal{H}^0} + H_0^{00} + \varepsilon V^{00} \\ &\quad - \frac{\varepsilon^2}{2} \sum_{n,\tilde{n},\ell,\ell',m} |\tilde{n}^{00}\rangle \langle \tilde{n}^{00}| \tilde{V}_{\ell'}^{01} |m^{11}\rangle \langle m^{11}| \tilde{V}_\ell^{10} |n^{00}\rangle \left(\frac{e^{i(\ell+\ell')\theta}}{E_m^{11} - E_n^{00} + \ell\hbar\omega} + \frac{e^{-i(\ell+\ell')\theta}}{E_m^{11} - E_n^{00} + \ell'\hbar\omega} \right) \langle n^{00}|. \end{aligned} \quad (182)$$

We can easily extend this formula to the multifrequency case by adapting the notations: $\omega \rightarrow \underline{\omega}$, $\theta \rightarrow \underline{\theta}$, $\ell \rightarrow \underline{\ell}$, and $\ell' \rightarrow \underline{\ell}'$ (see also Section II E).

E. Effective Hamiltonian for two-photon quasi-resonant processes in atoms: The two-photon RWA

We illustrate the preceding formulation to construct an effective Hamiltonian for the example of a two-photon transition in atoms by a laser pulse, with no single-photon resonances.

Since this effective Hamiltonian will be parametrized by the laser amplitude and its frequency, it will be relevant for processes with chirped laser pulses.

We consider an atom, of Hamiltonian H_0 , illuminated by a laser of polarization \vec{e} , amplitude \mathcal{E} and frequency ω , such that two atomic states $|a\rangle$ and $|b\rangle$ (of respective energies E_a and E_b giving $H_0 = \text{diag}[E_a, E_b]$ in the basis $\{|a\rangle, |b\rangle\}$) are in two-photon quasi-resonance:

$$E_a + 2\hbar\omega + \hbar\Delta = E_b. \quad (183)$$

One considers the electric dipole moment $\vec{\mu} = e \sum_i \vec{r}_i$, with \vec{r}_i the position of each electron i and e the elementary electric charge. The Floquet Hamiltonian reads

$$K = -i\hbar\omega \frac{\partial}{\partial\theta} + H_0 - \vec{\mu} \cdot \vec{e} \mathcal{E} \cos\theta. \quad (184)$$

We partition the Floquet Hamiltonian such that the states $|a\rangle$ and $|b\rangle$ span the Hilbert subspace \mathcal{H}^0 and the other atomic states $\{|1\rangle, \dots, |N\rangle\}$ the Hilbert subspace \mathcal{H}^1 .

Denoting $\mu_{nn'} = \langle n | \vec{\mu} \cdot \vec{e} | n' \rangle_{\mathbf{r}}$, with \mathbf{r} standing for the electron coordinates, and applying Eq. (182), we obtain for the second order effective Floquet Hamiltonian

$$K_{\text{eff}} = -i\hbar\omega \frac{\partial}{\partial\theta} + H_0 + \mathcal{E}V(\theta) \quad (185)$$

with

$$\mathcal{E}V(\theta) = -\mathcal{E} \begin{pmatrix} \mu_{aa} & \mu_{ab} \\ \mu_{ba} & \mu_{bb} \end{pmatrix} \cos\theta - \frac{\mathcal{E}^2}{2} \begin{pmatrix} \mathcal{V}_{aa}(\theta) & \mathcal{V}_{ab}(\theta) \\ \mathcal{V}_{ba}(\theta) & \mathcal{V}_{bb}(\theta) \end{pmatrix} \quad (186)$$

and

$$\mathcal{V}_{nn} = \cos^2\theta \sum_m \left(\frac{|\mu_{nm}|^2}{E_m - E_n - \hbar\omega} + \frac{|\mu_{nm}|^2}{E_m - E_n + \hbar\omega} \right), \quad (187a)$$

$$\mathcal{V}_{ab} = \frac{1}{4} \sum_m \mu_{am} \mu_{mb} \sum_{\ell, \ell' \in \{-1, 1\}} \left(\frac{e^{i(\ell+\ell')\theta}}{E_m - E_b + \ell\hbar\omega} + \frac{e^{-i(\ell+\ell')\theta}}{E_m - E_a + \ell'\hbar\omega} \right). \quad (187b)$$

To extract from the effective Floquet Hamiltonian (185) an effective dressed Hamiltonian independent of θ , we can apply a contact transformation consisting in averaging the Hamiltonian (185) with respect to $K_0 := -i\hbar\omega \partial/\partial\theta + H_0$, i.e. in diagonalizing it with respect to θ and to the basis $\{|a\rangle, |b\rangle\}$. Since $V(\theta) = \sum_{\ell \in \{-2, \dots, 2\}} \tilde{V}_\ell e^{i\ell\theta}$, this could be done using $W(\theta) = \sum_\ell \tilde{W}_\ell e^{i\ell\theta}$ satisfying (179), with, for example, the a, b component of the mode $\ell = 2$

$$\mathcal{E} \langle a | \tilde{W}_2 | b \rangle = \frac{\Omega_{ab}}{E_b - E_a - 2\hbar\omega}, \quad (188)$$

where we denote the effective two-photon Rabi frequency

$$\Omega_{ab} = -\frac{\mathcal{E}^2}{8} \sum_m \mu_{am} \mu_{mb} \left(\frac{1}{E_m - E_a - \hbar\omega} + \frac{1}{E_m - E_b + \hbar\omega} \right). \quad (189)$$

This leads to a *quasi-divergence* of the W which occurs *when the numerator is equal or larger than the denominator in absolute value*. It is due to the quasiresonance $E_b - E_a - 2\hbar\omega = \hbar\Delta$ and occurs thus when $|\Omega_{ab}| \gtrsim \hbar|\Delta|$. We thus apply instead the two-photon RWT $R = \text{diag}[1, \exp(-2i\theta)]$, giving the Hamiltonian $R^\dagger K_{\text{eff}} R$. We are now able to average this Floquet Hamiltonian with respect to K_0 since the small denominators of the associated W have been removed. Instead of diagonalizing fully this Hamiltonian by the contact transformation, we construct an effective dressed Hamiltonian by just averaging with respect to θ [this corresponds to applying the contact transformation $\exp(\mathcal{E}W)$ with $W = -i \int_0^\theta \left(R^\dagger V(\theta) R - \overline{R^\dagger V(\theta) R} \right)$ and $\overline{f(\theta)} = \left(\frac{1}{2\pi} \int_0^{2\pi} d\theta f(\theta) \right)$ and we retain terms up to \mathcal{E}^2 . The effective dressed Hamiltonian (independent of θ) obtained reads (using the energy reference $E_a = 0$)

$$H_{\text{eff}} = \begin{pmatrix} S_a & \Omega_{ab} \\ \Omega_{ab}^* & S_b + \hbar\Delta \end{pmatrix} \quad (190)$$

with the effective two-photon Rabi frequency (189) and the dynamical Stark shift of the state n :

$$S_n = -\frac{\mathcal{E}^2}{4} \sum_m \left(\frac{|\mu_{nm}|^2}{E_m - E_n - \hbar\omega} + \frac{|\mu_{nm}|^2}{E_m - E_n + \hbar\omega} \right). \quad (191)$$

The effective two-photon Rabi frequency is well approximated by

$$\Omega_{ab} \approx -\frac{\mathcal{E}^2}{4} \sum_m \frac{\mu_{am}\mu_{mb}}{E_m - E_a - \hbar\omega}, \quad (192)$$

which is an expression equivalent to (189) with a correction of the order $\hbar\Delta/(E_m - E_a - \hbar\omega)$.

We remark that this effective Hamiltonian (190) constructed by the combination of a partitioning of the Floquet Hamiltonian, of a two-photon RWT, and of a final θ -averaging can be seen as a *two-photon RWA*, which extends the usual (one-photon) RWA [39, 40]. We have thus rederived a well-known result, using stationary techniques that allows us to estimate easily the order of the neglected terms. This method allows us also to calculate higher order corrections. We apply it in the next subsection to calculate effective Hamiltonians for molecule illuminated by strong laser fields.

F. Effective Hamiltonian for rotational excitations in diatomic molecules

To determine an effective dressed Hamiltonian characterizing a molecule excited by strong laser fields, we have to apply the standard construction of the free effective Hamiltonian (such as the Born Oppenheimer approximation) taking into account the interaction with the field non-perturbatively (if resonances occur). This leads to four different time-scales in general: (i) for the motion of the electrons, (ii) for the vibrations of the nuclei, (iii) for the rotation of the nuclei, and (iv) for the frequency of the interacting field. It is well known that it is a good strategy to take into account of the time scales from the fastest to the slowest one.

We consider below an example in diatomic molecules where the field frequency is low with respect to the electronic excitation, but high with respect to the vibrations and consequently also with respect to the rotations. This will lead to Raman rotational excitations in the ground vibrational state of the ground electronic state (i.e. the ground vibronic state). The laser frequency is such that the ground electronic state is not one- nor two- photon resonant with other electronic states.

The resulting effective Hamiltonian [see Eq. (216)] has been used to show the adiabatic alignment of molecules by a laser field (see for example [32, 41]). The same technique can be used to construct an effective Hamiltonian but with a field frequency resonant with vibration. This Hamiltonian has been used to show the adiabatic orientation of polar molecules by a laser field and its second harmonic in quasi-resonance with the first excited vibrational state [42].

1. The Born-Oppenheimer Floquet Hamiltonian

The Born-Oppenheimer approximation allows to decouple the electronic and nuclear motions of the free molecule of the Hamiltonian H_0 . Solving the Schrödinger equation $H_0\Psi = E\Psi$ with respect to the electron coordinates $\mathbf{r} = \{\vec{r}_1, \vec{r}_2, \dots\}$, gives rise to the electronic states $\Psi_n(\mathbf{r}, \mathbf{R}) = \langle \mathbf{r} | n(\mathbf{R}) \rangle$, $n = 0, \dots, N_e$, of respective energies $\{E_n^{(e)}(\mathbf{R})\}$ as functions of the nuclear coordinates \mathbf{R} , with the electronic scalar product defined as $\langle n(\mathbf{R}) | n'(\mathbf{R}) \rangle_{\mathbf{r}} = \int d\mathbf{r} \Psi_n^*(\mathbf{r}, \mathbf{R}) \Psi_{n'}(\mathbf{r}, \mathbf{R})$. We assume a finite N_e bound electronic states. The Floquet Hamiltonian of the molecule perturbed by a field (of frequency ω , of amplitude \mathcal{E} and of linear polarization \vec{e}), in the dipole coupling approximation, and in a coordinate system of origin at the center of mass of the molecule, can be written as

$$K = -i\hbar\omega \frac{\partial}{\partial \theta} + H_0 - \vec{\mu} \cdot \vec{e} \mathcal{E} \cos \theta, \quad \vec{\mu} = e \sum_i \vec{r}_i \quad (193)$$

with \vec{r}_i the position of each electron i and e the elementary electric charge. The Born-Oppenheimer approximation allows to write H_0 as decoupled electronic states:

$$H_0 = T^{(n)} + \text{diag} \left[E_0^{(e)}(\mathbf{R}), E_1^{(e)}(\mathbf{R}), \dots, E_{N_e}^{(e)}(\mathbf{R}) \right], \quad (194)$$

where $T^{(n)}$ is the kinetic energy of the nuclei. We can write the dipole moment in the basis of these electronic states:

$$\vec{\mu} = \sum_{n,n'} |n(\mathbf{R})\rangle \vec{\mu}_{nn'}(\mathbf{R}) \langle n'(\mathbf{R})|, \quad \vec{\mu}_{nn'}(\mathbf{R}) = \langle n(\mathbf{R}) | \vec{\mu} | n'(\mathbf{R}) \rangle_{\mathbf{r}}. \quad (195)$$

$\vec{\mu}_{00}(\mathbf{R})$ is the permanent dipole moment of the ground electronic state, also denoted as $\vec{\mu}_{00}(\mathbf{R}) \equiv \vec{\mu}_0(\mathbf{R})$.

For a process with two lasers, the Floquet Hamiltonian is (see Section II E)

$$K = -i\hbar\omega \cdot \frac{\partial}{\partial \theta} + H_0 - \vec{\mu} \cdot [\vec{e}_1 \mathcal{E}_1 \cos \theta_1 + \vec{e}_2 \mathcal{E}_2 \cos \theta_2]. \quad (196)$$

2. Raman processes in the ground vibronic state by a single laser: Rotational excitations

We assume that the frequency of the laser is such that no excited electronic state is coupled by a one- or two-photon resonance with the ground electronic state.

a. Effective Hamiltonian in the ground electronic surface. The partitioning is in this case as follows: the electronic state $|n=0\rangle$ spans the Hilbert subspace \mathcal{H}_e^0 and the other electronic states $\{|1\rangle, \dots, |N_e\rangle\}$ the Hilbert subspace \mathcal{H}_e^1 . The dipole moment can be decomposed into diagonal and non-diagonal parts: respectively $\vec{\mu}_{nn}$ and $\vec{\mu}_{nn'}, n \neq n'$. Denoting $\vec{\mu}_{nn'} = [\mu_{1,nn'}, \mu_{2,nn'}, \mu_{3,nn'}]$ and $\vec{e} = [e_1, e_2, e_3]$ and applying Eq. (182), we obtain for the second order effective Floquet Hamiltonian connected to the ground electronic state

$$K_{\text{eff}}^{(e)} = -i\hbar\omega \frac{\partial}{\partial \theta} + T^{(n)} + E_0^{(e)} - \vec{\mu}_0 \cdot \vec{e} \mathcal{E} \cos \theta - \frac{1}{2} \mathcal{E}^2 \cos^2 \theta \sum_{i,j,m \neq 0} \left(\frac{e_i \mu_{i,0m} e_j \mu_{j,m0}}{E_m^{(e)} - E_0^{(e)} + \hbar\omega} + \frac{e_i \mu_{i,0m} e_j \mu_{j,m0}}{E_m^{(e)} - E_0^{(e)} - \hbar\omega} \right) \quad (197a)$$

$$= -i\hbar\omega \frac{\partial}{\partial \theta} + T^{(n)} + E_0^{(e)} - \vec{\mu}_0 \cdot \vec{e} \mathcal{E} \cos \theta - \frac{1}{2} \vec{e} \cdot \left(\overset{\leftrightarrow}{\alpha} \vec{e} \right) \mathcal{E}^2 \cos^2 \theta, \quad (197b)$$

with the *dynamical electronic polarizability* tensor $\overset{\leftrightarrow}{\alpha}$ of components

$$\alpha_{ij} = \sum_{m \neq 0} \left(\frac{\mu_{i,0m} \mu_{j,m0}}{E_m^{(e)} - E_0^{(e)} + \hbar\omega} + \frac{\mu_{i,0m} \mu_{j,m0}}{E_m^{(e)} - E_0^{(e)} - \hbar\omega} \right). \quad (198)$$

This allows to define an effective dipole moment $\vec{\mu}_{\text{eff}}$ as the sum of the permanent and induced dipole moments

$$\vec{\mu}_{\text{eff}} = \vec{\mu}_0 + \frac{1}{2} \overset{\leftrightarrow}{\alpha} \vec{e} \mathcal{E} \cos \theta, \quad (199)$$

such that the effective Floquet Hamiltonian can be written as

$$K_{\text{eff}}^{(e)} = -i\hbar\omega \frac{\partial}{\partial \theta} + T^{(n)} + E_0^{(e)} - \vec{\mu}_{\text{eff}} \cdot \vec{e} \mathcal{E} \cos \theta. \quad (200)$$

For a linear molecule, when the system of coordinates is chosen such that the third axis is along the molecular axis, the electronic polarizability tensor (in the molecular frame) is diagonal :

$$\overset{\leftrightarrow}{\alpha} = \text{diag} [\alpha_{\perp}, \alpha_{\perp}, \alpha_{\parallel}]. \quad (201)$$

Transforming the polarizability into the laboratory frame and denoting Θ the angle between the molecular axis and the polarization axis of the laser, we obtain the effective Floquet Hamiltonian in the ground electronic state of the linear molecule:

$$K_{\text{eff}}^{(e)} = -i\hbar\omega \frac{\partial}{\partial \theta} + T^{(n)} + E_0^{(e)}(R) - \mu_0(R) \mathcal{E} \cos \Theta \cos \theta - \frac{1}{2} (\alpha_{\parallel}(R) + \Delta\alpha(R) \sin^2 \Theta) \mathcal{E}^2 \cos^2 \theta \quad (202)$$

with $\Delta\alpha(R) = \alpha_{\perp}(R) - \alpha_{\parallel}(R)$, where $\Theta \in [0, \pi]$, $\varphi \in [0, 2\pi[$ are the angles of the usual spherical coordinates with origin at the center of mass of the molecule, and R is the internuclear distance.

It is usually a good approximation to consider the *static electronic polarizability* [i.e. Eq. (198) with $\omega = 0$] instead of the dynamical one when we are in the limit of a low frequency with respect to the electronic states:

$$E_n^{(e)} - E_0^{(e)} \gg \hbar\omega. \quad (203)$$

b. Effective Hamiltonian in the ground vibrational state Using the Born-Oppenheimer approximation (or equivalently the high frequency approximation, see Section III B) to effectively eliminate the fast vibrational motion with respect to the slow rotational one, we can obtain the Hamiltonian for the rotation of the free molecule in the ground electronic state by diagonalizing with respect to the vibrations of the nuclei (described here by the internuclear distance R), taking the angles Θ and φ as parameters. To this end, we split the kinetic energy of the nuclei into vibrational and rotational parts $T^{(n)} = T_{\text{vib}}^{(n)} + T_{\text{rot}}^{(n)}$, where $T_{\text{rot}}^{(n)}$ depends also on the vibrational coordinate R . We diagonalize $T_{\text{vib}}^{(n)} + E_0^{(e)}(R)$ and denote the eigenvalues by $E_0^{(v)}, \dots, E_{N_v}^{(v)}$ and the basis of eigenvectors by $\{|v=0\rangle, |v=1\rangle, \dots, |v=N_v\rangle\}$ where we assume N_v bound vibrational states. The Born-Oppenheimer approximation consists in neglecting the terms of $T_{\text{rot}}^{(n)}$ that are nondiagonal with respect to this vibrational basis of eigenvectors.

We assume that the laser frequency is far from any resonance between the ground vibrational state and the excited ones, such that the partitioning is very similar to the one made with the electronic states: the vibrational state $|v=0\rangle$ spans the Hilbert subspace \mathcal{H}_v^0 and the other vibrational states $\{|1\rangle, \dots, |N_v\rangle\}$ the Hilbert subspace \mathcal{H}_v^1 . We obtain for the second order effective Floquet Hamiltonian connected to the ground vibrational state of the ground electronic state

$$K_{\text{eff}}^{(v)} = -i\hbar\omega \frac{\partial}{\partial\theta} + T_{\text{rot},00}^{(n)} + E_0^{(v)} - \mu_{0,00}\mathcal{E} \cos\Theta \cos\theta - \frac{1}{2} \left(\alpha_{\parallel,00} + \Delta\alpha_{00} \sin^2\Theta + \alpha_0^{(v)} \cos^2\Theta \right) \mathcal{E}^2 \cos^2\theta, \quad (204)$$

where $\alpha_0^{(v)}$ is the effective polarizability in the ground vibrational state induced by the other vibrational states, given by

$$\alpha_0^{(v)} = \sum_{v \neq 0} \left(\frac{|\mu_{0,0v}|^2}{E_v^{(v)} - E_0^{(v)} + \hbar\omega} + \frac{|\mu_{0,0v}|^2}{E_v^{(v)} - E_0^{(v)} - \hbar\omega} \right), \quad (205)$$

where we have denoted $T_{\text{rot},vv'}^{(n)} := \langle v|T_{\text{rot}}^{(n)}|v'\rangle_R$, $\mu_{0,vv'} = \langle v|\mu_0(R)|v'\rangle_R$, $\alpha_{\parallel,vv'} = \langle v|\alpha_{\parallel}(R)|v'\rangle_R$, $\alpha_{\perp,vv'} = \langle v|\alpha_{\perp}(R)|v'\rangle_R$ and $\Delta\alpha_{vv'} = \alpha_{\perp,vv'} - \alpha_{\parallel,vv'}$. It is usually a good approximation to take only the contribution of the first excited vibrational state $E_1^{(v)}$ in the summation of $\alpha_0^{(v)}$ since the higher couplings are much smaller: $\mu_{0,01} \gg \mu_{0,02} \gg \mu_{0,03} \dots$

c. Effective Hamiltonian for rotational excitations We now finally consider the rotational coordinates for the free Hamiltonian in the ground vibrational state of the ground electronic state and will consider that the field is able to populate a priori many rotational states, which we treat thus as essential states. Neglecting $T_{\text{rot},vv'}^{(n)}$ for $v \neq v'$ according to the Born-Oppenheimer approximation, we approximate the ground vibronic state as a rigid rotor with the vibrational energies independent of the rotational coordinates (higher corrections corresponding for example to centrifugal distortion can be obtained from the non-diagonal terms $T_{\text{rot},vv'}^{(n)}$ for $v \neq v'$):

$$T_{\text{rot},00}^{(n)} := B_0 \hat{J}^2, \quad B_0 = \langle v=0|B|v=0\rangle_R \quad (206a)$$

with $B(R)$ the rotational constant, and the angular momentum operator

$$\hat{J}^2 = -\frac{1}{\sin\Theta} \frac{\partial}{\partial\Theta} \left(\sin\Theta \frac{\partial}{\partial\Theta} \right) - \frac{1}{\sin^2\Theta} \frac{\partial^2}{\partial\varphi^2}. \quad (207)$$

Choosing $E_0^{(v)} = 0$, we obtain the effective Floquet Hamiltonian

$$K_{\text{eff}}^{(v)} = -i\hbar\omega \frac{\partial}{\partial\theta} + B_0 \hat{J}^2 + V_{\text{eff}}^{(v)}(\theta, \Theta), \quad (208)$$

with

$$V_{\text{eff}}^{(v)}(\theta, \Theta) = -\mu_{0,00}\mathcal{E} \cos\Theta \cos\theta - \frac{1}{2} \left(\alpha_{\parallel,00} + \Delta\alpha_{00} \sin^2\Theta + \alpha_0^{(v)} \cos^2\Theta \right) \mathcal{E}^2 \cos^2\theta. \quad (209)$$

We consider the *high frequency limit* with respect to the rotation

$$\hbar\omega \gg B_0, \quad (210)$$

and apply the results of Section III B with the Hamiltonian written as

$$K_{\text{eff}}^{(v)}/\hbar\omega = -i \frac{\partial}{\partial\theta} + \epsilon \left[B_0 \hat{J}^2 + V_{\text{eff}}^{(v)}(\theta, \Theta) \right], \quad (211)$$

with the small parameter $\epsilon := 1/\hbar\omega$ and identifying the quantities of Section III B: $x \equiv \Theta$, $H_0 \equiv B_0\hat{J}^2$, $V_1 \equiv V_{\text{eff}}^{(v)}$. We first apply the contact transformation $S_1 = \exp(\epsilon W_1)$ with $W_1(\Theta, \theta) = -i \int^\theta (V_{\text{eff}}^{(v)} - \overline{V_{\text{eff}}^{(v)}}) d\theta$ and the average with respect to θ : $\overline{V_{\text{eff}}^{(v)}}(\Theta) = \frac{1}{2\pi} \int_0^{2\pi} d\theta V_{\text{eff}}^{(v)}(\theta, \Theta)$. Splitting $\hat{J}^2 := T_\Theta + T_\varphi$, we obtain the exact result (i.e. the terms of order ϵ^n , $n > 3$, are exactly zero):

$$S_1^\dagger \frac{K_{\text{eff}}^{(v)}}{\hbar\omega} S_1 = -i \frac{\partial}{\partial \theta} + \epsilon \left(B_0 \hat{J}^2 + \overline{V_{\text{eff}}^{(v)}} \right) + \epsilon^2 [B_0 T_\Theta, W_1] + \frac{\epsilon^3}{2} [[B_0 T_\Theta, W_1], W_1]. \quad (212)$$

We apply again a contact transformation $S_2 = \exp(\epsilon^2 W_2)$ with $W_2(\Theta, \theta) = -i \int^\theta (V_2 - \overline{V_2}) d\theta$, and

$$V_2 = [B_0 T_\Theta, W_1] + \frac{\epsilon}{2} [[B_0 T_\Theta, W_1], W_1], \quad (213)$$

which averages with respect to θ and gives, to second order in $1/\hbar\omega$,

$$K_{\text{eff}}^{(\text{ro})} = -i\hbar\omega \frac{\partial}{\partial \theta} + B_0 \hat{J}^2 + \overline{V_{\text{eff}}^{(v)}} + \epsilon \overline{[B_0 T_\Theta, W_1]} + \frac{\epsilon^2}{2} \overline{[[B_0 T_\Theta, W_1], W_1]}. \quad (214)$$

We calculate

$$\overline{V_{\text{eff}}^{(v)}} = -\frac{\mathcal{E}^2}{4} \left(\alpha_{\parallel,00} + \Delta\alpha_{00} \sin^2 \Theta + \alpha_0^{(v)} \cos^2 \Theta \right), \quad \overline{[T_\Theta, W_1]} = 0, \quad (215a)$$

$$W_1 = \frac{i\mathcal{E}^2}{8} \left(\alpha_{\parallel,00} + \Delta\alpha_{00} \sin^2 \Theta + \alpha_0^{(v)} \cos^2 \Theta \right) \sin 2\theta + i\mathcal{E}\mu_0 \cos \Theta \cos \theta, \quad (215b)$$

$$\overline{[[T_\Theta, W_1], W_1]} = -2 \overline{\left(\frac{\partial W_1}{\partial \Theta} \right)^2}, \quad (215c)$$

$$= \frac{\mathcal{E}^4}{64} \left(\Delta\alpha_{00} - \alpha_0^{(v)} \right)^2 \sin^2 2\Theta + \mu_0^2 \mathcal{E}^2 \sin^2 \Theta \quad (215d)$$

and obtain the effective Floquet Hamiltonian of second order in $1/\hbar\omega$ and of second order in field amplitude \mathcal{E} [43]

$$K_{\text{eff}}^{(\text{ro})} = -i\hbar\omega \frac{\partial}{\partial \theta} + B_0 \hat{J}^2 - \frac{\mathcal{E}^2}{2} \left[\frac{\alpha_{\parallel,00} + \alpha_0^{(v)}}{2} + \left(\frac{\Delta\alpha_{00} - \alpha_0^{(v)}}{2} - \frac{B_0 \mu_0^2}{(\hbar\omega)^2} \right) \sin^2 \Theta \right]. \quad (216)$$

Since we consider a linear polarization, the coupling does not depend on the angle φ and we can thus consider this Hamiltonian (216) acting on a state of the form $\psi(\theta, \varphi; t) = \phi(\theta; t) e^{iM\varphi/\sqrt{2\pi}}$, with M the projection of the angular momentum \hat{J} on the field polarization axis, which allows to identify \hat{J}^2 to $B_0 T_\Theta + M^2/\sin^2 \Theta$.

IV. ADIABATIC FLOQUET THEORY

The models we have discussed so far correspond to continuous (CW) lasers with a fixed sharp frequency and constant intensity. They can be easily adapted to the case of pulsed lasers that have slowly varying envelopes. They can furthermore have a chirped frequency, i.e. a frequency that changes slowly with time. For periodic (or quasiperiodic) semiclassical Hamiltonians, the Floquet states are the stationary states of the problem. Processes controlled by chirped laser pulses include additional time dependent parameters (the pulse envelopes and swept frequencies), whose time-scales are slow with respect to the optical frequencies. A first step is to relate the usual semiclassical time dependent Schrödinger equation to the time dependent dressed Schrödinger equation, defined by the Floquet Hamiltonian. Since this equation do not have the fast optical time dependence we can treat it with adiabatic principles, by studying the properties of the spectrum of the Floquet Hamiltonian as a function of the slow parameters.

We first derive the time dependent dressed Schrödinger equation generated by the Floquet Hamiltonian, relevant for processes induced by chirped laser pulses (see Section IV A). The adiabatic principles to solve this equation are next described in Section IV B.

A. The dressed Schrödinger equation for chirped laser pulses

We consider here for simplicity one chirped laser mode. Extension to multimode process is direct. The slow parameters of characteristic time τ are the laser pulse envelope $\Lambda(t)$ and frequency $\omega(t)$. The time dependent phase can be written as

$$\theta + g(t), \quad \text{with} \quad g(t) = \omega(t)t \quad (217)$$

We consider a semiclassical Hamiltonian that depends on these slow parameters

$$\hat{H}^{[\Lambda(t), \omega(t)]}(t) = H^{\Lambda(t)}(\theta + g(t)). \quad (218)$$

For instance for the dipole coupling of Eq. (1) with a pulse envelope

$$\mathcal{E}\left(\frac{t}{\tau}\right) = \Lambda\left(\frac{t}{\tau}\right) \mathcal{E}_{\max} \quad (219)$$

and chirped frequency $\omega(t/\tau)$, we take the semiclassical Hamiltonian

$$\hat{H}^{[\Lambda(\frac{t}{\tau}), \omega(\frac{t}{\tau})]}(t) = H_0 - \mathcal{E}\left(\frac{t}{\tau}\right) \mu \cos\left(\theta + \omega\left(\frac{t}{\tau}\right)t\right). \quad (220)$$

The parameter τ is a measure of the total duration of the pulse. For instance we can take Gaussian pulses

$$\Lambda_{\text{Gaussian}}\left(\frac{t}{\tau}\right) = e^{-(t/\tau)^2}. \quad (221)$$

If we take a pulse of the form

$$\Lambda_{\text{trig}}\left(\frac{t}{\tau}\right) = \begin{cases} \sin^2\left(\pi\frac{t-t_i}{\tau}\right), & \text{if } t \in [t_i, t_i + \tau] \\ 0 & \text{elsewhere,} \end{cases} \quad (222)$$

usually called *trig pulse*, the parameter τ is the total length of the pulse. We use the square to ensure the continuity of the first derivative which avoids additional nonadiabatic losses as we will discuss.

Remark. For some arguments involving adiabatic evolution pulses that have a well-defined beginning and end present conceptual advantages, since they allow clear-cut statements. For other considerations (like the Dykhne-Davis-Pechukas analysis needed in Section VC) one needs real analytic pulse shapes, which excludes shapes that are identically zero on the complement of a finite interval.

We derive the Floquet Hamiltonian K associated to this semiclassical Hamiltonian by starting with the following definition of the corresponding propagator, which is the natural generalization of (13)

$$U^K(t, t_0; \theta) := \mathcal{T}_{-g(t)} U(t, t_0; \theta) \mathcal{T}_{g(t_0)}, \quad (223)$$

where $\mathcal{T}_{g(t)}$ is the translation operator which acts on $\mathcal{L}_2(S^1, d\theta)$ as $\mathcal{T}_{g(t)}\xi(\theta) = \xi(\theta + g(t))$.

The operator U is the propagator of the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} U(t, t_0; \theta) = H^{\Lambda(t)}(\theta + g(t)) U(t, t_0; \theta) \quad (224)$$

if and only if U^K satisfies the dressed Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} U^K(t, t_0; \theta) = K^{[\Lambda(t), \omega_{\text{eff}}(t)]} U^K(t, t_0; \theta), \quad (225)$$

where

$$\omega_{\text{eff}}(t) = \frac{d\theta(t)}{dt} = \frac{dg(t)}{dt} = \omega(t) + \dot{\omega}t \quad (226)$$

and

$$K^{[\Lambda(t), \omega_{\text{eff}}(t)]}(\theta) = H^{\Lambda(t)}(\theta) - i\hbar\omega_{\text{eff}}(t)\frac{\partial}{\partial\theta}. \quad (227)$$

In terms of states, Eq. (223) gives the correspondence between $\phi(t; \theta)$ the solution of Eq. (224) and $\psi(t, \theta)$ the solution of Eq. (225):

$$\phi(t; \theta) = \mathcal{T}_{g(t)}\psi(t, \theta) = \psi(t, \theta + g(t)). \quad (228)$$

The above result is proved in Appendix A.1. We point out the appearance of an *effective* instantaneous frequency in the Floquet Hamiltonian (227).

B. Adiabatic and diabatic evolution of Floquet dressed states

The preceding analysis is well adapted when one considers slowly varying laser parameters. One can study the dressed Schrödinger equation invoking adiabatic principles by analyzing the Floquet Hamiltonian as a function of the slow parameters.

We distinguish the adiabatic evolution for non-resonant processes, for resonant processes at zero field and for processes with a dynamical resonance. For non-resonant processes the adiabatic transport of the dressed states is simple: The dynamics follows, up to a phase, the instantaneous dressed state whose eigenenergy is continuously connected to the one associated to the initial dressed state. This adiabatic transport will be generalized if more than one dressed state is involved in the dynamics.

A zero-field resonance can be explored adiabatically by the dynamics in different ways. One considers first a laser pulse of resonant (or quasi-resonant) carrying frequency leading to two degenerate (or quasi-degenerate) dressed states at early times, such that the dynamics has to be described in the subspace spanned by these two states. The process can be described as follows: When the field rises, this degeneracy is *dynamically lifted*, which induces a sharing of the population between the two instantaneous dressed states whose eigenenergies are continuously connected to the initial degenerate ones. This process will be the origin of the creation of coherent superposition of states by adiabatic passage (see Section VD). We will see that this lifting of degeneracy is instantaneous for one- and two-photon exact resonance processes. These two branches are next *followed adiabatically* by the dynamics if the pulse envelopes are slow enough. When the pulse later falls, the dynamics goes through the inverse process of *creation of degeneracy* which induces the interference of the two branches at the very end of the process.

One can see in this example the necessity to consider an adiabatic transport along more than one dressed state.

An alternative way to explore the zero-field resonance is to chirp a laser pulse which is switched on and off adiabatically, sufficiently far from the resonance. The chirp is such that the frequency is swept through the resonance when the field is on. The resonance appears in a dressed eigenenergy diagram (as a function of time or as a function of the field parameters) as an *avoided crossing*.

An avoided crossing will mainly limit the application of the adiabatic theorem: if the dynamics is not slow enough, dynamical transitions, so-called non-adiabatic transitions, will be induced between the dressed states forming the avoided crossing. A local Landau-Zener analysis can be invoked to determine this local non-adiabatic transition. Adiabatic passage along the avoided crossing will induce in general a transition in the bare states.

The dynamical resonances, which occur beyond a threshold of field amplitude, also usually appear as avoided crossings (see Section VI).

All these different types of resonances will be characterized geometrically in the next section.

1. Adiabatic evolution

It is convenient to consider explicitly the time-scale in the slow parameters: $\Lambda(s)$ and $\omega_{\text{eff}}(s)$, where $s = t/\tau$ is a reduced time, τ a characteristic time for the slow parameters and t is the physical time. The slow parameters are gathered in a formal vector $\mathbf{r}(s) = [\Lambda(s), \omega_{\text{eff}}(s)]$. The dressed Schrödinger equation reads

$$i\hbar\frac{\partial\psi(\theta, t)}{\partial t} = K^{\mathbf{r}(s)}\psi(\theta, t). \quad (229)$$

We denote $P(t) = \sum_{m \in \mathcal{S}} |\psi_m^{\mathbf{r}(s)}\rangle \langle \psi_m^{\mathbf{r}(s)}|$ the projector at time t in \mathcal{S} , a subspace in \mathcal{K} , in which we want to apply the adiabatic evolution. The adiabatic theorem can be formulated as:

$$\lim_{\tau \rightarrow \infty} U^K(t, t_0; \theta) P(t_0) = \lim_{\tau \rightarrow \infty} P(t) U^K(t, t_0; \theta), \quad (230)$$

if the instantaneous eigenenergies $\lambda_m^{\mathbf{r}(s)}$, $m \in \mathcal{S}$ are far enough from the other eigenenergies for all time $t \geq t_0$. In terms of eigenvectors, if one assumes a unique eigenvector $|\psi_m^{\mathbf{r}(s)}\rangle$ associated to the eigenenergy $\lambda_m^{\mathbf{r}(s)}$, one has $P(t) = |\psi_m^{\mathbf{r}(s)}\rangle \langle \psi_m^{\mathbf{r}(s)}|$ and the preceding formulation becomes :

If the system is at time $t_0 = \tau s_0$ in the Floquet instantaneous eigenstate $\psi(\theta, t_0) = \psi_m^{\mathbf{r}(s_0)}(\theta)$, then in the adiabatic limit $\tau \rightarrow \infty$ the state solution $\psi(\theta, t)$ of (229) is up to a phase given by the instantaneous Floquet state whose eigenenergy is continuously connected to the initial one at t_0 :

$$\psi(\theta, t) \simeq \exp \left[i \delta_m^{\mathbf{r}(s)}(t) \right] \psi_m^{\mathbf{r}(s)}(\theta), \quad (231)$$

where

$$\delta_m^{\mathbf{r}(s)}(t) = -\frac{1}{\hbar} \int_{t_0}^t du \lambda_m^{\mathbf{r}(u/\tau)} + i \int_{\mathbf{r}(s_0)}^{\mathbf{r}(s)} d\mathbf{r} \cdot \langle \psi_m^{\mathbf{r}} | \nabla_{\mathbf{r}} \psi_m^{\mathbf{r}} \rangle_{\mathcal{K}} \quad (232)$$

is the sum of respectively the dynamical phase and the Berry geometrical phase.

The dynamical phase depends on the trajectory followed in the space parameter and on its speed. The geometrical phase does not depend on its speed. Since the phase of the instantaneous Floquet states is not uniquely specified at each \mathbf{r} , one can always choose the geometrical phase as zero by requiring that at each time $\dot{\mathbf{r}} \cdot \langle \psi_m^{\mathbf{r}} | \nabla_{\mathbf{r}} \psi_m^{\mathbf{r}} \rangle_{\mathcal{K}} = 0$. However, if one follows a closed loop in parameter space the eigenvector at the end of the loop will differ from the initial one by a phase. This phase, which depends only on the geometry of the loop but not on the speed is the geometrical Berry phase [44]. If only one parameter is varied, the closed-loop geometrical phase is 0. If two parameters are varied, it can be 0 or π . If more than two parameters are varied, it can take any value.

The adiabatic theorem is valid in two quite different situations, which can be illustrated with a two-level example:

(i) Well separated instantaneous eigenvalues. In this case, if the initial condition is an instantaneous eigenstate, the evolution in the adiabatic limit follows the corresponding branch.

(ii) Exact crossing of eigenvalues. In this case the adiabatic evolution follows the initial branch across the intersection.

Thus, in both cases in the adiabatic limit the population is carried at all times by a single branch of instantaneous eigenstates. A quite general formulation of the adiabatic theorem, which imposes only smoothness conditions on the instantaneous eigenprojections has been presented recently by Avron and Elgart [45, 46].

In the applications to the control of molecular processes the property that is most often required is that the population stays on a single branch. The case that is most detrimental is when two or several branches do not cross but come close to each other, e.g. in the form of narrowly avoided crossings. In this case, for a finite speed of the parameters there are *nonadiabatic transitions* between the branches, i.e. the population is spread among them. This behavior will be discussed in more detail below.

More than one Floquet state can be involved in the dynamics, for example if the initial condition is a linear combination of the instantaneous eigenvectors. These Floquet states span a subspace \mathcal{S} and the adiabatic transport can be formulated in terms of eigenvectors:

$$\psi(\theta, t) \simeq \sum_{m \in \mathcal{S}} c_m \exp \left[i \delta_m^{\mathbf{r}(s)}(t) \right] \psi_m^{\mathbf{r}(s)}(\theta), \quad (233)$$

where the c_m are complex numbers determined by the initial condition

$$c_m = \langle \exp \left(i \delta_m^{\mathbf{r}(s_0)}(t_0) \right) \psi_m^{\mathbf{r}(s_0)}(\theta) | \psi(\theta, t_0) \rangle \quad (234)$$

A sketch of an argument that leads to the adiabatic theorem for the Floquet Hamiltonian of a N -level system is given in Appendix C.

2. Non-resonant deviations from adiabaticity: Perturbation theory, superadiabatic schemes and Dykhne-Davis-Pechukas formula

Deviations from strict adiabatic evolution given by the adiabatic theorem are of the order of $1/\tau$ (in amplitude) and can thus be estimated for short time by time-dependent perturbation theory in the adiabatic basis, which does not diverge for non-resonant processes, i.e. if there is no degeneracy nor quasi-degeneracy (appearing as avoided crossings) of the quasienergies. These deviations can be due (i) to the fact that τ is finite and (ii) to the possible

non-smoothness of the parameters. These cases have been considered in [47] for nonsmooth pulse ends in a two-level model driven by a non-resonant field. This study shows that adiabatic evolution is a good approximation even for a pulse of a few optical cycles. It also shows that the first order correction, which involves the coupling of the Floquet zone considered with the other zones, captures well the small deviations, that appear as oscillations (see Section 3.1 of [47]).

It is however known that in fact the adiabatic passage is in general much more efficient when considered at the end of the process. This is well understood in two-level systems for which one has the following result: *for smooth parameters and nondegenerate eigenvalues, the nonadiabatic corrections in the asymptotic adiabatic limit $\tau \rightarrow \infty$ are of order $e^{-|\text{const.}|\tau}$, exponential in τ , i.e. beyond all orders in $1/\tau$ at the end of the process.*

This result is due to Dykhne [48] and Davis and Pechukas [49] and has been extended to N -level systems [50]. The conditions of validity of the so-called Dykhne-Davis-Pechukas (DDP) formula has been established in [51, 52]. This formula allows to calculate in the adiabatic asymptotic limit the probability of the non-adiabatic transitions. This formula captures for example the result of the Landau-Zener formula, that we study below.

An alternative interpretation of this exponential nonadiabatic corrections has been given through *superadiabatic schemes*. The superadiabatic schemes allow to transform the problem to more adapted new basis (the so-called superadiabatic basis), where transition amplitudes proportional to powers of $1/\tau$ are removed. The scheme can be either iterative or by expansion in power series of $1/\tau$. This series expansion has been introduced by Berry for parametrically time-dependent quantum systems [53]. The iterative scheme [54–57] consists in constructing iteratively Schrödinger equations by successive appropriate unitary transformations of the effective dressed Hamiltonians. The first step corresponds to the instantaneous diagonalization (C4) of the Hamiltonian giving the new exact Schrödinger equation (C6), containing nonadiabatic couplings of first order in $1/\tau$. The next steps are diagonalizations of the new Hamiltonians which reduce the nonadiabatic couplings to higher orders. Neither the series nor the iterations converge in general. However Berry showed that, for this asymptotic series in two-level systems, an optimal order, corresponding to the minimization of the nonadiabatic couplings, gives an optimal superadiabatic basis with respect to which the transition amplitude acquires a universal error-function-like form. It is universal in the sense that it does not depend on the details of the Hamiltonian. This optimal superadiabatic basis coincides with the free basis (and also the adiabatic basis) at the beginning and at the end of the process when the fields are off. This means that if there are no degeneracies or quasi-degeneracies at the beginning and the end of the process, *the adiabatic passage is in fact supported by a superadiabatic transport between the beginning and the end of the process.* The nonadiabatic corrections are then given at the end of the process by the Berry's universal error function times an exponential in τ , in agreement with the DDP analysis [53, 57]. This approach has been successfully applied for a two-level atom strongly perturbed by a non-resonant field, in the full Floquet representation [47]. The resonant stimulated Raman adiabatic passage (STIRAP) process in a three-level system (that is studied below) is an example which has degeneracies of the eigenvalues at the beginning and the end of the process. It has been shown in [57] through an effective two-level model that in this case, the nonadiabatic correction at the end of the process is given, in addition to the DDP exponential term, by a *perturbative* term, whose dominant contribution is of first order in $1/\tau$.

Degeneracy and avoided crossing of the eigenvalues can be treated in a specific way, as shown below. Optimization of adiabatic evolution will be studied in section VC with the use of geometric arguments.

Nonsmoothness of the parameters usually leads to nonadiabatic corrections in transition amplitude of order p if the nonsmoothness is characterized by a discontinuous p -th derivative. Nonsmooth pulse ends can be investigated [58] in the simplified model

$$H(t) = \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega(t) \\ \Omega(t) & 2\Delta(t) \end{bmatrix}, \quad (235)$$

where we assume a real and positive Ω , which represents a two-level atom (with states $|1\rangle$ and $|2\rangle$) interacting with a one-photon quasi-resonant pulse in the rotating wave approximation [39, 40]. We consider a coupling characterized by a Rabi frequency $\Omega(t) = \Omega_0 \sin^2(\pi t/\tau)$, having discontinuous second derivatives at the beginning and at the end of the pulse. The frequency of the field is chirped in such a way that the distance between the two eigenenergies is kept constant: $\Delta(t) = \frac{|t|}{\tau} \sqrt{\Omega_0^2 - \Omega^2(t)}$ (this choice will appear clearer in Section VC). With this choice the nonadiabatic corrections are due uniquely to the nonsmoothness at the beginning and at the end. In the adiabatic limit the population mostly transferred from $|1\rangle$ to $|2\rangle$. For the nonadiabatic corrections in probability at the end of the pulse (i.e. the probability of the population to return to state $|1\rangle$), the first order nonadiabatic corrections in the adiabatic asymptotic limit $\tau \rightarrow \infty$, are given, after integrating twice by parts, by

$$P_1 \approx \frac{1}{4} \left(\frac{\pi}{\tau \Omega_0} \right)^4 \sin^2(\Omega_0 \tau). \quad (236)$$

This gives, as expected, asymptotic non-adiabatic corrections in probability that scale as $(1/\tau)^4$, since the discontinuity is in the second derivatives.

3. Resonant laser fields – Lifting of degeneracy

Processes that are resonant at zero field (i.e. with a atomic Bohr frequency that is an integer multiple of the laser frequency) can be investigated through an effective Hamiltonian of the model constructed from a multi-level atom driven by a quasi-resonant pulsed and chirped radiation field (referred to as a pump field). If one considers a n -photon process between the considered atomic states $|1\rangle$ and $|2\rangle$ (of respective energy E_1 and E_2), one can construct an effective hamiltonian with the two dressed states $|1;0\rangle$ (dressed with 0 photon) and $|2;-n\rangle$ (dressed with $-n$ photons) coupled by the n -photon Rabi frequency $\Omega(t)$ (of order n with respect to the field amplitude, and that we assume real and positive) and a dynamical Stark shift of the energies. It reads in the two-photon RWA [see Section III E and the Hamiltonian (190)], where we assume Ω real and positive for simplicity,

$$H(t) = \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega(t) \\ \Omega(t) & 2\Delta(t) \end{bmatrix}, \quad (237)$$

with the effective detuning

$$\Delta(t) = \Delta_0(t) + S(t), \quad (238)$$

where $S(t)$ is the relative dynamical Stark shift (of second order) due to the contribution of the other states and $\Delta_0(t)$ the detuning associated to the multiphoton near-resonant process, which is time-dependent if a chirp is applied. The population resides initially in the atomic state $|1\rangle$.

Note that the Hamiltonian (237) is a good approximation for the one- and two-photon processes (as shown in Section III E for the two-photon case), but that it is only a rough approximation for higher multiphoton processes, since the Stark shifts should contain additional terms of higher order to be consistent with the order of the effective Rabi frequency.

There is a quasi-resonance in this system if there exist times t for which $\Omega(t)$ is of the same order as $\Delta(t)$, as described more precisely in Section III E.

a. Adiabatic evolution. It is important to note that for this model (237) we can write the conditions for adiabatic behavior in detail using the procedure described in Appendix C: One obtains the transformed Schrödinger equation (C6):

$$i\hbar \frac{\partial}{\partial t} \tilde{\psi}(t) = \begin{bmatrix} \lambda(t) & i\gamma(t) \\ -i\gamma(t) & -\lambda(t) \end{bmatrix} \tilde{\psi}(t), \quad (239)$$

with

$$\lambda(t) = \frac{\hbar}{2} \sqrt{\Delta^2(t) + \Omega^2(t)} \quad (240)$$

and the nonadiabatic coupling

$$\gamma(t) = \frac{\hbar}{2} \frac{\Omega(t)\dot{\Delta}(t) - \dot{\Omega}(t)\Delta(t)}{\Delta^2(t) + \Omega^2(t)}. \quad (241)$$

The conditions for adiabatic evolution are satisfied if the nonadiabatic coupling is much smaller than the separation of the eigenvalues

$$|\gamma(t)| \ll \hbar \sqrt{\Omega^2(t) + \Delta^2(t)}. \quad (242)$$

If the detuning is constant, estimating $\dot{\Omega}(t) \sim \Omega_0/\tau$ with $\Omega_0 = \max_t \Omega(t)$ and taking $\Omega_0 \sim \Delta$, we obtain that *the dynamics is adiabatic if one assumes a large detuning with respect to $1/\tau$* , where τ characterizes the length of the pulse:

$$\tau\Delta \gg 1. \quad (243)$$

The dynamics is thus in this case at all times adiabatic in the sense that it mainly follows the dressed eigenstate whose eigenvalue is continuously connected to the one associated to the initial dressed state. This adiabatic transport results at the end of the pulse in an (almost) complete return in the initially populated state. It is important to point out that the dynamics is affected by the resonance in the sense that the excited bare state $|2\rangle$ is highly populated during the pulse if Ω is of the same order as Δ or larger at the peak laser amplitude. For two-level systems, the nonadiabatic small corrections lost to the other eigenstate have been extensively studied (see for example [59] and references therein).

b. Lifting and creation of degeneracy – Instantaneous splitting and recombination of population. In the opposite case

$$\tau\Delta \ll 1, \quad (244)$$

a dynamical splitting of the dynamics between the resonant dressed states occurs. One can reinterpret the well-known π -pulse formula for a one-photon process and extend it for multiphoton processes [60, 61]. In the case of an exact n -photon resonance, defined by (244), the two relevant dressed states $|1; 0\rangle$ and $|2; -n\rangle$ can be considered, before the rising of the pulse, as exactly degenerate with respect to the dynamics, associated to the dressed energy $E_1 = E_2 - n\hbar\omega$. The pulse rising induces a *dynamical splitting* of the population along two eigenstate branches. The splitting is *instantaneous* only in the case of exact one-photon resonance $n = 1$ and in the exact two-photon case $n = 2$. These cases are simple since the non-adiabatic coupling is exactly zero. Thus we can calculate exactly the solution of the Schrödinger equation for the two-level effective Hamiltonian.

The one-photon resonance case induces an equal sharing of the dynamics along the two eigenstate branches, which allows to recover the π -pulse formula

$$P_2 \equiv |\langle 2; -1 | \psi(t_f) \rangle|^2 = \sin^2 \frac{1}{2} \int_{t_i}^{t_f} |\Omega(t)| dt. \quad (245)$$

One can generalize it for the exact resonant case $n = 2$: one has (for α real)

$$\Delta(t) = S(t) = \alpha \mathcal{E}^2(t), \quad \Omega(t) = \beta \mathcal{E}^2(t), \quad \beta = |\beta| e^{-i\varphi}, \quad (246)$$

and the effective Hamiltonian (237) written as

$$H(t) = \frac{\hbar}{2} \mathcal{E}^2(t) \begin{bmatrix} 0 & \beta \\ \beta^* & 2\alpha \end{bmatrix}. \quad (247)$$

At each time, the time independent unitary transformation (having on its column the dressed states $|\psi_+\rangle$ and $|\psi_-\rangle$)

$$T = \begin{bmatrix} \cos(\zeta/2) & -\sin(\zeta/2) \\ e^{i\varphi} \sin(\zeta/2) & e^{i\varphi} \cos(\zeta/2) \end{bmatrix}, \quad (248)$$

with

$$\tan \zeta = -\frac{|\beta|}{\alpha}, \quad 0 \leq \zeta < \pi, \quad (249)$$

diagonalizes the Hamiltonian $H(s)$:

$$T^\dagger H(t) T = \begin{bmatrix} \lambda_+^\mathcal{E} & 0 \\ 0 & \lambda_-^\mathcal{E} \end{bmatrix} \equiv D(t), \quad (250)$$

with

$$\lambda_\pm^\mathcal{E} = \frac{\hbar}{2} \mathcal{E}^2 \left(\alpha \pm \sqrt{\alpha^2 + |\beta|^2} \right). \quad (251)$$

This can be interpreted as the lifting of the degeneracy

$$|1; 0\rangle = \cos(\zeta/2) |\psi_+\rangle - \sin(\zeta/2) |\psi_-\rangle, \quad (252a)$$

$$|2; -2\rangle = e^{-i\varphi} [\sin(\zeta/2) |\psi_+\rangle + \cos(\zeta/2) |\psi_-\rangle]. \quad (252b)$$

Since the population resides initially in the atomic state $|1\rangle$, one obtains a splitting of the dynamics along the two dressed states (with non equal weight in general):

$$|\psi(t)\rangle = \cos(\zeta/2) \exp \left[-\frac{i}{\hbar} \int_{t_i}^t du \lambda_+^\mathcal{E}(u) \right] |\psi_+\rangle - \sin(\zeta/2) \exp \left[-\frac{i}{\hbar} \int_{t_i}^t du \lambda_-^\mathcal{E}(u) \right] |\psi_-\rangle. \quad (253)$$

Note that Eq. (253) is exact, not an adiabatic approximation, since for the Hamiltonian (247) the nonadiabatic coupling is exactly zero. At the end of the pulse, the inverse mechanism of *instantaneous recombination of population* occurs at the *creation of degeneracy*

$$|\psi(t_f)\rangle = \left[\cos \gamma(t_f) + i \frac{\alpha}{\sqrt{\alpha^2 + |\beta|^2}} \sin \gamma(t_f) \right] |1; 0\rangle - i \frac{e^{i\varphi} |\beta|}{\sqrt{\alpha^2 + |\beta|^2}} \sin \gamma(t_f) |2; -2\rangle, \quad (254)$$

with the phase

$$\gamma(t_f) = \frac{1}{2\hbar} \int_{t_i}^{t_f} du \left[\lambda_+^{\mathcal{E}(u)} - \lambda_-^{\mathcal{E}(u)} \right] = \frac{1}{2} \sqrt{\alpha^2 + |\beta|^2} \int_{t_i}^{t_f} dt \mathcal{E}^2(t). \quad (255)$$

It can be interpreted as an interference of the two branches, with relative weight determined by $\gamma(t_f)$, which is equal to half the area between the two eigenvalues. One obtains the generalized two-photon π -pulse formula:

$$P_2 = \frac{|\beta|^2}{\alpha^2 + |\beta|^2} \sin^2 \left[\frac{1}{2} \sqrt{\alpha^2 + |\beta|^2} \int_{t_i}^{t_f} \mathcal{E}^2(t) dt \right], \quad (256)$$

which means that if

$$\sqrt{\alpha^2 + |\beta|^2} \int_{t_i}^{t_f} \mathcal{E}^2(t) dt = \pi, \quad (257)$$

one obtains the maximal population transfer to the state $|2; -2\rangle$. There is no complete transfer except in the limiting case $\alpha/|\beta| \rightarrow 0$. This process is not robust with respect to the pulse amplitude, since any deviation will in general change the area.

If one takes an area different from π , it leads to a final coherent superposition of states. For example, in the case of a one-photon process, one has [using formula (254) with $\alpha = 0$ and $\Omega = \beta\mathcal{E}$]

$$|\psi(t_f)\rangle = \cos \left(\int_{t_i}^{t_f} \frac{|\Omega(t)|}{2} dt \right) |1; 0\rangle - ie^{i\varphi} \sin \left(\int_{t_i}^{t_f} \frac{|\Omega(t)|}{2} dt \right) |2; -1\rangle. \quad (258)$$

and the area $\int_{t_i}^{t_f} |\Omega(t)| dt = \pi/2$ leads to a superposition of states with equal sharing in probability

$$|\psi(t_f)\rangle = \frac{1}{\sqrt{2}} (|1; 0\rangle - ie^{i\varphi} |2; -1\rangle). \quad (259)$$

Again, this creation of superposition of states is not robust with respect to the pulse amplitude. We will study in Section V D a way to create a superposition of states whose coefficients are robust in probability (i.e. squared absolute value of the coefficients).

We have described the picture with the simplified effective two-level model (237). However, it is still valid in the more general case of a strong field resonant n -multiphoton ($n > 2$) process, although the effective two-level model is rather inaccurate as already mentioned. In this case, one has to consider the full eigenenergies of the Floquet Hamiltonian that are relevant for the process (for example calculated numerically), denoted as $\lambda_+^{\mathcal{E}(t)}$ and $\lambda_-^{\mathcal{E}(t)}$, continuously connected to the degenerate energies $\lambda_+^{\mathcal{E}(t_i)} = \lambda_-^{\mathcal{E}(t_i)} = E_1 = E_2 - n\hbar\omega$. The associated Floquet states, which in general depend on the pulse amplitude, are denoted $|\psi_+^{\mathcal{E}(t)}\rangle$ and $|\psi_-^{\mathcal{E}(t)}\rangle$. The splitting of the dynamics along the two branches in this case is not instantaneous but in general dynamical. The splitting does not necessarily coincide with the lifting of the degeneracy. We assume here that it occurs however approximately *instantaneously* at a time $t_s > t_i$ (associated with the complex coefficients denoted a_+ and a_- such that $|a_+|^2 + |a_-|^2 = 1$), and that before this time, the solution is first shifted adiabatically into the Floquet state that is continuously connected to the initial one [60]:

$$|\psi(t_s)\rangle \simeq \exp \left(-\frac{i}{\hbar} \int_{t_i}^{t_s} du \lambda_-^{\mathcal{E}(u)} \right) |\psi_1^{\mathcal{E}(t_s)}\rangle \quad (260a)$$

$$\simeq \exp \left(-\frac{i}{\hbar} \int_{t_i}^{t_s} du \lambda_-^{\mathcal{E}(u)} \right) (a_+ |\psi_+^{\mathcal{E}(t_s)}\rangle + a_- |\psi_-^{\mathcal{E}(t_s)}\rangle), \quad (260b)$$

where we have denoted before the splitting of the dynamics, for $t < t_s$, the Floquet states $|\psi_1^{\mathcal{E}(t)}\rangle$ and $|\psi_2^{\mathcal{E}(t)}\rangle$, continuously connected respectively to $|1; 0\rangle$ and $|2; -n\rangle$, and assumed associated to the eigenenergies respectively $\lambda_-^{\mathcal{E}(t)}$ and $\lambda_+^{\mathcal{E}(t)}$. These two branches are next *followed adiabatically* if the pulse envelopes are slow enough, which gives (up to an irrelevant global phase):

$$|\psi(t)\rangle \simeq a_+ \exp \left(-\frac{i}{\hbar} \int_{t_s}^t du \lambda_+^{\mathcal{E}(u)} \right) |\psi_+^{\mathcal{E}(t)}\rangle + a_- \exp \left(-\frac{i}{\hbar} \int_{t_s}^t du \lambda_-^{\mathcal{E}(u)} \right) |\psi_-^{\mathcal{E}(t)}\rangle. \quad (261)$$

When the pulse later falls, the dynamics goes through the inverse process of recombination which occurs symmetrically at time $t'_s = t_f - t_s$ (if we assume a symmetric envelope) such that

$$\left| \psi_+^{\mathcal{E}(t'_s)} \right\rangle = a_+^* \left| \psi_1^{\mathcal{E}(t'_s)} \right\rangle - a_- \left| \psi_2^{\mathcal{E}(t'_s)} \right\rangle, \quad (262a)$$

$$\left| \psi_-^{\mathcal{E}(t'_s)} \right\rangle = a_-^* \left| \psi_1^{\mathcal{E}(t'_s)} \right\rangle + a_+ \left| \psi_2^{\mathcal{E}(t'_s)} \right\rangle. \quad (262b)$$

The resulting final transfer can be written as [60, 62]

$$P_2 \simeq 4 |a_+ a_-|^2 \sin^2 \left[\frac{1}{2} \int_{t_s}^{t_f - t_s} du \left(\lambda_+^{\mathcal{E}(u)} - \lambda_-^{\mathcal{E}(u)} \right) \right]. \quad (263)$$

Since in general the relative distance $\lambda_+^{\mathcal{E}} - \lambda_-^{\mathcal{E}}$ between the eigenenergies is small at the beginning and at the end of the pulse (before the splitting of the population and after the recombination), the formula is well approximated by

$$P_2 \simeq 4 |a_+ a_-|^2 \sin^2 \left[\frac{1}{2} \int_{t_i}^{t_f} du \left(\lambda_+^{\mathcal{E}(u)} - \lambda_-^{\mathcal{E}(u)} \right) \right]. \quad (264)$$

Thus the transfer probability depends on (i) the way in which the population is split and recombined and (ii) the difference of the dynamical phases. In the context of complete transfer, the process has been named generalized or multiphoton π -pulse and has been tested numerically for a five-photon resonance in a Morse potential [60]. This formula (264) also displays generalized Rabi oscillations.

We remark that this multiphoton process, like the one-photon process described by Eq. (245) and the two-photon process described by (256), are not robust with respect to the pulse area.

c. Intermediate quasi-resonant regimes – Dynamical splitting of population. The intermediate quasi-resonant regimes, defined as

$$\tau \Delta \sim 1, \quad (265)$$

leading to a lifting (or creation) of a quasi-degeneracy, is still an open question. In this case, the unitary transformation T (248) is time dependent and as a consequence the splitting of population is not instantaneous and leads to a non trivial dynamics. It has only been studied numerically in, for example, [62, 63].

4. Diabatic versus adiabatic dynamics around eigenenergy crossings and avoided crossings

As mentioned above, an avoided crossing can result from a chirping process or from a dynamical resonance induced by a field. An avoided crossing appears *locally* in the spectrum between two dressed states. One considers in general that the dynamics is *globally* adiabatic with respect to the other states in the subspace spanned by the dressed states forming the avoided crossing. The adiabatic approximation might fail *inside this subspace* when the dynamics encounters this avoided crossing.

If the coupling between the two dressed eigenvectors is zero, the eigenvalue crossing appears as a true crossing. This means that the branches ignore each other and the adiabatic approximation still holds through the true crossing.

If the coupling is different from zero, the dynamics can either *follow* the avoided crossing (*adiabatic* evolution), *cross* it (*diabatic* evolution) or partially cross it, depending on the speed of the dynamics with respect to the shape of the avoided crossing.

We assume that the model depends on one slow time-dependent parameter, denoted $r(t)$, and that the shape of the avoided crossing as a function of r is well described around the avoided crossing $r = r_c$ (occurring at time $t = t_c$) by its width h and its curvature C (see Fig. 1). We choose the parametrization such that $r_c = 0$. The eigenenergies read

$$\lambda_{\pm}^r = \pm h \sqrt{1 + \left(\frac{r}{\delta r} \right)^2}. \quad (266)$$

The curvature is defined by

$$C = \left| \frac{\partial^2 \lambda_{\pm}}{\partial r^2} (r = 0) \right| = \frac{h}{(\delta r)^2}. \quad (267)$$

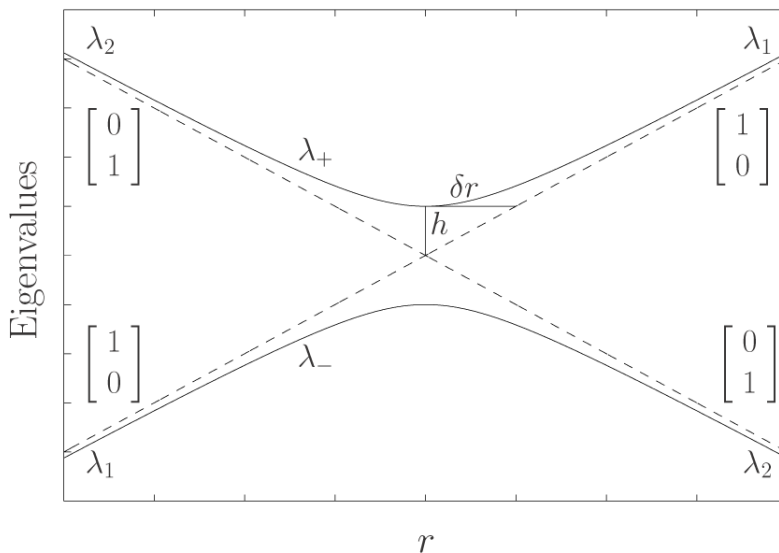


FIG. 1: Diagram of an avoided crossing of width $2h$ and of curvature $C = h/(\delta r)^2$.

We label these two continuous branches by the instantaneous Floquet states $\psi_-^{r(t)}$ and $\psi_+^{r(t)}$. The two eigenvalues λ_{\pm}^r can be deduced from an effective local dressed Hamiltonian

$$H_{\text{eff}} = h \begin{bmatrix} r/\delta r & 1 \\ 1 & -r/\delta r \end{bmatrix}, \quad (268)$$

in the basis

$$\psi_1 \equiv \psi_-^{r(t \rightarrow -\infty)} \equiv \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \psi_2 \equiv \psi_+^{r(t \rightarrow -\infty)} \equiv \begin{bmatrix} 0 \\ 1 \end{bmatrix}. \quad (269)$$

We can approximately characterize the dynamics by linearizing it in time around the avoided crossing: $r(t) = \dot{r}_c(t - t_c)$ and apply the Landau-Zener formula [64, 65] to calculate the probability to jump from the branch ψ_- to ψ_+ [66]:

$$P_{-\rightarrow+} = \exp\left(-\pi \frac{h \times \delta r}{\dot{r}_c}\right). \quad (270)$$

The asymptotic transition probability $P_{-\rightarrow+}$ is higher for (i) a thinner avoided crossing, (ii) a steeper curvature and (iii) a faster passage.

An avoided crossing gives rise to three qualitatively different regimes, that we can analyze considering the system starting in the initial state $\psi(t \rightarrow -\infty) = \psi_1$:

- (a) If the speed is slow enough ($\dot{r}_c \ll h \times \delta r$), the dynamics is *adiabatic*, i.e. $P_{-\rightarrow+} \approx 0$ (meaning that the system goes into the state ψ_2 far after the avoided crossing);
- (b) If the speed is fast enough ($\dot{r}_c \gg h \times \delta r$), the dynamics is *diabatic*, i.e. $P_{-\rightarrow+} \approx 1$ (meaning that the system stays in the state ψ_1 far after the avoided crossing);
- (c) Any intermediate speed leads to a sharing of the dynamics into the two branches, which gives rise afterwards to two dynamical states which have their own adiabatic evolution.

Formula (270) defines thus the efficiency of the diabatic passage. We remark that the Landau-Zener formula gives the information for the whole range of gap distances, from the limit of exact crossings to widely separated ones.

If we apply this analysis locally in the Floquet spectrum, it provides the matching between the adiabatic evolution far from any avoided crossings and a local adiabatic or diabatic behavior around them.

We conclude that the only unfavorable situation for adiabatic following is the intermediate regime in which the population is split among the branches. In systems encountered in applications there are often many levels that

display exact and avoided crossings of different sizes. In order to have an adiabatic transfer concentrated on a single branch, it is required to choose the adiabatic speed in such a way that the population either goes completely across (in narrow avoided crossings) or completely stays in the same branch by going slowly enough at wide avoided crossings. *This gives a strategy for the design of adapted laser pulses.*

We remark that the preceding argument is based on the hypothesis that successive avoided crossings, involving the same or different branches, can be treated sequentially, independently of each other. There are cases where several avoided crossings interfere with each other, and the simple sequential Landau-Zener analysis does not apply (see for example [67]).

V. TOPOLOGY OF THE DRESSED EIGENERGY SURFACES

In order to achieve a given population transfer between the initial and target states by adiabatic passage, one has additionally to develop a global picture showing the possible paths that link these states, to design the appropriate field parameters as a function of time which will allow the desired adiabatic passage. We will describe how these connectivity properties of the dressed states are determined by the topology of the dressed state energy surfaces as a function of the time-dependent external field parameters [68, 69].

Adiabatic passage can result in a robust population transfer if one uses adiabatic variations of at least two *effective* parameters of the total laser fields. They can be the amplitude and the detuning of a single laser (chirping) or the amplitudes of two delayed pulses [stimulated Raman adiabatic passage (STIRAP), see [70] for a review]. The different eigenenergy surfaces are connected to each other by conical intersections, which are associated with resonances (which can be either zero field resonances or dynamical resonances appearing beyond a threshold of the the field intensities). The positions of these intersections determine the possible sets of paths that link an initial state and the different target states. The paths can be classified into topological equivalence classes. Two paths are topologically equivalent if one can be deformed into the other without cutting it nor leaving the surfaces. All paths linking the initial and target states that are in the same topology class are equivalent in the adiabatic limit. The topological aspect is the key of the robustness of the process in the sense that the final transfer does not depend on the precise shapes or areas of the laser pulses nor on precise tuning of laser frequencies.

The topology of the surfaces is essentially determined by the resonances, which produce avoided crossings of surfaces and conical intersections. When the surfaces do not interact (zero coupling), one can also observe one-dimension intersections. The main ingredients of adiabatic transport are a *global adiabatic passage* along *one* eigenstate combined with *local diabatic evolution* near conical intersections (or with local adiabatic evolution through the exact conical intersections). We will illustrate these properties using several simple examples.

A. Topology of adiabatic passage by a chirped pulse and SCRAP

The concept of the topology of adiabatic passage can be illustrated in the simple model of an effective two-level atom interacting with a one-photon or two-photon near-resonant pulse in the two-photon RWA [see Section III E and the Hamiltonian (190)]

$$H(t) = \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega(t) \\ \Omega(t) & 2\Delta(t) \end{bmatrix}, \quad (271)$$

where $\Omega(t)$ (assumed here a positive real) stands for a one- or two-photon Rabi frequency of a pump laser and $\Delta(t) = \Delta_0(t) + S(t)$ is the sum of $\Delta_0(t)$, the detuning from the one- or two-photon resonance, and $S(t)$ the dynamical Stark shift produced by the other states. One can consider two types of processes occurring in this effective two-level system:

(a) *Direct chirping*: the detuning from the resonance $\Delta_0(t)$ is time dependent due to an active sweeping of the laser frequency (see e.g. Ref. [71] for an effective two-photon chirping). If one considers moreover a one-photon chirp, the dynamical Stark shift $S(t)$ can be neglected.

(b) *Stark chirped rapid adiabatic passage (SCRAP)*: the quasi-resonant laser frequency (pump laser) is not chirped (the detuning Δ_0 is time independent). The effective chirping results from a total dynamical Stark shift $S(t) = S_S(t) + S_P(t)$, with $S_S(t)$ due to an auxiliary laser field (non resonant with any levels of the system), referred to as a Stark laser [72, 73] and $S_P(t)$ due to the pump laser itself. If one considers a one-photon quasi-resonance for the pump laser, the dynamical Stark shift $S_P(t)$ can be neglected.

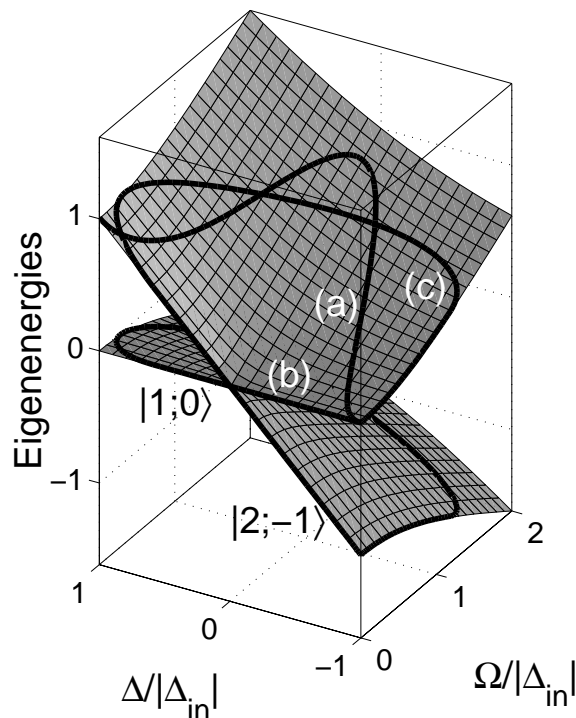


FIG. 2: Surfaces of eigenenergies (in units of $|\Delta_{in}|$) as functions of $\Omega/|\Delta_{in}|$ and $\Delta/|\Delta_{in}|$ (dimensionless). Three different paths, denoted (a), (b) and (c) are depicted: (a) corresponds to a direct chirping and (b) and (c) to SCRAP.

The processes associated to this Hamiltonian (271) can be completely described in the diagram of the two eigen-surfaces

$$\lambda_{\pm}(\Omega, \Delta) = \frac{\hbar}{2} \left(\Delta \pm \sqrt{\Omega^2 + \Delta^2} \right) \quad (272)$$

which represent the eigenenergies of (271) as functions of the instantaneous effective Rabi frequency Ω and the detuning Δ (see Fig. 2). All the quantities are normalized with respect to a characteristic detuning denoted $|\Delta_{in}|$. They display a conical intersection at $\Omega = 0, \Delta = 0$ induced by the crossing of the lines corresponding to the states $|1;0\rangle$ and $|2;-1\rangle$ for $\Omega = 0$ and varying Δ . In the plane $\Omega = 0$, the states $|1;0\rangle$ and $|2;-1\rangle$ do not interact. The crossing of these states in this plane $\Omega = 0$ can be seen consequently as a *mute resonance*. Thus *adiabatic passage through the intersection leaves the system in the same state*. The way of passing around or through this conical intersection is the key of the successful transfer. Three generic curves representing all the possible passages with a negative initial detuning $-|\Delta_{in}|$ are shown in Fig. 2. Note that the three other equivalent curves with a positive initial detuning have not been drawn. The path (a) corresponds to a direct chirping of the laser frequency from the initial detuning $-|\Delta_{in}|$ to the final one $+|\Delta_{in}|$. The paths (b) and (c) correspond to SCRAP with $\Delta_0 = -|\Delta_{in}|$ for the case of a one-photon resonant pump. For the path (b), while the quasi-resonant pump pulse is off, another laser pulse (the Stark pulse, which is far from any resonance in the system) is switched on and induces positive Stark shifts $S(t) > 0$ (the Stark pulse frequency is chosen with this aim). The Stark pulse makes thus the eigenstates get closer and induces a resonance with the pump frequency. This resonance is mute since the pump pulse is still off, which results in the true crossing in the diagram. The pump pulse is switched on after the passage through the crossing while the Stark pulse decreases. This induces this time the passage through the non-mute resonance, generally characterized by an avoided crossing (which is located behind the true crossing in Fig. 2, see also Fig. 3b). Finally the pump pulse is switched off. As shown in the diagram, the adiabatic following of the path (b), combining the passage through the true crossing and through an avoided crossing, induces the complete population transfer from state $|1\rangle$ to state $|2\rangle$. The path (c) is similar to the path (b) but with the pulse sequence reversed: It leads exactly to the same effect. In this case, the pump pulse is indeed switched on first (making the eigenstates repel each other as shown in the diagram) before the Stark pulse $S(t) > 0$, which is then switched off after the pump pulse.

In summary, the three paths (a), (b) and (c) represent fully adiabatic passage from state $|1; 0\rangle$ to state $|2; -1\rangle$; (a) passes around the conical intersection, (b) and (c) pass both once around the conical intersection and once through it.

We remark that the topology gives information on the dynamics for purely adiabatic passage. For real pulses of finite duration one has to complement these information with the analysis of the effects of non-adiabatic corrections.

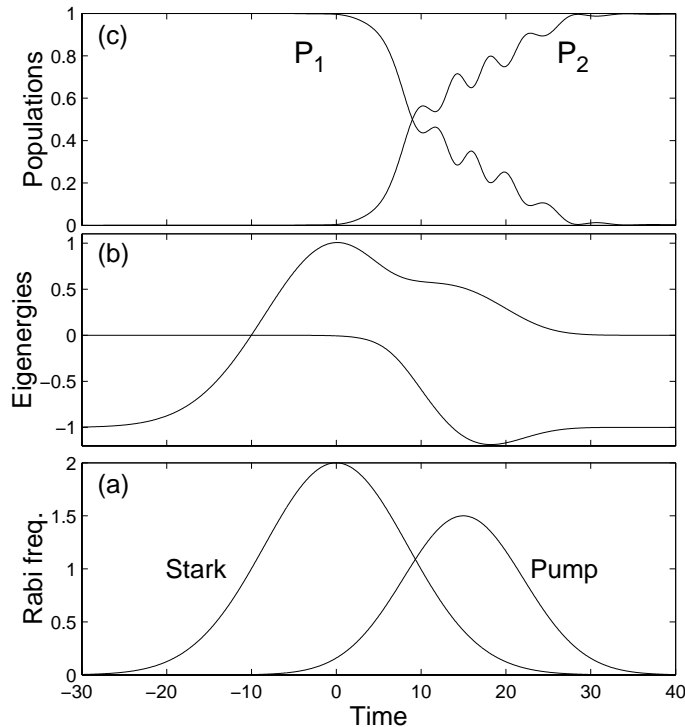


FIG. 3: Numerical calculation illustrating the SCRAP process with Gaussian pulses for the pulse peaks $\Omega_0/|\Delta_{\text{in}}| = 1.5$, $S_0/|\Delta_{\text{in}}| = 2$, the delay $t_d/|\Delta_{\text{in}}| = 15$, and the pulse lengths $\tau_p/|\Delta_{\text{in}}| = 10$, $\tau_s/|\Delta_{\text{in}}| = 12$ (corresponding approximately to the path (b) of Fig. 2): (a) Population histories $P_n(t) = |\langle n|\psi\rangle|^2$ for $n = 1, 2$ as a function of time in units of $1/|\Delta_{\text{in}}|$. Population transfer $P_2(\infty)$ to the bare state $|2\rangle$ is nearly complete. (b) The associated eigenenergies λ_{\pm}/\hbar (272) in units of $|\Delta_{\text{in}}|$. (c) The Rabi frequencies $\Omega(t)$ and $S(t)$ (in units of $|\Delta_{\text{in}}|$) respectively associated to pump and Stark pulses.

B. Robustness of adiabatic passage as a consequence of the topological properties of the eigensurfaces

The process (a) is robust with respect to fluctuations of the two parameters since it is based on the passage of the dynamics around the conical intersection. Thus neither a precise path nor any phase condition are required. Adiabaticity conditions have additionally to be fulfilled for the success of a path. They are here given by (242). In the next subsection, we discuss optimized paths that minimize this nonadiabatic loss.

The processes (b) and (c) require an additional analysis around the crossing when the dynamics slightly misses it. One has to consider the neighborhood of the conical intersection as a thin avoided crossing. In this case, the dynamics meets locally a thin avoided crossing instead of an exact crossing. This avoided crossing has to be passed *adiabatically* for the success of the process. The Landau-Zener analysis of Section IV B 4 gives an estimation of the efficiency of the diabatic passage through Eq. (270) approximating the local dynamics around an avoided crossing with the linear time-dependent detuning $\Delta(t) = \hat{\Delta}(t_c)(t - t_c) \equiv \hat{\Delta}_c(t - t_c)$ and the coupling $\Omega(t) = \Omega(t_c) \equiv \Omega_c$, with t_c the time when the avoided crossing is passed. The condition to achieve the diabatic passage locally can thus be formulated as

$$\hat{\Delta}_c \gg \pi\Omega_c^2/2. \quad (273)$$

Thus adiabatic passage in multi-level systems can be considered in general as *global adiabatic passage combined with local diabatic evolutions near conical intersections*. In multi-level systems, near a conical intersection, where one

considers a local ideal diabatic evolution, it is essential that the evolution also be adiabatic with respect to the other states.

The peak amplitudes, the delay between the two fields and the pulse shapes are chosen such that the conditions (242) and (273) are met in the concerned regions. Detailed conditions to achieve diabatic and adiabatic passage can be found in [73, 74] for the example of delayed Gaussian pulses.

We remark that if condition (273) is not satisfied, which is the case if one misses the conical intersection in an intermediate regime ($\Omega_c^2 \approx \dot{\Delta}_c$), the Landau-Zener formula shows that the dynamics splits the population into the two surfaces near the intersection. This gives rise afterwards to two states which will have their own adiabatic evolution.

In Fig. 3, we have performed a numerical calculation of the dynamics corresponding to the path (b) and which confirms the preceding analysis. We have solved the time dependent Schrödinger equation: $i\partial\psi/\partial t = (H/\hbar)\psi$ in units of a characteristic detuning $|\Delta_{\text{in}}|$, with Gaussian pulses for the pump and Stark lasers of respective characteristic length τ and τ_s : $\Omega(t) = \Omega_0 \exp[-(t - t_d)^2/\tau^2]$ $S(t) = S_0 \exp[-t^2/\tau_s^2]$. The pump is time-shifted by t_d . Fig. 3b clearly shows a crossing followed by the avoided crossing. Using Gaussian pulses (which are never zero) imply that we never have true crossings. However, the delay is chosen such that one has a diabatic passage through the thin avoided crossing which thus appears as a true crossing in Fig. 3b for the scale of the dynamics. We have used $\tau_p|\Delta_{\text{in}}| = 10 \gg 1$ and $\tau_s|\Delta_{\text{in}}| = 12 \gg 1$ to ensure the adiabatic passage condition (243) far after the crossing.

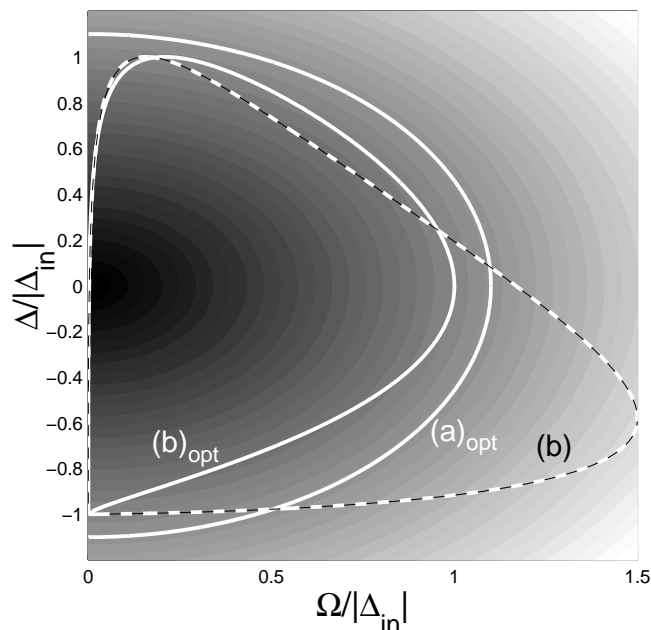


FIG. 4: Contour plot of the difference of the eigenenergies as a function of $\Omega/|\Delta_{\text{in}}|$ and $\Delta/|\Delta_{\text{in}}|$. Three different paths have been drawn: an optimal path (a)_{opt} (i.e. on a level line) corresponding to the topologically equivalent path (a) of Fig. 2 (with the final detuning $\Delta_0 = 1.1|\Delta_{\text{in}}|$), the path (b) corresponding to the numerical calculation of Fig. 3, and a path (b)_{opt} close to an optimal one corresponding to the numerical calculation of Fig. 5.

C. Optimization of adiabatic passage

Since in real experiments, pulses of finite area are used, it is useful to analyze the conditions that will optimize the adiabatic passage, i.e. the conditions that will allow to minimize the nonadiabatic losses with a minimal pulse area. Adiabatic passage can be optimized by inspection of the eigenenergy surfaces as functions of the time-dependent parameters of the coupling. A contour plot of the difference of the eigenenergy surfaces exhibits *level lines*. In Fig. 4, we have displayed level lines (as contours) corresponding to the eigenenergy surfaces of Fig. 2. For this example, they are half circles given by

$$\Omega^2 + \Delta^2 = \Delta_0^2, \quad (274)$$

with radius Δ_0 and center $\Omega = 0$, $\Delta = 0$. The radius Δ_0 corresponds to the chirp width for a one-photon chirping process in a two-level atom.

In [58], it was shown, for a class of two-level models, that *the passage along these level lines in the adiabatic regime minimizes the non-adiabatic correction*. The analysis is based on the Dykhne-Davis-Pechukas (DDP) formula [48, 49, 51, 52] (requiring analytic pulses) The nonadiabatic correction that is minimized is the dominant contribution given by the DDP formula [58].

This means that for a one-photon chirping process, if we choose the pulse shape $\Lambda(t)$, giving the Rabi frequency

$$\Omega(t) = \Omega_0 \Lambda(t), \quad (275)$$

the optimized detuning is then given by

$$\Delta(t) = \Delta_0 \frac{|\tau|}{\tau} \sqrt{1 - \Lambda^2(\tau)}, \quad \Delta_0 = \Omega_0, \quad (276)$$

such that the distance between the quasienergies is kept constant and equal to $\hbar\Delta_0$ during the process.

The adiabatic criterion is thus reduced to the choice of a level line, which has to be far enough from the origin. For a one-photon chirping process, this corresponds to the choice of the chirp width Δ_0 such that

$$\Delta_0 \tau \gg 1, \quad (277)$$

with τ the length of the pulse, according to (243). In practice one observes that adiabaticity can be achieved for quite small pulse areas. For instance, for Gaussian pulses, the precise adiabaticity condition is $\Delta_0 \tau \gg 1/(2\sqrt{2}) \approx 0.35$. For the choice $\Delta_0 \tau = 1.75 (= 5 \times 0.35)$, one observes a nonadiabatic loss in probability of only $P_1(+\infty) \approx 0.0015$ [58].

This result gives the strategy to choose appropriate time-dependent parameters to achieve the adiabatic passage with a minimum pulse area.

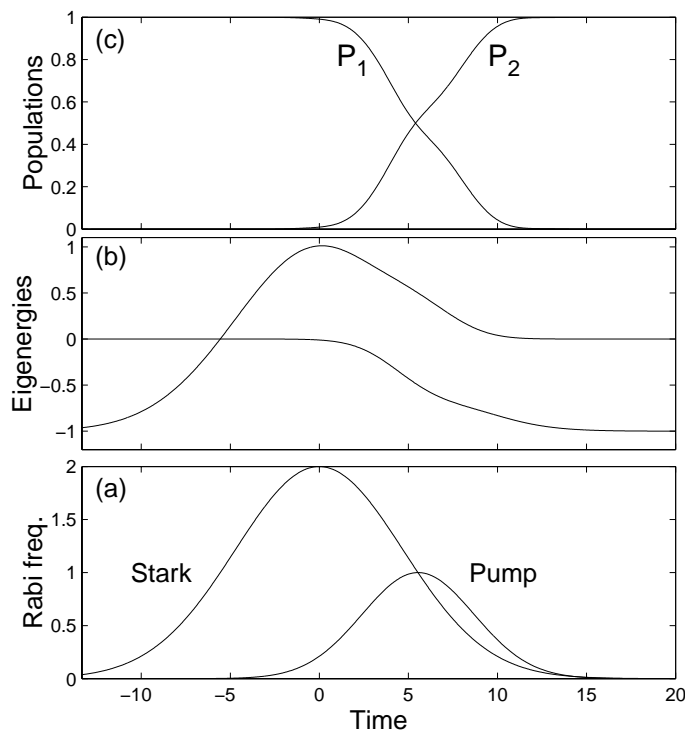


FIG. 5: As in Fig. 3 but for Gaussian pulses giving parameters close to optimal, corresponding to the path $(b)_{\text{opt}}$ in Fig. 4: pulse peaks $\Omega_0/|\Delta_{\text{in}}| = 1$, $S_0/|\Delta_{\text{in}}| = 2$, the delay $t_d/|\Delta_{\text{in}}| = 8.3$, and the (smaller) pulse lengths $\tau_p/|\Delta_{\text{in}}| = 6.7$ $\tau_s/|\Delta_{\text{in}}| = 10$. One can note the almost parallel eigenenergies after the crossing.

This can be applied for the SCRAP process described above. We choose again Gaussian pulses, but with parameters such that the path is now close to the optimal one, i.e. a level line. The numerical calculation is shown in Fig. 5 and

the associated path $(b)_{\text{opt}}$ in Fig. 4. We can see that for smaller pulse areas compared to the ones used in Fig. 3, we obtain a better population transfer, which is moreover monotonic.

D. Resonant processes – Creation of coherent superposition of states – Half-SCRAP

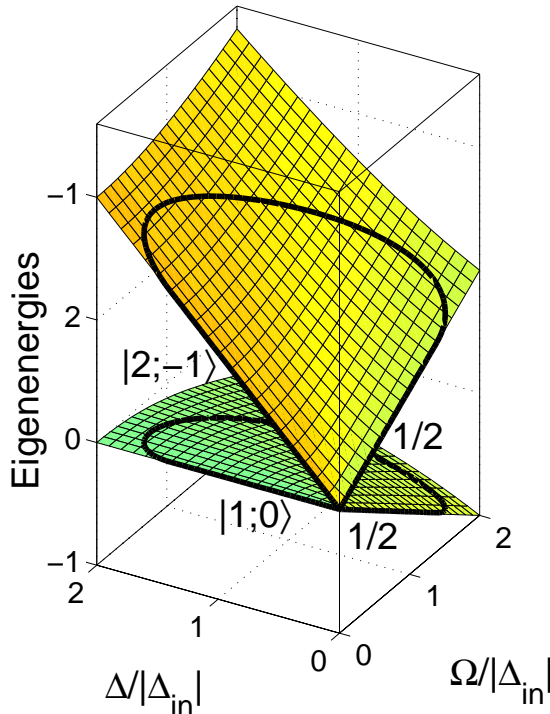


FIG. 6: Surfaces of eigenenergies (in units of $|\Delta_{\text{in}}|$) as functions of $\Omega/|\Delta_{\text{in}}|$ and $\Delta/|\Delta_{\text{in}}|$ for positive Δ . The coefficients $1/2$ refer to the equal sharing of the lifting of degeneracy in the $\Delta = 0$ -plane.

When the processes involve a zero-field resonance, one has to add the ingredient of lifting of degeneracy. This means that we have to consider the dynamics starting (or ending) near the conical intersection in a *direction not parallel to the $\Omega = 0$ -plane*. This can be seen in Fig. 6 where the surfaces of Fig. 2 have been redrawn for positive detunings (case of a one-photon resonance). When the dynamics starts this way, it is characterized by two adiabatic paths, one on each surface. They will lead in general to coherent superpositions of states.

An essential point is that the result of the lifting (or creation) of degeneracy depends on the direction of the dynamics as already discussed in Section IV B 3 for the case of one laser.

We study an exact resonant process ($\Delta_0 = 0$) starting (or ending) thus exactly at the conical intersection. We consider the cases that can be calculated analytically, with the Hamiltonian

$$H(t) = \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega(t) \\ \Omega^*(t) & 2\Delta(t) \end{bmatrix} : \quad (278)$$

- (i) a one-photon resonant pump (in this case, the Stark shift $S_P(t)$ can be neglected) giving the detuning $\Delta(t) = S_S(t)$ and the Rabi frequency $\Omega(t) = -\mu\mathcal{E}(t)/\hbar$, $\mu = |\mu|e^{-i\varphi}$;
- (ii) a two-photon resonant pump giving $\Delta(t) = S_P(t) + S_S(t)$ with the effective two-photon Rabi frequency $\Omega(t) = \beta\mathcal{E}^2(t)$, $\beta = |\beta|e^{-i\varphi}$ and its associated relative Stark shift $S_P(t) = \alpha\mathcal{E}^2(t)$.

We denote the eigenvalues

$$\lambda_{\pm} = \frac{\hbar}{2} \left(\Delta \pm \sqrt{\Delta^2 + |\Omega|^2} \right), \quad (279)$$

and the corresponding dressed eigenvectors $|\psi_{\pm}\rangle$. In the Δ (assumed positive) direction (i.e. for $\Omega = 0$), the lifting

or creation of degeneracy occurs trivially along a unique surface:

$$|1; 0\rangle = |\psi_-\rangle, \quad (280a)$$

$$|2; -n\rangle = |\psi_+\rangle. \quad (280b)$$

All the other directions lead to a lifting of degeneracy with a sharing of population into the two surfaces. The one-photon process gives in the Ω direction, or equivalently in the field-amplitude \mathcal{E} direction:

$$|1; 0\rangle = \frac{1}{\sqrt{2}} (|\psi_+\rangle - |\psi_-\rangle), \quad (281a)$$

$$|2; -1\rangle = \frac{e^{-i\varphi}}{\sqrt{2}} (|\psi_+\rangle + |\psi_-\rangle), \quad (281b)$$

which implies a lifting of the degeneracy occurring along the two surfaces with an equal weight. The lifting of degeneracy of the two-photon process in the field-amplitude \mathcal{E} direction does not occur in the Ω direction due to the Stark shifts, as seen in Section IV B 3:

$$|1; 0\rangle = \cos(\zeta/2) |\psi_+\rangle - \sin(\zeta/2) |\psi_-\rangle, \quad (282a)$$

$$|2; -2\rangle = e^{-i\varphi} [\sin(\zeta/2) |\psi_+\rangle + \cos(\zeta/2) |\psi_-\rangle], \quad (282b)$$

with

$$\tan \zeta = -\frac{|\beta|}{\alpha}, \quad 0 \leq \zeta < \pi. \quad (283)$$

The creation of degeneracy of the one-photon process is conversely given by

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} (|1; 0\rangle + e^{i\varphi} |2; -1\rangle), \quad (284a)$$

$$|\psi_-\rangle = \frac{1}{\sqrt{2}} (-|1; 0\rangle + e^{i\varphi} |2; -1\rangle), \quad (284b)$$

and the one of the two-photon process by

$$|\psi_+\rangle = \cos(\zeta/2) |1; 0\rangle + e^{i\varphi} \sin(\zeta/2) |2; -2\rangle, \quad (285a)$$

$$|\psi_-\rangle = -\sin(\zeta/2) |1; 0\rangle + e^{i\varphi} \cos(\zeta/2) |2; -2\rangle, \quad (285b)$$

to which dynamical phases have to be added.

We analyze two kinds of paths which, starting in state $|1; 0\rangle$, will lead to a coherent superposition of states:

(a) First, lifting of degeneracy in the Δ direction [according to (280a)] giving one dressed state involved in the dynamics, next adiabatic following on this dressed state along the lower surface with $\Omega \neq 0$ and finally creation of degeneracy for decreasing Ω [according to (284a) for the one-photon process and to (285a) for the two-photon process]. In Fig. 6, a particular path of the one-photon process has been drawn (i.e. creation of degeneracy for $\Delta = 0$), yielding a coherent superposition of states with equal weights in absolute value.

(b) First, lifting of degeneracy in a direction not parallel to the $\Omega = 0$ plane, which gives two dressed states involved in the dynamics [according to (281a) for the one-photon process and to (282a) for the two-photon process], next *independent* adiabatic following on these dressed states (along both the lower and upper surface) and finally creation of degeneracy in the Δ direction [according to (280)]. In Fig. 6, one can see the two path associated to this (one-photon) case, yielding also a coherent superposition of states with equal weights in absolute value.

These two cases are produced by two different sequences: respectively (a) first the Stark pulse and next the pump pulse (referred to as Stark-pump sequence), and (b) first the pump pulse and next the Stark pulse (referred to as pump-Stark sequence). The phases associated to the superposition of states resulting from these two different sequences are not identical. For the sequence Stark-pump, we start (at time t_i) with the lifting of degeneracy $|\psi(t_i)\rangle = |\psi_+\rangle$, which leads at the final time t_f to (up to an irrelevant global phase)

$$|\psi(t_f)\rangle = \cos(\zeta/2) |1; 0\rangle + e^{i\varphi} \sin(\zeta/2) |2; -n\rangle. \quad (286)$$

For the sequence pump-Stark, we start with the lifting of degeneracy $|\psi(t_i)\rangle = \cos(\zeta/2) |\psi_+\rangle - \sin(\zeta/2) |\psi_-\rangle$. Using the adiabatic transport for each branch, the state solution reads at the end

$$|\psi(t_f)\rangle = \cos(\zeta/2) |2; -n\rangle - e^{i \int_{t_i}^{t_f} ds (\lambda_+(s) - \lambda_-(s))} \sin(\zeta/2) |1; 0\rangle. \quad (287)$$

Thus the two sequences lead to the same superposition in probabilities but with different phases. The sequence pump-Stark leads to an additional *non-robust* phase difference $\int_{t_i}^{t_f} ds [\lambda_+(s) - \lambda_-(s)]$ coinciding with the dynamical phase difference.

If one considers an initial coherent state for the photon field instead of a photon-number state, the superpositions of states have the additional optical phase, giving for (286)

$$|\phi(t_f)\rangle = \cos(\zeta/2) |1\rangle + e^{i\varphi} \sin(\zeta/2) e^{-in\omega t} |2\rangle, \quad (288)$$

and for (287)

$$|\phi(t_f)\rangle = \cos(\zeta/2) e^{-in\omega t} |2\rangle - e^{i \int_{t_i}^{t_f} ds (\lambda_+(s) - \lambda_-(s))} \sin(\zeta/2) |1\rangle, \quad (289)$$

with $n = 2$ for the two-photon process.

This process leading to a coherent superposition of states has been suggested in [63] and named *half-scrap*, since it is very similar to the scrap process except it starts (or ends) in resonance.

The question of robustness with respect to the detuning for resonant processes is not yet completely clarified (see numerical studies in [63]).

This half-Scrap could be generalized for a n -multiphoton process ($n > 2$) in a multi-level system, with the use of the full quasienergies and Floquet states (calculated numerically).

E. Topology of Stimulated Raman adiabatic passage (STIRAP) and STIRAP-like processes

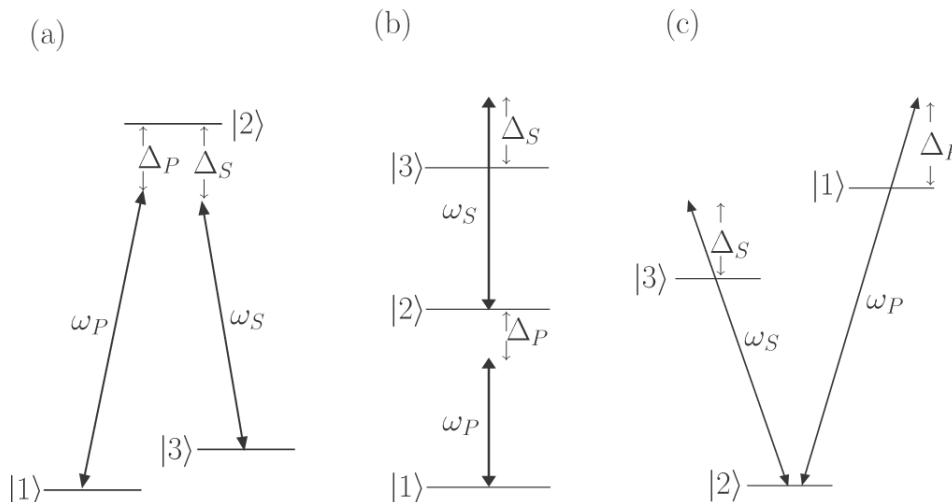


FIG. 7: Diagram of linkage patterns between three atomic states showing pump (P) and Stokes (S) transitions and the various detunings for (a) Λ , (b) ladder and (c) V systems.

The adiabatic passage induced by two delayed laser pulses, the well known process of STIRAP [70], produces a population transfer in Λ systems (see Fig. 7a). The pump field couples the transition 1-2 and the Stokes field couples the transition 2-3. It is known that, with the initial population in state $|1\rangle$, a complete population transfer is achieved with delayed pulses, either (i) with a so-called counterintuitive temporal sequence (Stokes pulse before pump) for various detunings as identified in Refs [74, 75], or (ii) with two-photon resonant (or quasi-resonant) pulses but far from the one-photon resonance with the intermediate state $|2\rangle$, for any pulse sequence (demonstrated in the approximation of adiabatic elimination of the intermediate state [76]). Here we analyze the STIRAP process through the topology of the associated surfaces of eigenenergies as functions of the two field amplitudes. Our results are also valid for ladder and V systems.

We also obtain the following results related to STIRAP: (i) We can explain the transfer of population to state $|3\rangle$ with intuitive (as well as with counterintuitive) specific quasi-resonant pulses *without invoking the approximation of adiabatic elimination*. (ii) With specific quasi-resonant pulses, we can *selectively* transfer the population to state $|2\rangle$ for an *intuitive* sequence or to state $|3\rangle$ for a *counterintuitive* sequence, and (iii) with an intuitive or counterintuitive

sequence, we can *selectively* transfer the population to state $|2\rangle$ or to state $|3\rangle$ playing on the *detunings* and on the *ratio of the peak pulse amplitudes*.

We also analyze the counterpart of the preceding processes in V systems (see Fig. 7c): the initial population being in state $|2\rangle$, we show that with specific non-resonant pulses, (i) we can *selectively* transfer the population to state $|1\rangle$ for an intuitive sequence or to state $|3\rangle$ for a counterintuitive sequence; (ii) we can *selectively* transfer the population to state $|1\rangle$ or to state $|3\rangle$ playing on the ratio of the peak pulse amplitudes.

The topology will allow us to classify all the possibilities of complete population transfer by adiabatic passage for a three-level system interacting with two delayed pulses, as it was done for the two-level system interacting with a chirped laser pulse.

The most general dressed Hamiltonian in the rotating wave approximation for these processes reads [70]

$$H(t) = \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_P(t) & 0 \\ \Omega_P(t) & 2\Delta_P & \Omega_S(t) \\ 0 & \Omega_S(t) & 2(\Delta_P - \Delta_S) \end{bmatrix}, \quad (290)$$

with $\Omega_j(t)$, $j = P, S$ (assumed real and positive) the one photon Rabi frequencies associated respectively to the pump pulse (of carrier frequency ω_P) and the Stokes pulse (of carrier frequency ω_S). We have assumed that the states $|1\rangle$ and $|3\rangle$ have no dipole coupling and that spontaneous emission is negligibly small on the time scale of the pulse duration. The rotating wave approximation is valid if $\hbar\Omega_P(t) \ll |E_2 - E_1|$ and $\hbar\Omega_S(t) \ll |E_3 - E_2|$, where E_j , $j = 1, 2, 3$ are the energies associated to the bare states $|j\rangle$.

The detunings Δ_P and Δ_S are one-photon detunings with respect to the pump and Stokes frequencies respectively and

$$\delta = \Delta_P - \Delta_S \quad (291)$$

is the two-photon detuning.

For Λ , ladder and V systems (see respectively Fig. 7a, b and c), the one-photon detunings Δ_P , Δ_S are respectively defined as

$$\Lambda : \hbar\Delta_P = E_2 - E_1 - \hbar\omega_P, \quad \hbar\Delta_S = E_2 - E_3 - \hbar\omega_S, \quad (292a)$$

$$\text{Ladder} : \hbar\Delta_P = E_2 - E_1 - \hbar\omega_P, \quad \hbar\Delta_S = E_2 - E_3 + \hbar\omega_S, \quad (292b)$$

$$V : \hbar\Delta_P = E_2 - E_1 + \hbar\omega_P, \quad \hbar\Delta_S = E_2 - E_3 + \hbar\omega_S, \quad (292c)$$

which determines the dressed basis in which the dressed Hamiltonian (290) has been written: respectively $\{|1; 0, 0\rangle, |2; -1, 0\rangle, |3; -1, 1\rangle\}$, $\{|1; 0, 0\rangle, |2; -1, 0\rangle, |3; -1, -1\rangle\}$ and $\{|1; 0, 0\rangle, |2; 1, 0\rangle, |3; 1, -1\rangle\}$. In the following, we consider the population of the atomic states.

In what follows we study the topology of the eigenenergy surfaces for various generic sets of the parameters. The topology depends on the detunings which determine the relative position of the energies at the origin. We study various *quasi-resonant* pulses in the sense that the detunings are smaller than or of the order of the associated peak Rabi frequencies, that is,

$$\Delta_P \lesssim \max_t(\Omega_P), \quad \Delta_S \lesssim \max_t(\Omega_S), \quad (293a)$$

$$\delta \lesssim \max_t(\Omega_P), \quad \delta \lesssim \max_t(\Omega_S). \quad (293b)$$

1. Transfer to a unique state

Allowing large enough amplitudes leads to three generic cases for $\delta > 0$ and three other cases for $\delta < 0$, which are equivalent by symmetry.

Two typical examples are displayed in Figs. 8 and 9. In both cases, the surface continuously connected to the state $|2\rangle$ is isolated from the two other surfaces which present a conical intersection for $\Omega_S = 0$ and for $\Omega_P = 0$, respectively. This crossing corresponds to a mute resonance as described above for chirping. (A resonance is called mute if the frequencies are in resonance but the corresponding coupling term is zero or small in the Hamiltonian).

The topologies shown on the respective figures 8 and 9 are generic for the condition

$$\Delta_P \Delta_S > 0, \quad (294)$$

with respectively

$$|\Delta_P| < |\Delta_S| \quad \text{and} \quad |\Delta_P| > |\Delta_S|. \quad (295)$$

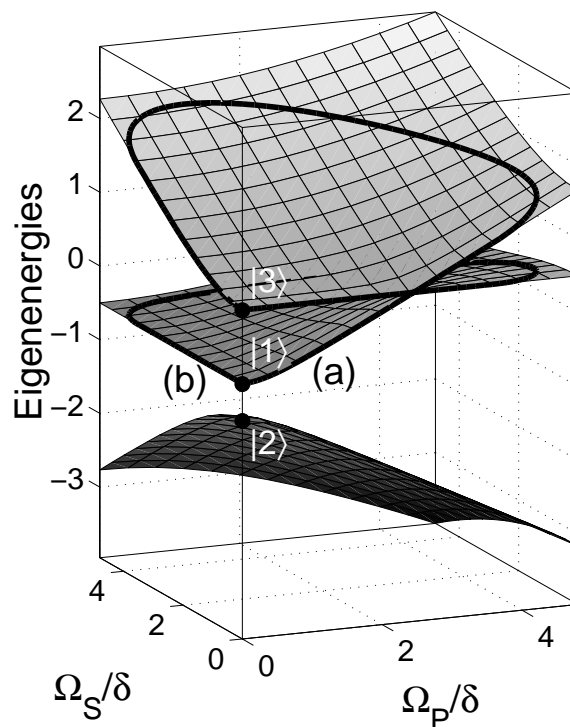


FIG. 8: Surfaces of eigenenergies (in units of δ) as functions of Ω_P/δ and Ω_S/δ when the dressed states (denoted λ_1 , λ_2 and λ_3 , respectively connected to E_1 , E_2 and E_3 for fields off) are such that $\lambda_2 < \lambda_1 < \lambda_3$, with $\Delta_P = -\delta/2$ and $\Delta_S = -3\delta/2$. The paths (a) and (b) (constructed with delayed pulses of the same length and peak amplitude) correspond respectively to the intuitive and counterintuitive pulse sequences in Λ or ladder systems (for which the initial population resides in state $|1\rangle$).

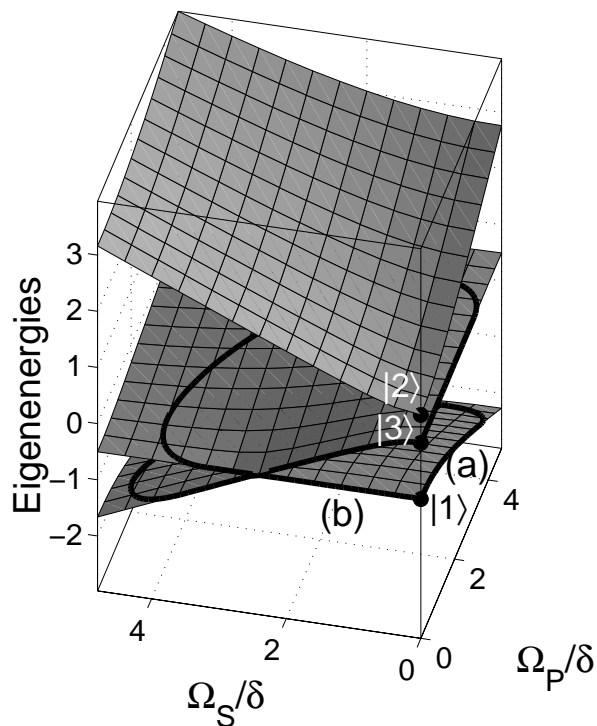


FIG. 9: Surfaces of eigenenergies (in units of δ) as functions of Ω_P/δ and Ω_S/δ for the case $\lambda_1 < \lambda_3 < \lambda_2$, with $\Delta_P = 3\delta/2$ and $\Delta_S = \delta/2$. The paths (a) and (b) (with pulses of the same length and peak amplitude) correspond respectively to the intuitive and counterintuitive pulse sequences in Λ or ladder systems.

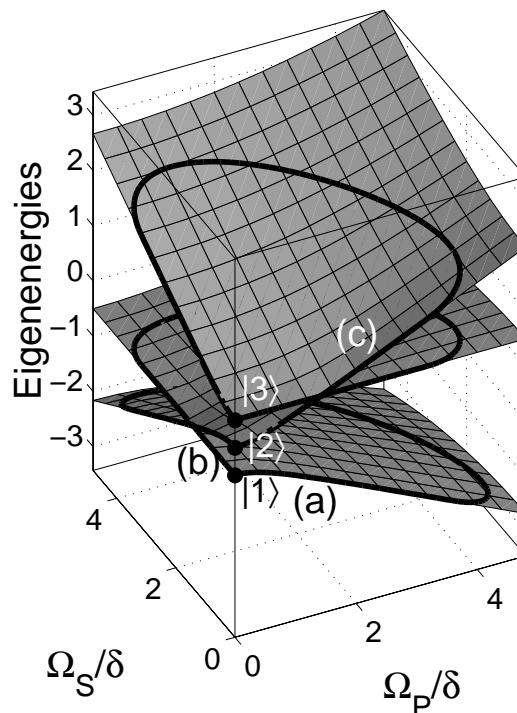


FIG. 10: Surfaces of eigenenergies (in units of δ) as functions of Ω_P/δ and Ω_S/δ for the case $\lambda_1 < \lambda_2 < \lambda_3$, with $\Delta_P = \delta/2$ and $\Delta_S = -\delta/2$. The paths (a) and (b) (with pulses of the same length and peak amplitude) correspond respectively to the intuitive (transfer to |2>) and counterintuitive (transfer to |3>) pulse sequences in Λ or ladder systems leading to the selective transfer. The paths (a) and (c) correspond to the selective transfer in V systems (for which the initial population resides in |2>), respectively to |1> and |3>.

In the following, we describe in detail the case of Fig. 8. For the process in Λ or ladder systems, where the initial population resides in state |1>, two different adiabatic paths lead to the complete population transfer, depending on the pulse sequence. The path denoted (a) corresponds to an intuitive sequence for the rise of the pulses. The pump pulse is switched on first, making the levels connected to the states |1> and |2> repel each other (dynamical Stark shift) until the level connected to |1> crosses the level connected to |3>. The Stokes pulse is switched on after the crossing. Next the two pulses can decrease in any order. The path (b) is associated to a counterintuitive sequence for the decrease of the pulses. The two pulses can be switched on in any order. The pump pulse has to decrease through the crossing when the Stokes pulse is already off. These two results are valid even without application of adiabatic elimination. The conditions of global adiabaticity are similar to the ones of the chirped frequency case (242). As discussed in Section IV B 4, an analysis of the diabatic evolution near the conical intersections can be made locally with the Landau-Zener approximation (270).

The V systems are uninteresting in these cases since the final population comes back to the state |2> for any pulse sequence.

Another typical example is displayed in Fig. 10. The topology shown on this figure is generic for the condition

$$\Delta_P \Delta_S < 0. \quad (296)$$

In this configuration, two conical intersections involve the intermediate surface, one with the lower surface and the other one with the upper surface. This topology gives here more possibilities for transfer: *the combined choice of the pulse sequence and the ratio of the peak amplitudes allows the selective transfer into the two other states.*

Figure 10 shows that, for the process in Λ (or ladder) systems, two different adiabatic paths lead to different complete population transfers, depending on the pulse sequence. The path (a) corresponds to an intuitive pulse sequence (for the decrease of the pulses) and allows to populate at the end the state |2>. The Stokes and pump pulses can be switched on in any sequence and the pump pulse is switched off before the Stokes one. The path (b) corresponds to a counterintuitive pulse sequence (for the rise of the pulses) and allows to populate at the end the

state $|3\rangle$. The Stokes pulse is switched on before the pump and the Stokes pulse has to be switched off before the pump. We can thus selectively populate the states $|2\rangle$ or $|3\rangle$ provided the peak amplitudes are sufficiently strong to induce the adiabatic path to cross the intersection involved.

For the process in V systems, the paths (a) and (c) of Fig. 10 show the respective selective transfer into the states $|1\rangle$ or $|3\rangle$.

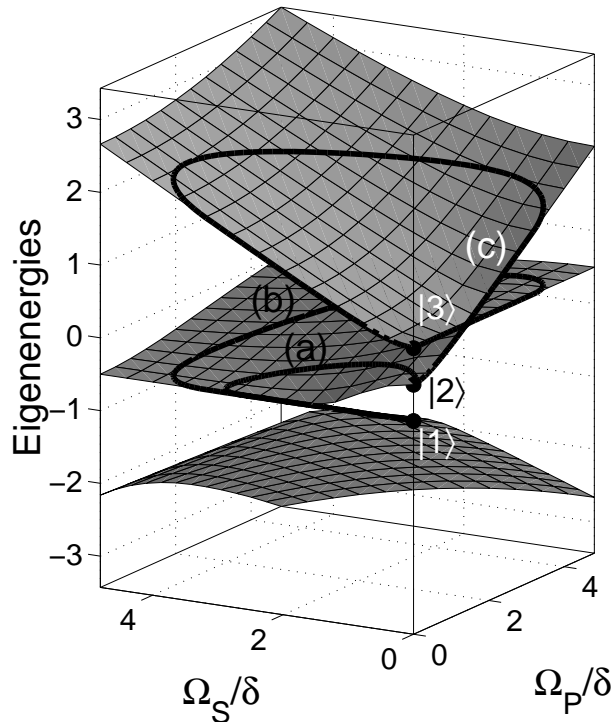


FIG. 11: Surfaces of eigenenergies (in units of δ) with the same parameters as Fig. 10 showing the selective transfer with pulses of different peak amplitudes and length. For counterintuitive sequences in Λ or ladder systems, the path (b) [corresponding to the path (b) of Fig. 10] shows the transfer to $|3\rangle$, and the path (a) (with pulses of different length and peak amplitude) characterizes the transfer to $|2\rangle$. The paths (a) and (c) correspond to the selective transfer in V systems.

Figure 11 corresponds to the same topology of Fig. 10 but with a different path (a). Figure 11 shows that, for Λ (or ladder) systems, we can selectively populate the states $|2\rangle$ or $|3\rangle$ if the pulse sequences are designed differently in their order and their peak amplitude. Path (b) corresponds to path (b) of Fig. 10 and allows to populate at the end the state $|3\rangle$. Path (a) corresponds to a longer pump pulse (still switched on after the Stokes pulse) of smaller peak amplitude which allows to populate at the end the state $|2\rangle$. Note that we can obtain a similar path (a) with a counterintuitive pulse sequence and equal peak amplitudes if the detuning Δ_P is taken smaller so that the crossing for $\Omega_S = 0$ is pushed to a higher pump pulse amplitude Ω_P .

For V systems, Fig. 11 shows that this selectivity [paths (a) and (c)] also occurs (for any sequence of the pulses).

Figure 12 shows numerical calculations that illustrate some of the predictions of the above analysis. It displays the populations of the states $|2\rangle$ and $|3\rangle$ at the end of the pulses for intuitive and counterintuitive sequences with a large pulse area. The boundaries of the areas of efficient transfer (black areas) are predicted quite accurately by the topology analysis: They are determined by (i) the straight lines (thick full lines) $\Delta_P = 0$ and $\Delta_S = 0$ coming from the inequalities (294) and (296) and (ii) the branches of the hyperbolas (dashed lines)

$$\Delta_S = \Delta_P - \frac{(\Omega_{\max})^2}{4\Delta_P}, \quad (297a)$$

$$\Delta_P = \Delta_S - \frac{(\Omega_{\max})^2}{4\Delta_S}, \quad (297b)$$

which are determined from the positions of the conical intersections. Figure 12 shows that the efficiency of the robust

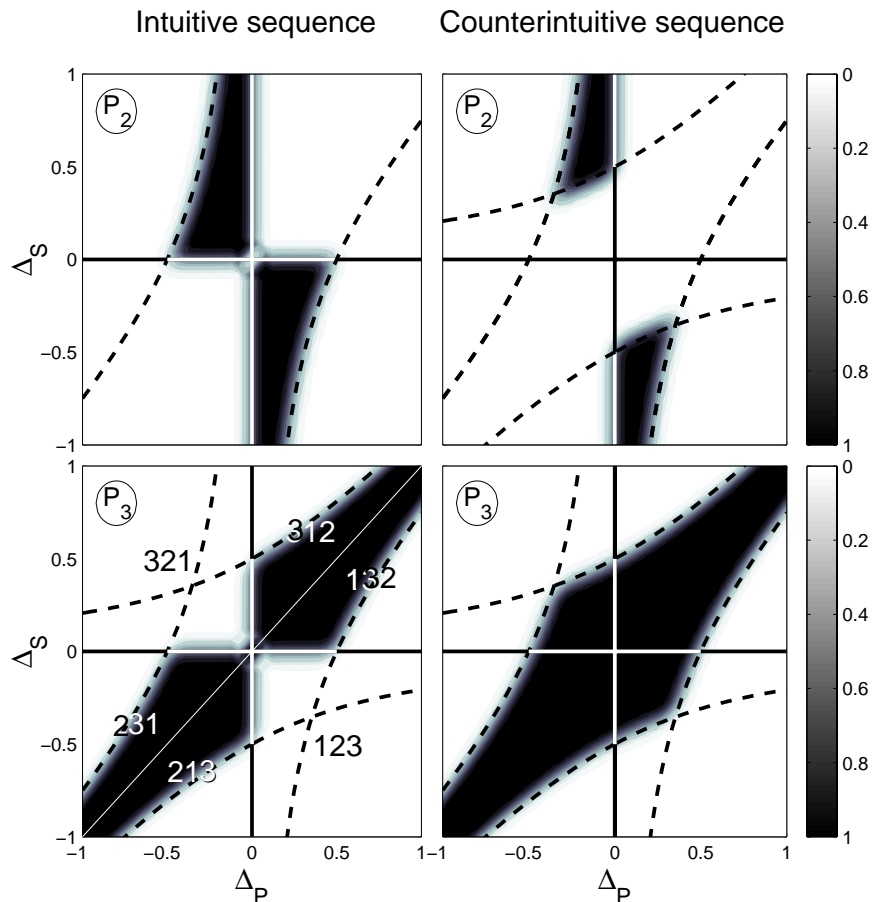


FIG. 12: Transfer efficiencies P_2 to $|2\rangle$ (upper row) and P_3 to $|3\rangle$ (lower row) as functions of the detunings Δ_P and Δ_S (in units of Ω_{\max}) at the end of the pulses for the intuitive (left column) and counterintuitive (right column) sequences of delayed sine-squared pulses with the same peak amplitude Ω_{\max} and a large temporal area $\Omega_{\max}\tau = 500$ (τ is the pulse length and the delay is $\tau/2$). The efficient population transfers are bounded by $\Delta_P = 0$ and $\Delta_S = 0$ (thick full lines) and the branches of hyperbolas (dashed lines). The areas bounded by the full lines are labelled by the cases 213, 132, 123, ... (These number sets are associated to the eigenenergies for zero field amplitudes from the smallest to the biggest, for example 213 means $\lambda_2 < \lambda_1 < \lambda_3$.) The three first ones correspond respectively to Figs 8, 9 and 10.

population transfer to the states $|2\rangle$ or $|3\rangle$ is identical for the intuitive and counterintuitive sequences except in two regions: (i) areas bounded by $\Delta_P\Delta_S < 0$ and the branches of the hyperbolas, where the population is transferred in a robust way to state $|2\rangle$ for the intuitive sequence or to state $|3\rangle$ for the counterintuitive sequence and (ii) an area (smaller for longer pulse areas) near the origin where *non adiabatic effects* are strong for the intuitive sequence and where the population transfer depends precisely on the pulse areas of this intuitive sequence (see the comments below). *Non adiabatic effects*, which are smaller for larger pulse areas, also occur near the straight line boundary regions. *Non diabatic effects* arise as well near the hyperbolic boundaries.

For the concrete realization with finite pulses of moderate areas, we have to analyze the precise influence of non adiabatic and non diabatic effects. We discuss here these non adiabatic effects referring to Fig. 8 supposing that the detunings are small enough with respect to the speed of the process to yield non adiabatic transitions:

In the intuitive case, at the beginning of the process, the states $|1\rangle$ and $|2\rangle$ are coupled by the pump pulse, and thus non adiabatic transitions can occur near the origin between the surfaces connected to $|1\rangle$ and $|2\rangle$. In the counterintuitive case, at the beginning of the process, state $|1\rangle$ is not coupled to the other levels and there are no non adiabatic transitions near the origin. At the end of the process, the adiabatic path ending in $|3\rangle$ is not coupled to the other levels, implying again absence of non adiabatic transitions near the origin. We thus recover the well known fact that resonant STIRAP (with very small detunings) is more favorable with a counterintuitive pulse sequence and leads to

Rabi oscillations in the intuitive case.

2. Transfer to a coherent superposition of states

We study the various superposition of states that can be created by adiabatic passage in a robust way with respect to variations of the field amplitude, using the topological analysis with resonances of Section VD (see also Section IV B 3 for the case of one laser). We assume that one starts (at time $t = t_i$) with a coherent state for the photon field and in the atomic state $|1\rangle$. We study here the Λ -system. Our results are easily extended to the other system (ladder and V), using the appropriate signs accompanying the field frequencies. We study the creation of a superposition of states at the final time $t = t_f$.

This can be analyzed with the help of Fig. 8, where we have taken $\Delta_P = 0$. The intuitive pump-Stokes sequence induces first a lifting of degeneracy with equal sharing between the dressed states $|\psi_+\rangle$ (the upper one, associated to the eigenenergy λ_+) and $|\psi_-\rangle$ (the lower one, associated to the eigenenergy λ_-) initially connected to $|1\rangle$ and $|2\rangle$. If we assume that the peak pump field amplitude is *beyond* the conical intersection, then the branches $|\psi_-\rangle$ and $|\psi_+\rangle$ respectively connect $-|2\rangle$ and $|3\rangle$ at the end. When $\Delta_S < 0$ (as in Fig 8), this leads at the end of the process to the coherent superposition with a dynamical phase (up to an irrelevant global phase)

$$|\psi(t_f)\rangle = \frac{1}{\sqrt{2}} \left[|3\rangle - e^{i \int_{t_i}^{t_f} ds(\lambda_+(s) - \lambda_-(s))} e^{-i\omega_S(t_i - t_f)} |2\rangle \right]. \quad (298)$$

When $\Delta_S > 0$, we obtain

$$|\psi(t_f)\rangle = \frac{1}{\sqrt{2}} \left[|3\rangle + e^{-i \int_{t_i}^{t_f} ds(\lambda_+(s) - \lambda_-(s))} e^{-i\omega_S(t_i - t_f)} |2\rangle \right]. \quad (299)$$

The counterintuitive Stokes-pump sequence leads to the transfer to the unique state $|3\rangle$.

If we assume that the peak pump field amplitude is *below* the conical intersection, then the branches $|\psi_-\rangle$ and $|\psi_+\rangle$ respectively connect $-|2\rangle$ and $|1\rangle$ at the end. This leads to coherent superpositions between the states $|1\rangle$ and $|2\rangle$.

If we have additionally $\Delta_S = 0$, the counterintuitive sequence gives the standard STIRAP (transfer to state $|3\rangle$) and the intuitive sequence induces interferences of the branches at the end of the processes, that do not lead to robust superposition of states.

We now analyze Fig. 9, where we assume $\Delta_S = 0$. When $\Delta_P > 0$ (as in Fig 9), this leads at the end of the process to the coherent superposition without dynamical phase (but still with the optical phase):

$$|\psi(t_f)\rangle = \frac{1}{\sqrt{2}} \left[|3\rangle - e^{-i\omega_S(t_i - t_f)} |2\rangle \right]. \quad (300)$$

When $\Delta_S > 0$, we obtain

$$|\psi(t_f)\rangle = \frac{1}{\sqrt{2}} \left[|3\rangle + e^{-i\omega_S(t_i - t_f)} |2\rangle \right]. \quad (301)$$

The topological analysis thus shows that *it is not possible with two quasi-resonant delayed lasers to end in a superposition of states between the lowest states $|1\rangle$ and $|3\rangle$ in a robust way*. We can remark that in [77], it has been shown that one can create such a superposition, however in a non-robust way but still by adiabatic passage, by modifying the end of the STIRAP process (with the counterintuitive sequence), maintaining a fixed ratio of Stokes and pump pulse amplitudes.

The numerical calculations of Figure 12 show the predicted superpositions of states at $\Delta_P = 0$ and $\Delta_S = 0$. They also show that a final superposition between $|1\rangle$ and $|3\rangle$ is possible on some pieces of the hyperbolas (dashed lines). However they are not robust since the equation of these hyperbolas (297) depend on the peak field amplitudes.

VI. STATE-SELECTIVITY BY BICHROMATIC PULSES

The tools described in the preceding sections have been applied to investigate different kinds of control processes, such as the control of tunneling [62, 78, 79], the vibrational state selectivity in molecules (see e.g. [47, 61]) up to its dissociation in the ground electronic state[80], the alignment [32, 41] and orientation [42, 43] of molecules, the deflection of atomic beams [68, 81], and the creation of entangled states in two coupled spins 1/2 [82, 83]. These processes are based on the possibility to select a given dressed state in the system during or after the laser pulses.

In this section we will describe the application of these methods to some examples of population transfer by delayed bichromatic pulses in two and three level systems. Bichromatic effects with CW lasers in population trapping have been also investigated in [84].

We study processes with two fields of different carrier frequencies ω_1 and ω_2 which act in resonance (or in quasi-resonance) on the same atomic transition, which are referred to as *bichromatic processes*. They induce dynamical resonances in the system due to the beat frequency

$$\delta = \omega_1 - \omega_2. \quad (302)$$

We consider Hamiltonians of the form

$$H(\underline{\omega}t + \underline{\theta}) = H_0 - \mathbf{d} \cdot \left[\sum_{j=1}^2 \mathbf{e}_j \mathcal{E}_j(t) \cos(\omega_j t + \theta_j) \right] \quad (303)$$

where H_0 is the Hamiltonian of the free atomic system of energies E_ℓ , $\ell = 1, \dots, N$ associated to the states $\{|\ell\rangle\}$ spanning the Hilbert space $\mathcal{H} = \mathbb{C}^N$ on which H_0 and the dipole moment operator \mathbf{d} act. The total electric field, containing two carrier frequencies $\underline{\omega} = (\omega_1, \omega_2)$, is characterized by unit polarization vectors \mathbf{e}_j , smooth pulse-shaped envelope functions of time $\underline{\mathcal{E}}(t) = [\mathcal{E}_1(t), \mathcal{E}_2(t)]$ and the initial phases $\underline{\theta} = (\theta_1, \theta_2)$. The interaction is thus characterized by the time-dependent Rabi frequencies $\Omega_j^{(m\ell)}(t) = -\langle m | \mathbf{d} \cdot \mathbf{e}_j | \ell \rangle \mathcal{E}_j(t) / \hbar$, $j = 1, 2$ when the frequency ω_j is quasi-resonant between the states $|m\rangle$ and $|\ell\rangle$. One additionally assumes that the fields are weak enough such that $|\hbar\Omega_j^{(m\ell)}(t)| \ll |E_\ell - E_m|$ for all times, meaning that the nonresonant terms can be neglected. The fields are however sufficiently strong such that, for some $|m\rangle$ and $|\ell\rangle$, the peak Rabi frequency is comparable to the beat frequency: $\max_t |\Omega_j^{(m\ell)}(t)| \sim |\delta|$. The resonant terms with respect to the frequency difference δ will be kept, since they will produce dynamical resonances.

In the Floquet representation

$$K = -i\hbar\underline{\omega} \cdot \frac{\partial}{\partial \underline{\theta}} + H(\underline{\theta}), \quad (304)$$

the effective Hamiltonian will be derived with the following change of variables

$$\begin{cases} \theta = \theta_1 - \theta_2 \\ \theta_a = \theta_2 \end{cases}, \quad (305)$$

giving

$$\begin{cases} \partial/\partial\theta_1 = \partial/\partial\theta \\ \partial/\partial\theta_2 = \partial/\partial\theta_a - \partial/\partial\theta \end{cases}$$

and

$$K = -i\hbar\omega_2 \frac{\partial}{\partial\theta_a} - i\hbar\delta \frac{\partial}{\partial\theta} + H(\underline{\theta}). \quad (306)$$

We will apply specific rotating wave transformations R that will allow to identify resonant terms and to eliminate the nonresonant ones. We obtain an effective one-mode Floquet Hamiltonian of the form

$$K_{\text{eff}} = -i\hbar\delta \frac{\partial}{\partial\theta} + H_{\text{eff}}(\theta) \simeq R^\dagger K R, \quad (307)$$

that will take into account non trivial resonant bichromatic effects with respect to the frequency δ . Although the field intensities are moderate, the system exhibits dynamical resonances that in the case of a single laser are usually encountered only in a strong-field regime.

The dynamics of the dressed atom is determined by the effective one-mode time dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(\theta, t) = K_{\text{eff}}(t) \psi(\theta, t), \quad (308)$$

where $\psi(\theta, t)$ is a N -element column vector. The exact solution will thus be approximated by $R\psi(\theta, t)$.

These bichromatic resonances and their consequences will be studied in two- and three-level systems.

A. Two-level systems – Topological quantization of atomic beam deflection

1. The effective Hamiltonian

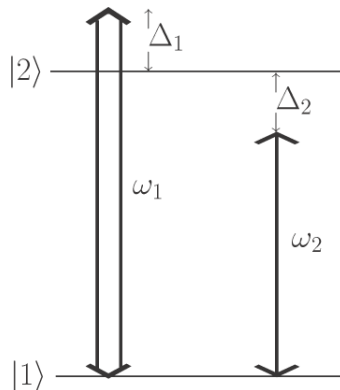


FIG. 13: Diagram of linkage patterns between two atomic states.

We consider a two-level system ($E_2 > E_1$) [68] driven by two quasi-resonant fields of detunings $\Delta_j \equiv (E_2 - E_1)/\hbar - \omega_j$, $j = 1, 2$, as depicted in Fig. 13. We assume that the dipole moment couples only the two levels: $\langle 1 | \mathbf{d} \cdot \mathbf{e}_j | 1 \rangle = \langle 2 | \mathbf{d} \cdot \mathbf{e}_j | 2 \rangle = 0$. The two characteristic Rabi frequencies denoted $\Omega_j(t) = -\langle 1 | \mathbf{d} \cdot \mathbf{e}_j | 2 \rangle \mathcal{E}_j(t)/\hbar$, $j = 1, 2$ involve the same transition 1 – 2. In the basis $\{|1\rangle, |2\rangle\}$, the Hamiltonian reads

$$H(\underline{\theta}) = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} + \hbar(\Omega_1(t) \cos \theta_1 + \Omega_2(t) \cos \theta_2) \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}. \quad (309)$$

The beat frequency is here $\delta \equiv \omega_1 - \omega_2 = \Delta_2 - \Delta_1$. We study the non-perturbative regime $|\delta| \lesssim \max_t |\Omega_j(t)| \ll (E_2 - E_1)/\hbar$, $j = 1, 2$.

We use the rotating wave transformation dressing the state $|2\rangle$ with minus one ω_1 -photon:

$$R = \begin{bmatrix} 1 & 0 \\ 0 & e^{-i\theta_1} \end{bmatrix}. \quad (310)$$

Applying this transformation to the Floquet Hamiltonian (304) gives

$$\begin{aligned} R^\dagger K R &= -i\hbar\omega \cdot \frac{\partial}{\partial \underline{\theta}} + \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_1 \\ \Omega_1 & 2\Delta_1 \end{bmatrix} + \frac{\hbar\Omega_2}{2} \begin{bmatrix} 0 & e^{-i(\theta_1 - \theta_2)} \\ e^{i(\theta_1 - \theta_2)} & 0 \end{bmatrix} \\ &+ \frac{\hbar\Omega_1}{2} \begin{bmatrix} 0 & e^{-2i\theta_1} \\ e^{2i\theta_1} & 0 \end{bmatrix} + \frac{\hbar\Omega_2}{2} \begin{bmatrix} 0 & e^{-i(\theta_1 + \theta_2)} \\ e^{i(\theta_1 + \theta_2)} & 0 \end{bmatrix}, \end{aligned} \quad (311)$$

which can be approximated, after the transformation (305), by the effective Floquet Hamiltonian [81]

$$K_{\text{eff}} = -i\hbar\delta \frac{\partial}{\partial \theta} + \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_1 \\ \Omega_1 & 2\Delta_1 \end{bmatrix} + \frac{\hbar\Omega_2}{2} \begin{bmatrix} 0 & e^{-i\theta} \\ e^{i\theta} & 0 \end{bmatrix}. \quad (312)$$

Since $-i\hbar\omega_2 \partial/\partial \theta_a$ is decoupled from the rest of the Floquet Hamiltonian, it acts trivially and can be omitted. This effective model is valid only if two different frequencies are assumed. The derivative term represents the relative number of photon pairs, one ω_1 -photon minus one ω_2 -photon. Thus the absorption of one “effective photon” of frequency δ in the effective model (312) corresponds in the complete model (304) to the absorption of one photon of frequency ω_1 and the emission of one photon of frequency ω_2 . If the two laser fields are counterpropagating, perpendicularly to the atomic beam, this double photon exchange results in a net transfer of momentum to the atom of $\hbar(\omega_1 + \omega_2)/c$ which manifests as a deflection of the beam.

The second term of the effective Hamiltonian (312) is the usual RWA Hamiltonian (associated to the ω_1 field), with eigenvalues $2\lambda_{\pm}^0 = \hbar\Delta_1 \pm \hbar\sqrt{(\Delta_1)^2 + (\Omega_1)^2}$. The third term can be viewed as a perturbation of this RWA Hamiltonian.

The analysis of the dynamics consists of (i) the calculation of the dressed eigenenergy surfaces of the effective quasienergy operator as a function of the two Rabi frequencies Ω_1 and Ω_2 , (ii) the analysis of their topology, and (iii) the application of adiabatic principles to determine the dynamics of processes in view of the topology of the surfaces.

2. Eigenenergy surface topology

In the following, we will consider for simplicity the case $\Delta_1 = -\Delta_2$ so that $\delta = -2\Delta_1$. For frozen values of the two fields Ω_1 and Ω_2 , we calculate dressed states and dressed energies by diagonalizing K_{eff} . The eigenelements can be labelled with two indices: one, denoted n , refers to the levels of the atom, and another one denoted k , refers to the relative photon numbers. The index k stands for the number of the ω_1 -photons absorbed and the number of ω_2 -photons emitted. The eigenvalues and eigenvectors have the following property of periodicity:

$$\lambda_{n;k,-k} = \lambda_{n;0,0} + k\hbar\delta, \quad |n;k,-k\rangle_{\text{eff}} = |n;0,0\rangle_{\text{eff}} \exp(ik\theta).$$

The eigenelements appear as two families, each of which consists of an infinite set of eigenvalues with equal spacing $\hbar\delta$. The eigenstates of K_{eff} , $|1;k,-k\rangle_{\text{eff}}$ and $|2;k,-k\rangle_{\text{eff}}$, can thus be labelled by $|1;k,-k\rangle$ and $|2;-1+k,-k\rangle$, $k \in \mathbb{Z}$ in the original basis of (304). If one starts with the initial state $|n_i;0,0\rangle$, the state $|n_f;k_1,k_2\rangle$ at the end of the process will characterize the atom in the state $|n_f\rangle$ with emission of k_i photons of frequency ω_i if $k_i > 0$ or absorption of k_i photons if $k_i < 0$, $i = 1, 2$.

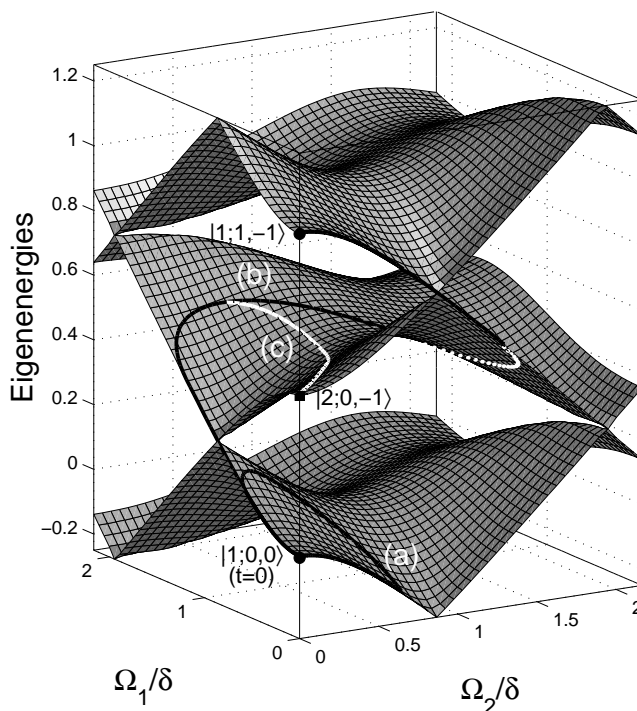


FIG. 14: Dressed eigenenergy surfaces (in units of δ) as functions of Ω_1 and Ω_2 for $\delta = -2\Delta_1 = 2\Delta_2$. Three different paths (denoted a, b and c) depending on the temporal evolution of the pulses are depicted.

On Fig. 14, we display eigenenergy surfaces, calculated numerically, as functions of the scaled Rabi frequencies Ω_1/δ and Ω_2/δ , assumed positive without loss of generality. Together with the adiabatic analysis, the topology of these surfaces gives insight into the various atomic population and photon transfers that can be produced by choosing appropriately the temporal evolution of the pulses. The process starts in the dressed state $|1;0,0\rangle$, i.e. the lowest atomic state with zero ω_1 and ω_2 photons. Its energy is shown as the starting point of various paths. We define the *transfer state* as the Floquet eigenvector which is adiabatically followed, i.e. on which the dressed population resides during the dynamics. There are two infinite families of quasienergy surfaces, that are constructed by the translations by $\hbar\delta k$, $k \in \mathbb{Z}$ of two surfaces. Any two neighboring surfaces have points of contact that are conical intersections. In the present model all the points of intersection are located either at the line $\Omega_1 = 0$ or at the line $\Omega_2 = 0$, corresponding to the situations where only one of the laser fields is interacting with the atom. Besides these true crossings, the quasienergy surfaces display avoided crossings. These true crossing and avoided crossings are associated with dynamical resonances as we will show below.

Three kinds of adiabatic paths can occur in this topology, as shown in Fig. 14 which displays three examples of adiabatic paths leading to three different final atomic population and photon transfers. They are labelled as (a), (b) and (c).

For the curve (a), the shifts of the eigenvalues are smaller than the energy of the first intersections. As a consequence, the path stays on a single surface, and at the end the system returns to the initial state, without any final transfer of photons nor of the atomic population.

The curve (b) corresponds to shifts that are larger than the first intersections. The crossing of the first intersection as Ω_1 increases with $\Omega_2 = 0$ brings the dressed system into the first upper quasienergy surface. Turning on and increasing the amplitude Ω_2 (while Ω_1 decreases) moves the path across this surface. When the second field Ω_2 decreases, the curve crosses an intersection (with $\Omega_1 = 0$) that brings the system to the third level surface, on which the curve stays until the end of the pulse Ω_2 . The transfer state is finally connected to state $|1; 1, -1\rangle$: there is no transfer of atomic population, but one ω_2 -photon has been absorbed and one ω_1 -photon has been emitted at the end of the process. This path is produced with two delayed pulses of approximately the same peak amplitudes. Two dynamical resonances occur in this system. Each is crossed twice, appearing as one true crossing and one avoided crossing. This appears clearer in the temporal representation of the quasienergies shown in Fig. 16b (see below for details of the dynamics). They can be described as follows: the field 1 dynamically shifts the eigenvalues which become resonant with the field 2. This resonance is mute when the field 2 is off (left true crossing) and becomes effective when the field 2 is on (left avoided crossing). The second dynamical resonance occurs symmetrically from dynamical Stark shift due to field 2 which makes the eigenvalues resonant with the field 1. The topology shows the connection of the adiabatic paths related to the preceding dynamical resonances.

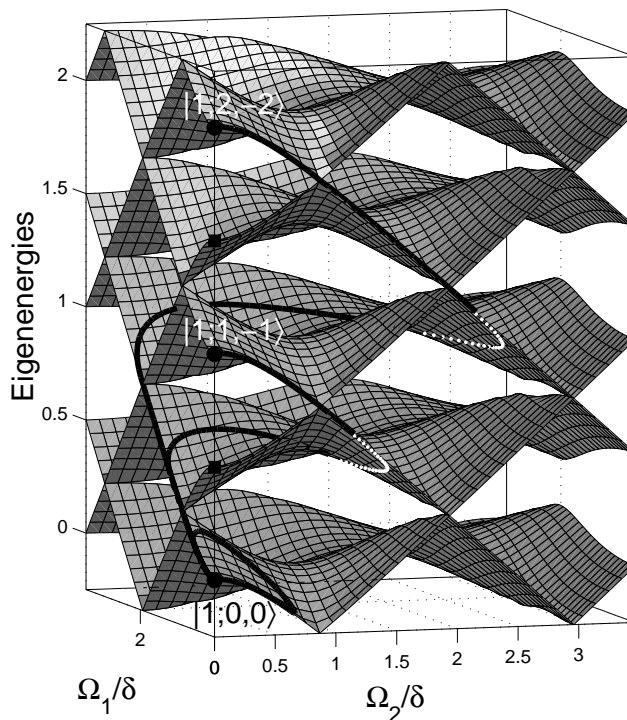


FIG. 15: Same figure as 14, but for stronger field amplitudes

If the field amplitudes are taken even larger, such that two dynamical resonances are crossed (corresponding to the true crossings when Ω_1 rises with $\Omega_2 = 0$ and when Ω_2 decreases with $\Omega_1 = 0$), the final state is $|1; 2, -2\rangle$, i.e. there is no atomic population transfer but an absorption of two ω_2 -photons and an emission of two ω_1 -photons. This path is shown in Fig. 15. This kind of process can be generalized to paths yielding the connectivity of the transfer state to $|1; k, -k\rangle$, i.e. the emission of k ω_1 -photons and the absorption of k ω_2 -photons (k positive for pulse 1 before pulse 2 and negative for pulse 2 before pulse 1), with no atomic population transfer.

The path (c) in Fig. 14 involves a crossing of one conical intersection of the two described above. The first resonance

is crossed by the rising pulse 1 (with $\Omega_2 = 0$). The second pulse is chosen with a smaller peak amplitude in order to avoid the passage through the resonance that would lead the system to the third level surface. This leads to an atomic population transfer, accompanied with absorption of one ω_2 -photon, since the path ends at $|2; 0, -1\rangle$. This can be generalized for upper and lower paths: the connectivity leads to $|2; -1 + k, -k\rangle$, with k positive (pulse 1 before smaller pulse-2 amplitude) or negative or zero integer (pulse 2 before smaller pulse-1 amplitude).

The topology of the quasienergy surfaces thus shows which appropriate delays and peak amplitudes induce desired atomic population and photon transfers. In the adiabatic regime, these loops can be classified into topologically inequivalent classes. If the evolution is adiabatic, all paths of a given class lead to the same end effect. This property underlies the robustness of the process.

3. Analytical construction of the dressed eigenenergies

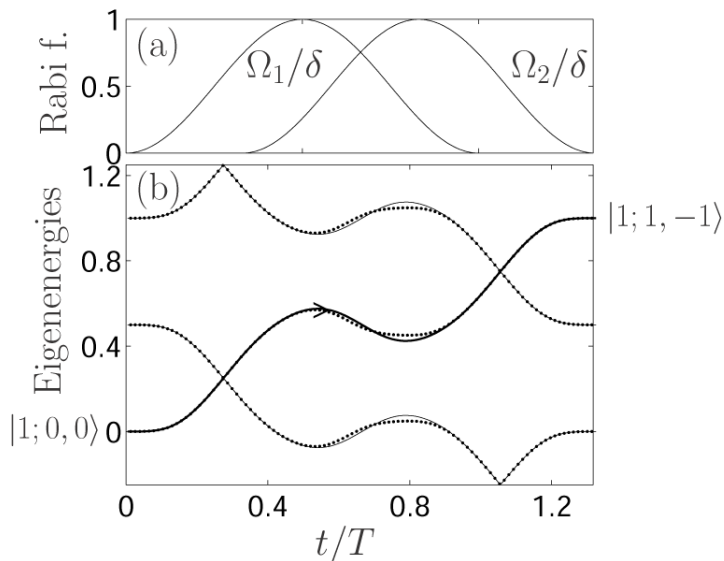


FIG. 16: (a) Rabi frequencies (in units of δ) from squared trig function envelopes. (b) Dressed eigenenergy curves (in units of δ), corresponding to the path b of Fig. 14 ($\Omega_{\max} = 1.5\delta$) from formula (313) (dotted lines) and exact numerical result (full line). The arrow indicates the adiabatic path (big line).

With the technique combining the rotating wave transformations and contact transformations developed in Section III C, one can treat accurately the dynamical resonances and construct approximately the quasienergies. If we take into account the first two dynamical resonances by appropriate RWT's [associated with the path (b)], one obtains the following explicit expression for the dressed energy surfaces

$$\frac{\lambda_{\pm,k}}{\hbar} = \frac{\Delta_1}{2} + k\delta \mp \left[\frac{1}{4} (\sqrt{A} - \delta)^2 + \frac{(\varepsilon^2 \Omega_1 \lambda_-^0)^2}{\hbar^2 A} \right]^{\frac{1}{2}} \quad (313)$$

with $A = \left\{ \left[(\Delta_1)^2 + (\Omega_1)^2 \right]^{1/2} - \delta \right\}^2 + 4(\varepsilon \lambda_-^0 / \hbar)^2$ and $2\varepsilon = -\Omega_2 / \sqrt{(\Delta_1)^2 + (\Omega_1)^2}$. Figure 16b displays these eigenvalues as functions of time for the dynamics described below. They are in close agreement with the exact eigenvalues calculated numerically from the Hamiltonian (312). The explicit consideration of the small perturbative corrections from the full model (304) by contact transformations does not change the topology of the surfaces in the sense that the conical intersections are not removed but only slightly shifted.

This systematic method can also be applied to treat the next dynamical resonances occurring for higher field amplitudes.

4. Dynamics and topological quantization of the number of exchanged photons

The path described above can be constructed by two smooth pulses, associated to the Rabi frequencies $\Omega_1(t)$ and $\Omega_2(t)$, with a time delay τ . To a sequence of such pulses corresponds a closed loop in the parameter plane Ω_1 and Ω_2 . Each of the two black curves (labelled a and b) correspond to a sequence of two smooth pulses of equal length T and equal peak Rabi frequencies $\Omega_{\max} \equiv \max_t [\Omega_1(t)] = \max_t [\Omega_2(t)]$, separated by a delay such that the pulse 1 is switched on before the pulse 2. This path has been redrawn as a function of time on Fig. 16b, using \sin^2 envelopes of length $T = 100/\delta$ and a delay of $\tau = T/3$, shown on Fig. 16a. Details of this dynamics of bichromatic processes, in particular in relation with the initial condition for the photon field, are given and discussed in the next subsection. The path (c) needs two pulses with different peak amplitudes.

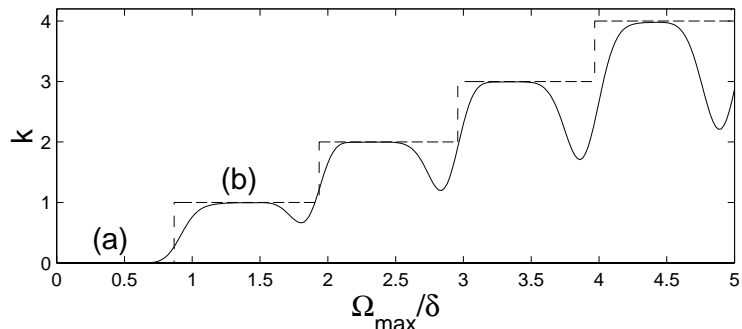


FIG. 17: Comparison of the number k of effective photons emitted at the end of the process [Eq. 314] (dashed line) with the average number of effective photons from the exact numerical result (full line). The plateaux labelled (a) and (b) refer to the two paths of Fig. 14 for pulse length $T = 100/\delta$ and delay $\tau = T/3$.

For equal peak amplitudes, we display in Fig. 17 the final average effective number k of exchanged photons as a function of the peak Rabi frequencies, calculated numerically by solving the dressed time-dependent Schrödinger equation. This shows the consequence of the topology described above. Since the connectivity of the transfer state to $|1; k, -k\rangle$ is based on the crossings, we can determine analytically the final number of effective photons k as a function of the peak Rabi frequencies Ω_{\max}/δ (taken equal) in the purely adiabatic regime:

$$k = \text{Integer part of } \sqrt{(\Omega_{\max}/\delta)^2 + (\Delta_1/\delta)^2}. \quad (314)$$

It predicts the adiabatic plateaux of Fig. 17, that can be interpreted as a topological quantization of the number of exchanged photons. The dips are due to nonadiabatic Landau-Zener transitions when the pulse overlap is in the neighborhood of the intersections. With a configuration of counterpropagating laser fields, perpendicular to an atomic beam, this translates into the possibility of deflection of the beam by the quantized transfer of a momentum $k\hbar(\omega_1 + \omega_2)/c$.

B. Three-level systems

The full semi-classical Hamiltonian (303) contains

$$H_0 = \begin{bmatrix} E_1 & 0 & 0 \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \end{bmatrix}, \quad \mathbf{d} = \begin{bmatrix} 0 & \mathbf{d}_{12} & 0 \\ \mathbf{d}_{21} & 0 & \mathbf{d}_{23} \\ 0 & \mathbf{d}_{32} & 0 \end{bmatrix}, \quad (315)$$

which are respectively the Hamiltonian of the free three-level system, acting on the Hilbert space $\mathcal{H} = \mathbb{C}^3$ spanned by the vector set $\{|1\rangle, |2\rangle, |3\rangle\}$, and the dipole moment operator (coupling transitions 1-2 and 2-3, but not 1-3). We take for simplicity equal coupling for the transitions 1-2 and 2-3. The system is characterized by the time-dependent Rabi frequencies $\hbar\Omega_1(t) = -\langle 1|\mathbf{d} \cdot \mathbf{e}_1|2\rangle\mathcal{E}_1(t) = -\langle 2|\mathbf{d} \cdot \mathbf{e}_1|3\rangle\mathcal{E}_1(t)$ and $\hbar\Omega_2(t) = -\langle 1|\mathbf{d} \cdot \mathbf{e}_2|2\rangle\mathcal{E}_2(t) = -\langle 2|\mathbf{d} \cdot \mathbf{e}_2|3\rangle\mathcal{E}_2(t)$. We

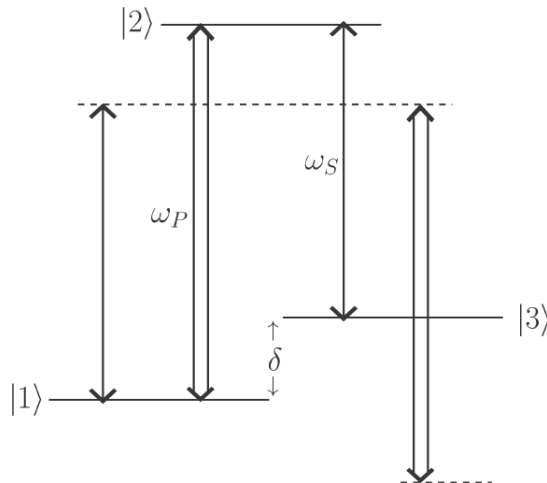


FIG. 18: Diagram of linkage patterns between three atomic states (full horizontal lines), showing pump (P or 1) and Stokes (S or 2) laser frequencies.

consider the situation where the frequency ω_1 is one-photon quasi-resonant with the 1-2 transition, and the frequency ω_2 is one-photon quasi-resonant with the 2-3 transition. We study the intermediate field intensities regime

$$|\delta| \lesssim \max_t [|\Omega_1(t)|, |\Omega_2(t)|] \ll (E_2 - E_1)/\hbar, (E_3 - E_2)/\hbar. \quad (316)$$

In particular we consider Λ -systems, depicted in Fig. 18, where the lasers 1 and 2 are respectively called *pump* and *Stokes* lasers. We use here resonant frequencies $\hbar\omega_1 = E_2 - E_1$, $\hbar\omega_2 = E_2 - E_3$ so that the two-field combination maintains the two-photon resonance between the states $|1\rangle$ and $|3\rangle$, as for the usual STIRAP process [70]. We have thus here $\delta \equiv \omega_1 - \omega_2 = (E_3 - E_1)/\hbar$. The main results of this part can be found in [38, 85, 86].

1. The effective Hamiltonian

To obtain the effective Floquet Hamiltonian, we apply the rotating wave transformation (RWT)

$$R(\underline{\theta}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & e^{-i\theta_1} & 0 \\ 0 & 0 & e^{i(\theta_2 - \theta_1)} \end{bmatrix}, \quad (317)$$

to obtain (setting $E_1 = 0$ as the reference of the energies)

$$R^\dagger K R = -i\hbar\underline{\omega} \cdot \frac{\partial}{\partial \underline{\theta}} + \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_1 & 0 \\ \Omega_1 & 0 & \Omega_2 \\ 0 & \Omega_2 & 0 \end{bmatrix} + V_1(\underline{\theta}) \quad (318)$$

with

$$V_1(\underline{\theta}) = \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_1 e^{-2i\theta_1} & 0 \\ \Omega_1 e^{2i\theta_1} & 0 & \Omega_2 e^{2i\theta_2} \\ 0 & \Omega_2 e^{-2i\theta_2} & 0 \end{bmatrix} + \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_2 e^{-i(\theta_1 + \theta_2)} & 0 \\ \Omega_2 e^{i(\theta_1 + \theta_2)} & 0 & \Omega_1 e^{i(\theta_1 + \theta_2)} \\ 0 & \Omega_1 e^{-i(\theta_1 + \theta_2)} & 0 \end{bmatrix} \\ + \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_2 e^{-i(\theta_1 - \theta_2)} & 0 \\ \Omega_2 e^{i(\theta_1 - \theta_2)} & 0 & \Omega_1 e^{-i(\theta_1 - \theta_2)} \\ 0 & \Omega_1 e^{i(\theta_1 - \theta_2)} & 0 \end{bmatrix}. \quad (319)$$

The usual RWA consists in neglecting the $\underline{\theta}$ -dependent operator V_1 . The first term of V_1 (319) contains the counter-rotating terms of the pump laser on the 1-2 transition and of the Stokes laser on the 2-3 transition. The next two terms

correspond to the interactions of the pump laser on the 2-3 transition and of the Stokes laser on the 1-2 transition. Following the hypothesis (316), we neglect the first two terms and keep the last term which becomes large (see [38] for details) when $\max_t [|\Omega_1(t)|, |\Omega_2(t)|]$ approaches or overcomes $|\delta|$. The (approximate) effective one-mode Floquet Hamiltonian is thus

$$K_{\text{eff}} = -i\hbar\delta\frac{\partial}{\partial\theta} + \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_1 & 0 \\ \Omega_1 & 0 & \Omega_2 \\ 0 & \Omega_2 & 0 \end{bmatrix} + \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_2 e^{-i\theta} & 0 \\ \Omega_2 e^{i\theta} & 0 & \Omega_1 e^{-i\theta} \\ 0 & \Omega_1 e^{i\theta} & 0 \end{bmatrix}. \quad (320)$$

The derivation term is the relative number operator for pairs of photons, one pump-field photon minus one Stokes-field photon. The second term is the well-known RWA Hamiltonian (dressed Hamiltonian used in the usual STIRAP) and the third one can be viewed as a perturbation of this RWA Hamiltonian.

We choose to have zero pump and Stokes photon at the beginning of the process. The initial condition is thus $|1; 0, 0\rangle$, which corresponds here to $|\psi(t = t_i)\rangle = |1; 0\rangle$ for the effective one-mode Schrödinger equation (308). At each value of Ω_1 and Ω_2 , the eigenvalues of K_{eff} can be decomposed as $\lambda_{n; -k, k} = \lambda_{n; 0, 0} - k\delta = \lambda_{n; 0, 0} - k\omega_1 + k\omega_2$ and their respective eigenvectors as $|n; -k, k\rangle_{\text{eff}} = |n; 0, 0\rangle_{\text{eff}} \exp[-ik\theta]$. The eigenstates of K_{eff} $|1; -k, k\rangle_{\text{eff}}$, $|2; -k, k\rangle_{\text{eff}}$ and $|3; -k, k\rangle_{\text{eff}}$ can thus be respectively labelled by $|1; -k, k\rangle$, $|2; -1 - k, k\rangle$ and $|3; -1 - k, k + 1\rangle$ $k \in \mathbb{Z}$ in the original basis of (304). If one starts with the initial state $|n_i; 0, 0\rangle$, the state $|n_f; k_1, k_2\rangle$ at the end of the process will characterize the atom in the state $|n_f\rangle$ with emission of k_i photons of frequency ω_i if $k_i > 0$ or absorption of k_i photons if $k_i < 0$, $i = 1, 2$. The eigenvalues appear as three families with periodic replicas (with period $2\pi/\delta$) and yield one-mode Floquet zones which can interact each other.

2. Eigenenergy surface topology

In Fig. 19, we display quasienergy surfaces, calculated numerically, as functions of the scaled Rabi frequencies Ω_1/δ and Ω_2/δ (assumed positive without loss of generality). The process starts in the dressed state $|1; 0, 0\rangle$, i.e. the lowest atomic state with zero ω_1 and ω_2 photons. Its energy (which is zero in Fig. 19) is shown as the starting point of various paths. There are three infinite families of quasienergy surfaces, constructed by the translations by $\hbar\delta k$, $k \in \mathbb{Z}$ of three surfaces. The surfaces exhibit conical intersections between two neighbours. In the present model all the points of intersection are located either at the line $\Omega_1 = 0$ or at the line $\Omega_2 = 0$, corresponding to the situations where only one of the laser fields is interacting with the atom. Besides these true crossings, the quasienergy surfaces display avoided crossings. These crossings and avoided crossings are also associated with dynamical resonances of the same type as the ones shown above in the two-level system.

The lifting of the degeneracy in the Ω_1 or Ω_2 directions is the same as in the case of the usual STIRAP, since this lifting of degeneracy occurs for very small field intensities: The lifting of degeneracy is such that the state solution is adiabatically connected to $|1; 0, 0\rangle$ in the Ω_2 direction. We study below the conditions yielding complete population transfer from $|1\rangle$ to $|3\rangle$, for pulses in counterintuitive orders, i.e. for delayed Ω_1 (pump pulse) switching on *after* Ω_2 (Stokes pulse).

Figure 19 shows that for $\max_t \Omega_1(t) \sim \max_t \Omega_2(t) < \delta$, we recover a STIRAP-type path (denoted as path a), i.e. connecting $|1; 0, 0\rangle$ to $|3; -1, 1\rangle$. The creation of degeneracy is indeed such that the middle state (connected to the energy zero) is adiabatically connected to $|3; -1, 1\rangle$ in the Ω_1 direction. The upper and lower states (connected to the energy zero) are respectively connected to the superpositions of states: $(|1; 0, 0\rangle + |2; -1, 0\rangle)/\sqrt{2}$ and $(|1; 0, 0\rangle - |2; -1, 0\rangle)/\sqrt{2}$, in the Ω_1 direction. In the case of path a, the last term of the Hamiltonian (320) can be seen as a small perturbation of the RWA Hamiltonian of the standard resonant STIRAP. This has been studied in details in [38]. The effect of this perturbation is a distortion of the path (see Fig. 21b for a time evolution of this path). The dynamics associated to this path is studied below.

Increasing the intensity of Ω_2 , we obtain a path (path b in Fig. 19) connecting $|1; 0, 0\rangle$ to the superposition of states $(|1; -1, 1\rangle + |2; -2, 1\rangle)/\sqrt{2}$ (of energy $-\delta$). Increasing again the intensity of Ω_2 , we obtain a path (path c) connecting $|1; 0, 0\rangle$ to $|3; -3, 3\rangle$ (of energy -2δ). This is similar to the usual STIRAP in the sense that this path allows to transfer the atomic population from $|1\rangle$ to $|3\rangle$, however with the nontrivial effect of an absorption of three ω_1 -photons and an emission of three ω_2 -photons. For higher intensities of Ω_2 we can generalize the preceding connections. In summary, the topology shows two kinds of adiabatic connections: (i) from $|1; 0, 0\rangle$ to $(|1; -(2k+1), 2k+1\rangle + |2; -(2k+2), 2k+1\rangle)/\sqrt{2}$ and (ii) from $|1; 0, 0\rangle$ to $|3; -(2k+1), 2k+1\rangle$, $k \geq 0$.

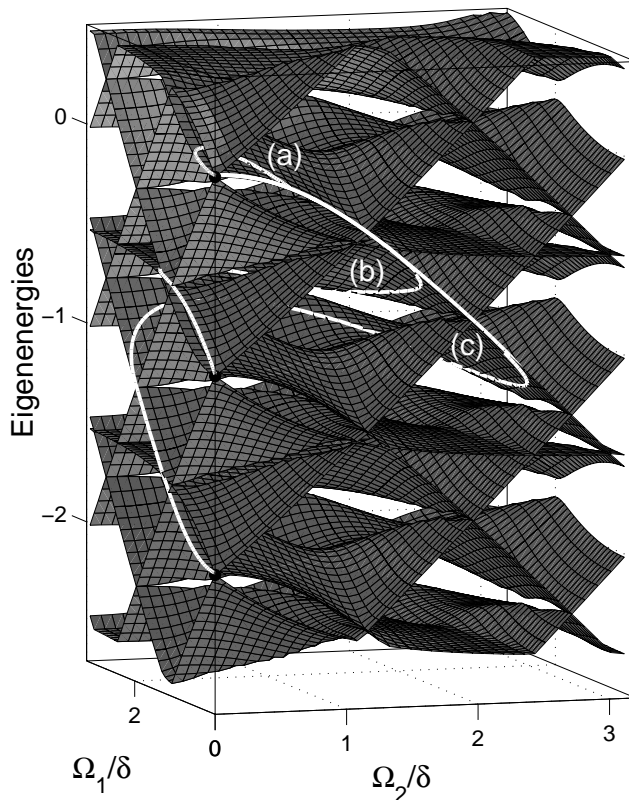


FIG. 19: Dressed eigenenergy surfaces (in units of δ) as functions of Ω_1/δ and Ω_2/δ . Three characteristic paths are shown, all starting at the same state of energy zero, and with a sequence of pulses $\Omega_1 - \Omega_2$ of different peak amplitudes: path (a) corresponding to a STIRAP-like process, whose dynamics is shown in Figs 20 and 21, is of relatively small amplitude and makes a small loop in a single eigenenergy surface; path (b) giving a superposition of states $(|1; -1, 1\rangle + |2; -2, 1\rangle)/\sqrt{2}$ (of energy $-\delta$); and path (c) giving a STIRAP-like process accompanied with three ω_1- photons absorbed and three ω_2- photons emitted, whose dynamics is shown in Figs 22 and 23.

3. Dynamics

We study the dynamics for the complete transfer to state $|3\rangle$. The dynamics is considered either with the semiclassical Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \phi(t) = H_{\text{eff}}(t) \phi(t), \quad (321)$$

with the effective time dependent Hamiltonian, constructed with K_{eff} (320)

$$H_{\text{eff}} = \frac{\hbar}{2} \begin{bmatrix} 0 & \Omega_1 + \Omega_2 e^{-i\delta t} & 0 \\ \Omega_1 + \Omega_2 e^{i\delta t} & 0 & \Omega_2 + \Omega_1 e^{-i\delta t} \\ 0 & \Omega_2 + \Omega_1 e^{i\delta t} & 0 \end{bmatrix} \quad (322)$$

or with the dressed Schrödinger equation (308) with the effective time dependent quasienergy Hamiltonian (320). We recall that the semiclassical Schrödinger equation (321) is equivalent to the dressed Schrödinger equation (308) with a coherent state as the initial condition for the photon field. Studying the dressed Schrödinger equation (308) with a number state as the initial condition for the photon field allows to characterize the dynamics by each path considered above. It is important to note that in these examples *the information on the number of photons exchanged with the*

system, obtained from the calculation with the number state as the initial condition, is still valid at the end of the pulse for a coherent state as an initial condition.

We consider two specific conditions, one for which the semiclassical and the dressed approaches are equivalent (which is the case for the STIRAP configuration) with respect to the number of photons exchanged at the end of the process, and another one for which the dressed theory brings the additional information of multiphoton processes.

To ensure that the interactions have a finite duration, we consider truncated \sin^2 envelopes. Time and frequency are scaled with respect to δ . The scaled pulse length is set to $T = 100/\Omega_0$ and the delay $\tau = 0.33T$. The pulses have to be applied in the so-called counterintuitive order: the ω_2 – Stokes pulse precedes the ω_1 – pump pulse with the delay τ . To fulfill the standard adiabatic condition, the relevant Rabi frequencies Ω have to be sufficiently large $\Omega T \gg 1$.

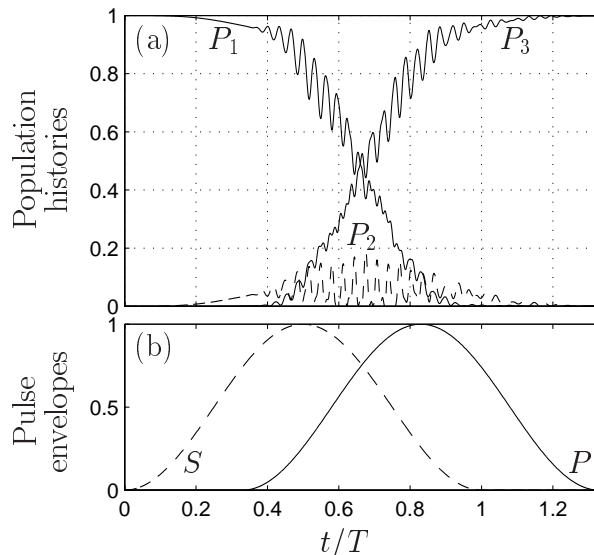


FIG. 20: From the semiclassical Schrödinger equation, (a) population histories $P_n(t)$ for $n = 1, 2, 3$ with $\delta = 2\Omega_0$ and $\Omega_{\max} = \Omega_0$ (top frame) and excitation by trig function pulse envelopes (of length $T = 100/\Omega_0$ and delay $0.33T$) with pump (full line) before Stokes (dashed line) shown in bottom frame (b). Population transfer $P_3(\infty)$ to bare state $|3\rangle$ is nearly complete.

For the parameters $\delta = 2\Omega_0$ and $\Omega_{\max} = \Omega_0$, corresponding to the path (a) on the surfaces in Fig. 19, we show in Fig. 20 the solution of the semiclassical Schrödinger equation (321). It features a STIRAP-like process inducing a complete population transfer for this choice of the delays. Two zones of the quasienergy spectrum associated to the surfaces of Fig. 19 are pictured as a function of time in Fig. 21b. We notice that the state $|1; 0, 0\rangle$ is adiabatically connected to the final target state $|3; -1, 1\rangle$. This implies a complete population transfer from the bare state $|1\rangle$ to the bare state $|3\rangle$ with absorption of one pump photon and emission of one Stokes photon at the end of the process.

This is confirmed by the numerical solution of the dressed Schrödinger equation (308) with a number state as the initial condition for the photon field $|1; 0, 0\rangle$: It shows that the solution dressed statevector $\psi(t)$ (the transfer state, which in the bare basis is given by $R\psi(\theta, t)$) mainly projects on the transfer eigenvector during the process. Additional informations of the dressed solution during time are shown on Fig. 21a and 21c. Figure 21a displays the probabilities of being in the bare states 1, 2 and 3:

$$P_n = \sum_{k_P, k_S} |\langle n; k_P, k_S | R | \psi(t) \rangle_{\mathcal{H}}|^2, \quad n = 1, 2, 3 \quad (323a)$$

$$= \frac{1}{(2\pi)^2} \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 |\langle n | R \psi(t) \rangle_{\mathcal{H}}|^2. \quad (323b)$$

Figure 21c shows the respective probabilities of one and two ω_1 – pump photon absorption $\mathcal{P}_{P,-1}$, $\mathcal{P}_{P,-2}$, and of one ω_2 – Stokes photon emission and absorption $\mathcal{P}_{S,1}$, $\mathcal{P}_{S,-1}$, defined with the respective formulas of the probabilities of ℓ ω_1 – photons emissions and of ℓ ω_2 – photons emissions

$$\mathcal{P}_{P,\ell} = \sum_{n, k_2} |\langle n; \ell, k_2 | R | \psi(t) \rangle_{\mathcal{H}}|^2, \quad (324a)$$

$$\mathcal{P}_{S,\ell} = \sum_{n, k_1} |\langle n; k_1, \ell | R | \psi(t) \rangle_{\mathcal{H}}|^2. \quad (324b)$$

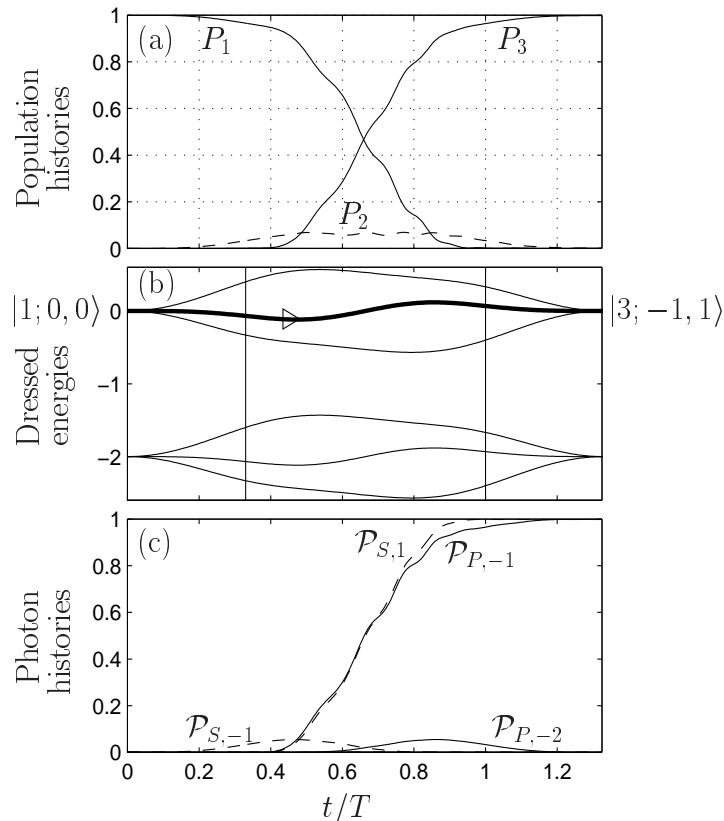


FIG. 21: From the dressed Schrödinger equation, with the same parameters as in Fig. 20, (a) population histories $P_n(t)$ for $n = 1, 2, 3$ (top frame), (c) photon histories (bottom frame), associated to the dressed spectrum in middle frame (b). The arrow characterizes the transfer eigenvector. Vertical lines indicate where the pump pulse starts and the Stokes pulse ends.

The other probabilities of photon emissions or absorptions are negligible. During the process, we remark that small transient ω_1 - and ω_2 - photon absorption probabilities arise. An early ω_2 - photon absorption is observed, coinciding exactly with the (negative) shift of the transfer eigenvector. The first effects of the ω_2 - pulse are indeed (i) to split the unpopulated dressed states connected to $|2\rangle$ and $|3\rangle$, and (ii) to produce a Stark shift of the dressed state connected to $|1\rangle$ (the early part of the transfer state), which is equivalent to a partial absorption of a ω_2 - photon. Symmetrically, a late ω_1 - photon absorption occurs. It is due to a (positive) Stark shift of the dressed state connected to $|3\rangle$ (the late part of the transfer state). Arising near the end of the process, for which one ω_1 - photon has already been absorbed, it leads to a partial absorption of a second ω_1 - photon. At the end of the process the complete population transfer from state $|1\rangle$ to state $|3\rangle$ is accompanied by the loss of a ω_1 - photon and the gain of a ω_2 - photon. Thus the final result is not different from the semiclassical result.

Comparing Figs. 20a and 21a, we notice that, as expected, the solution of the dressed Schrödinger equation, with a number state as initial condition for the photon field, *averages* the solution of the semiclassical Schrödinger equation, with respect to the formula (323b).

We now study the situation when the detuning from the transition frequencies satisfies $\delta < \Omega_{\max}$ so that different Floquet zones cross.

To that effect, we choose the parameters $\delta = 2\Omega_0$ and $\Omega_{\max} = 4.4\Omega_0$, corresponding to the path c on the surfaces in Fig. 19. As shown on Fig. 22, the solution of the semiclassical Schrödinger equation (321) leads to nearly complete population transfer from state $|1\rangle$ to state $|3\rangle$. The analysis of the surfaces shows that the state $|1; 0, 0\rangle$ connects $|3; -3, 3\rangle$. Thus the complete population transfer from the bare state $|1\rangle$ to the bare state $|3\rangle$ must be accompanied with absorption of three pump photons and emission of three Stokes photons at the end of the process. This is confirmed by the numerical solution of the dressed Schrödinger equation (308) with the initial state as a number state for the photon field $|1; 0, 0\rangle$, shown in Fig. 23a: the dressed statevector $\psi(t)$ approximately projects on the transfer eigenvectors during the process. It shows the probabilities of being in the bare states 1, 2 and 3. Figure 23c shows the respective probabilities of one, two, three and four ω_1 - photon absorptions, of one ω_2 - photon absorption, and of one, two and three ω_2 - photon emissions, calculated with the formulas (324). The other probabilities of photon

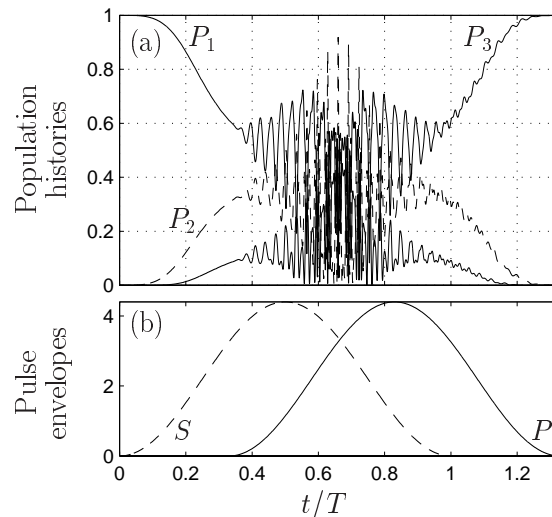


FIG. 22: From the semiclassical Schrödinger equation, (a) population histories $P_n(t)$ for $n = 1, 2, 3$ with $\delta = 2\Omega_0$ and $\Omega_{\max} = 4.4\Omega_0$ and (b) pulse excitation. Population transfer $P_3(\infty)$ to bare state $|3\rangle$ is nearly complete.

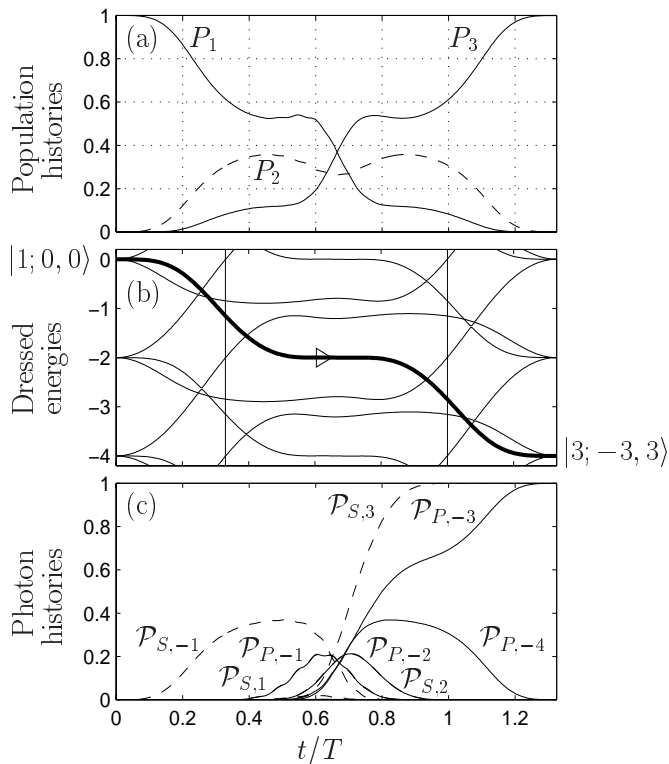


FIG. 23: From the dressed Schrödinger equation, with the same parameters as in Fig. 22, (a) population histories $P_n(t)$ for $n = 1, 2, 3$ (top frame) and (c) photon histories (with $\mathcal{P}_{P,-1} \approx \mathcal{P}_{S,1}$ and $\mathcal{P}_{P,-2} \approx \mathcal{P}_{S,2}$), associated to the dressed spectrum in middle frame (b).

emissions or absorptions are negligible. As in the preceding case, we observe an early Stokes photon absorption and a late pump photon absorption characterizing Stark shifts of the dressed state connected to $|1\rangle$ and the one connected to $|3\rangle$ respectively. Moreover in this case the field is so strong that it induces absorption (respectively emission) of one, two and then three pump (respectively Stokes) photons. The complete population transfer from state $|1\rangle$ to state $|3\rangle$ is now accompanied by the loss of three ω_1 -photons and the gain of three ω_2 -photons at the end of the process.

APPENDIX A: MATHEMATICAL COMPLEMENTS

1. Relation between the semi-classical and the Floquet evolution

We want to show the relation (13) of section II A in a more general setting in which the semi-classical Hamiltonian can have other time dependent parameters, and in which the frequency can be chirped. This is the general setting needed for the treatment of adiabatic evolution with chirped pulses in Section IV A, Eq. (223). We consider a semi-classical Hamiltonian of the form

$$H^{\mathbf{r}(t)}(\underline{\Theta}(t)), \quad (\text{A1})$$

where $\mathbf{r}(t)$ represents a set of parameters that can have an arbitrary time dependence, and $\underline{\Theta}(t) = (\Theta_1(t) \dots \Theta_d(t))$ represents d phases corresponding to d lasers acting on the molecule.

Furthermore we consider a more general form of the time dependence of the phase

$$\underline{\Theta}(t) = \underline{\theta} + \underline{g}(t). \quad (\text{A2})$$

In the case of a chirped frequency we have e.g. $\underline{\Theta}(t) = \underline{\theta} + \underline{v}(t) t$. As mentioned in Section IV A the effective instantaneous frequency is defined as $\underline{\omega}_{\text{eff}}(t) = d\underline{\Theta}(t)/dt = d\underline{g}(t)/dt = \underline{v}(t) + \underline{\dot{v}}(t) t$. If we define the generalized translation operator

$$\left(\mathcal{T}_{\underline{g}(t)}\Psi\right)(\underline{\theta}) = \left(e^{\underline{g}(t)\frac{\partial}{\partial \underline{\theta}}}\Psi\right)(\underline{\theta}) = \Psi(\underline{\theta} + \underline{g}(t)), \quad (\text{A3})$$

the semiclassical Hamiltonian can be written as

$$H^{\mathbf{r}(t)}(\underline{\Theta}(t)) = \mathcal{T}_{\underline{g}(t)}H^{\mathbf{r}(t)}(\underline{\theta})\mathcal{T}_{-\underline{g}(t)}. \quad (\text{A4})$$

Proposition. *The operator U is the propagator of the semi-classical Schrödinger equation (lifted to the enlarged space \mathcal{K})*

$$i\hbar\frac{\partial}{\partial t}U(t, t_0; \underline{\theta}) = H^{\mathbf{r}(t)}(\underline{\Theta}(t))U(t, t_0; \underline{\theta}), \quad U(t, t; \underline{\theta}) = \mathbb{1}_{\mathcal{H}}, \quad (\text{A5})$$

if and only if the operator U_K , defined by

$$U_K(t, t_0; \underline{\theta}) = \mathcal{T}_{-\underline{g}(t)}U(t, t_0; \underline{\theta})\mathcal{T}_{\underline{g}(t_0)}, \quad (\text{A6})$$

satisfies

$$i\hbar\frac{\partial}{\partial t}U_K(t, t_0; \underline{\theta}) = K^{\mathbf{r}(t)}U_K(t, t_0; \underline{\theta}), \quad U_K(t, t; \underline{\theta}) = \mathbb{1}_{\mathcal{K}}, \quad (\text{A7})$$

with

$$K^{\mathbf{r}(t)} = -i\hbar\underline{\omega}_{\text{eff}}(t) \cdot \frac{\partial}{\partial \underline{\theta}} + H^{\mathbf{r}(t)}(\underline{\theta}), \quad (\text{A8})$$

where $\underline{\omega}_{\text{eff}}(t)$ are the effective instantaneous frequencies

$$\underline{\omega}_{\text{eff}}(t) = d\underline{\Theta}(t)/dt = d\underline{g}(t)/dt. \quad (\text{A9})$$

The Floquet Hamiltonian $K^{\mathbf{r}(t)}$ acts on the enlarged Hilbert space $\mathcal{K} = \mathcal{H} \otimes \mathcal{L}_2(\mathbf{T}^d, d\underline{\theta}/2\pi)$, where \mathbf{T}^d is the d -dimensional unit torus.

Proof: We first remark that

$$\frac{\partial}{\partial t}\mathcal{T}_{\underline{g}(t)} \equiv \frac{\partial}{\partial t}e^{\underline{g}(t)\frac{\partial}{\partial \underline{\theta}}} = \frac{d\underline{g}(t)}{dt} \cdot \frac{\partial}{\partial \underline{\theta}}\mathcal{T}_{\underline{g}(t)} \equiv \mathcal{T}_{\underline{g}(t)}\underline{\omega}_{\text{eff}} \cdot \frac{\partial}{\partial \underline{\theta}} \quad (\text{A10})$$

We start with (A5) and invert eq. (A6)

$$U(t, t_0; \underline{\theta}) = \mathcal{T}_{\underline{g}(t)}U_K(t, t_0; \underline{\theta})\mathcal{T}_{-\underline{g}(t_0)}. \quad (\text{A11})$$

The time derivative of U can be expressed as

$$\frac{\partial}{\partial t}U = \frac{\partial}{\partial t}\mathcal{T}_{\underline{g}(t)}U_K\mathcal{T}_{-\underline{g}(t_0)} = \mathcal{T}_{\underline{g}(t)}\underline{\omega}_{\text{eff}} \cdot \frac{\partial}{\partial \underline{\theta}}U_K\mathcal{T}_{-\underline{g}(t_0)} + \mathcal{T}_{\underline{g}(t)}\frac{\partial U_K}{\partial t}\mathcal{T}_{-\underline{g}(t_0)} \quad (\text{A12})$$

which after insertion into (A5) and using (A4) yields

$$i\hbar\mathcal{T}_{\underline{g}(t)}\left(\underline{\omega}_{\text{eff}} \cdot \frac{\partial}{\partial \underline{\theta}}U_K + \frac{\partial U_K}{\partial t}\right)\mathcal{T}_{-\underline{g}(t_0)} = \mathcal{T}_{\underline{g}(t)}H^{\text{r}(t)}(\underline{\theta})\mathcal{T}_{-\underline{g}(t)}\mathcal{T}_{\underline{g}(t)}U_K\mathcal{T}_{-\underline{g}(t_0)} \quad (\text{A13})$$

which by multiplication from the left by $\mathcal{T}_{-\underline{g}(t)}$ and from the right by $\mathcal{T}_{\underline{g}(t_0)}$ yields (A7). The inverse implication follows from the same argument run backwards.

2. The structure of eigenvectors and eigenvalues of Floquet Hamiltonians – the concept of dressed Hamiltonian

In this section we show that the Floquet eigenvectors have the following general structure

$$\psi_{m,\underline{k}}(x, \underline{\theta}) = C(x, \underline{\theta}) [\phi_m^B(x) \otimes e^{i\underline{k}\cdot\underline{\theta}}], \quad (\text{A14})$$

where $C(x, \underline{\theta})$ is a unitary operator in \mathcal{K} , and $\phi_m^B(x) \in \mathcal{H}$ are the eigenvectors of a time and $\underline{\theta}$ independent operator B acting on \mathcal{H} . The eigenvalues can be written in the form

$$\lambda_{m,\underline{k}} = \lambda_m^B + \hbar\underline{k} \cdot \underline{\omega}, \quad (\text{A15})$$

where λ_m^B are the eigenvalues of B . The eigenelements can thus be classified by two labels: m , related to the molecule, and \underline{k} , related to the photon field.

We remark that if λ is an eigenvalue of K with eigenvector ψ , then for any $\underline{k} \in \mathbb{Z}^d$, $\lambda + \hbar\underline{k} \cdot \underline{\omega}$ is also an eigenvalue with corresponding eigenvector $e^{i\underline{k}\cdot\underline{\theta}}\psi$. This is an immediate consequence of the form of $K = -i\hbar\underline{\omega} \cdot \frac{\partial}{\partial \underline{\theta}} + H(x, \underline{\theta})$. In the periodic case this leads to a periodic structure of the spectrum. For instance, if we take an N -level model for the molecule, the Floquet spectrum will consist of a group of N eigenvalues that are repeated at a distance $k\omega$ for all $k \in \mathbb{Z}$, i.e. an infinite number of times. This periodic structure can be called Floquet zones, or Brillouin zones in analogy to a similar property in crystals. Although the Floquet Hamiltonian has an infinite number of eigenvalues and eigenvectors, once N are known, all the others can be constructed trivially. As the examples in Sections VI show, the energies of two different Brillouin zones can overlap and even lead to resonances that strongly couple the zones, leading to non trivial physical effects.

In the quasiperiodic case of two or several incommensurate frequencies the Floquet eigenvalues cover the real line densely, and the overlap between Brillouin zones is much more intricate.

This structure of the eigenvectors and eigenvalues of Floquet Hamiltonians can be understood by considering an alternative interpretation of the Floquet eigenvalue problem:

We look for a unitary transformation $C(x, \underline{\theta}) : \mathcal{H} \rightarrow \mathcal{H}$ (with $\underline{\theta}$ interpreted as a parameter) such that the semi-classical Schrödinger equation is transformed into an equation with a time-independent Hamiltonian B , i.e. such that

$$U^B(t, t_0; \underline{\theta}) = C(\underline{\Theta}(t))^{-1}U(t, t_0; \underline{\theta})C(\underline{\Theta}(t_0)) \quad (\text{A16})$$

satisfies

$$i\hbar\frac{\partial}{\partial t}U^B(t, t_0; \underline{\theta}) = BU^B(t, t_0; \underline{\theta}), \quad (\text{A17})$$

where $B = B(x)$ is a constant operator (i.e. independent of t and $\underline{\theta}$), acting on \mathcal{H} . If such a transformation exists, then

$$U(t, t_0; \underline{\theta}) = C(\underline{\Theta}(t))e^{-iB(t-t_0)/\hbar}C(\underline{\Theta}(t_0))^{-1} \quad (\text{A18})$$

and B can be expressed in terms of $C(\underline{\Theta}(t))$ and $H(\underline{\Theta}(t))$:

$$B = C(\underline{\Theta}(t))^{-1}H(\underline{\Theta}(t))C(\underline{\Theta}(t)) - i\hbar C(\underline{\Theta}(t))^{-1}\frac{\partial C(\underline{\Theta}(t))}{\partial \underline{\theta}} \cdot \frac{d\underline{\Theta}(t)}{dt}. \quad (\text{A19})$$

Acting with $\mathcal{T}_{-\underline{\omega}t}$ from the left on (A18) and with $\mathcal{T}_{\underline{\omega}t_0}$ from the right, one obtains that C induces a unitary transformation of the Floquet Hamiltonian in the enlarged space \mathcal{K}

$$\begin{aligned}\mathcal{T}_{-\underline{\omega}t}U(t, t_0; \underline{\theta})\mathcal{T}_{\underline{\omega}t_0} &\equiv e^{-iK(t-t_0)/\hbar} \\ &= C(\underline{\theta})\mathcal{T}_{-\underline{\omega}t}e^{-iB(t-t_0)/\hbar}\mathcal{T}_{\underline{\omega}t_0}C(\underline{\theta})^{-1} \\ &= C(\underline{\theta})e^{-(i/\hbar)(t-t_0)(-i\hbar\underline{\omega}\cdot\partial/\partial\underline{\theta}+B)}C(\underline{\theta})^{-1},\end{aligned}\tag{A20}$$

i.e.

$$K = C(\underline{\theta})(-i\hbar\underline{\omega}\cdot\frac{\partial}{\partial\underline{\theta}} + B)C(\underline{\theta})^{-1}.\tag{A21}$$

Hence, the determination of the eigenelements of K in \mathcal{K} is reduced to the determination of those of B in \mathcal{H} . When such a transformation $C(\underline{\theta})$ can be found, the operator B is called the *dressed Hamiltonian*. Although it acts only on the molecular Hilbert space \mathcal{H} , it contains the information on the photons, that “dress” the molecule. The transformation $C(\underline{\theta})$ can be interpreted as a change of representation. We remark that the transformation $C(x, \underline{\theta})$, and thus the dressed Hamiltonian B , is clearly not unique since $C(x, \underline{\theta})$ can be composed with any unitary transformation that acts inside \mathcal{H} .

We consider only the situation in which B has a purely discrete spectrum : $B\phi_m^B = \lambda_m^B\phi_m^B$. Since $-i\hbar\underline{\omega}\cdot\frac{\partial}{\partial\underline{\theta}}$ commutes with B , and its eigenelements are $\hbar\underline{k}\cdot\underline{\omega}$ and $e^{i\underline{k}\cdot\underline{\theta}}$, $\underline{k} \in \mathbb{Z}^M$, we can conclude that the eigenvalues and eigenvectors of K have the general structure given in Eqs. (A15),(A14). Since the sets of functions $\{\phi_m^B\}$ and $\{e^{i\underline{k}\cdot\underline{\theta}}\}$ are complete orthonormal bases of their respective spaces \mathcal{H} and $\mathcal{L}_2(\mathbf{T}^d, d\underline{\theta}/2\pi)$, and since C is unitary, we conclude that $\{\psi_{m,\underline{k}}\}$ forms a complete basis of \mathcal{K} .

In order to arrive at the eigenvalue equation for K we remark that since B is hermitian in \mathcal{H} there is a unitary transformation T that diagonalizes it in a reference base $\{|f_m\rangle\}$ of \mathcal{H} (which e.g. in the case of a two-level model can be represented in coordinates by $\{(1, 0), (0, 1)\}$):

$$T^\dagger BT = D = \sum_m \lambda_m^B |f_m\rangle\langle f_m|.\tag{A22}$$

T can be thought of as a matrix whose columns are the components of the eigenvectors of B expressed in the basis $\{|f_m\rangle\}$:

$$T = \sum_m |\phi_m^B\rangle\langle f_m|,\tag{A23}$$

which allows to write

$$\psi_{m,\underline{k}}(x, \underline{\theta}) = C(x, \underline{\theta})(T \otimes \mathbb{1}_{\mathcal{L}})|f_m \otimes e^{i\underline{k}\cdot\underline{\theta}}\rangle.\tag{A24}$$

Inserting (A22) into (A21) we obtain

$$K = C(\underline{\theta})T(-i\hbar\underline{\omega}\cdot\frac{\partial}{\partial\underline{\theta}} + D)T^\dagger C(\underline{\theta})^{-1}\tag{A25}$$

or

$$KC(\underline{\theta})T = C(\underline{\theta})T(-i\hbar\underline{\omega}\cdot\frac{\partial}{\partial\underline{\theta}} + D).\tag{A26}$$

Applying both sides of this operator relation to the elements of the basis $f_m \otimes e^{i\underline{k}\cdot\underline{\theta}}$ and using the fact that

$$(-i\hbar\underline{\omega}\cdot\frac{\partial}{\partial\underline{\theta}} + D) |f_m \otimes e^{i\underline{k}\cdot\underline{\theta}}\rangle = (\lambda_m^B + \hbar\underline{k}\cdot\underline{\omega})|f_m \otimes e^{i\underline{k}\cdot\underline{\theta}}\rangle,\tag{A27}$$

we arrive at the eigenvalue equation for K :

$$K\psi_{m,\underline{k}}(x, \underline{\theta}) = \lambda_{m,\underline{k}}\psi_{m,\underline{k}}(x, \underline{\theta}).\tag{A28}$$

Remark: Systems for which such a transformation $C(x, \underline{\theta})$ exists are called *reducible*. Due to the Floquet theorem this is always the case for time-periodic Hamiltonians (for finite or infinite dimensional \mathcal{H}). However, in the case of several incommensurate frequencies (quasiperiodic Hamiltonian) reducibility is not always satisfied, even for finite dimensional \mathcal{H} [33, 34][35, 36] [19]. We remark that for finite dimensional \mathcal{H} reducibility is equivalent to the property of K having no continuous spectrum[19].

3. Relation between eigenvectors and diagonalization transformations

The preceding arguments are an adaptation of the following elementary relations of finite dimensional linear algebra, which we illustrate with two dimensional hermitian matrices: We will use the notation S, A, D for the operators and $\tilde{S}, \tilde{A}, \tilde{D}$ for the corresponding matrix representations in a reference orthonormal basis $\{|e_1\rangle, |e_2\rangle\}$. We will use $|\psi\rangle$ for the intrinsic vectors, and $\tilde{\psi}$ for their column vectors of components with respect to the reference basis. Accordingly, $\tilde{e}_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\tilde{e}_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. We consider a hermitian operator A represented by the matrix \tilde{A} . This operator can be diagonalized with respect to the reference basis by a unitary transformation S represented by a matrix \tilde{S} : $\tilde{S}^\dagger \tilde{A} \tilde{S} = \tilde{D}$, where $\tilde{D} = \text{diag}(\lambda_1, \lambda_2)$. The eigenvalue equations can be written in matrix form as

$$\tilde{A} \tilde{S} = \tilde{S} \tilde{D}. \quad (\text{A29})$$

The components of the normalized eigenvectors $\tilde{\psi}_1 = \begin{pmatrix} u_1 \\ v_1 \end{pmatrix}$, $\tilde{\psi}_2 = \begin{pmatrix} u_2 \\ v_2 \end{pmatrix}$ can be identified as the column vectors of the matrix

$$\tilde{S} = \begin{pmatrix} u_1 & u_2 \\ v_1 & v_2 \end{pmatrix} \equiv (\text{column}(\tilde{\psi}_1) \quad \text{column}(\tilde{\psi}_2)), \quad (\text{A30})$$

since

$$\tilde{A} \tilde{S} = (\text{column}(\tilde{A} \tilde{\psi}_1) \quad \text{column}(\tilde{A} \tilde{\psi}_2)), \quad (\text{A31})$$

and

$$\tilde{S} \tilde{D} = (\text{column}(\tilde{\psi}_1 \lambda_1) \quad \text{column}(\tilde{\psi}_2 \lambda_2)). \quad (\text{A32})$$

Equation (A29) is equivalent to $\tilde{A} \tilde{\psi}_j = \lambda_j \tilde{\psi}_j$, $j = 1, 2$.

In order to extend these relations to operators in an infinite dimensional Hilbert space, we first write them in terms of operators S, A, D instead of in terms of their matrix representations $\tilde{S}, \tilde{A}, \tilde{D}$. The diagonalization formula is

$$S^\dagger A S = D, \quad (\text{A33})$$

where D is an operator that is diagonal in the reference basis, i.e. $\langle e_i | D | e_j \rangle = \delta_{ij} \lambda_j$. The diagonalization equation (A33) is equivalent to the eigenvalue equation written in operator form:

$$A S = S D. \quad (\text{A34})$$

The relation with the eigenvectors was made in the matrix representation by the statement that the column vectors of the matrix S that diagonalizes A are the components $\tilde{\psi}_j$ of the eigenvectors with respect to the reference basis. Extracting the j -th column vector of a matrix \tilde{S} is done by letting the matrix act on the coordinates \tilde{e}_j of the j -th basis element: $\tilde{S} \tilde{e}_j = j$ -th column of \tilde{S} . In terms of operators this translates into the statement that the j -th eigenvector can be expressed as

$$|\psi_j\rangle = S |e_j\rangle \quad (\text{A35})$$

since, indeed

$$A S |e_j\rangle = S D |e_j\rangle = S \lambda_j |e_j\rangle = \lambda_j S |e_j\rangle. \quad (\text{A36})$$

The operator S that diagonalizes A in the basis $\{|e_1\rangle, |e_2\rangle\}$ can be written as

$$S = \sum_j |\psi_j\rangle \langle e_j|. \quad (\text{A37})$$

We remark that in this formulation the choice of the reference basis is fixed but arbitrary. We use this formulation in the discussion of the adiabatic theorem in Appendix C.

APPENDIX B: COHERENT STATES IN THE FLOQUET REPRESENTATION

In this Appendix we show that the coherent states are represented in Floquet theory by a generalized function $\Phi_{\theta_0}(\theta)$, which is real, and depends on $\theta - \theta_0$, where $\theta_0 \in \mathbb{S}^1$ is a fixed angle, and

$$(\Phi_{\theta_0}(\theta))^2 = 2\pi\delta(\theta - \theta_0). \quad (\text{B1})$$

This can be obtained as follows. The photon field coherent states are eigenvectors of the annihilation operator

$$a|\alpha\rangle = \alpha|\alpha\rangle, \quad \alpha = |\alpha|e^{-i\theta_0}. \quad (\text{B2})$$

In the usual Fock number state representation they are given, up to a phase factor, by

$$|\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle. \quad (\text{B3})$$

In the phase representation they can be written as

$$\begin{aligned} \Phi_{\theta_0}^{(\bar{n})}(\theta) &= e^{i\zeta} e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} e^{i(n-\bar{n})\theta} \\ &= e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{|\alpha|^n}{\sqrt{n!}} e^{i(n-\bar{n})(\theta-\theta_0)} \end{aligned} \quad (\text{B4})$$

(where ζ is an arbitrary constant phase that we have chosen as $\zeta = \bar{n}\theta_0$). In order to obtain the representation of coherent states in Floquet theory we have to take $|\alpha| = \sqrt{\bar{n}}$, since the average photon number in a coherent state is given by $|\alpha|^2$, and then apply the limit $\bar{n} \rightarrow \infty$.

This can be rigorously done using directly the representation (B4), as was shown in [9]. Here we discuss an alternative construction, that is formal but gives a useful intuition. We use an approximate expression of the coherent states for large \bar{n} , obtained in [8], by developing

$$a_{\bar{n},\theta} = \sqrt{\bar{n}} e^{-i\theta} \sqrt{1 - \frac{1}{\bar{n}} i \frac{\partial}{\partial \theta}} \underset{\bar{n} \rightarrow \infty}{\rightsquigarrow} \sqrt{\bar{n}} e^{-i\theta} \left(1 - \frac{1}{2\bar{n}} i \frac{\partial}{\partial \theta} \right), \quad (\text{B5})$$

This leads to the following asymptotic expression [8] for the normalized coherent state corresponding to $\alpha = \sqrt{\bar{n}} e^{-i\theta_0}$, obtained as solution of $e^{-i\theta} (1 - i/(2\bar{n})\partial/\partial\theta) \Phi_{\theta_0}^{(\bar{n})} = e^{-i\theta_0} \Phi_{\theta_0}^{(\bar{n})}$:

$$\Phi_{\theta_0}^{(\bar{n})} \underset{\bar{n} \rightarrow \infty}{\rightsquigarrow} \frac{1}{\nu} \exp \{ -2\bar{n} [1 - \cos(\theta - \theta_0) - i(\sin(\theta - \theta_0) - (\theta - \theta_0))] \} \quad (\text{B6})$$

where the normalization constant is

$$\nu^2 = e^{-4\bar{n}} I_0(4\bar{n}) \quad (\text{B7})$$

with I_0 a Bessel function, which behaves asymptotically as

$$I_0(4\bar{n}) = \int_0^{2\pi} \frac{d\theta}{2\pi} \exp(4\bar{n} \cos \theta) \underset{\bar{n} \rightarrow \infty}{\rightsquigarrow} \frac{e^{4\bar{n}}}{(8\pi\bar{n})^{1/2}}. \quad (\text{B8})$$

Therefore

$$\left| \Phi_{\theta_0}^{(\bar{n})}(\theta) \right|^2 \underset{\bar{n} \rightarrow \infty}{\rightsquigarrow} (8\pi\bar{n})^{1/2} \exp \{ -4\bar{n} [1 - \cos(\theta - \theta_0)] \}, \quad (\text{B9})$$

noticing that the function $\exp \{ -4\bar{n} [1 - \cos(\theta - \theta_0)] \}$ behaves like $\exp \{ -2\bar{n}(\theta - \theta_0)^2 \}$ for $\bar{n} \rightarrow \infty$, we get

$$\left| \Phi_{\theta_0}^{(\bar{n})}(\theta) \right|^2 \underset{\bar{n} \rightarrow \infty}{\rightsquigarrow} 2\pi\delta(\theta - \theta_0), \quad (\text{B10})$$

where $\delta(\theta - \theta_0)$ is the usual Dirac delta function.

We remark that since the phase term in (B4) (or in (B6)) is odd in $\theta - \theta_0$, we obtain that $\Phi_{\theta_0}^{(\bar{n})}(\theta) \rightarrow \Phi_{\theta_0}(\theta)$ with $\Phi_{\theta_0}(\theta)$ real and

$$\left(\Phi_{\theta_0}^{(\bar{n})}(\theta)\right)^2 \xrightarrow{\bar{n} \rightarrow \infty} 2\pi\delta(\theta - \theta_0). \quad (\text{B11})$$

Furthermore, using the well-known properties of the expectation values of N^m on coherent states, we obtain

$$\left\langle \Phi_{\theta_0}^{(\bar{n})}(\theta) \left| -i \frac{\partial}{\partial \theta} \right| \Phi_{\theta_0}^{(\bar{n})}(\theta) \right\rangle_{\mathcal{L}} = 0, \quad \text{for all } \bar{n}, \quad (\text{B12})$$

$$\left\langle \Phi_{\theta_0}^{(\bar{n})}(\theta) \left| (-i)^m \frac{\partial^m}{\partial \theta^m} \right| \Phi_{\theta_0}^{(\bar{n})}(\theta) \right\rangle_{\mathcal{L}} \xrightarrow{\bar{n} \rightarrow \infty} \infty, \quad m \geq 2. \quad (\text{B13})$$

The subscripts in the scalar product symbols ($\langle \cdot | \cdot \rangle_{\mathcal{L}}$) indicate on which space they act. We conclude thus that in Floquet theory the photon coherent states are represented by the ‘‘square root of a δ -function’’, that we denote by $\Phi_{\theta_0}(\theta) = (2\pi)^{1/2}\delta_{1/2}(\theta - \theta_0)$. Since we will be interested in expectation values, only $|\Phi_{\theta_0}|^2$ will appear in our calculations. The formal calculus rules for $\delta_{1/2}(\theta - \theta_0)$ are given in Ref. [9].

APPENDIX C: THE ADIABATIC THEOREM FOR FLOQUET HAMILTONIANS

In this Appendix we sketch an argument that leads to the adiabatic theorem for an N -level system with a Floquet Hamiltonian denoted $K^{\mathbf{r}}$ which generates the dressed Schrödinger equation (Eq. (229) of Section IV).

$$i\hbar \frac{\partial \psi(\theta, t)}{\partial t} = K^{\mathbf{r}(s)} \psi(\theta, t). \quad (\text{C1})$$

We have to show that in the adiabatic limit up to corrections of order $\mathcal{O}(1/\tau)$, the evolution is approximated by

$$\psi(\theta, t) \simeq \sum_{m \in \mathcal{S}} c_m \exp \left[i\delta_m^{\mathbf{r}(s)}(t) \right] \psi_m^{\mathbf{r}(s)}(\theta), \quad (\text{C2})$$

where the c_m are complex numbers determined by the initial condition

$$c_m = \left\langle \exp \left[i\delta_m^{\mathbf{r}(s_0)}(t_0) \right] \psi_m^{\mathbf{r}(s_0)}(\theta) \mid \psi(\theta, t_0) \right\rangle \quad (\text{C3})$$

Let $\{\psi_m^{\mathbf{r}(s)}\}$ be an orthonormal basis of instantaneous eigenvectors of $K^{\mathbf{r}(s)}$, which we assume to be sufficiently smooth as a function of s . We define the unitary operator $\mathbf{S}^{\mathbf{r}(s)} := \sum_m |\psi_m^{\mathbf{r}(s)}\rangle \langle \psi_m^{\mathbf{r}(s_0)}|$, where s_0 is the initial time. This operator transforms the Floquet Hamiltonian by

$$\mathbf{D}^{\mathbf{r}(s)} := \left(\mathbf{S}^{\mathbf{r}(s)} \right)^\dagger K^{\mathbf{r}(s)} \mathbf{S}^{\mathbf{r}(s)}, \quad (\text{C4})$$

into an operator $\mathbf{D}^{\mathbf{r}(s)}$, which for all s is diagonal in the basis taken at s_0 , $\{\psi_m^{\mathbf{r}(s_0)}\}$. Defining transformed states by

$$\tilde{\psi}(\theta, s) = \left(\mathbf{S}^{\mathbf{r}(s)} \right)^\dagger \psi(\theta, \tau s). \quad (\text{C5})$$

the Schrödinger equation (C1) can be rewritten as

$$\frac{i\hbar}{\tau} \frac{\partial \tilde{\psi}(\theta, s)}{\partial s} = \left[\mathbf{D}^{\mathbf{r}(s)} - \frac{i\hbar}{\tau} \left(\mathbf{S}^{\mathbf{r}(s)} \right)^\dagger \frac{\partial \mathbf{S}^{\mathbf{r}(s)}}{\partial s} \right] \tilde{\psi}(\theta, s) \quad (\text{C6})$$

The last term of the right-hand side of Eq. (C6) characterizes the *nonadiabatic couplings* between the instantaneous Floquet states (off-diagonal terms, of the form $|\psi_\ell^{\mathbf{r}(s_0)}\rangle \langle \psi_\ell^{\mathbf{r}(s)} | \dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} \psi_m^{\mathbf{r}(s)} \rangle_{\mathcal{K}} \langle \psi_m^{\mathbf{r}(s_0)}|$, $\ell \neq m$) and the Berry phase

(real diagonal terms). In the adiabatic limit $\tau \rightarrow \infty$, one can neglect the nonadiabatic couplings, i.e. the nondiagonal terms that are of order $\mathcal{O}(1/\tau)$:

$$\frac{i\hbar}{\tau} \frac{\partial \tilde{\psi}(\theta, s)}{\partial s} \simeq \left[\mathbf{D}^{\mathbf{r}(s)} - \frac{i\hbar}{\tau} \text{diag}_{(s_0)} \left(\left(\mathbf{S}^{\mathbf{r}(s)} \right)^\dagger \frac{\partial \mathbf{S}^{\mathbf{r}(s)}}{\partial s} \right) \right] \tilde{\psi}(\theta, s), \quad (\text{C7})$$

where $\text{diag}_{(s_0)}$ denotes the diagonal part with respect to the initial time basis $\{\psi_m^{\mathbf{r}(s_0)}\}$. Developing $\psi(\theta, t)$ at an initial time $t_0 = \tau s_0$ in the eigenvector basis of $K^{\mathbf{r}(s_0)}$, spanning the subspace \mathcal{S} :

$$\psi(\theta, \tau s_0) = \sum_{m \in \mathcal{S}} c_m \psi_m^{\mathbf{r}(s_0)}(\theta), \quad (\text{C8})$$

the equation is easily solved and one recovers Eq. (233). We remark that in many applications the initial time s_0 is taken before the rise of the laser pulse. In this case, since the interaction is off, the initial basis coincides with the eigenvectors of the free molecule multiplied by those of the field. The operator $\mathbf{D}^{\mathbf{r}(s)}$ of Eq. (C4) can then be written as

$$\mathbf{D}^{\mathbf{r}(s)} = -i\hbar\omega \frac{\partial}{\partial \theta} + \mathbf{d}^{\mathbf{r}(s)} \quad (\text{C9})$$

where $\mathbf{d}^{\mathbf{r}(s)}$ is an operator in \mathcal{H} that is diagonal in the basis of the eigenvectors of the free molecule.

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