# High-order adiabatic representations of quantum systems through a perturbative construction of dynamical invariants

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A perturbative series is derived for the systematic construction of a dynamical invariant (Lewis invariant) for a time-dependent Hamiltonian which is characterized by a time-scale parameter $\tau$, as appears in the usual formulation of the adiabatic theorem. The derivations make efficient use of the quantum averaging method, and the perturbative series obtained permits the construction of the invariant in successive orders in $\epsilon \sim 1/\tau$, corresponding to high-order adiabatic approximations. The series can be considered and resummed analytically to all orders, yielding an exact invariant for an harmonic oscillator linearly driven by an external field. For a nondegenerate two-level system, approximate invariants have been obtained up to the fifth order and illustrate how the adiabatic approximations of increasing orders successively approach the exact dynamics. The construct is applicable also to Floquet Hamiltonians and, in this context, it furnishes high-order adiabatic representations for the time evolution of Floquet states associated with a material system in an aperiodic laser pulse. We illustrate in particular how an exact Floquet dynamical invariant, defining exact adiabatic transports of Floquet states, is obtained for a laser-driven harmonic vibrational mode.

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## I. INTRODUCTION

Adiabaticity in quantum mechanics has always been associated with a slow variation of the Hamiltonian with respect to the time variable as expressed by the celebrated adiabatic theorem [1,2]. An adiabatic evolution is one in which the time-dependent state vector, in principle a solution of the time-dependent Schrödinger equation, is approximated by an eigenvector of the instantaneous Hamiltonian. The adiabatic theorem establishes how this adiabatic representation of the time evolution converges towards the exact one as the time scale $\tau$ over which the Hamiltonian varies tends to infinity. Thus, the concept of adiabaticity has mostly been evoked to define an approximation to the exact time evolution of the time-dependent quantum system. On the other hand, the advents of ultrashort, intense laser pulses [3,4] allow the investigations of the dynamics of laser-driven atomic and molecular systems occurring in conditions that hardly justify the use of the adiabatic approximation. Yet, one would like to be able to approach these dynamical problems by some sort of generalization of the adiabaticity concept. This is desired first for interpretative purposes; for example, to view the fast time evolution of the laser-driven system as the adiabatic transport of some state amounts to interpret the dynamics in terms of laser-induced structure changes [5]. Such a generalization would also be desirable for computational tasks: for example, one can make use of the generalized concept to define an adaptive basis set for an expansion of the time-dependent wave function that remains minimal at all times, an objective long sought for in quantum molecular dynamics [6–9].

To define such a generalization, we will first consider an exact adiabatic separation between the time and the spatial variables to be achieved whenever a time-dependent, Hermitian operator $\mathcal{I}(t)$ could be constructed such that the exact time-evolution operator is diagonal or, more generally, block diagonal in the eigenbasis of $\mathcal{I}(t)$. This operator can be viewed as an effective Hamiltonian, as done in Refs. [10,11]. Although its eigenvalues may vary in time, here we will refer to this operator rather as a dynamical invariant of the system, for its definition reminds one of what is known as a Lewis invariant [12–14]. In more recent literature, dynamical invariants, in fact Lewis invariants, have been evoked mostly in relation with the concept of geometric phases and its generalizations [15–17]. A comprehensive account of the spectral properties of these invariants can be found in Ref. [16] which uses the concept of dynamical invariant to define geometrically equivalent quantum systems.

It is to be expected that finding a dynamical invariant for a given time-dependent problem is as difficult as solving (analytically) the time-dependent Schrödinger equation itself. Indeed, exact, closed-form analytical expressions for the invariant had been found only for certain particular classes of systems [10–14]. In spite of this, little work has been devoted to the construction of the invariant by a perturbative method. We derive here a perturbation series to construct such an invariant *systematically* for a time-dependent Hamiltonian with a discrete spectrum. The series permits the generation of the invariant in successive orders in an adiabatic parameter $\epsilon = \tau_0/\tau$, where $\tau$ is a time-scale parameter characterizing the time variation of $\mathcal{H}(t)$, $\tau_0$ an intrinsic time scale of the system, i.e., $\tau_0 = 2\pi/\omega_0$, $\omega_0$ being a frequency which characterizes a typical separation within the energy spectrum of the system. In zeroth order, the invariant is defined by the time-dependent Hamiltonian, i.e., the transports of its eigen-

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states correspond to the usual adiabatic approximation described above. In any other orders, the construction defines the sought-for generalization of the adiabaticity concept. A similar series, using the same adiabatic parameter, has previously been evoked to establish the connection between the so-called Lewis phases, associated with the exact adiabatic transport of the invariant's eigenstates, and Berry phases, associated with the approximate transports of the Hamiltonian's eigenstates [17]. By identifying the adiabatic parameter $\epsilon$ defined above as the small parameter of the theory, the present perturbation series distinguishes itself from a perturbation treatment where the small parameter is generically attached rather to a perturbation potential (denoting an added interaction, neglected at zeroth order) [18].

The development of the perturbative series is given in Sec. III. It makes extensive use of the so-called quantum averaging technique, introduced by Scherer [19,20]. This technique, reviewed in Appendix A, has recently been used in a study of resonant and nonresonant interactions in field-driven systems described in the Floquet representation [21,22]. How the developed perturbative series actually works is illustrated in detail in Sec. III, where we show that, when resummed to all orders, the series yields the exact dynamical invariant for a linearly driven harmonic oscillator modeling a vibrational mode interacting with a strong laser field. In contrast, for a laser-driven nondegenerate two-level system, the perturbative series cannot be resummed analytically to all orders. However, with the help of a symbolic programming language, the series can be considered up to a high order, yielding an approximate invariant denoting a high-order adiabatic representation of the dynamics of this system. We examine, for a number of laser frequency conditions, how this representation approaches the exact dynamics (calculated numerically), as the order of the perturbative series is increased.

The construct is applicable also to Floquet Hamiltonians, describing a material system in an aperiodic pulse, and, in this context, it furnishes high-order adiabatic representations for the time evolution of Floquet states. Section IV starts with a review of a recent reformulation of Floquet theory that is particularly well suited for the present purposes [23,24]. We then illustrate how an exact Floquet dynamical invariant, defining exact adiabatic transports of Floquet states, can be obtained for the particular case of a laser-driven harmonic vibrational mode and discuss elements of restructuring that are expected to arise generically as one goes from the zeroth-order adiabatic approximation to the high-order adiabatic Floquet representations.

Section V concludes the paper with perspectives of applications of the formal constructs of the preceding sections. These range from its use in the development of new numerical tools, in particular for the description of time-resolved orbital dynamics of laser-driven multielectron systems, to its application in quantum control problems involving systems modeled by finite level schemes and/or coupled harmonic oscillators.

## II. PERTURBATION SERIES FOR A DYNAMICAL INVARIANT

### A. Dynamical invariants

Consider a system described by a time-dependent Hamiltonian $\mathcal{H}(t)$. A Lewis invariant of this system is defined [12–14] to be a time-dependent observable $\mathcal{I}(t)$ which is related to the Hamiltonian by (atomic units will be used throughout the paper)

$$[\mathcal{H},\mathcal{I}] - i\partial_t\mathcal{I} = 0, \tag{1}$$

Let $|\varphi_{l,\nu};t\rangle$, $\nu=1,2,\ldots,g_l$, be the (orthonormalized) eigenvectors of $\mathcal{I}$ associated with the eigenvalue $\epsilon_l(t)$ of degeneracy $g_l$, i.e.,

$$\mathcal{I}|\varphi_{l,\nu};t\rangle = \epsilon_l(t)|\varphi_{l,\nu};t\rangle, \quad \nu = 1,2,\ldots,g_l. \tag{2}$$

By differentiating both sides of Eq. (2), projecting the resulting equation on another eigenstate $|\varphi_{k,\nu'};t\rangle$, then adding to the result the identity

$$i\langle\varphi_{k,\nu};t|[\mathcal{H},I]|\varphi_{l,\nu'};t\rangle = i[\epsilon_l(t)-\epsilon_k(t)]\langle\varphi_{k,\nu};t|\mathcal{H}|\varphi_{l,\nu'};t\rangle,$$

one readily obtains

$$[\epsilon_l(t)-\epsilon_k(t)]\langle\varphi_{k,\nu};t|\mathcal{H}-i\partial_t|\varphi_{l,\nu'};t\rangle = \langle\varphi_{k,\nu};t|[\mathcal{H},I] - i\partial_t\mathcal{I}|\varphi_{l,\nu'};t\rangle + i\delta_{kl}\delta_{\nu,\nu'}\partial_t\epsilon_l(t). \tag{3}$$

From this, we can make two statements. First, with $k=l$ in Eq. (3), the definition of the Lewis invariant, Eq. (1), implies that its eigenvalues $\epsilon_k$ are constant in times, i.e., the observable is invariant during the time evolution of the system. Second, setting $k\neq l$ in Eq. (3), we obtain

$$\langle\varphi_{k,\nu};t|\mathcal{H}-i\partial_t|\varphi_{l,\nu'};t\rangle = \frac{\langle\varphi_{k,\nu};t|[\mathcal{H},I]-i\partial_t\mathcal{I}|\varphi_{l,\nu'};t\rangle}{\epsilon_l-\epsilon_k}, \tag{4}$$

so that, with Eq. (1), the matrix element of $[\mathcal{H}-i\partial_t]$ between an arbitrary pair of eigenvectors, $|\varphi_{k,\nu};t\rangle, |\varphi_{l,\nu'};t\rangle$ (with eigenvalues $\epsilon_k\neq\epsilon_l$, of respective degeneracy $g_k$, $g_l$), of $\mathcal{I}$ will vanish exactly. This is what makes the introduction of $\mathcal{I}$ so interesting, as its eigenvectors are transported diagonally, or, in the presence of degeneracy, block diagonally, during the time-evolution of the system. To see this, consider the expansion of an arbitrary time-dependent state $|\Psi(t)\rangle$ in this basis

$$|\Psi(t)\rangle = \sum_l \sum_{\nu=1}^{g_l} c_{l,\nu}(t)|\varphi_{l,\nu};t\rangle. \tag{5}$$

Substituting this into the time-dependent Schrödinger equation,

$$i\partial_t|\Psi(t)\rangle = \mathcal{H}|\Psi(t)\rangle, \tag{6}$$

then projecting onto a basis vector $|\varphi_{k,\nu};t\rangle$, we readily obtain

$$i\partial_t c_{k,\nu}(t) = \sum_{\nu'=1}^{g_k} \alpha^{(k)}_{\nu,\nu'} c_{k,\nu'}(t), \tag{7}$$

where

$$\alpha^{(k)}_{\nu,\nu'}(t) = \langle \varphi_{k,\nu'};t|\mathcal{H}(t) - i\epsilon\partial_t|\varphi_{k,\nu};t\rangle, \quad (8)$$

i.e., the time evolutions of the coefficients $c_{k,\nu}(t)$ are decoupled with respect to the first index $k$ (which distinguishes different eigenvalues of $\mathcal{I}$). Only states belonging to degenerate eigenvalues are coupled to each other through the matrix $\alpha^{(k)}$. In the particular case the system is prepared initially in an eigenstate associated with a nondegenerate eigenvalue, it will remain in this state at all times, i.e., this time evolution can be described as an exact adiabatic transport of this eigenstate. More formally, the time-evolution operator of the system is exactly given by the block-diagonal form [16]

$$U(t,t_0) = \sum_k \sum_{\nu,\nu'} u^{(k)}_{\nu,\nu'}(t,t_0)|\varphi_{k,\nu'};t\rangle\langle\varphi_{k,\nu};t_0|, \quad (9a)$$

where, for a given $k$, the $g_k \times g_k$ unitary matrix $u^{(k)}$ (of elements $u^{(k)}_{\nu,\nu'}$) is the solution of the matrix equation

$$i\frac{du^{(k)}(t,t_0)}{dt} = \alpha^{(k)}(t)u^{(k)}(t_0,t_0), \quad u^{(k)}(t,t_0) = 1. \quad (9b)$$

It is this diagonal (or block-diagonal) character of the time evolution, when expressed in the eigenbasis of $\mathcal{I}(t)$, which is of interest here. In this respect, we note that only the decoupling condition of Eq. (4) is to be satisfied, and we may introduce a more general definition of $\mathcal{I}(t)$ by [10,11]

$$[[\mathcal{H},\mathcal{I}] - i\partial_t\mathcal{I},\mathcal{I}] = 0, \quad (10)$$

as this is sufficient to ensure that the off-diagonal matrix elements defined by (4) vanish identically. This definition no longer implies that the eigenvalues of $\mathcal{I}(t)$ are constant in time. In Refs. [10,11], it is considered an effective Hamiltonian; In the present paper, keeping in mind its connection with the Lewis invariant, we will still be referring to this operator as a dynamical invariant.

Now, Eq. (10) says that $[\mathcal{H},\mathcal{I}]-i\partial_t\mathcal{I}$ is diagonal in the eigenbasis of $I$. Thus, defining $\Pi_I V$ to be the diagonal part of $V$ in this eigenbasis [see Appendix A, Eqs. (A3) and (A4); the notations used here are borrowed from Ref. [21]], the definition of the dynamical invariant may be rewritten in the more convenient, compact form

$$(1 - \Pi_{\mathcal{I}})\{[\mathcal{H},\mathcal{I}] - i\partial_t\mathcal{I}\} = 0. \quad (11)$$

Let $\tau$ be a time-scale parameter characterizing the time variation of $\mathcal{H}(t)$. Also, under the assumption that $\mathcal{H}(t)$ admits a discrete spectrum at all times $t\in[0,\tau]$, we define $\omega_0$ to be a frequency which characterizes the typical energy separation between the eigenvalues of $\mathcal{H}(t)$. We introduce an adiabatic parameter $\epsilon$ by

$$2\pi\epsilon = \frac{\tau_0}{\tau}, \quad \tau_0 = \frac{2\pi}{\omega_0}. \quad (12)$$

Making the change of variable

$$s = \frac{t}{\tau} = \omega_0\epsilon t, \quad i\partial_t = i\omega_0\epsilon\partial_s, \quad (13)$$

and defining $H(s)$ and $I(s)$ through

$$H(s) = \frac{1}{\omega_0}\mathcal{H}(\tau s), \quad (14)$$

$$I(s) = \mathcal{I}(\tau s), \quad (15)$$

we may rewrite the condition (10) in the form

$$(1 - \Pi_I)\{[H(s),I] - i\epsilon\partial_s I\} = 0, \quad (16)$$

which will constitute the starting point of the perturbation theory we now develop for the dynamical invariant $I$, with the adiabatic parameter $\epsilon$ playing the role of the small parameter of the associated perturbative series.

### B. Perturbation series for the dynamical invariant

We write this series in the form

$$I = I^{(0)} + \sum_{k=1}^{\infty}\epsilon^k\delta I^{(k)} = \sum_{k=0}^{\infty}\epsilon^k\delta I^{(k)}, \quad (17)$$

where $\delta I^{(k)}$, $k\neq 0$, denotes the $k$th-order correction to $I$ and $I^{(0)}=\delta I^{(0)}=H$. When restricted to a finite order $k=N$, the sum on the right-hand side of (17) defines the $N$th-order approximation to the invariant, which will be designated $I^{(N)}$. The exact invariant $I$ is the limit of this at $N\to\infty$, $I=I^{(\infty)}$.

Now, let $X_0$ be a particular solution to the equation

$$(1 - \Pi_I)X = 0. \quad (18)$$

Then, clearly, $X=X_0+\Pi_I O$, with $O$ an arbitrary operator, also satisfies this equation [since $\Pi_I$ is a projector, $(\Pi_I)^2 O=\Pi_I O$]. Thus, the condition defining a dynamical invariant reformulated in (16) can be satisfied by the general form

$$[H,I] - i\epsilon\partial_s I = -i\epsilon\Pi_I[\partial_s I + R], \quad (19)$$

where the arbitrary operator $R$ is of order $\epsilon^0$. Since this operator can be chosen at will, we will require it to ensure that Eq. (19) be equivalent to

$$[H,I] - i\epsilon(1 - \Pi_H)\{\partial_s I + R\} = 0, \quad (20)$$

We require this because handling equations involving the superoperator $\Pi_H$ associated with $H$ is easier than equations containing $\Pi_I$ associated with the yet unknown $I$, such as Eqs. (16) and (19). Comparing Eqs. (20) and (19), we find then that $R$ must satisfy

$$(\Pi_I - \Pi_H)(\partial_s I + R) = -R. \quad (21)$$

We now write $R$ in power series in $\epsilon$,

$$R(s) = \sum_{k=0}^{\infty}\epsilon^k G^{(k)}(s), \quad (22)$$

and, estimating that $\Pi_I-\Pi_H$ (acting on a given operator) is of order $\epsilon$ while $\Pi_{I^{(k)}}-\Pi_{I^{(k-1)}}$ would be of order $\epsilon^k$, we write

$$\Pi_I - \Pi_H = \sum_{k=1}^{\infty}\epsilon^k\mathcal{Y}_k, \quad (23)$$

$$\epsilon^k \mathcal{Y}_k = \Pi_{I^{(k)}} - \Pi_{I^{(k-1)}}. \tag{24}$$

With the expansions of Eqs. (23), (22), and (17), we obtain, on the one hand,

$$[H, \delta I^{(k)}] - i(1-\Pi_H)(\partial_s \delta I^{(k-1)} + G^{(k-1)}) = 0, \tag{25}$$

from the condition that the coefficient of the $\epsilon^k$ term (at a given order $k$) in Eq. (20) vanishes exactly, for all $\epsilon$. On the other hand, Eq. (21) gives

$$G^{(k)} = -\sum_{k'=1}^{k} \mathcal{Y}_{k'}(\partial_s \delta I^{(k-k')} + G^{(k-k')}), \quad G^{(0)} = 0 \tag{26}$$

This recurrence relation allows us to construct the various terms of $R$ up to order $k$ from the knowledge of the $G^{(k')}$ terms and of the correction terms $\delta I^{(k')}$ of lower order. Once $\delta I^{(k-1)}$ and $G^{(k-1)}$ are known, $\delta I^{(k)}$ is obtained by solving Eq. (25), which is of the form

$$[K_0, X] + (V - \Pi_{K_0} V) = 0, \tag{27}$$

with

$$K_0 = H, \quad V = -i(\partial_s \delta I^{(k-1)} + G^{(k-1)}).$$

As recalled in Appendix A, and shown in Ref. [21], the general solutions of an operator equation of the general form of Eq. (27) [this is exactly Eq. (A11) of Appendix A with $V' = (V - \Pi_{K_0} V)$], is formally known and are given by

$$X = W^{K_0}[(1-\Pi_{K_0})V] + C, \tag{28a}$$

where

$$W^{K_0}[(1-\Pi_{K_0})V] = \lim_{T\to\infty}\left(\frac{-i}{T}\right)\int_0^T d\sigma' \int_0^{\sigma'} d\sigma \mathcal{U}_{K_0}(\sigma)(1 - \Pi_{K_0})V\mathcal{U}_{K_0}^{-1}(\sigma), \tag{28b}$$

as defined in Eq. (A5), $[U_{K_0}(\sigma) = \exp(-iK_0\sigma)]$, and $C$ is an arbitrary operator that commutes with $K_0$.

Applying these general relations to the specific case where $K_0 = H$, $V = -i(\partial_s \delta I^{(k-1)} + G^{(k-1)})$ and $C = 0$, we can finally define the $k$th-order correction $\delta I^{(k)}$ recursively through

$$\delta I^{(k)} = -iW^H[(1-\Pi_H)(\partial_s \delta I^{(k-1)} + G^{(k-1)})] = \lim_{T\to\infty}\left(\frac{-1}{T}\right)\int_0^T d\sigma' \int_0^{\sigma'} d\sigma e^{-iH(s)\sigma}(1-\Pi_H)(\partial_s \delta I^{(k-1)} + G^{(k-1)})e^{+iH(s)\sigma} \tag{29}$$

starting with $\delta I^{(0)} = I^{(0)}(s) = H(s)$. By construction, all these correction terms are nondiagonal in the eigenbasis of $H(s)$, according to Eq. (A8),

$$\Pi_H \delta I^{(k)} = 0. \tag{30}$$

## III. EXAMPLES: SIMPLE MODEL SYSTEMS

### A. Field-driven harmonic oscillator

Consider first a laser-driven harmonic oscillator, described by the time-dependent Hamiltonian

$$\mathcal{H}(t) = \frac{p^2}{2} + \frac{\omega_0^2}{2}q^2 + \tilde{f}_0 \cos(\omega_L t)p, \tag{31a}$$

or, in terms of dimensionless operators $Q = \omega_0^{1/2} q$, $P = \omega_0^{-1/2} p$, and $s = t/\tau = (\omega_L/2\pi)t$,

$$H(s) = \frac{1}{2}(P^2 + Q^2) + f_0 \cos(2\pi s)P, \quad f_0 = \omega_0^{-1/2}\tilde{f}_0, \tag{31b}$$

$$H(s) = H_0 + f_0 \cos(2\pi s)P, \tag{31c}$$

where $H_0 = (1/2)(P^2 + Q^2)$ is the unperturbed (field-free) Hamiltonian, $\omega_0$ is the oscillator natural frequency and $\omega_L$, that of the laser field. In this case, $\tau = 2\pi/\omega_L$ and $2\pi\epsilon = \omega_L/\omega_0$.

For this system, a quick inspection of the results of the lowest order calculations, together with the structure of the recurrence relations of Eqs. (29) and (26) indicates that, at any given order $k$, $I^{(k)}$ will be of the form

$$I^{(k)}(s) = \frac{1}{2}(P^2 + Q^2) + \eta^{(k)}(s)P + \zeta^{(k)}(s)Q \tag{32}$$

up to a time-dependent $c$ number. The system's Hamiltonian, $H = I^{(0)}(s)$, is of that form with $\eta^{(0)} = f_0 \cos(2\pi s)$ and $\zeta^{(0)} = 0$. It is then useful to note the following relations:

$$\mathcal{U}_{I^{(k)}}(\sigma)Q\mathcal{U}_{I^{(k)}}^{\dagger}(\sigma) = (Q + \zeta^{(k)})\cos\sigma - (P + \eta^{(k)})\sin\sigma, \tag{33a}$$

$$\mathcal{U}_{I^{(k)}}(\sigma)P\mathcal{U}_{I^{(k)}}^{\dagger}(\sigma) = (P + \eta^{(k)})\cos\sigma + (Q + \zeta^{(k)})\sin\sigma - \eta^{(k)}, \tag{33b}$$

where $\mathcal{U}_{I^{(k)}}(\sigma) = \exp[-iI^{(k)}(s)\sigma]$, from which we readily find

$$\Pi_{I^{(k)}} Q = 0, \tag{34a}$$

$$\Pi_{I^{(k)}} P = -\eta^{(k)}. \tag{34b}$$

We thus see that $G^{(k)}$ will always be a $c$ number that can be ignored in Eqs. (25) and (29). The same relations, (33a) and (33b), with $k=0$ ($I^{(0)} = H$) also give

$$W^H[(1-\Pi_H)Q] = P + \eta^{(0)} = P + f_0\cos(2\pi s), \tag{35a}$$

$$W^H[(1-\Pi_H)P] = -(Q + \zeta^{(0)}) = -Q. \tag{35b}$$

With all this, we readily get

$$\delta I^{(1)} = W^H[(1-\Pi_H)\partial_s H] = \partial_s \eta^{(0)} W^H[(1-\Pi_H)P] = 2\pi f_0 \sin(2\pi s)Q \tag{36}$$

and

$$\delta I^{(2)} = W^H[(1-\Pi_H)\partial_s \delta I^{(1)}] = (2\pi)^2 f_0 \cos(2\pi s) W^H[(1-\Pi_H)Q] = (2\pi)^2[f_0\cos(2\pi s)P + f_0^2\cos^2(2\pi s)] = (2\pi)^2 f_0 \cos(2\pi s)P, \tag{37}$$

where the $c$ number $(2\pi)^2 f_0^2 \cos^2(2\pi s)$ has been dropped in writing the last line. By induction, we infer the general forms of correction terms of even and odd orders,

$$\delta I^{(2m)}(s) = \mathcal{C}_{2m} f_0 \cos(2\pi s) P, \quad m \geq 1, \tag{38a}$$

$$\delta I^{(2m+1)}(s) = \mathcal{C}_{2m+1} f_0 \sin(2\pi s) Q, \quad m \geq 0. \tag{38b}$$

From the relation between $\delta I^{(k+1)}$ and $\delta I^{(k)}$, Eq. (29), the results of Eqs. (35a) and (35b) and from $\mathcal{C}_1 = 2\pi$, it follows that $\mathcal{C}_{k+1} = 2\pi \mathcal{C}_k \Rightarrow \mathcal{C}_k = (2\pi)^k$, $\forall$ $k$. We can finally write the perturbative series to all orders, using (38a) and (38b), and recalling that $2\pi\epsilon = \omega_L/\omega_0$. Not surprisingly, the series can be resummed analytically to all orders, for $\omega_L < \omega_0$, to give

$$I^{(\infty)}(s) = \frac{1}{2}(P^2 + Q^2) + \left(\frac{\omega_0^2}{\omega_0^2 - \omega_L^2}\right) f_0 \cos(2\pi s) P + \frac{\omega_L}{\omega_0}\left(\frac{\omega_0^2}{\omega_0^2 - \omega_L^2}\right) f_0 \sin(2\pi s) Q. \tag{39}$$

By evaluating explicitly the commutator $[H(s), I^{(\infty)}(s)]$ and the derivative $\partial_s I^{(\infty)}(s)$, it can readily be verified that this satisfies

$$[H(s), I^{(\infty)}(s)] - i\epsilon \partial_s I^{(\infty)}(s) = 0$$

exactly for all $\omega_L \neq \omega_0$. Note that even though the perturbative series, considered to all orders, converges only for $\omega_L < \omega_0$, it has nevertheless yielded an exact dynamical invariant for the more general case of a harmonic oscillator driven by any nonresonant field.

### B. Laser-driven two-level system

Consider now a two-level system driven by a laser field described by a Hamiltonian of the form

$$\mathcal{H}(t) = \omega_0[|2\rangle\langle 2| - |1\rangle\langle 1|] + f_0 \cos(\omega_L t)[|2\rangle\langle 1| + |1\rangle\langle 2|], \tag{40}$$

which can also be conveniently rewritten in terms of spin operators

$$S_x = |2\rangle\langle 1| + |1\rangle\langle 2|, \quad S_y = i(|2\rangle\langle 1| - |1\rangle\langle 2|),$$

$$S_z = |2\rangle\langle 2| - |1\rangle\langle 1|,$$

satisfying the usual cyclic commutation relations. Thus

$$\mathcal{H}(t) = \omega_0 S_z + f_0 \cos(\omega_L t) S_x. \tag{41}$$

Introducing a reduced time $s$ defined by $s = t/\tau = \omega_0 \epsilon t$ [25], where $\tau = 1/\omega_L$ and $\epsilon = \omega_L/\omega_0$,

$$H(s) = S_z + f \cos s S_x, \tag{42}$$

with $f = f_0/\omega_0$. In this case, we expect any operator, be it one of the $\delta I^{(k)}$'s or one of the $G^{(k)}$'s, and in particular each approximant $I^{(k)}$ itself, to be a linear combination of the Pauli matrices, i.e., is a function of the type

$$F(a,b,c) = a S_x + b S_y + c S_z. \tag{43}$$

It is then convenient to note that such an operator can be presented in the form

$$F(a,b,c) = \lambda e^{-i\alpha S_y} e^{-i\beta S_x} S_z e^{+i\beta S_x} e^{+i\alpha S_y}, \tag{44}$$

denoting the diagonalization of the matrix representing $F$ in the eigenbasis of $S_z$. The parameters $\alpha$ and $\beta$ associated with the two rotations generated by $S_x$ and $S_y$ are thus given by

$$\alpha = \arctan\left(\frac{a}{c}\right), \quad \beta = \arcsin\left(\frac{-b}{\lambda}\right), \tag{45a}$$

$$\lambda = \sqrt{a^2 + b^2 + c^2}. \tag{45b}$$

Using this representation, when $F$ designates one of the $I^{(k)}$'s, we can express the propagator associated with $F$ as a sequence of rotations of spin operators

$$e^{-iF\sigma} = e^{-i\alpha S_y} e^{-i\beta S_x} e^{-i\lambda S_z \sigma} e^{+i\beta S_x} e^{+i\alpha S_y}. \tag{46}$$

This allows the calculations of quantities of the forms $\Pi_F O$ and $W^F[(1-\Pi_F)O]$ that are needed to implement the perturbative schemes [cf. Eqs. (26) and (29)], by known rules concerning these rotations.

With $F = H$, we readily find

$$\Pi_H(\partial_s H) = -\frac{f^2 \sin(2s)}{2 + f^2[1 + \cos(2s)]}(S_z + f \cos s S_x) \tag{47}$$

then

$$\delta I^{(1)}(s) = W^H[-i(1 - \Pi_H)\partial_s H] = \frac{f \sin s}{1 + f^2 \cos^2 s} S_y. \tag{48}$$

The result of Eq. (47) implies that $G^{(1)}$ is nontrivial (not a $c$ number as in the previous case of the linearly forced harmonic oscillator), it being indeed found to be

$$G^{(1)}(s) = \left(\frac{f \sin s}{1 + f^2 \cos^2 s}\right)^2 f \cos s S_y + O(\epsilon),$$

and the following result is obtained, after some calculations, for the leading term of the second-order correction

$$\delta I^{(2)}(s) = W^H[-i(1 - \Pi_H)(\partial_s \delta I^{(1)} + G^{(1)})] = -\frac{f \cos s\{1 + f^2[2 - \cos(2s)]\}}{(1 + f^2 \cos^2 s)^3} \times (-S_x + f \cos s S_z) + O(\epsilon^2). \tag{49}$$

The calculations become more and more complex as $k$ increases, but with a program written in the MATHEMATICA symbolic language, we have been able to generate the corrections $\delta I^{(k)}$ to a high order (results of calculations up to $k = 5$ are reported below). The resulting approximant to the dynamical invariant, $I^{(k)}$, given by Eq. (17) with the sum restricted to its first $k$ terms, is then diagonalized (in the eigenbasis of $S_z$) and its two eigenvectors $|\varphi_k(s)\rangle$, $k = 1, 2$ are used to construct the time evolution operator through (no degeneracy was found at any time for this system)

$$U(s,s_0) = \sum_{k=1}^{2} e^{-i\int_{s_0}^{s} ds' \lambda_k(s')} |\varphi_k(s)\rangle\langle\varphi_k(s_0)|, \tag{50a}$$

$$\lambda_k(s) = \langle\varphi_k(s)|H(s) - i\epsilon\partial_s|\varphi_k(s)\rangle. \tag{50b}$$

We also calculate $U(s,s_0)$ numerically by accumulating $e^{-iH(s_i)\delta s}$ evaluated over each of the small time slices $[s_i, s_{i+1}=s_i+\delta s]$, $i=0,\ldots,N-1$ unto which the time interval $[s_0,s]$ is divided, with $s_N=s$. Considering a time evolution out of the ground state $|1\rangle$, of the field-free system as initial state, we then calculate the probability that the system makes a transition to state $|2\rangle$, at any time $s$,

$$P_{12}(s) = |\langle 2|U(s,s_0)|1\rangle|^2, \tag{51}$$

using either of the two representations of $U(s,s_0)$ described above. All the calculations are made in MATHEMATICA 5.2, including the numerical propagation over short time slices, which we take to have an extension $\delta s=10^{-3}\epsilon$, corresponding to a 1000th division of the optical cycle.

The results of these calculations for $f=0.1$ (the Rabi frequency is one-tenth of the Bohr frequency) are exhibited in Fig. 1, for $\epsilon=0.1$ [panel (a)], $\epsilon=0.3$ [panel (b)], and $\epsilon=0.5$ [panel (c)], corresponding to an adiabatic dynamical regime and two increasingly nonadiabatic situations. The left-hand panel of each figure gives the population of the excited state as a function of time (up to an optical cycle) as calculated using $I^{(k)}$, $k=1-5$, and as obtained in the convergent numerical calculation. The right-hand panel gives the relative error in $P_{12}$ at $s=\pi$, $t=T_L/2$, ($T_L=2\pi/\omega_L$ is the period of the field), considered as a function of the order $k$ of the adiabatic representation. It is not surprising that in the $\epsilon=0.1$ case, Fig. 1(a), the series converges very quickly (radius of convergence $\simeq 2$), and even the zeroth-order adiabatic approximation, $I\simeq H(s)$ performs pretty well. In the $\epsilon=0.3$ and 0.5 cases, Figs. 1(b) and 1(c), one needs to go at least up to the fifth-order to reach convergence. The zeroth-order adiabatic approximation is clearly inadequate except at the beginning of the dynamics, which is highly nonadiabatic in the eigenbasis of $H(s)$.

It is interesting to examine how the approximate invariant of a given order differs from $H(s)$. The first two corrections ($k=1,2$) have been given explicitly above. More generally, it was found that the leading term in the odd-order corrections $\delta I^{(k)}$ is proportional to $S_y$ while that in the even-order ones is always some combination of $S_x$ and $S_z$. As expected, the analytical expressions of the coefficients of the three spin operators rapidly become impractical to exhibit as $k$ increases. To see in more detail how the various $I^{(k)}$ differs from $H(s)$, we show in Fig. 2 the variations, with respect to the time parameter $s$, of the coefficients $c_x, c_y, c_z$ of $S_x, S_y, S_z$ in $F=I^{(k)}$, in the representation of Eq. (43) for the case $\epsilon=0.3$, $f=0.1$. Figure 2(a) shows the trajectories traced out by $c_x, c_y, c_z$, for $k=0$, 1, and 5, as $s$ sweeps over the range corresponding to an optical cycle, Due to the particular form chosen for $H(s)$ ($c_x=f\cos s$, $c_y=0$, $c_z=1$), this trajectory is just a straight line in zeroth order. This representation illustrates vividly the nonadiabaticity of the dynamics which is reflected in the deviation of the trajectories of $I^{(k)}$ from the straight-line trajectory of $H(s)$. Figure 2(b) shows, over the same range of $s$, the variations $\Delta c_j^{(k)}=c_j^{(k)}-c_j^{(k-1)}$ $(j=x,y,z)$, of these coefficients in going from order $k-1$ to order $k$. Actually, only nonzero variations $\Delta c_j^{(k)}(s)$ are shown in the figure: For $c_x$ and $c_z$, a nonzero variation is found only for even values of $k$, while for $c_y$, the coefficient of $S_y$, such a variation is found for odd values of $k$ only.

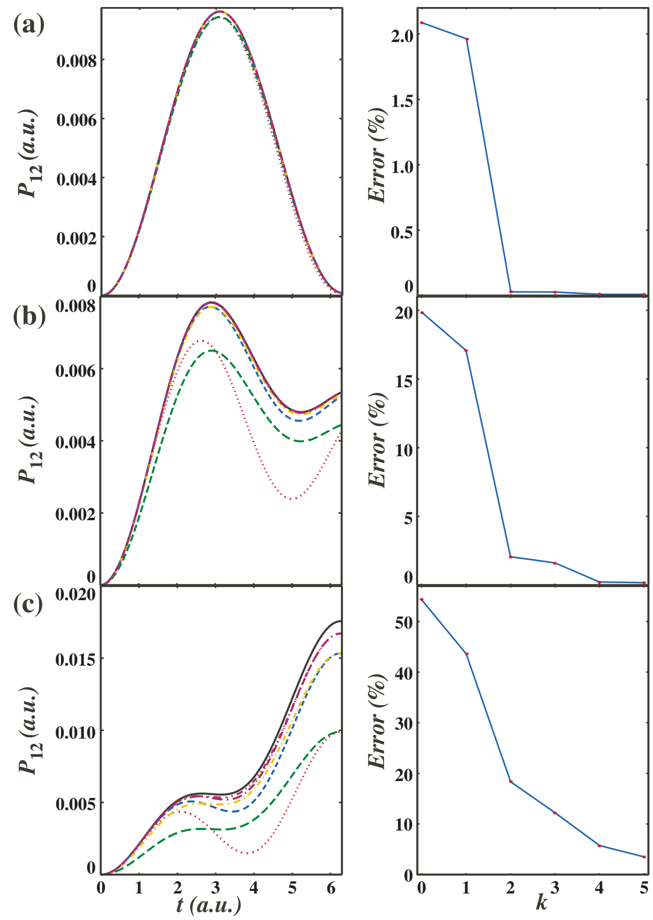


FIG. 1. (Color online) Transition probability $P_{12}$ as a function of time $t$, for the two-level system driven by a field, for $\epsilon=0.1$ and $f=0.1$ in (a), $\epsilon=0.3$ and $f=0.1$ in (b), and $\epsilon=0.5$ and $f=0.1$ in (c). The results of the numerical propagation are shown by a black solid line, those calculated using the $k$th-order dynamical invariant are shown as red dots for $k=0$, green dashed line for $k=1$, blue dashed line for $k=2$, orange dotted-dashed line for $k=3$, brown dotted-dashed line for $k=4$, and violet dotted-dashed line for $k=5$. The right-hand panel shows, as a function of the perturbation order $k$, the relative error in $P_{12}$ at $t=T_L/2$ with respect to the results of the numerical propagation.

## IV. DYNAMICAL INVARIANT FOR A FLOQUET HAMILTONIAN

### A. Time-dependent Floquet Hamiltonian

An interesting problem, encountered in the theoretical treatments of laser-induced dynamics in atoms and molecules, concerns the concept of adiabatic transport of Floquet

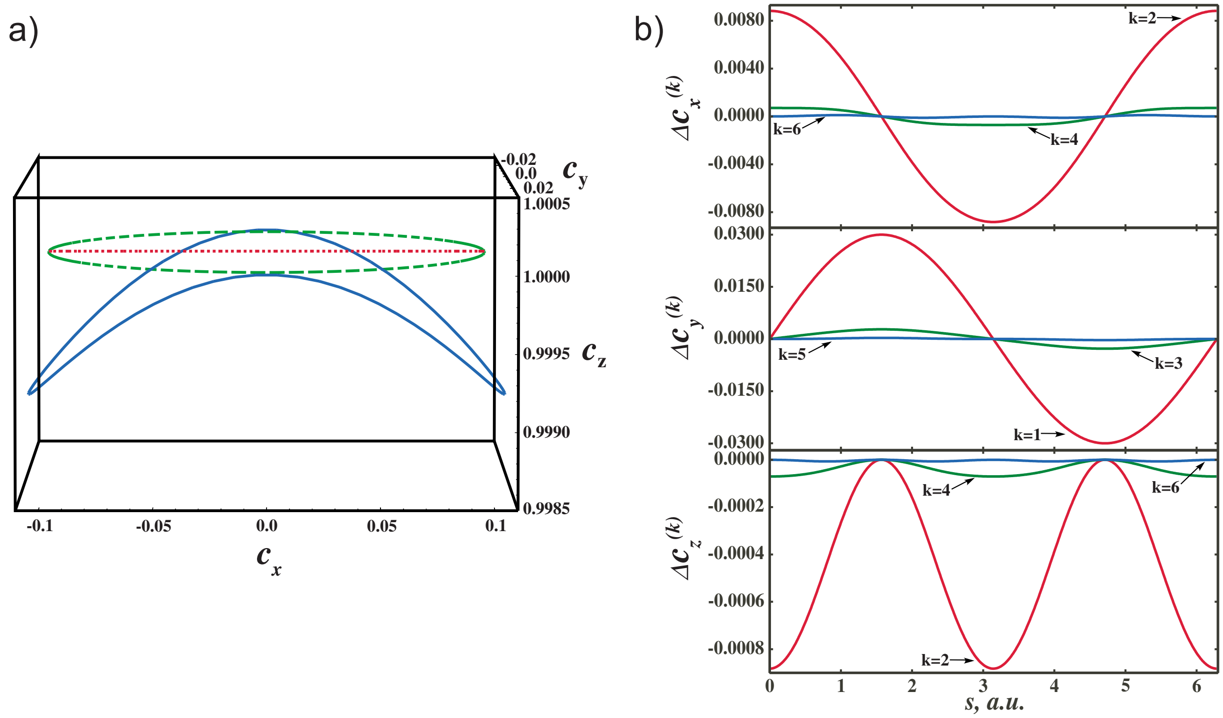


FIG. 2. (Color online) Evolutions, with respect to the time parameter $s$, of the coefficients $c_x$, $c_y$, and $c_z$ of $S_x$, $S_y$, $S_z$, respectively, in $I^{(k)}$, $k=1-6$, in the representation of Eq. (43) for the case $\epsilon=0.3$, $f=0.1$. (a) Trajectories traced out by these coefficients in a three-dimensional representation, for $k=0$ (red dotted line), $k=1$ (green dashed line), and $k=5$ (blue solid line). (b) Variations $\Delta c_j^{(k)}=c_j^{(k)}-c_j^{(k-1)}$ $(j=x,y,z)$ of these coefficients in going from order $k-1$ to order $k$ as a function of time. A nonzero $\Delta c_{x(z)}^{(k)}$ is found only for even values of $k$ (explicitly shown are the curves for $k=2$ in red, $k=4$ in green, and $k=6$ in blue), while a nonzero $\Delta c_y^{(k)}$ is obtained only for odd values of $k$ (explicitly shown are results for $k=1$ in red, $k=3$ in green, and $k=5$ in blue).

states. Let us first recall how these are defined: If a time-dependent Hamiltonian exhibits a time periodicity $\mathcal{H}(t+T)=\mathcal{H}(t)$ (here $T=2\pi/\omega_L$ is the period of the incident laser field for instance), then Floquet theorem establishes the existence of solutions of the time-dependent Schrödinger equation which are of the form

$$|\Psi_k(t)\rangle = e^{-iE_k^{\mathrm{Fl}}t}|\Phi_k(t)\rangle,$$

where $E_k^{\mathrm{Fl}}$, called quasienergy, and $|\Phi_k(t+T)\rangle=|\Phi_k(t)\rangle$ are eigenvalues and eigenvectors of the Floquet Hamiltonian,

$$\mathcal{K} = \mathcal{H}(t) - i\frac{\partial}{\partial t}. \tag{52}$$

An interesting view of the Floquet representation has recently been given [23,24], in which $\mathcal{H}(t)$ is considered to be a member of a family of Hamiltonians $\mathcal{H}(t+\theta/\omega_L)$ parametrized by an initial phase angle $\theta$. This representation is reminiscent of the $(t,t')$ formulation of the Floquet theory [26] and, with respect to certain aspects at least, it could be made equivalent to the $(t,t')$ formulation by the simple identification $\theta=\omega_L t'$. As detailed in Ref. [23], by promoting $\theta$ to the role of dynamical variable, and regarding $\mathcal{H}(t+\theta/\omega_L)$ as the image of a time independent (but $\theta$ parametrized) $\mathcal{H}(\theta)$ under a translation of $\theta$ by $\omega_L t$, allows one to view the Floquet Hamiltonian $\mathcal{K}$ as a time-independent operator,

$$\mathcal{K} = \mathcal{H}(\theta) - i\omega_L\frac{\partial}{\partial\theta} = \mathcal{H}(\theta) + \omega_L p_\theta, \tag{53}$$

defined over an enlarged Hilbert space constructed by taking the tensor product between the system's (atomic or molecular) Hilbert space with the space of square integrable, periodic functions of $\theta$. In this view, $p_\theta=-i\partial_\theta$ is the momentum operator canonically conjugate to the angle $\theta$, so that

$$[p_\theta,\theta] = -i.$$

The lift of the time-evolution operator associated with $\mathcal{H}(t)$ in the enlarged Hilbert space is unitarily related to the Floquet time-evolution operator $\mathcal{U}_{\mathcal{K}}(t-t_0)$ by a simple translation in the angle variable $\theta$.

We are here interested in the case when the time dependence of the Hamiltonian is not truly periodic, but is characterized by a slow modulation of the field amplitude $F(t)$. Under the translation of $\theta$ by $-\omega_L t$, the Hamiltonian $\mathcal{H}(t+\theta/\omega_L)$ is mapped into a new Hamiltonian, $H^{F(t)}(\theta)$, that remains time dependent through the variation of $F(t)$. One can then show that the exact time evolution in the Floquet representation is governed by the now explicitly time-dependent Floquet Hamiltonian [24,27]

$$\mathcal{K}(t) = \mathcal{H}^{F(t)}(\theta) - i\omega_L\frac{\partial}{\partial\theta} = \mathcal{H}^{F(t)}(\theta) + \omega_L p_\theta. \tag{54}$$

A number of interesting applications of the adiabatic theorem to time-dependent Floquet Hamiltonians can be found in the literature, for bound systems [24,27–29], as well as for non-Hermitian open systems [30], and correspond to a zeroth-order adiabatic approximation in the Floquet representation. In fact, an adiabaticity hypothesis of this type underlies most discussions of laser-driven dynamics in terms of the dressed atom-molecule picture when a finite, shaped pulse is involved. A natural question arises then, in relation with concerns of finite pulse-shape effects [31,32], as to how to extend the adiabatic theorem as it applies to the time-evolution operator associated with $\mathcal{K}(t)$ and, more precisely, how to define the concept of higher-order adiabatic transport of Floquet states. The concept of dynamical invariant, associated with $\mathcal{K}(t)$ rather than with $\mathcal{H}(t)$, provides the answer. We thus consider here the problem of constructing a dynamical invariant for this case, i.e., to solve

$$(1-\Pi_{\mathcal{I}})\{[\mathcal{K}(s),\mathcal{I}]-i\epsilon\partial_s\mathcal{I}\}=0, \tag{55}$$

for $\mathcal{I}(s)$, defining again the dimensionless time variable $s=t/\tau\in[0,1]$, $\tau$ representing now a time scale (assumed longer than the longest period $\sup[2\pi/\omega_L(t)]$) characterizing the modulation of the field parameters. It is clear that the derivations and results in Sec. II can be applied to this case entirely with $\mathcal{K}(t)$ replacing $\mathcal{H}$ uniformly. We now illustrate how this construct works in the case of a laser-driven harmonic oscillator with amplitude modulations, i.e., with a constant $\omega_L$.

### B. Pulsed-laser-driven model systems

Consider, for example, a time-dependent Floquet Hamiltonian of the form

$$\mathcal{K}(s)=\frac{p^2}{2}+\frac{\omega_0^2}{2}q^2+\omega_0^{1/2}f(s)(\cos\,\theta p+\omega_0\sin\,\theta q)+\omega_L p_\theta. \tag{56}$$

In terms of the dimensionless position and momentum variables $P,Q$ defined in Sec. III A, this yields

$$K(s):=\frac{1}{\omega_0}\mathcal{K}(s)=K_0+f(s)(\cos\,\theta P+\sin\,\theta Q), \tag{57}$$

where

$$K_0=\frac{P^2}{2}+\frac{Q^2}{2}+\frac{\omega_L}{\omega_0}p_\theta. \tag{58}$$

It is useful to note that $K(s)$ can be unitarily related to the time-independent separable Floquet Hamiltonian $K_0$ by

$$K(s)=\mathcal{W}^\dagger(s)K_0\mathcal{W}(s), \tag{59}$$

where

$$\mathcal{W}(s):=\exp\{-i[\alpha(s)\sin\,\theta P+\beta(s)\cos\,\theta Q]\}\exp[-i\Xi(\theta,s)], \tag{60a}$$

$$\alpha(s):=-\omega_0\frac{\omega_L+\omega_0}{\omega_L^2-\omega_0^2}f(s), \tag{60b}$$

$$\beta(s):=\frac{\omega_L\omega_0}{\omega_L^2-\omega_0^2}f(s), \tag{60c}$$

$$\Xi(\theta,s):=\frac{1}{2\omega_L}\left[\left(\frac{\beta^2}{2}+f\beta\right)\left(\theta+\frac{1}{2}\sin\,2\theta\right)+\left(\frac{\alpha^2}{2}-f\alpha\right)\left(\theta-\frac{1}{2}\sin\,2\theta\right)\right]. \tag{60d}$$

From this unitary relation [Eq. (59)], and defining

$$O(\sigma):=\mathcal{U}_{K(s)}(\sigma)^\dagger O\mathcal{U}_{K(s)}(\sigma),$$

$$O_0(\sigma):=\mathcal{U}_{K_0}(\sigma)^\dagger O\mathcal{U}_{K_0}(\sigma)$$

$(O=Q,P,\theta,p_\theta)$, we first find that

$$Q(\sigma)=Q_0(\sigma)+F_q(\theta,\sigma), \tag{61a}$$

$$P(\sigma)=P_0(\sigma)+F_p(\theta,\sigma), \tag{61b}$$

where $Q_0(\sigma)=Q\cos\,\sigma-P\sin\,\sigma$, $P_0(\sigma)=P\cos\,\sigma+Q\sin\,\sigma$, are independent of $\theta$, while $F_q$, $F_p$ are functions of $\sigma$ which involve only the variable $\theta$ and contain neither the canonically conjugate momentum $p_\theta$, nor the oscillator's dynamical variables $Q$, $P$.

From Eqs. (61a) and (61b), we further obtain

$$\Pi_K Q=\lim_{T\to\infty}\left(\frac{1}{T}\right)\int_0^T d\sigma F_q(\theta,\sigma), \tag{62a}$$

$$\Pi_K P=\lim_{T\to\infty}\left(\frac{1}{T}\right)\int_0^T d\sigma F_p(\theta,\sigma), \tag{62b}$$

i.e., $\Pi_K Q$, $\Pi_K P$ depend solely on the variable $\theta$. To emphasize this when needed, such a function will be denoted generically by $\{\theta\}$ in the following.

Since

$$\partial_s K(s)=f'(s)(\cos\,\theta P+\omega_0\sin\,\theta Q) \tag{63}$$

[we will use the notations $f'(s):=df(s)/ds$, $f''(s):=d^2f(s)/ds^2$, $f^{(n)}:=d^nf(s)/ds^n$, $n\geq 3$], we find, using Eqs. (61a), (61b), (62a), and (62b) in Eq. (29), with $K$ replacing $H$ throughout [e.g., $\delta I^{(0)}=K(s)$ instead of $H$, and $\Pi_H\to\Pi_K$],

$$\delta I^{(1)}=-f'\frac{\omega_0}{\omega_0-\omega_L}(\cos\,\theta Q-\sin\,\theta P)+\{\theta\}^{(1)}. \tag{64}$$

Equation (26) then gives a $G^{(1)}$ that involves $\theta$ only, so that we expect $\delta I^{(2)}$, and in fact all the subsequent $\delta I^{(l)}$'s, to comprise a part that is linear in $Q$ and $P$ and which arises from the terms $Q_0(\sigma)$, $P_0(\sigma)$ in the above, and a part depending solely on $\theta$. Each $\delta I^{(l)}$ can thus be written as

$$\delta I^{(k)}=(\delta I^{(k)})_{p,q}+\{\theta\}^{(k)}. \tag{65}$$

where the notation $(A)_{p,q}$ is to designate that part of $A$ which depends nontrivially on $Q$ and $P$, and the final result for the Floquet dynamical invariant will be of the form

$$I^{(\infty)}(s) = K(s) + \sum_{k=1}^{\infty} \epsilon^k (\delta I^{(k)})_{p,q} + \{\theta\}_{\mathrm{tot}},$$

all the terms depending solely on $\theta$ at the various orders having been gathered into $\{\theta\}_{\mathrm{tot}}$. Since these terms can ultimately be removed by a simple unitary transformation (on $I^{(\infty)}$) of the form

$$\exp[i\Gamma(\theta,s)],$$

with the function $\Gamma(\theta,s)$ defined by

$$\frac{\omega_L}{\omega_0}\frac{\partial\Gamma(\theta,s)}{\partial\theta} = \{\theta\}_{\mathrm{tot}},$$

we can simply ignore all $\{\theta\}$ terms, as well as all $c$ numbers, at every step of the following derivations.

As for the $(\delta I^{(k)})_{p,q}$ terms, the following general results have been obtained:

$$(\delta I^{(2p)})_{p,q} = (-1)^p f^{(2p)} \left(\frac{\omega_0}{\omega_0-\omega_L}\right)^{2p} (\sin\,\theta Q + \cos\,\theta P), \tag{66}$$

$$(\delta I^{(2p-1)})_{p,q} = (-1)^p \left(\frac{\omega_0}{\omega_0-\omega_L}\right) f^{(2p-1)} \left(\frac{\omega_0}{\omega_0-\omega_L}\right)^{2(p-1)} \times(\cos\,\theta Q - \sin\,\theta P), \tag{67}$$

for all $p \geq 1$.

In the particular case of a $\sin^2$ pulse, given by

$$f(s) = f_0 \sin^2[\Omega t(s)] = f_0 \sin^2(2\pi s), \quad \tau = \frac{2\pi}{\Omega}, \quad \epsilon = \frac{\Omega}{2\pi\omega_0} \tag{68}$$

the infinite perturbative series [of the $(\delta I^{(k)})_{p,q}$] can be resummed analytically to give

$$(I^{(\infty)})_{p,q}(s) = K(s) + \frac{f_0(\omega_0-\omega_L)}{(\omega_0-\omega_L)^2 - 4\Omega^2}\Bigg[\left(\Omega \sin(4\pi s)\sin\,\theta - \frac{2\Omega^2}{(\omega_0-\omega_L)}\cos(4\pi s)\cos\,\theta\right)P + \left(\Omega \sin(4\pi s)\cos\,\theta + \frac{2\Omega^2}{(\omega_0-\omega_L)}\cos(4\pi s)\sin\,\theta\right)Q\Bigg].$$

By evaluating explicitly the commutator $[K(s),(I^{(\infty)})_{p,q}(s)]$, and the derivative $\partial_s(I^{(\infty)})_{p,q}(s)$, it can readily be verified that this satisfies

$$[K(s),(I^{(\infty)})_{p,q}(s)] - i\epsilon\frac{\partial(I^{(\infty)})_{p,q}(s)}{\partial s} = 0$$

exactly.

That the series, in the case of a forced harmonic oscillator, gives a solution that verifies exactly the original definition of the Lewis invariant, Eq. (1), either with respect to $H(s)$ (Sec. III A), or with respect to the Floquet Hamiltonian $K(s)$, is remarkable. This is due to the fact that the contributions (to $I$) of the $G_k$ factors in Eqs. (22) and (20) are trivial in this case, they being $c$ numbers in the non-Floquet problem of Sec. III A and are independent of $Q$, $P$ in the present problem.

In the uncoupled eigenbasis of $K_0$, spanned by kets of the product forms $|v,n\rangle = |v\rangle|n\rangle$, where $|v\rangle$ is one of the usual number states of the field-free harmonic oscillator, and $|n\rangle$ is an eigenvector of $p_\theta$,

$$p_\theta|n\rangle = n|n\rangle, \quad \langle\theta|n\rangle = \frac{1}{\sqrt{2}}e^{in\theta},$$

the matrix representation of $I^{(k)}(s)$, $k=1,2,\ldots,\infty$, i.e., the "Floquet scheme" of any order, involves couplings of the basis vectors with selection rule $\Delta v = \pm 1$, $\Delta n = \pm 1$. This coupling pattern does not change as one goes from $K(s)$ to $I^{(k)}(s)$, $k=1,2,\ldots,\infty$, because the couplings added by each successive correction term $(\delta I^{(k)})_{p,q}$ remain linear in $Q$ and $P$ and sinusoidal with respect to $\theta$. Only the strength of the couplings in this Floquet scheme, and the way they are modulated with respect to the time parameter $s$ or $t$ have changed in going from the zeroth-order adiabatic representation to the exact one associated with $I^{(\infty)}(s)$.

This simple high-order adiabatic Floquet structure is peculiar to the linearly forced harmonic oscillator. It is to be expected that, for other systems, the constructed invariant of some order $k > 0$ would have added, in a less trivial manner, new couplings in the Floquet scheme that correspond to new multiphoton processes. Consider, for example, the two-level system of Sec. III B, with now a pulse envelope $f(s)$ modulating the periodic interaction term in Eq. (42), so that in the Floquet formalism, one would replace $H(s)$ by

$$K(s) = S_z + f(s)(\cos\,\theta)S_x + \frac{\omega_L}{\omega_0}p_\theta, \tag{69}$$

which gives, in zeroth order, a Floquet scheme with the two eigenstates of $S_z$ (dressed by "photon" states $|n\rangle$) coupled to each other with $\Delta n = \pm 1$. In this zeroth-order Floquet representation, transitions from one level to another are thus accompanied by energy exchanges with the field which correspond to the absorption or emission of one photon at a time. Considering just the first-order correction $\delta I^{(1)}$, we have been able to show, at least for field intensities which remain modest at all times $[f(s) < 1]$ and in a low-frequency regime $(\omega_L < \omega_0)$, that the nonadiabatic effects of the field modulation by the pulse envelope $f(s)$ induce new couplings in the first-order adiabatic representation that permit the direct (nonsequential) exchange of three photons, through a term varying as $(\cos 3\theta)S_y$ in $\delta I^{(1)}$. (See Appendix B.) At higher field intensities and/or in a higher frequency regime, even with a restriction to the first-order correction, we expect this to be enriched by further coupling terms, denoting new multiphoton pathways which result from the (partial) resummation of nonadiabatic couplings that arise from the aperiodic modulation of the field amplitude. This enrichment is also expected as one goes to a higher-order representation.

## V. DISCUSSIONS AND CONCLUSIONS

We have derived a perturbative series for the construction of an approximate dynamical invariant of a time-dependent quantum system. The approximate invariant obtained at a given order of the perturbation theory systematically defines a higher adiabatic representation of the system's dynamics.

The dynamical invariant is defined here by Eq. (10) rather than by Eq. (1), and this generalization played a crucial role in the development of the perturbative procedure given in detail in Sec. II B. The generalized invariant, defined by Eq. (10), no longer has constant eigenvalues and new degeneracy's can arise during the time evolution; great care must therefore be exercised to follow the evolution of these eigenvalues, even though they do not play a direct, explicit role in the time-resolved dynamics. (Even Berry phases associated with the higher-order adiabatic evolutions described by the eigenstates of the invariant do not involve these eigenvalues.) The time-dependent systems we have considered explicitly as examples in Sec. III do not give rise to degenerate eigenvalues at any time: In the case of the forced harmonic oscillator, the invariant has been constructed to infinite order and to this order, it satisfies the original definition of the Lewis invariant, Eq. (1), so that its eigenvalues are time independent. Moreover, at any order, the invariant is unitarily linked to the field-free Hamiltonian, and its eigenvalues are the field-free, nondegenerate quantized energy levels of the field-free oscillator. The time-dependent Floquet problems defined in Sec. IV are more susceptible to give rise to degenerate situations. In the explicit example of the forced harmonic oscillator, the invariant is, in any order, unitarily equivalent to the uncoupled Floquet Hamiltonian $K_0$. Thus, no degeneracy will be found in this case, as long as the ratio between the field frequency $\omega_L$ and the vibrational frequency of the oscillator $\omega_0$ is not a rational number.

We have illustrated the working of the present perturbative series on two types of systems, the choices of which are motivated by their simplicity. Indeed, the solutions to the perturbation equations (26) and (29) require the calculations of the flow of basic operators under $\mathcal{U}_{H(s)}(\sigma)$ for an infinite "time" $\sigma$. This is presently possible only for dynamical systems possessing a finite Lie algebra. In the case of the harmonic oscillator in the non-Floquet version, an exact Lewis invariant is long known [12–14], and this has also been an element of motivation for its consideration as a test system. It turns out that this case is particularly simple, due to the irrelevance of the $G^{(k)}$ terms in the equations to be solved at each iteration, as these operators are all $c$ numbers. The two-level system represents a more difficult application of the present scheme. We have exploited the simplicity of the algebra of spin operators and spin rotations, to work out the corrections to $\mathcal{I}$ to a high order, with the help of a program written in the MATHEMATICA symbolic language. We illustrated in this particular case how the invariant, constructed in a finite order, defines a high-order adiabatic approximation to the exact time evolution. The approach employed in this case of a two-level system to implement the perturbative scheme will also be applicable in future generalizations to $N$ level systems, using the commutation properties of the generators of the SU($N$) unitary group. Such a generalization is particularly relevant to the development of efficient computational tools for the calculations of time-dependent electronic structure of laser-driven many-electron atoms or molecules described in a finite orbital basis. This restriction to a finite orbital basis implies that only laser-driven dynamics among molecular bound states could be considered. The description of ionization will require a separate treatment, for example, by considering dynamical Feschbach-type couplings between time-dependent bound states and ionization continua. Such a treatment clearly lies beyond the scope of the formalism presented here.

To our knowledge, no attempts have been made previously to define and construct a dynamical invariant for a Floquet Hamiltonian that depends on time through an aperiodic modulation of an otherwise periodic potential. Such an invariant, even approximate, is highly desirable as its structure and the structure of its eigenstates would give direct insight on the effects of what could be called time nonadiabaticity, or pulse shape effects on multiphoton processes. This is important for the generalization of laser control schemes that relied on the concept of adiabatic transport of Floquet states, the so-called STIRAP process [33,24] for instance. We have been able to generate an exact Floquet dynamical invariant only for the forced harmonic oscillator case. For the Floquet two-level system, a preliminary exploration has been presented in Appendix B and is limited to the first-order correction. In a future work, we plan to use in a systematic way, the connection between SU(2) and the rotation group in $R^3$ to obtain a geometric interpretation of the perturbative construction. This may help in finding closed form, higher-order solutions for this system.

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## APPENDIX A: QUANTUM AVERAGING THEOREM

We give here a review of the quantum averaging technique on which are based the formal developments of the perturbative series given in Sec. II.

Let

$$\mathcal{U}_{K_0}(x) = \exp(-iK_0 x) \tag{A1}$$

be the evolution operator generated by the Hermitian operator $K_0$. This Hamiltonian-like operator $K_0$ may actually depend on time, but it is explicitly considered independent of the timelike variable $x$. We also assume that $K_0$ has a completely discrete spectrum, and denote $|k,\nu\rangle$, $\nu=1,2,\ldots,g_k$ its (complete, orthonormal) eigenvectors of $K_0$ associated with a $g_k$-fold eigenvalue (labeled by $k$). Let $V$ be an operator that is bounded under the flow of $\mathcal{U}_{K_0}$, in the sense

$$\lim_{T\to\infty}\frac{\mathcal{U}_{K_0}^{-1}(T)V\mathcal{U}_{K_0}(T)-V}{T}=0. \tag{A2}$$

Define

$$\Pi_{K_0}V=\lim_{T\to\infty}\left(\frac{1}{T}\right)\int_0^T dx\,\mathcal{U}_{K_0}(x)V\mathcal{U}_{K_0}^{-1}(x), \tag{A3}$$

then

$$\Pi_{K_0}V=\sum_{k,\nu,\nu'}|k,\nu\rangle V_{k,\nu,k,\nu'}\langle k,\nu'|, \tag{A4}$$

where

$$V_{k,\nu,k,\nu'}:=\langle k,\nu|\hat{V}|k,\nu'\rangle.$$

Thus, $\Pi_{K_0}V$ is that part of $V$ that is diagonal in the eigenbasis of $K_0$. Let now $W^{K_0}(V)$ be the following operator:

$$W^{K_0}(V)=\lim_{T\to\infty}\left(\frac{-i}{T}\right)\int_0^T d\sigma'\int_0^{\sigma'} d\sigma\,\mathcal{U}_{K_0}(\sigma)V\mathcal{U}_{K_0}^{-1}(\sigma). \tag{A5}$$

We then have

$$[K_0,W^{K_0}(V')]+V'=0, \tag{A6}$$

where

$$V'=(1-\Pi_{K_0})V, \tag{A7}$$

and

$$\Pi_{K_0}W^{K_0}(V')=0, \tag{A8}$$

$$[K_0,\Pi_{K_0}V]=0. \tag{A9}$$

We shall refer to the results of (A6) and (A8), due to Scherer [19,20], as the quantum averaging theorem. The notation defined through (A3) is that of Ref. [21]; along with (A9) it emphasizes that $\Pi_{K_0}$ is a projector on the kernel of the map $ad_{K_0}: V\mapsto[K_0,V]$, i.e., it associates to any operator $V$, bounded under the flow of $K_0$, its diagonal part in the eigenbasis of $K_0$. Adding to $W^{K_0}(V)$, defined by Eq. (A5), an arbitrary operator $C$ that commutes with $K_0$,

$$X=W^{K_0}(V')+C,\quad \Pi_{K_0}C=0, \tag{A10}$$

in fact gives the general solutions of the operator equation [21]

$$[K_0,X]+V'=0, \tag{A11}$$

solutions which exist, if and only if,

$$\Pi_{K_0}V'=0. \tag{A12}$$

The particular solution $X=W^{K_0}(V')$ is strictly nondiagonal in the eigenbasis of $K_0$ according to Eq. (A8).

## APPENDIX B: FLOQUET FIRST-ORDER INVARIANT FOR A PULSE-DRIVEN TWO-LEVEL SYSTEM

In the case of the two-level Floquet Hamiltonian

$$K(s)=S_z+f(s)\cos\theta S_x+\frac{\omega_L}{\omega_0}p_\theta, \tag{B1}$$

we can find three functions $\alpha_0(s,\theta)$, $\beta_0(s,\theta)$, and $\lambda_0(s,\theta)$, such that

$$K(s)=e^{-i\alpha_0 S_y}e^{-i\beta_0 S_x}K_0e^{+i\beta_0 S_x}e^{+i\alpha_0 S_y}, \tag{B2}$$

where

$$K_0:=\left(\lambda_0 S_z+\frac{\omega_L}{\omega_0}p_\theta\right). \tag{B3}$$

These functions are solutions of

$$\frac{\omega_L}{\omega_0}\partial_\theta\alpha_0-\lambda_0\sin\beta_0=0, \tag{B4a}$$

$$\frac{\omega_L}{\omega_0}\sin\alpha_0\partial_\theta\beta_0-\lambda_0\cos\beta_0\cos\alpha_0=-1, \tag{B4b}$$

$$\frac{\omega_L}{\omega_0}\cos\alpha_0\partial_\theta\beta_0+\lambda_0\cos\beta_0\sin\alpha_0=f(s)\cos\theta. \tag{B4c}$$

We are particularly interested in the case $(\omega_L/\omega_0)<1$, $f(s)<1$, $\forall\ s$, corresponding to a low frequency, relatively weak field situation. In this case, the functions $\alpha_0(s,\theta)$, $\beta_0(s,\theta)$, and $\lambda_0(s,\theta)$ will be dominated by the adiabatic solutions given by [these are the same as found in Eqs. (45a) and (45b) of Sec. III B, for the non-Floquet problem]

$$\beta_0(s,\theta)\simeq 0, \tag{B5a}$$

$$\alpha_0(s,\theta)\simeq\arctan[f(s)\cos\theta], \tag{B5b}$$

$$\lambda_0(s,\theta)\simeq\sqrt{1+f(s)^2\cos^2\theta}. \tag{B5c}$$

Using known rules for the rotations of spin matrices, we get, from Eq. (B2),

$$\begin{aligned}\Pi_K[\partial_s K(s)]&=\partial_s f(s)e^{-i\alpha_0 S_y}e^{-i\beta_0 S_x}[\Pi_{K_0}(\cos\theta\cos\alpha_0 S_x)\\&\quad-\Pi_{K_0}(\cos\theta\sin\alpha_0 S_z)]e^{+i\beta_0 S_x}e^{+i\alpha_0 S_y}\\&\equiv\partial_s f(s)[\Pi_{K_0}(\cos\theta\cos\alpha_0 S_x)\\&\quad-\Pi_{K_0}(\cos\theta\sin\alpha_0 S_z)],\end{aligned} \tag{B6}$$

where we have introduced the notation $\equiv$ to denote a unitary equivalence through the sequence of the two rotations (of the spin matrices) of angles $\alpha_0$ and $\beta_0$ generated by $S_y$ and $S_x$, respectively. Similarly, we have

$$\begin{aligned}\delta I^{(1)}&=-iW^K[(1-\Pi_K)\partial_s K]\\&\equiv-i\partial_s f(s)\{W^{K_0}[(1-\Pi_{K_0})\cos\theta\cos\alpha_0(s,\theta)S_x]\\&\quad-W^{K_0}[(1-\Pi_{K_0})\cos\theta\sin\alpha_0(s,\theta)S_z]\}.\end{aligned} \tag{B7}$$

Defining

$$O(\sigma)=\mathcal{U}_{K_0}(\sigma)^{\dagger}O\mathcal{U}_{K_0}(\sigma), \quad O=S_x,S_y,S_z,\theta,p_\theta,$$

where $\mathcal{U}_{K_0}(\sigma)=\exp[-iK_0(s)\sigma]$, it can easily be shown that

$$\theta(\sigma)=\theta-\frac{\omega_L}{\omega_0}\sigma,$$

$$S_x(\sigma)=S_x\cos\left(\int_0^{\sigma}\lambda_0[s,\theta(\sigma')]d\sigma'\right)+S_y\sin\left(\int_0^{\sigma}\lambda_0[s,\theta(\sigma')]d\sigma'\right),$$

$$S_y(\sigma)=S_y\cos\left(\int_0^{\sigma}\lambda_0[s,\theta(\sigma')]d\sigma'\right)-S_x\sin\left(\int_0^{\sigma}\lambda_0[s,\theta(\sigma')]d\sigma'\right),$$

$$S_z(\sigma)=S_z.$$

These relations allow us to evaluate the integrals involved in the $\Pi_{K_0}$ and $W^{K_0}$ terms in Eqs. (B6) and (B7). In the limit $(\omega_L/\omega_0)<1$, $f(s)<1,\forall s$, using the approximate relations (B5a)–(B5c), we first find that only the second $\Pi_{K_0}$ term in Eq. (B6) is nonzero. The detailed expression of $\delta I^{(1)}$ then expands into three terms,

$$\begin{aligned}\delta I^{(1)}\equiv \partial_s f(s)\Bigg\{&S_x\left[\lim_{T\to\infty}\left(\frac{1}{T}\right)\int_0^T d\sigma\int_0^{\sigma}d\sigma'\cos[\theta(\sigma')]\cos\{\alpha_0[s,\theta(\sigma')]\}\cos\left(\int_0^{\sigma'}\lambda_0[s,\theta(\sigma'')]d\sigma''\right)\right]\\&+S_y\left[\lim_{T\to\infty}\left(\frac{1}{T}\right)\int_0^T d\sigma\int_0^{\sigma}d\sigma'\cos[\theta(\sigma')]\cos\{\alpha_0[s,\theta(\sigma')]\}\sin\left(\int_0^{\sigma'}\lambda_0[s,\theta(\sigma'')]d\sigma''\right)\right]\\&-S_z\left[\lim_{T\to\infty}\left(\frac{1}{T}\right)\int_0^T d\sigma\int_0^{\sigma}d\sigma'\{\cos[\theta(\sigma')]\}\sin\{\alpha_0[s,\theta(\sigma')]\}-\Pi_{K_0}[\cos\theta\sin\alpha_0(s,\theta)]\right]\Bigg\}\end{aligned} \tag{B8}$$

and we find, again in the weak-field low-frequency approximation, that the coefficients of $S_z$ and $S_x$ vanish (the integrals contained therein are finite) while, up to order $f^2$, the remaining term yields

$$\delta I^{(1)}\equiv-\frac{f^2}{16}\left(\frac{\omega_0^2}{\omega_0^2-\omega_L^2}\cos\theta-\frac{\omega_0^2}{\omega_0^2-9\omega_L^2}\cos(3\theta)\right)S_y+O(f^2). \tag{B9}$$


[1] T. Kato, J. Phys. Soc. Jpn. **5**, 435 (1950).
[2] A. Messiah, *Quantum Mechanics* (Wiley, North-Holland, New York, 1958), Vol. II.
[3] T. Brabec and F. Krausz, Rev. Mod. Phys. **72**, 545 (2000).
[4] A. Apolonski, P. Dombi, G. G. Paulus, M. Kakehata, R. Holzwarth, Th. Udem, Ch. Lemell, K. Torizuka, J. Burgdörfer, T. W. Hänsch, and F. Krausz, Phys. Rev. Lett. **92**, 073902 (2004).
[5] T. T. Nguyen-Dang, N. A. Nguyen, and N. Mireault, THEOCHEM **591**, 101 (2002).
[6] J. V. Tietz and S. I. Chu, Chem. Phys. Lett. **101**, 446 (1983).
[7] J. Chang and R. E. Wyatt, J. Chem. Phys. **85**, 1826 (1986).
[8] G. Jolicard, Annu. Rev. Phys. Chem. **46**, 83 (1995).
[9] J. P. Killingbeck and G. Jolicard, J. Phys. A **36**, R105 (2003).
[10] T. T. Nguyen-Dang, J. Chem. Phys. **90**, 2657 (1989).
[11] T. T. Nguyen-Dang, S. Manoli, and H. Abou-Rachid, Phys. Rev. A **43**, 5012 (1991).
[12] H. R. Lewis, Phys. Rev. Lett. **18**, 510 (1967).
[13] H. R. Lewis, J. Math. Phys. **9**, 1976 (1968).
[14] H. R. Lewis, Jr. and W. B. Riesenfeld, J. Math. Phys. **10**, 1458 (1969).
[15] A. Mostafazadeh, J. Phys. A **31**, 9975 (1998).
[16] A. Mostafazadeh, J. Phys. A **34**, 4493 (2001).
[17] D. B. Monteoliva, H. J. Korsch, and J. A. Nunez, J. Phys. A **27**, 6897 (1994).
[18] H. R. Lewis and W. E. Lawrence, Phys. Rev. A **55**, 2615 (1997).
[19] W. Scherer, J. Phys. A **30**, 2825 (1997).
[20] W. Scherer, J. Phys. A **27**, 8231 (1994).
[21] H. Jauslin, S. Guérin, and S. Thomas, Physica A **279**, 432 (2000).
[22] M. Amniat-Talab, S. Guérin, and H. Jauslin, J. Math. Phys. **46**, 042311 (2005).
[23] S. Guérin, F. Monti, J. M. Dupont, and H. Jauslin, J. Phys. A **30**, 7193 (1997).
[24] S. Guérin and H. Jauslin, Adv. Chem. Phys. **125**, 147 (2003).
[25] Note that this definition differs from the general one given in Eq. (13). The new definition greatly simplifies the symbolic calculations presented below. It also implies that $s$ ranges from 0 to $2\pi$ as $t$ sweeps over an optical cycle. Also, $\epsilon$ (instead of $2\pi\epsilon$) is directly identified with $\omega_L/\omega_0$.
[26] U. Peskin and N. Moiseyev, J. Chem. Phys. **99**, 4590 (1993).
[27] K. Drese and M. Holthaus, Eur. Phys. J. D **5**, 119 (1999).
[28] H. P. Breuer, K. Dietz, and M. Holthaus, Phys. Rev. A **47**, 725

(1993).
[29] H. P. Breuer and M. Holthaus, J. Phys. Chem. **97**, 12634 (1993).
[30] A. Fleischer and N. Moiseyev, Phys. Rev. A **72**, 032103 (2005).
[31] G. Jolicard, D. Viennot, and J. P. Killingbeck, J. Phys. Chem. **108**, 8580 (2004).
[32] D. Viennot, G. Jolicard, J. P. Killingbeck, and M.-Y. Perrin, Phys. Rev. A **71**, 052706 (2005).
[33] K. Bergmann, H. Theuer, and B. W. Shore, Rev. Mod. Phys. **70**, 1003 (1998).