Generalized π pulses

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We show that the concept of π pulses can be extended to multilevel systems. Generalized π pulses selectively excite a target state via a mechanism that is closely related to the familiar excitation dynamics in a two-level system. The corresponding generalized area theorem does not refer to the "area under the pulse envelope," but to an integral over a difference of instantaneous quasienergies. Nevertheless, there are the same possibilities of pulse shaping for the generalized pulses as for their two-level counterparts. A semiclassical interpretation of the resonance condition leads to an analytical approximation to the relevant quasienergies, and shows that the excitation mechanism is universal.

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I. INTRODUCTION

Recent advances in laser technology have drawn attention to an intriguing question: Is it possible to use specifically "designed" laser pulses to achieve coherent control of molecular dynamics [1–3]? One of the main tasks in this line of research is to find principles for "guiding the evolution of a quantum system" [4] by strong laser fields, so that certain desired molecular processes can be induced with high efficiency.

For a quantum system with only two relevant levels, such a principle is well known. A "π pulse," applied on resonance, leads to complete inversion [5]. These π pulses are not unique. An infinity of pulses with different shapes, but the same area under the pulse envelope, can have the same effect. Nowadays, pulse shaping has become an important tool for NMR spectroscopy [6,7].

In this paper, we show that it is possible to extend the basic idea of π pulses to transitions in multilevel systems. Generalized π pulses induce complete selective excitation of a prescribed target state, and, exactly as for their two-level analogs, there is a significant freedom in the choice of the pulse shape. Accordingly, this freedom can be exploited in the design of optimal laser pulses.

The outline of our work is as follows. First, we briefly review the theory of two-level π pulses and show how these are related to their multilevel counterparts. We then give an example of a generalized π pulse, together with an illustration of the possibilities of pulse shaping. In Sec. IV we discuss the resonance condition for the generalized pulses from a semiclassical point of view. In Sec. V we turn to compositions of π pulses, which lead to controlled transitions between distant states, and briefly sketch a possible extension of the method. The final section contains a concluding discussion.

II. A NEW LOOK AT AN OLD PROBLEM

As a starting point for the discussion of generalized π pulses, let us briefly recapitulate some familiar facts. The Schrödinger equation for a two-level system which interacts with a periodic electric field of strength F_0 and frequency ω,

$$i\hbar\frac{d}{dt}\begin{bmatrix}a_1(t)\\a_2(t)\end{bmatrix}=[H_0+H_{\rm int}(t)]\begin{bmatrix}a_1(t)\\a_2(t)\end{bmatrix}, \tag{2.1}$$

with (we assume $E_2>E_1$)

$$H_0=\begin{bmatrix}E_1 & 0\\ 0 & E_2\end{bmatrix} \tag{2.2}$$

and

$$H_{\rm int}(t)=-\mu F_0\cos(\omega t)\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}, \tag{2.3}$$

can be solved exactly, if the resonant, or "rotating-wave," approximation is made [8]. Denoting the two eigenstates of H_0 by

$$\varphi_1=\begin{bmatrix}1\\0\end{bmatrix},\quad \varphi_2=\begin{bmatrix}0\\1\end{bmatrix}, \tag{2.4}$$

the wave function can be written as

$$\psi(t)=a_1(t)\varphi_1+a_2(t)\varphi_2 . \tag{2.5}$$

In the particular case of exact resonance, $\hbar\omega=E_2-E_1$, and assuming the initial condition $\psi(t=0)=\varphi_1$, one obtains oscillations [9]

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$$|a_2(t)|^2=\sin^2\left[\frac{\Omega t}{2}\right], \tag{2.6}$$

with the Rabi frequency

$$\Omega=\frac{\mu F_0}{\hbar}. \tag{2.7}$$

Thus, after a time t_p determined by

$$t_p=\frac{\pi}{\Omega}, \tag{2.8}$$

we have inversion, i.e., $|a_2(t_p)|^2=1$.

For our purposes it is instructive to look at the same problem from a different angle [10]. Since the full Hamiltonian $H=H_0+H_{\rm int}(t)$ is periodic in time, there are periodically time-dependent Floquet states $u_{1,2}(t)$ and quasienergies $\varepsilon_{1,2}$, so that the wave function can also be expressed as

$$\psi(t)=c_1u_1(t)\exp(-i\varepsilon_1t/\hbar)+c_2u_2(t)\exp(-i\varepsilon_2t/\hbar). \tag{2.9}$$

Whereas in (2.5) the wave function had been expanded, with *time-dependent* coefficients, in a basis of time-independent eigenstates of H_0, we now are using a basis of periodically time-dependent eigenstates of $H_0+H_{\rm int}(t)-i\hbar\partial_t$ for an expansion with *time-independent* coefficients c_j. The time evolution is described by the dynamical phase factors $\exp(-i\varepsilon_jt/\hbar)$ (with $j=1,2$).

Again, in the rotating-wave approximation the Floquet states are easy to calculate; one finds (see also [11])

$$u_1(t)=\frac{1}{\sqrt{2\Omega_g}}\begin{bmatrix}\sqrt{\Omega_g+\Delta}\exp(i\omega t)\\ \sqrt{\Omega_g-\Delta}\end{bmatrix},$$
$$u_2(t)=\frac{1}{\sqrt{2\Omega_g}}\begin{bmatrix}-\sqrt{\Omega_g-\Delta}\exp(i\omega t)\\ \sqrt{\Omega_g+\Delta}\end{bmatrix}, \tag{2.10}$$

with the frequency detuning $\Delta=(E_2-E_1)/\hbar-\omega$, and

$$\Omega_g=[(\mu F_0/\hbar)^2+\Delta^2]^{1/2}; \tag{2.11}$$

the quasienergies are (modulo $\hbar\omega$)

$$\varepsilon_1=\tfrac{1}{2}(E_1+E_2)+\frac{\hbar\omega}{2}-\frac{\hbar\Omega_g}{2},$$
$$\varepsilon_2=\tfrac{1}{2}(E_1+E_2)+\frac{\hbar\omega}{2}+\frac{\hbar\Omega_g}{2}. \tag{2.12}$$

As expected, the case of exact resonance $\Delta=0$ is very simple. We then have

$$u_1(t)\exp(-i\varepsilon_1t/\hbar)=\frac{1}{\sqrt{2}}\begin{bmatrix}\exp(-iE_1t/\hbar)\\ \exp(-iE_2t/\hbar)\end{bmatrix}\exp(i\Omega t/2),$$
$$u_2(t)\exp(-i\varepsilon_2t/\hbar)=\frac{1}{\sqrt{2}}\begin{bmatrix}-\exp(-iE_1t/\hbar)\\ \exp(-iE_2t/\hbar)\end{bmatrix}\exp(-i\Omega t/2), \tag{2.13}$$

and it follows that the coefficients in the expansion (2.9) are given by

$$c_1=\frac{1}{\sqrt{2}},\quad c_2=-\frac{1}{\sqrt{2}}. \tag{2.14}$$

The important observation now is that the condition (2.8) can be written as

$$(\varepsilon_2-\varepsilon_1)t_p/\hbar=\pi. \tag{2.15}$$

This fact leads to an interesting interpretation of Rabi oscillations in the language of the Floquet theory. In the presence of an oscillating force, the initial state $\psi(t=0)=\varphi_1$ is split into a superposition of two Floquet states with equal amplitudes, $|c_1|^2=|c_2|^2=\frac{1}{2}$, and, according to (2.9), each of them acquires a dynamical phase which is determined by its quasienergy. Measuring the occupation probability of φ_2 at $t=t_p$ leads to an interference of these two components, so that the excitation probability is determined by the difference of the two dynamical phases. Equation (2.15) then simply states that maximal excitation, or inversion, corresponds to constructive interference.

Of course, from a mathematical point of view, both approaches (2.5) and (2.9) are completely equivalent. The Floquet approach, however, becomes particularly efficient if, instead of an oscillating electric field $\mathcal{E}(t)=F_0\cos(\omega t)$ with constant amplitude, there is a pulse $\mathcal{E}(t)=F(t)\cos(\omega t)$, provided that the characteristic time t_p during which the smooth envelope $F(t)$ changes is considerably longer than the period $T=2\pi/\omega$ of a single oscillation. In such a situation, the Hamiltonian no longer depends periodically on time. But if the amplitude $F(t)$ is "frozen" at a particular value F, we can define instantaneous quasienergies $\varepsilon_{1,2}^F$ and instantaneous Floquet states $u_{1,2}^F(t)$. The key point then is that the response to pulses with slowly changing envelopes is adiabatic, i.e., the occupation probabilities of the instantaneous Floquet states remain constant, and the dynamical phases are given by the time-integrated instantaneous quasienergies [12,13]. Therefore, if we consider a two-level system driven exactly on resonance by a pulse with an envelope $F(t)$ which starts from $F(0)=0$, reaches a maximal amplitude $F_{\max}$, and decreases back to $F(t_p)=0$ after a total pulse duration t_p, it follows immediately from (2.15) that the condition for inversion becomes

$$\frac{1}{\hbar}\int_0^{t_p}dt(\varepsilon_2^{F(t)}-\varepsilon_1^{F(t)})=\pi. \tag{2.16}$$

This expression can be rewritten to look more familiar. For a two-level system, we have [see (2.12)]

$$\varepsilon_2^{F(t)}-\varepsilon_1^{F(t)}=\mu F(t), \tag{2.17}$$

and therefore (2.16) takes the form

$$\frac{\mu}{\hbar}\int_0^{t_p}dt\,F(t)=\pi. \tag{2.18}$$

This is the well-known "area theorem" [8]: Inversion in a two-level system is obtained if the area under the pulse envelope, multiplied by the transition matrix element μ, and divided by Planck's constant, becomes equal to π. It

is important that the precise form of the envelope is irrelevant; it is only its area that counts. But whereas (2.17) and, as a consequence, (2.18) are valid only for a two-level system under the additional assumption of the rotating-wave approximation, the formulation (2.16) is much more general. The main purpose of this paper is to demonstrate that there are generalized π pulses which can induce a selective excitation of specific "target states" in a multilevel system. Such pulses are characterized by the condition (2.16), but *not* by (2.18). This result becomes particularly clear if one performs a Floquet expansion analogous to (2.9), whereas an eigenstate expansion like (2.5) only confuses the picture.

III. GENERALIZED π PULSES: AN EXAMPLE

As an example for the selective excitation of molecular vibrations by short pulses of infrared laser radiation, we now consider the model of a forced Morse oscillator

$$H(t)=\frac{p^2}{2m}+D(1-e^{-\beta x})^2+dx\,F(t)\cos(\omega t)\ , \tag{3.1}$$

with parameters of an H—F bond [14]: $m=1744.8$, $D=0.2251$, $\beta=1.174$, and $d=0.3099$ (all data in atomic units). Of course, this simple model is not intended to give a full description of the real HF molecule, but to demonstrate salient features of the generalized π pulses.

We now specify the pulse shape

$$F(t)=F_{\max}\sin^2\left[\frac{\pi t}{t_p}\right]\ , \tag{3.2}$$

where t_p denotes the pulse length, and choose the frequency $\hbar\omega=(E_5-E_0)/5$. This frequency corresponds to a "five-photon transition" from the vibrational ground state $n=0$ with energy E_0 to the fifth excited state $n=5$ with energy E_5. Finally, we choose a pulse length of 100 laser cycles, $t_p=100\times 2\pi/\omega$, which amounts to 0.922 ps. The Schrödinger equation

$$i\hbar\partial_t\psi(t)=H(t)\psi(t) \tag{3.3}$$

is then solved numerically. This model is strongly motivated by several previous studies [15–17].

Figure 1(a) shows the response of the Morse oscillator to such a pulse with peak amplitude $F_{\max}=0.0431$ a.u. Starting from the ground state, the probability appears to spread, and vibrational eigenstates up to $n=7$ become significantly populated during the pulse, but in the end almost all the probability flows to the state $n=5$. As a result of our particular pulse, the selective excitation of this state has been achieved.

Figure 1(a) can be regarded as the analog of (2.5) for the two-level system. The wave function $\psi(t)$ is expanded in a basis of the vibrational states φ_n, i.e., in the basis of the unperturbed eigenstates of the Morse oscillator,

$$\psi(t)=\sum_n a_n(t)\varphi_n\ , \tag{3.4}$$

and the occupation probabilities $|a_n(t)|^2$ are displayed. Two things are remarkable: The excitation mechanism appears to be incompatible with "sequential ladder climbing" (the occupation probability for $n=6$, which is the state *above* the target state, peaks even before that of $n=4$). In addition, the time evolution of the population does not show any symmetry, although the envelope function $F(t)$ is symmetric.

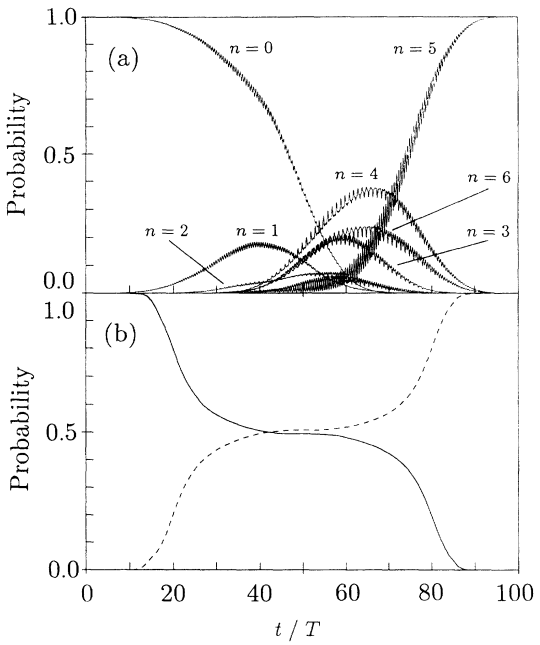

FIG. 1. (a) Occupation probabilities $|a_n(t)|^2$ of unperturbed Morse eigenstates φ_n during a laser pulse with the envelope (3.2), frequency $\omega=0.016489$ a.u., and maximal amplitude $F_{\max}=0.0431$ a.u. The pulse length t_p is 100 laser cycles, or 0.922 ps. (b) Occupation probabilities of the instantaneous Floquet states for the same laser pulse as investigated in (a). Only two Floquet states account for all the dynamics: the state u_0^F connected to the initial state $n=0$ (full line), and u_5^F (dashed line), which is connected to the target state $n=5$.

In order to obtain the counterpart of (2.9), namely, an expansion of the wave function $\psi(t)$ *for the very same pulse* in the basis of instantaneous Floquet states, one first has to freeze the amplitude $F(t)$ at constant values F and to consider the resulting one-parameter family $H^F(t)$ of strictly periodic Hamiltonian operators,

$$H^F(t)=\frac{p^2}{2m}+D(1-e^{-\beta x})^2+dx\,F\cos(\omega t)\ ,$$
$$0\le F\le F_{\max}\ . \tag{3.5}$$

Then the eigenvalue equation

$$[H^F(t)-i\hbar\partial_t]u_n^F(t)=\varepsilon_n^F u_n^F(t) \tag{3.6}$$

has to be solved for each fixed value of F, with periodic boundary conditions in time. Finally, the wave function $\psi(t)$, i.e., the solution to the time-dependent Schrödinger equation for the pulse $F(t)$, is projected at each moment t_0 onto the instantaneous Floquet states $u_n^{F(t_0)}(t)$. The result of this tedious procedure is shown in Fig. 1(b). The picture now is much simpler than the previous Fig. 1(a), although it describes the same situation. Only two Floquet states are populated during the pulse; these two

states are those which are connected to the initial state $n=0$ and the target $n=5$. Thus, seen from the "comoving frame of reference" provided by the instantaneous Floquet states, the excitation process can be described in terms of two-level dynamics. The symmetry of the occupation probabilities of the two Floquet states clearly reflects the symmetry of the pulse shape.

This dynamical behavior can be explained with the help of the instantaneous quasienergy spectrum [18], i.e. of the eigenvalues ε_n^F. It should be noted that because of the continuous part of the energy spectrum of the unperturbed Morse oscillator the Floquet states turn into resonances with finite lifetimes, and the quasienergies acquire negative imaginary parts [19]. However, in our case these imaginary parts are so small that they can be completely neglected in the following discussion, even though the continuum is properly taken care of in the numerical studies [17].

The quasienergy spectrum for the present example is shown in Fig. 2. Quasienergies are defined modulo $\hbar\omega$: if ε_n^F is a quasienergy of the Floquet state labeled by n, and if l is an arbitrary integer, then $\varepsilon_n^F + l\hbar\omega$ is a quasienergy that characterizes the same physical state. The quasienergies displayed in Fig. 2 are labeled such that $(n,-l)$ describes an eigenvalue that connects to $E_n - l\hbar\omega$ for vanishing amplitude F, where E_n is an unperturbed energy eigenvalue. A quasienergy spectrum describes both the "dressing" of the unperturbed quantum system by the photons of the laser field (via its modulo $\hbar\omega$ structure) and the ac Stark effect, i.e., the distortion of the original level structure with increasing field amplitude.

The particular choice $\hbar\omega=(E_5-E_0)/5$ of the frequency ω leads to a degeneracy (modulo $\hbar\omega$) of the quasienergies ε_i^F and ε_f^F of the initial state $i=0$, and that of the final target state $f=5$ at low amplitudes F. But, as seen in Fig. 2, this quasienergetic degeneracy is removed when the field strength becomes larger. Thus under the influence of the pulse $F(t)$ the wave function is first shifted adiabatically into the Floquet state $u_i^F(t)$ connected to the initial state; then, as the degeneracy is lifted, it is split into a superposition of the two Floquet states $u_i^F(t)$ and $u_f^F(t)$. After that, these two components of the wave function evolve adiabatically, and each of them acquires a dynamical phase which is determined by its quasienergy, exactly as in the case of the two-level system. At the end of the pulse, when the field strength becomes so low that the instantaneous quasienergies are almost degenerate again, both components interfere. Selective excitation of the target state corresponds to constructive interference. Therefore, the condition for the relative quantum phase reads [18]

$$\frac{1}{\hbar}\int_0^{t_p} dt(\varepsilon_i^{F(t)}-\varepsilon_f^{F(t)})=\pm\pi\ , \tag{3.7}$$

which is exactly identical to the condition (2.16) for the usual two-level π pulses.

However, in the present case the quasienergy difference is not simply proportional to the field strength, so that the "area theorem" in its conventional form (2.18) does not hold. For generalized π pulses this area theorem has to be replaced by (3.7).

In analogy to (2.6) for the excitation probability of a two-level system, the excitation probability can now be written as

$$P_{i\to f}=\sin^2\left[\frac{1}{2\hbar}\int_0^{t_p} dt(\varepsilon_i^{F(t)}-\varepsilon_f^{F(t)})\right]\ . \tag{3.8}$$

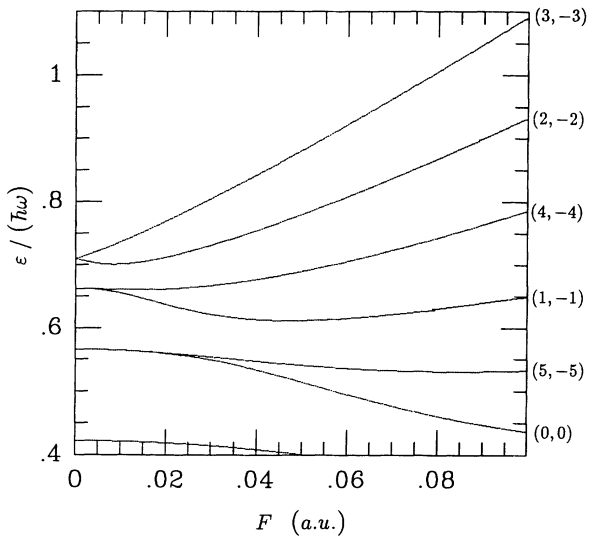

FIG. 2. Quasienergies (modulo $\hbar\omega$) for the Morse oscillator driven with frequency $\omega=0.016\,489$ a.u. and constant amplitude F. A label $(n,-l)$ on the right margin indicates that a quasienergy is connected to $E_n - l\hbar\omega$ for $F\to 0$, where E_n is the energy of the unperturbed eigenstate φ_n. The dynamics of generalized π pulses for the transition $n=0\to n=5$ is completely determined by the removal of the degeneracy of the quasienergies (0,0) and (5,−5).

Figure 3 demonstrates how well this formula works: The solid line denotes the theoretical excitation probability (3.8), calculated as function of the maximal amplitude $F_{\max}$ from the quasienergies shown in Fig. 2; little boxes indicate excitation probabilities that have been obtained from a numerical solution of the Schrödinger equation.

The perfect agreement between theory and "numerical experiment" shows that the basic adiabatic assumption, i.e., the separation of fast and slow time scales, can be valid even for subpicosecond laser pulses. Since the condition for the applicability of the adiabatic principle is $2\pi/\omega \ll t_p$, it is clear that substantial deviations from strict adiabaticity will eventually occur in very short pulses. An example for such deviations is shown in Fig. 4 for a pulse with $t_p=50\times 2\pi/\omega=0.461$ ps, only half as long as before. But even in this critical case, the qualitative agreement is still good.

Although condition (3.7) does not refer directly to the area under the pulse envelope, it leaves a similar freedom as the usual area theorem. Again, the precise form of the envelope function $F(t)$ is irrelevant, as long as it is smooth (so that the adiabatic approximation applies). All that matters is the value of the integrated difference between the instantaneous quasienergies, and an infinity of different envelopes can result in selective excitation. This freedom can be exploited in a systematic procedure to

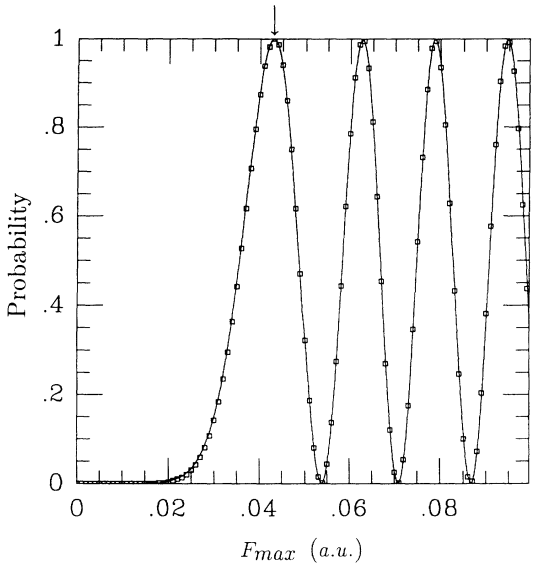

FIG. 3. Predicted excitation probabilities of the target state $n=5$ according to (3.8) (full line) and numerically computed values (boxes) for pulses (3.2) with frequency $\omega=0.016489$ a.u., and length $t_p=100T$, as functions of the maximal amplitude $F_{\max}$. The arrow indicates the π-pulse considered in Fig. 1.

"design" suitable laser pulses, in which possible physical restrictions can be taken into account.

A first example for this approach is already contained in Fig. 3. Let us suppose that we have a laser which delivers pulses with the shape (3.2) at the frequency $\hbar\omega=(E_5-E_0)/5$, and that the pulse length $t_p=100T$ is fixed ($T=2\pi/\omega$). The task then would be to determine a maximal field strength $F_{\max}$ that leads to selective excitation of the target state $n=5$. One can now proceed as follows. First, the instantaneous quasienergies have to be computed as functions of the field amplitude. Then the integral on the left-hand side of (3.7) has to be evaluated for the shape (3.2) as a function of $F_{\max}$. That value of $F_{\max}$ which makes the integral equal to $\pm\pi$ belongs to a generalized π pulse. In the example shown in Fig. 3, this procedure leads to the prediction that pulses with $F_{\max}=0.0431$ a.u. will induce a practically complete excitation of the target state. A numerical solution of the Schrödinger equation can finally be performed to check the result. Even in cases where the adiabatic approximation introduces a slight error, the pulses determined in this way will provide excellent starting points for further optimizations.

For another illustration of the designing process, let us consider pulses with a "plateau":

$$F(t)=\begin{cases} F_{\max}\sin^2\left[\dfrac{\pi t}{t_1}\right], & 0\le t<t_1/2 \\ F_{\max}, & t_1/2\le t<t_1/2+t_2 \\ F_{\max}\sin^2\left[\dfrac{\pi(t-t_2)}{t_1}\right], & t_1/2+t_2\le t\le t_1+t_2\ . \end{cases} \tag{3.9}$$

Suppose one could technically realize such pulses with a varying plateau length t_2, but one were restricted to $F_{\max}=0.04$ a.u. and $t_1=80T$. The same strategy as before then leads to the prediction that a plateau length $t_2\approx 14T$ will give rise to a π pulse; this prediction is confirmed in Fig. 5 by a numerical solution of Schrödinger's equation. If, in a different situation, one is forced to work with pulses with, say, $t_1=70T$ and $t_2=15T$, but there is still the freedom to adjust the maximal amplitude, then it can be deduced that $F_{\max}\approx 0.0405$ a.u. is the optimal choice (Fig. 6).

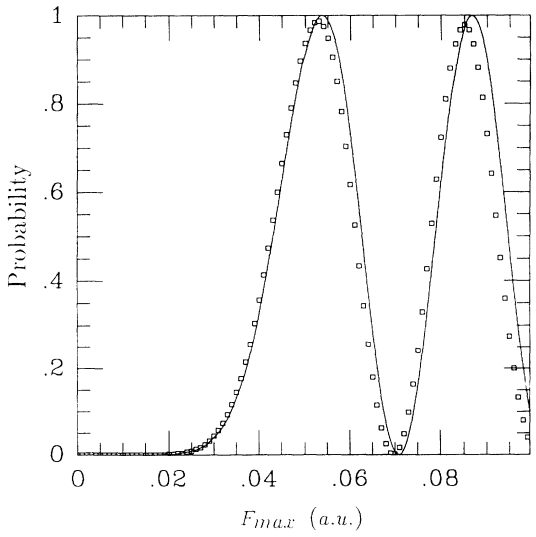

FIG. 4. Predicted excitation probabilities of the target state $n=5$ according to (3.8) (full line) and numerically computed values (boxes) for pulses (3.2) with frequency $\omega=0.016489$ a.u., length $t_p=50T$, as functions of the maximal amplitude $F_{\max}$.

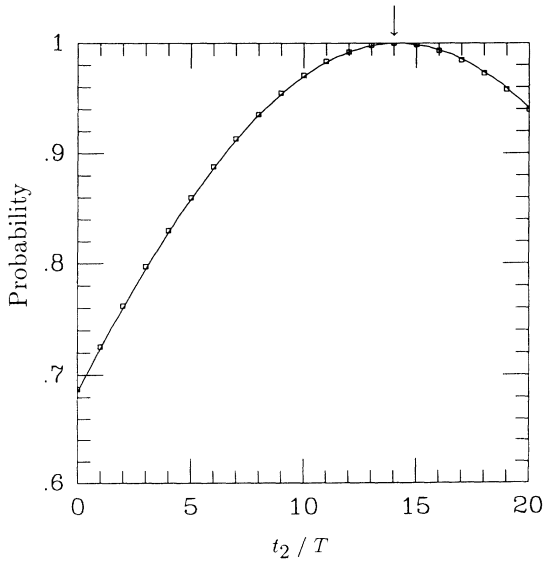

FIG. 5. An example for "designed" laser pulses: For the envelope (3.9), $F_{\max}=0.04$ a.u., and $t_1=80T$, formula (3.8) predicts that a pulse with a plateau length of $t_2=14T$ is a π pulse for the transition $n=0\rightarrow n=5$ (full line). The prediction is confirmed by numerical solutions of the Schrödinger equation (boxes).

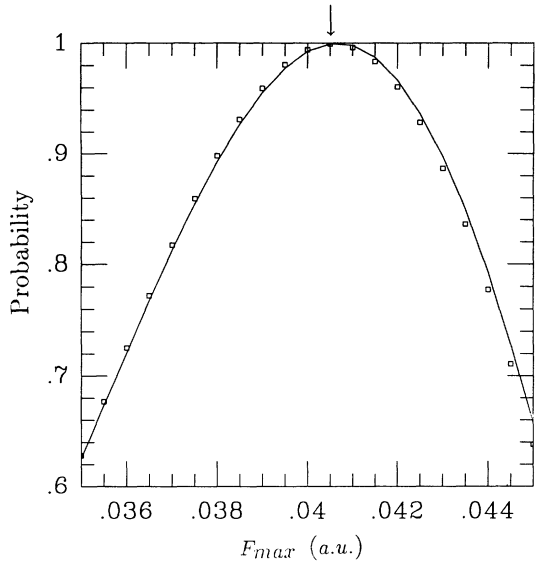

FIG. 6. Another example of designed pulses with the envelope (3.9): If $t_1=70T$ and $t_2=15T$ are kept fixed, then (3.8) predicts that the plateau field strength $F_{\max}=0.0405$ a.u. is optimal (full line). Again, the prediction is confirmed by numerical calculations (boxes).

These examples may suffice to demonstrate the flexibility of the present approach. From the viewpoint of numerical efficiency, it is important to stress that the quasienergies are, of course, independent of the pulse shape. Thus they have to be computed only once, and can then be used to calculate the integral (3.7) for *any* smooth envelope $F(t)$.

IV. UNDERSTANDING THE QUASIENERGY SPECTRUM: THE RESONANCE CONDITION

The particular choice of frequency in our example, $\hbar\omega=(E_5-E_0)/5$ to populate the fifth excited state, is not obvious. Although the approximate selection rule $\Delta n=\pm 1$, valid for the weakly anharmonic Morse oscillator, suggests that a "five-photon transition" could be the most efficient mechanism to excite the state $n=5$, it is by no means clear that this perturbative selection rule, which does not incorporate the effect of the pulse shape, has any meaning at all in the strong-field regime. In this section we will use a semiclassical argument to show that there is a nonperturbative effect which strongly favors the previous frequency choice, and explain the characteristic behavior of near-resonant instantaneous quasienergies (Fig. 2).

Expressed in action-angle variables (I,ϑ), the classical Hamiltonian function of the unperturbed Morse oscillator reads [20]

$$H_0(I)=\omega_0 I-\frac{\omega_0^2 I^2}{4D}\ , \tag{4.1}$$

with

$$\omega_0=\left[\frac{2D\beta^2}{m}\right]^{1/2}\ . \tag{4.2}$$

The frequency of classical oscillations is given by

$$\Omega(I)=\frac{dH_0}{dI}=\omega_0-\frac{\omega_0^2 I}{2D}\ . \tag{4.3}$$

When such a nonlinear oscillator is driven by an external periodic force with frequency ω, resonances emerge [21]. The most important of these resonances occurs if the oscillation frequency is equal to the driving frequency, i.e., at the action $I_{\rm res}$ determined by

$$\Omega(I_{\rm res})=\omega\ . \tag{4.4}$$

Semiclassically, the action $I_n=\hbar(n+\frac{1}{2})$ (starting from $n=0$) corresponds to the nth quantum state, and $E_n=H_0(I_n)$ are the quantized energy eigenvalues. It follows that a frequency which, quantum mechanically, couples an initial state i with a final state f by $(f-i)$ photons,

$$\hbar\omega=(E_f-E_i)/(f-i)\ , \tag{4.5}$$

leads on the classical level to the appearance of a 1:1 resonance precisely in the middle between I_i and I_f:

$$I_{\rm res}=\tfrac{1}{2}(I_f+I_i)\ . \tag{4.6}$$

A classical Poincaré surface for the situation considered in Sec. III $(i=0,f=5)$ is shown in Fig. 7 for a field strength of $F=0.03$ a.u. For the unperturbed oscillator, such a plot would merely show straight lines $I=$const (which, topologically, are circles, since the angles $\vartheta=0$ and 2π have to be identified). But now the existence of the 1:1 resonance leads to a significant reordering of the phase-space structure close to the resonant action. It is important to realize that the resonance-induced closed contours seen in Fig. 7 do *not* result from a continuous deformation of the unperturbed "circles" of constant ac-

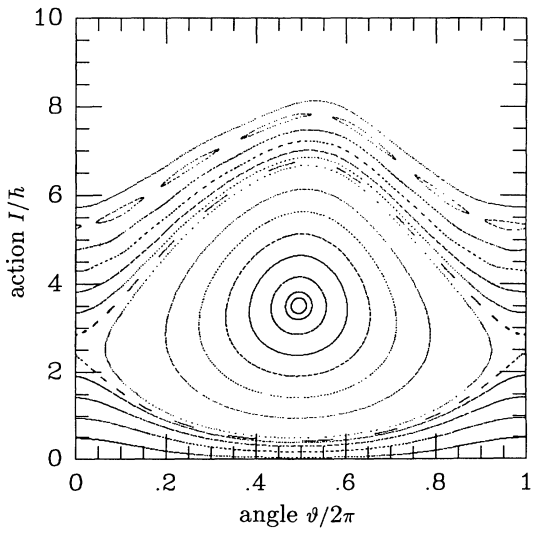

FIG. 7. Poincaré section for a classical Morse oscillator driven with amplitude $F=0.03$ a.u., and frequency $\omega=0.016\,489$ a.u.

tion. When the field strength F is increased, the unperturbed manifolds have to break up, and fragments from above and below $I_{\rm res}$ have to combine to produce the new invariant manifolds. In this way, the classical resonance couples the action $I_i = I_{\rm res} - \Delta I$ with $I_f = I_{\rm res} + \Delta I$, and there even exists a purely classical counterpart to transitions between the corresponding quantum states [22].

For a quantitative analysis we start from the full classical Hamiltonian

$$H(I,\vartheta) = H_0(I) + dFx(I,\vartheta)\cos(\omega t) \tag{4.7}$$

with constant amplitude F, and perform the usual resonance approximation [23]: $x(I,\vartheta)$ is expanded in a cosine series

$$x(I,\vartheta) = \frac{1}{\beta}\ln\left[\frac{\omega_0^2 - \omega_0\cos(\vartheta)\sqrt{\omega_0^2 - \Omega(I)^2}}{\Omega(I)^2}\right] = \sum_{n=0}^{\infty} x_n(I)\cos(n\vartheta)\ ; \tag{4.8}$$

then only the resonant term proportional to x_1 is kept. In addition, the unperturbed Hamiltonian is expanded quadratically around $I_{\rm res}$. In this way, we arrive at

$$H(I,\vartheta) \approx E_{\rm res} + \Omega(I_{\rm res})\Delta I + \frac{(\Delta I)^2}{2M} + \gamma\cos(\vartheta - \omega t)\ , \tag{4.9}$$

with

$$\Delta I = I - I_{\rm res}\ ,$$
$$E_{\rm res} = H_0(I_{\rm res})\ ,$$
$$M^{-1} = \left.\frac{d^2 H_0}{dI^2}\right|_{I_{\rm res}}\ ,$$
$$\gamma = \frac{dFx_1(I_{\rm res})}{2}\ .$$

In general, canonical transformations and quantization are noncommuting operations. But if we ignore this complication and naively quantize the conjugate pair $(\Delta I, \vartheta)$, we obtain the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(\vartheta,t) = \left[E_{\rm res} + \frac{\hbar\Omega(I_{\rm res})}{i}\frac{\partial}{\partial\vartheta} - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial\vartheta^2} + \gamma\cos(\vartheta - \omega t)\right]\psi(\vartheta,t)\ . \tag{4.10}$$

After a transformation $\vartheta - \omega t = z$ the term linear in the momentum vanishes because of the resonance condition $\Omega(I_{\rm res}) = \omega$, and we are left with

$$i\hbar\frac{\partial}{\partial t}\tilde{\psi}(z,t) = \left[E_{\rm res} - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial z^2} + \gamma\cos(z)\right]\tilde{\psi}(z,t)\ . \tag{4.11}$$

This is nothing but the Schrödinger equation for a particle with mass M which moves in a periodic cosine "lattice." A little reflection shows that the allowed *energy* eigenvalues for this system coincide (modulo $\hbar\omega$) with the *quasienergies* of the original problem. The ansatz

$$\tilde{\psi}(z,t) = \chi(v)\exp(-i\varepsilon t/\hbar) \tag{4.12}$$

with $v = z/2$ leads to the Mathieu equation [24]

$$\frac{d^2}{dv^2}\chi(v) + [\alpha - 2q\cos(2v)]\chi(v) = 0\ , \tag{4.13}$$

with the parameters

$$\alpha = \frac{8M}{\hbar^2}(\varepsilon - E_{\rm res}) \tag{4.14}$$

and

$$q = \frac{4M\gamma}{\hbar^2} = \frac{2MdFx_1(I_{\rm res})}{\hbar^2}\ . \tag{4.15}$$

Now the boundary conditions have to be taken into account: ϑ is an angle variable, so that $\psi(\vartheta,t)$ has to be 2π periodic in ϑ. Therefore, $\chi(v)$ must be a π-periodic Mathieu function, which imposes restrictions on the possible values of α and, thus, determines the (quasi) energies ε. For each given value of q, the parameter α has to belong to one of the sets of characteristic values [24] $\{a_0, a_2, a_4, \ldots\}$ or $\{b_2, b_4, b_6, \ldots\}$, which give rise to even or odd π-periodic solutions of the Mathieu equation. If we define

$$\alpha_k(q) = \begin{cases} a_k(q), & k = 0,2,4,\ldots \\ b_{k+1}(q), & k = 1,3,5,\ldots, \end{cases} \tag{4.16}$$

we can finally write the resonant quasienergies as

$$\varepsilon_k(q) = E_{\rm res} + \frac{\hbar^2}{8M}\alpha_k(q) \bmod \hbar\omega\ . \tag{4.17}$$

One can also formulate this result without taking recourse to classical mechanics [25]. To this end, we first determine the resonant quantum state $n_{\rm res}$, i.e., the state which fulfills the condition

$$E_n' = \hbar\omega \tag{4.18}$$

most closely (the prime indicates differentiation with respect to the quantum number n), and replace the mass parameter M by $\hbar^2/E''_{n_{\rm res}}$. The expansion coefficient $x_1(I_{\rm res})$ corresponds to the dipole matrix element $2\langle n_{\rm res}|x|n_{\rm res}+1\rangle$, so that the Mathieu parameter q becomes

$$q = \frac{4dF\langle n_{\rm res}|x|n_{\rm res}+1\rangle}{E''_{n_{\rm res}}}\ , \tag{4.19}$$

and the quasienergies are

$$\varepsilon_k(q) = E_{n_{\rm res}} + \tfrac{1}{8}E''_{n_{\rm res}}\alpha_k(q) \bmod \hbar\omega\ . \tag{4.20}$$

In this approximation, the quasienergy spectrum is characterized by only two parameters: $E''_{n_{\rm res}}$, which contains information about the unperturbed energy eigenvalues close to the resonant state, and q, which quantifies how this state is coupled to its nearest neighbors.

The Morse oscillator is a particular example where

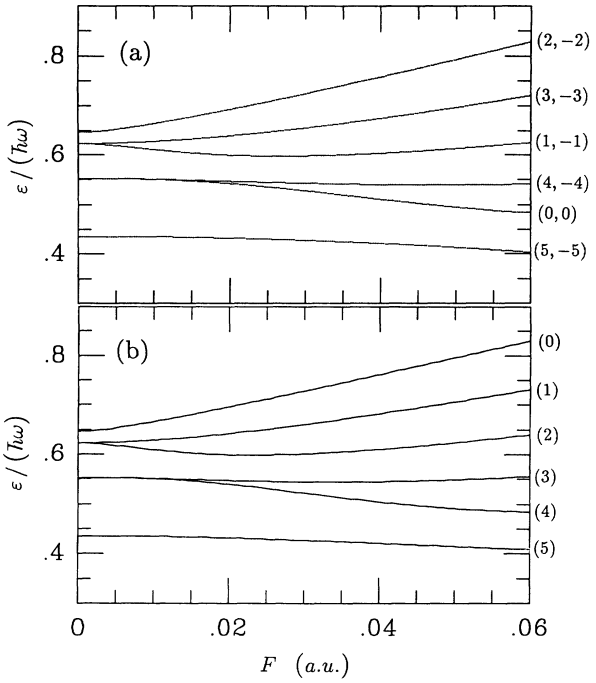

FIG. 8. (a) Quasienergies of resonant states for $\omega=0.016\,884$ a.u. Quantum numbers on the right have the same meaning as in Fig. 2. (b) Approximate quasienergies according to the Mathieu approximation (4.20). Numbers on the right are the quantum numbers k defined in (4.16).

these semiclassical techniques work well even for low quantum numbers. The unperturbed Hamiltonian depends only quadratically on the action, so that the quadratic expansion around $I_{\rm res}$ introduces no error. If the difference in quantum number between the initial state i and the final state f is even, the relation (4.18) can be satisfied exactly. For example, for $i=0$ and $f=4$ we have $n_{\rm res}=2$. Figure 8(a) shows the numerically computed, exact quasienergies for this case, whereas Fig. 8(b) shows the evaluation of (4.20). To obtain this figure, the Morse matrix element $\langle 2|x|3\rangle$ has been approximated by the corresponding matrix element of a harmonic oscillator with the same mass m and characteristic frequency ω_0 as the hydrogen fluoride oscillator.

The good agreement between numerical values and the analytical approximation is not the main point. In fact, it is usually much faster simply to compute the quasienergies than to search the required characteristic values in suitable tables [26]. More important is the understanding of principal features of quantum dynamics in strong laser fields. In this respect, the interpretation of the quantum number k introduced in (4.16) is instructive. As already pointed out above, the original quantum numbers n for the unperturbed Morse oscillator correspond to discretized values of the classical action,

$$\frac{1}{2\pi}\oint_{\zeta} p\,dx=\hbar(n+\tfrac{1}{2})\,, \tag{4.21}$$

where the closed quantization path ζ lies on a manifold of constant energy. In action-angle variables, ζ would be a straight line $I=$const stretching from $\vartheta=0$ to 2π. There are similar semiclassical quantization rules to calculate the quasienergies and Floquet states for periodically driven systems [27,28], but now the quantization procedure refers to the extended phase space $\{(p,x,t)\}$. In our case, the semiclassical rule which selects the correct "quantized" manifolds can be expressed as

$$\frac{1}{2\pi}\oint_{\gamma} p\,dx=\hbar(k+\tfrac{1}{2})\,. \tag{4.22}$$

The path γ has to lie in a plane of constant time t, and on an invariant manifold which exists in the presence of the driving force, i.e., on one of those contours seen in the Poincaré plot (Fig. 7). Because the resonance leads to new manifolds that are not merely deformations of the unperturbed energy manifolds, there are possibilities for the choice of γ which do not exist in the unperturbed system. Hence, the quantum number k in (4.22) can be unrelated to n in (4.21). In Fig. 7, $k=0$ refers to the circle with area $2\pi\hbar(\frac{1}{2})$, then $k=1$ to that with area $2\pi\hbar(\frac{3}{2})$, and so forth [29].

The semiclassical quantum number k that appears in (4.22) is the same number that has been introduced in (4.16). For example, the "ground state" $k=0$, corresponding to the innermost quantized circle in Fig. 7, is associated with the characteristic value a_0, which yields an even Mathieu function with one lobe. In a quasienergy spectrum, this ground state is the highest member of a resonant "fan;" the excited states with higher values of k lie successively *below* the ground state [see Fig. 8(b)]. This inversion is explained by the fact that the effective mass M of the Mathieu excitations is negative, since the unperturbed energy spacing decreases with increasing energy.

Thus our example of a π pulse which led to a transition from $n=0$ to 5 involves Mathieu excitations with $k=4$ and 5. More generally, a transition between n-states i and f requires neighboring Mathieu states $k=f-i$ and $k=f-i-1$. This has an important consequence. In order to mediate such a quantum transition, the resonance in the corresponding classical phase space has to be large enough to allow the semiclassical construction of a state with $k=f-i$, i.e., the area covered by the resonance should be at least $2\pi\hbar(f-i+\frac{1}{2})$. Thus the magnitude of the classical resonance determines the magnitude of the possible "quantum jump" $f-i$. This fact finally explains the distinguished role of the resonance with the frequency ratio $\Omega(I_{\rm res}):\omega=1:1$. There are other resonances for different rational frequency ratios, but their areas are, generally, (much) smaller at equal values of the field strength F [21]. Or, expressed differently, if it is possible at all to construct a generalized π pulse with a frequency that does not correspond to the 1:1 resonance, such a pulse might require unrealistically strong fields.

To finish this section, let us sum up. The instantaneous quasienergies, which determine the quantum phases of interfering Floquet states in a strong resonant laser pulse, can be understood by a semiclassical quantization of classical resonant phase-space structures, and are well approximated in terms of characteristic values of the Mathieu equation. For weakly anharmonic systems, like

the Morse oscillator, the classical 1:1 resonance is usually the largest, which implies that a frequency which couples initial and final quantum states i and f by $f-i$ photons is the best choice for a generalized π pulse.

V. COMPOSITION OF π PULSES AND FURTHER EXTENSIONS

If the distance (in quantum number) between initial and target states is too large, there is no π pulse for selective excitation, but careful numerical simulations [30–32] have shown that there is a simple possibility to bypass this problem. If a transition from, say, $n=0$ to 10 cannot be achieved in a single step, it may still be possible to use two laser pulses, a first one to induce the transition from $n=0$ to a suitable intermediate state, e.g., $n=5$, and then a second one to populate the target state [31]. In our language, both pulses must be π pulses, each of them tailored to one of the transitions.

It is remarkable that π pulses can be contracted. Although the excitation process is clearly divided into separate steps, a second pulse can start before the first one is over [30–32]. An example for this is given in Fig. 9, where we have used the model of the Morse oscillator with HF parameters again to study the excitation of the state $n=9$. First, the π pulse from Sec. III is used to populate $n=5$, then a second π pulse with frequency $\omega_2=(E_9-E_5)/4$ and envelope (3.2) excites the target. (Parameters for the second pulse are amplitude $F_{\max,2}=0.0142$ a.u., and pulse length $t_{p2}=100\times 2\pi/\omega_2$, corresponding to 1.175 ps.) The overlap of both pulses is 0.4 ps, i.e., the second pulse starts 0.4 ps before the first one finishes [Fig. 9(a)]. The differences $\varepsilon_5^F-\varepsilon_0^F$ and $\varepsilon_9^F-\varepsilon_5^F$ for the individual pulses are displayed in Fig. 9(b). The area under both curves is exactly equal to $\hbar\cdot\pi$, which manifests that both pulses really are π pulses. Figure 9(c) shows the populations of the Floquet states involved in the dynamics. The pattern for the first and second pulse is the same. Thus, although both pulses overlap significantly, they still act independently.

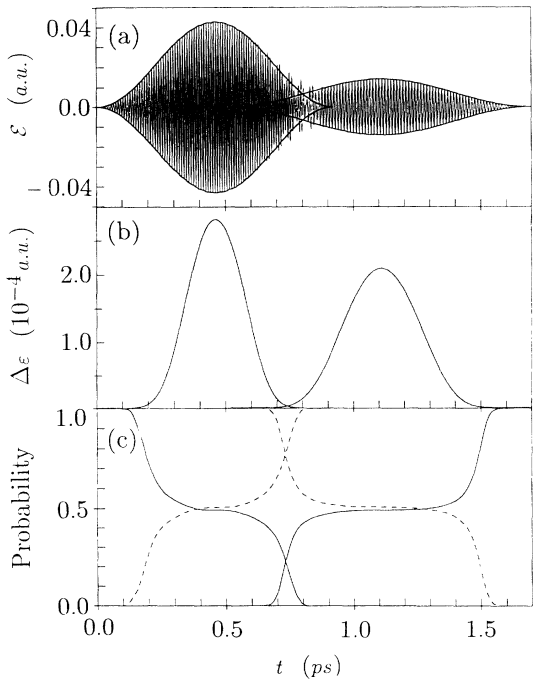

FIG. 9. (a) Overall electric field $\mathcal{E}(t)$ for a laser pulse composed from two π pulses for the transitions $0\rightarrow 5$ and $5\rightarrow 9$; the overlap is 0.4 ps. (b) Differences of the instantaneous quasienergies for the individual pulses. The area under each of the two curves is equal to $\hbar\cdot\pi$. (c) Occupation probabilities of the Floquet states involved in the excitation dynamics.

In a first approximation, this phenomenon can again be explained in terms of the instantaneous quasienergy spectra for the two independent pulses. The quasienergetic degeneracy for the second pulse is removed only in the fourth order of the instantaneous field strength F, that for the first pulse even only in the fifth order. Hence, as long as the field strengths are small, the relevant quasienergy differences are almost equal to zero; the interfering Floquet states collect their relative phases only in the strong-field regime. In a manner of speaking, the low-field regime is irrelevant. As long as the rising amplitude of the second pulse remains so weak during the overlap period that it does not influence the low-field degeneracy of the fading first one, both pulses are dynamically independent, regardless of whether or not they are partially superimposed.

In Fig. 10 we show the excitation probability of the target $n=9$ as a function of the pulse overlap. Up to an overlap of 0.42 ps the partial superposition has no effect, and a practically complete excitation of the target remains possible.

A thorough theoretical analysis of this example, however, requires a more elaborate approach. Quasienergies can also be introduced if a quantum system interacts simultaneously with two laser fields. Let H_0 be the Hamiltonian of the unperturbed system, and μ its dipole function. We follow the strategy of Sec. III and first "freeze" the two envelope functions $F_1(t)$ and $F_2(t)$ at some instantaneous values F_1 and F_2. The total Hamiltonian is then given by (we do not explicitly indicate spatial dependencies)

$$H(t)=H_0-F_1\mu\cos(\omega_1 t)-F_2\mu\cos(\omega_2 t+\delta)\ . \qquad (5.1)$$

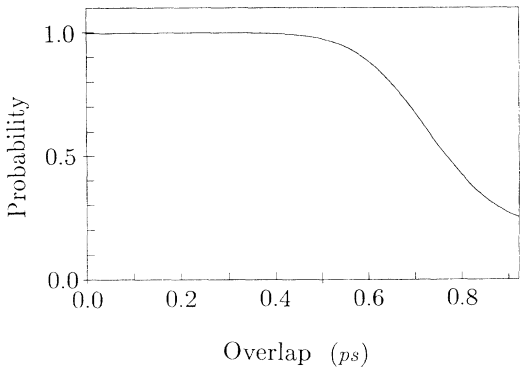

FIG. 10. Resulting excitation probability of the target state $n=9$ after compositions of two π pulses, as function of their overlap.

For simplicity we assume that the two frequencies ω_1 and ω_2 are not rationally related; δ is a relative phase. If we now introduce two *independent* time variables t_1 and t_2, we can employ the Floquet theorem to deduce that the equation

$$[\tilde{H}(t_1,t_2)-i\hbar\partial_{t_1}-i\hbar\partial_{t_2}]\tilde{\psi}(t_1,t_2)=0\ , \tag{5.2}$$

with

$$\tilde{H}(t_1,t_2):=H_0-F_1\mu\cos(\omega_1 t_1)-F_2\mu\cos(\omega_2 t_2+\delta) \tag{5.3}$$

has solutions of the form

$$\tilde{\psi}(t_1,t_2)=\tilde{u}(t_1,t_2)\exp(-i\varepsilon_1 t_1/\hbar)\exp(-i\varepsilon_2 t_2/\hbar)\ , \tag{5.4}$$

where the functions $\tilde{u}(t_1,t_2)$ are periodic in both t_1 and t_2:

$$\tilde{u}(t_1,t_2)=\tilde{u}(t_1+T_1,t_2)=\tilde{u}(t_1,t_2+T_2)\ , \tag{5.5}$$

with $T_j=2\pi/\omega_j$, $j=1$ and 2. The importance of this statement rests in the fact that the restrictions

$$\psi(t):=\tilde{\psi}(t,t) \tag{5.6}$$

solve the "original" Schrödinger equation

$$[H(t)-i\hbar\partial_t]\psi(t)=0\ . \tag{5.7}$$

It follows that we can formulate the eigenvalue problem

$$[H(t)-i\hbar\partial_t]u(t)=\varepsilon u(t) \tag{5.8}$$

with $\varepsilon=\varepsilon_1+\varepsilon_2$ [see (5.4)] and quasiperiodic boundary conditions, i.e., the eigenfunctions $u(t)$ have to be restrictions of doubly periodic functions to the diagonal, $u(t)=\tilde{u}(t,t)$. These eigenvalues ε and functions $u(t)$ are the instantaneous quasienergies and Floquet states for the two-frequency problem.

As usual, there is an adiabatic principle associated with this eigenvalue equation. If either amplitude F_1 and F_2, or both, varies slowly compared to T_1 and T_2, a system initially in a Floquet state will remain in the connected state and acquire a phase which is equal to the time-integrated instantaneous quasienergies. Thus it is straightforward to extend the method of "adiabatic guidance" to the case of two (or even more) laser fields. First the quasienergy surfaces $\varepsilon(F_1,F_2)$ have to be computed, then optimal envelopes $F_1(t),F_2(t)$ can be determined. In particular, it is in general *not* necessary to separate the two pulses, as in the previous example of composed π pulses. On the contrary, the simultaneous action of two strong laser fields can open up further possibilities for a controlled quantum-mechanical population transfer, which need to be studied in detail.

VI. DISCUSSION

The concept of π pulses, well known from two-level systems interacting with pulses of monochromatic radiation, can be extended to multilevel systems. The generalized π pulses provide instructive examples how strong laser fields can be used to manipulate quantum dynamics in a controlled manner. Although the two-state nature of the underlying excitation mechanism is not immediately obvious, it becomes clear after a transformation to a basis of instantaneous Floquet states. The generalized area theorem (3.7) does not refer to the "area under the pulse shape," but to a time-integrated difference of instantaneous quasienergies. Nevertheless, the spirit of the derivation of this result is the same as in the well-studied case of a two-level system. Moreover, there are the same possibilities for systematic pulse shaping. The semiclassical analysis of the resonance condition leads to approximation (4.20) for the quasienergies. This is a general result which holds not only for the Morse oscillator, but for arbitrary nonlinear, periodically forced systems. Correspondingly, the mechanism of generalized π pulses is universal, rather than system specific. It is important to realize the nonperturbative character of this mechanism. The external laser field is so strong that it does not merely shift the energy levels of the unperturbed system, but it alters the level structure to such an extent that new quantum numbers have to be introduced.

Our idealized discussion did not take into account several experimental problems. For example, in a laboratory experiment not all molecules will be exposed to the same laser field, either because of their random orientation or because of the spatial inhomogeneity of the intensity in a focused beam. Thus some molecules might experience fields which satisfy the condition for constructive interference, others might interfere destructively. But even then, each molecule would either remain in its initial state, or undergo a transition to the target state, but the population would not spread over other levels.

If a transition between distant states cannot be induced by a single π pulse, the process can be divided into smaller steps [30]. The π pulses for individual transitions can then be combined without any need for a phase relation between them, and they can partially be contracted without losing their individual effects. But the governing principle behind the generalized π pulses, namely adiabatic response of Floquet states, remains valid even when two (or more) strong laser pulses act simultaneously. It remains to be seen whether this fact can lead to even more efficient excitation schemes.

The numerical results of the present work are less important than the way in which they are interpreted. The Morse system is certainly too simple to describe the dynamics of real molecules in strong laser fields, but the strategy of dividing the problem into static (the computation of the instantaneous quasienergy "surfaces") and dynamic (the quantum evolution on these surfaces) parts is general. It would certainly be illuminating to discuss the dynamics of more realistic model systems with several degrees of freedom, including vibrational-rotational coupling, from this point of view.

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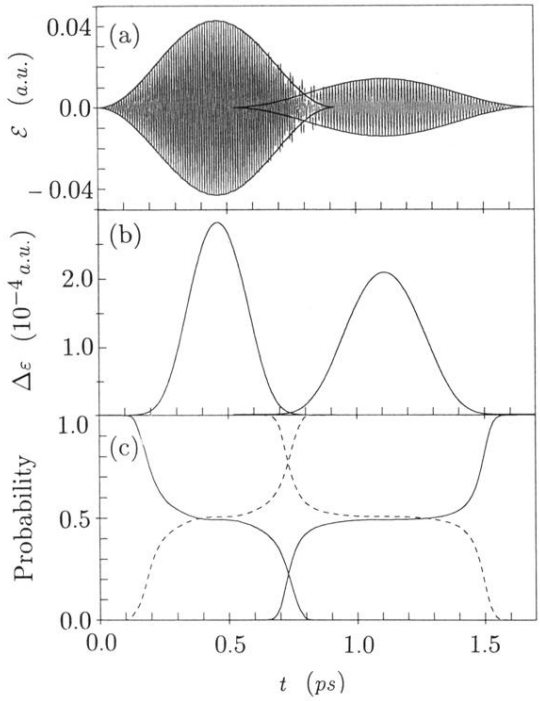

FIG. 9. (a) Overall electric field $\mathcal{E}(t)$ for a laser pulse composed from two π pulses for the transitions 0→5 and 5→9; the overlap is 0.4 ps. (b) Differences of the instantaneous quasienergies for the individual pulses. The area under each of the two curves is equal to $\hbar\cdot\pi$. (c) Occupation probabilities of the Floquet states involved in the excitation dynamics.