Counterdiabatic suppression of background state population in resonance leaking by controlling intermediate branching

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The counterdiabatic principle [M. Demirplak and S. A. Rice, J. Phys. Chem. A **107**, 9937 (2003)] is used in a pragmatic way to formulate a practical control strategy for perturbed population transfer. Interpreting the appearance of population in undesirable intruder or background states as phenomenological consequences of diabatic perturbations, such branching is suppressed as soon as it arises. By invoking a penalty term that is sensitive to any transitional population in undesirable levels, a correction field is created which *effectively* prevents diabatic behavior. This strategy is applied to the control of background state population in multiphoton excitations. For a model five-level system we show that leaking of a resonant three-photon transition to a background state can readily be suppressed by simple correction fields obtained from our intermediate-branching driven implementation of counterdiabatic control. *© 2006 American Institute of Physics*.
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I. INTRODUCTION

Leaking to background states can strongly quench resonant state-to-state molecular multiphoton excitation.[1] Under suitable conditions, even very weakly coupled background "intruder" states may draw population away from the target state, so that the target state population may become very small.[2,3] Furthermore, if the transition to the background state occurs through a lambda (Λ) configuration, the leaking process can be fairly robust.[3] Such a situation can arise if the resonance frequency of a primary multi- ($n-$) photon transition is degenerate or near degenerate with a resonant ($n+1$) photon transition to the intruder state (n photons absorbed, one photon emitted). Under the conditions of resonance leaking, a π pulse,[4] while still effecting complete depletion of the initial state, in general, will prepare a superposition state including target and intruder states, and possibly other intermediate levels.

The fact that resonance leaking involves overlapping or merging resonances implies that interference effects can be employed to control the multiphoton transition and to suppress leaking to the intruder state. We have previously described two control strategies using appropriately phase-adjusted pulse pairs,[3] an *a posteriori* "control-by-repair" method, pumping intruder population back to the target state well after the end of the first pulse, and a constructive method, employing interfering fractional π pulses.

In the present paper we explore an alternative strategy adapted from the counterdiabatic (cd) paradigm introduced by Demirplak and Rice[5,6] (see also Ref. 7). The paradigm asserts that for a given molecule-field system, to a first approximation an adiabatic transfer mechanism can be formulated within a suitable dynamic, i.e., time- and field-dependent basis set, and that a phase sensitive correction field can remove actual deviations from adiabatic passage along the transfer state caused by nonadiabatic transitions. This cd correction reestablishes adiabatic behavior at all times, giving rise to population transfer by "assisted adiabatic passage," with its associated advantages, in particular, its robustness with respect to field variations.

For two-level systems and selected three-level systems, explicit expressions for cd correction fields have been derived in Refs. 5 and 6; however, as the authors note, these solutions may not always be practical ones. For general N-level systems, analytic expressions or even suitable dynamical basis sets may be hard to obtain, and cd corrections will have to be found by other means, reverting in effect to guided numerical optimization. Similar considerations apply to purely experimental situations. In any case, the determination of practical control fields that retain at least some of the virtues of a full cd correction can be a useful alternative to straightforward pulse optimization.

We take the route towards control fields based on a pragmatic interpretation of the cd principle in two steps. Noting first that cd control fields have been shown to be reasonably robust,[6] we assert that control fields fairly close to exact cd ones may be obtained by constrained optimization of trial fields, provided that the latter are reasonably well chosen. For a concrete model system, dressed states can be constructed, diabatic perturbations can be located as crossings or avoided crossings in the dressed state energy correlation dia-

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grams, and trial fields can be placed into the intervals containing diabatic perturbations. Otherwise, the phenomenological consequences of the diabatic perturbations, notably transitional effects in the population dynamics, have to be addressed. Exerting control on this phenomenological level, the trial correction fields should be localized in the time intervals of perturbed dynamics, heralded by undesirable population branching, and their driving frequencies should be related to the branching transition(s). Pulse optimization can then be effected by maximizing the target population at the *end* of the pulse under a constraint, penalizing any undesirable *intermediate or transient* population, e.g., intruder or background state population.

In this paper, we demonstrate the successful application of the two methods of obtaining approximate cd correction fields by controlling intermediate branching to the suppression of background state population in a model five-level system (5LS). In Sec. II we introduce the 5LS, give a brief account of the theoretical and numerical backgrounds of our investigations, and analyze the dynamics of the leaking π-pulse transition in terms of quasienergy correlation diagrams obtained from adiabatic Floquet analysis.[8,9] In Sec. III our strategies to obtain approximate cd control fields are presented and discussed. First in Sec. III A we describe the construction of correction fields based only on information on the positions of crossings in the quasienergy correlation diagrams (denoted as "avoided-crossing related method" of obtaining approximate cd correction fields). Noting that such information may not be available in realistic situations, in Sec. III B we deal with the purely phenomenological variant of obtaining cd corrections and derive control fields from information on the population dynamics alone ("population-branching related method"). In both cases, in a first step we restrict the control fields to simple analytical pulse forms, which are adjusted by parameter optimization. If necessary, the control strategy can be extended to a two-step setup, further improving the analytical control fields by constrained optimal control.[10–13] Our paper ends with some conclusions and a summary given in Sec. IV.

II. THEORETICAL AND COMPUTATIONAL BACKGROUND

A. Model system and calculations

The model 5LS used to investigate resonance leaking is taken from Ref. 3. The level scheme consisting of a four-level Morse progression, states $|1\rangle$–$|4\rangle$, and a background (intruder) state $|5\rangle$ attached to the top Morse level in Λ configuration is shown in Fig. 1.[14] Also indicated are the parametrized dipole couplings. All remaining elements of the dipole matrix are zero, so that there are no overtone couplings along the progression. The parameters are adjusted from those for the bend progression of the HCN molecule, where the phenomenon of resonance leaking was observed in simulations of a realistic molecular system.[2]

In our simulations, the interaction of this 5LS with a laser pulse is described by a semiclassical molecule-field Hamiltonian, and the corresponding time-dependent Schrödinger equation is solved in the energy representation.

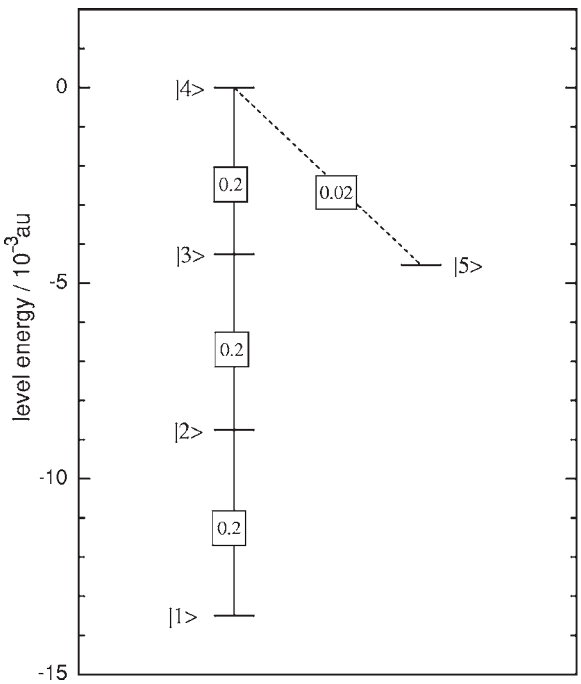

FIG. 1. The model five-level system. The dipole matrix elements (in a.u.) coupling neighboring levels are shown in the boxes. The background (intruder) state $|5\rangle$ is coupled weakly to the top of the strongly sequentially coupled anharmonic progression $|1\rangle$–$|4\rangle$.

A suitably polarized Gaussian π pulse[15–17] driving resonantly a multiphoton transition has the field strength,

$$E_\pi(t) = A_\pi \exp[-(t-T/2)^2/\sigma_\pi^2]\cos(\omega_\pi t), \tag{1}$$

where the parameters A_π and ω_π denote resonance conditions for a given pulse length specified by σ_π. Integration of the Schrödinger equation is performed over the time interval $[0,T]$. Setting $T=2.6\sigma_\pi$ (=3.125 times the full pulse width at half height, FWHH) ascertains that $E_\pi(t)$ is negligibly small for $t<0$ and for $t>T$. The same relative integration limits are used for all control fields described later in this paper.

B. Resonance leaking in the model system

In the model 5LS, for driving pulses in the picosecond range the three-photon transition (3-PT) from the initial state $|1\rangle$ to the target state $|4\rangle$ is affected by strong resonance leaking. In the present work, our reference case is a resonant Gaussian pulse with a FWHH of 2.92 ps. As shown in Fig. 2(a), such a pulse, given by Eq. (1) with amplitude A_π=0.001 261 a.u. and carrier frequency ω_π=0.004 500 527 a.u., populates the target state $|4\rangle$ and the intruder state $|5\rangle$ to 50% each. If by setting $\mu_{45}=0$ the intruder state is fully decoupled, the 3-PT in the resulting effective four-level system (4LS) induced by E_π is complete and smooth. This fairly unperturbed Rabi-type[4,15–17] three-photon π-pulse excitation with sinusoidal population dynamics represents the unperturbed "adiabatic" dynamics to be reestablished in the coupled system by a cd correction field.

Looking at the population dynamics for both cases in Fig. 2(a), we can infer that resonance leaking in the coupled 5LS occurs by depletion of the intermediately formed target population, so that overall the leaking process resembles a

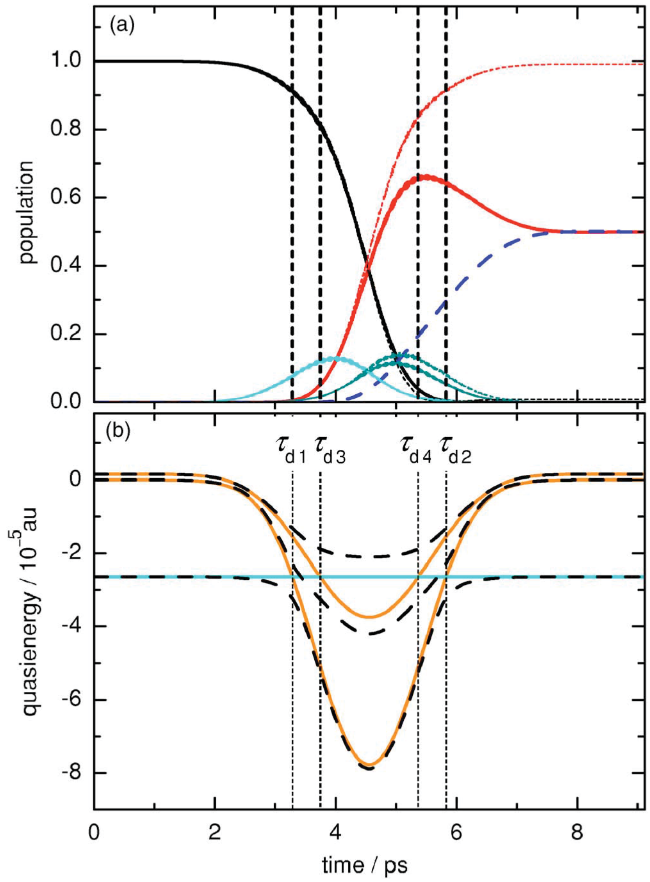

FIG. 2. (a) Population dynamics in the model five-level system induced by the resonant Gaussian π pulse (E_π). Short-dashed thin lines: reference adiabatic dynamics in the intruder state decoupled effective four-level system. Bold lines: leaking dynamics in the fully coupled system. The individual states are indicated. Intruder population is dashed for highlighting. (b) The corresponding adiabatic Floquet quasienergy correlation diagrams. Full lines: intruder state $|5\rangle$ decoupled (adiabatic); broken lines: fully coupled (diabatic). Asymptotic states are indicated near the right margin.

(3+1)-PT along a strongly anharmonic progression. We also note that the reference case itself shows small perturbations in form of some transitional population in the intermediate levels $|2\rangle$ and $|3\rangle$.

The relevant section of the quasienergy correlation diagrams from an adiabatic Floquet analysis[8,9] is shown in Fig. 2(b). The dressed states of the uncoupled system (full lines) provide a basis for describing the 3-PT. The two energy levels corresponding asymptotically to the initial state and the target state give rise to the adiabatic transfer state. They intersect the fully decoupled intruder state at the four crossing points $\tau_{d\,1}-\tau_{d\,4}$. In the coupled system, these crossings turn into avoided ones, giving rise to the new states shown as dashed lines, which are diabatic in terms of the uncoupled basis, all with strong contributions from the intruder state.

Several strong-field control schemes have been proposed to deal with such avoided crossing situations,[18] enforcing either some form of adiabatic passage,[19] or admitting nonadiabatic transitions and using coherent control[20] between the interfering parallel pathways (nonadiabatic passage[21]). The counterdiabatic strategy[5–7] is to reestablish dressed states resembling those for the uncoupled system [full lines in Fig. 2(b)] and to drive population transfer adiabatically in this basis ("assisted adiabatic passage").

C. Optimization of the control fields

In the construction of the control field, two facets have to be considered. The ultimate goal is to maximize the target population P_{tar} (P_4 in our example) at the end of the pulse, i.e., at time T. Among different possible control fields, our phenomenological implementation of a cd correction aims at quenching intruder state population P_{int} (P_5 in our example) at all times. In this spirit, we optimize the control field by minimizing the target function V,

$$V = -P_{\text{tar}}(T) + \lambda_{\text{int}} I_{\text{int}}, \tag{2}$$

which is a function of all adjustable parameters in (6) and possesses a possible global minimum of −1. The penalty term ($\lambda_{\text{int}} I_{\text{int}}$) contains the Lagrangian parameter λ_{int}, which can be preset to govern the balance between the two terms in (2), and I_{int} is the time-averaged intruder population,

$$I_{\text{int}} = T^{-1} \int_0^T P_{\text{int}}(t)\, dt, \tag{3}$$

In our optimizations, initially we obtain approximate cd correction fields $E_{\text{cd}}(t)$ composed from few simple pulses of Lorentzian or Gaussian form by optimization of the pulse parameters. Subsequent optimal control calculations performed to improve the control fields from step 1 start from the corrected total field $E_\pi(t)+E_{\text{cd}}(t)$. Standard methods of optimal control[15] are employed to obtain the control field E_{oc}. The objective function includes the intruder penalty term $\lambda_{\text{int}} I_{\text{int}}$ from Eq. (2), and we also include a penalty term $\lambda_{\text{fl}} T^{-1} F$ limiting the fluence $F=\int_0^T E(t)^2 dt$ of the control field.

III. RESULTS AND DISCUSSION

We now proceed to put the ideas laid out above into praxis and obtain approximate cd correction fields from indirect information on the diabatic perturbations of the multiphoton dynamics. In Sec. III A, we describe a strategy to obtain "avoided-crossing related" control fields by considering the crossings and avoided crossings in the dressed state energy correlation diagrams. In Sec. III B, we use only phenomenological information about the diabatic perturbations derived from the population dynamics to obtain "population-branching related" control fields. Optimal control based fields leaving the realm of cd corrections and giving rise to different mechanisms of excitation will be briefly described in Sec. III C.

A. Avoided-crossing related correction fields

The energy correlation diagrams in Fig. 2(a) suggest that reestablishing an approximately adiabatic transfer state requires the distortion of the diabatic states in the regions around avoided crossings. In line with the intended phenomenological approach, without employing a formal analysis (e.g., in terms of a generalized Floquet analysis[22]) we can infer that such distortions can be effected by introducing additional interactions generated by pulses placed close to the crossing points and strongly coupling the target state with the

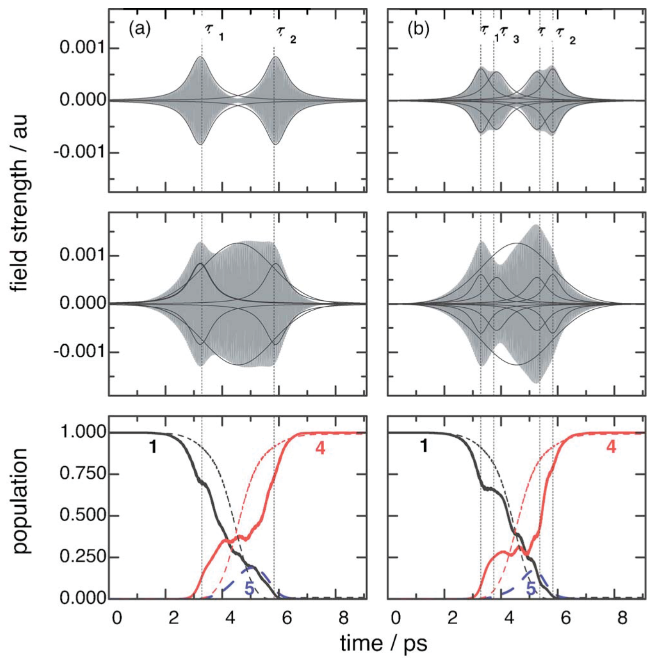

FIG. 3. Total control fields, correction fields, and associated population dynamics in the model five-level system for avoided-crossing related correction fields E_{cdac}. Column (a): two Lorentzian pulses placed at the crossing points $\tau_{d\,1}$ and $\tau_{d\,2}$. Column (b): four Lorentzian pulses placed at the crossing points $\tau_{d\,1}-\tau_{d\,4}$. The times $\tau_{d\,1}-\tau_{d\,4}$ are indicated as short-dashed vertical lines. Fields $E(t)$ are shown in gray; envelopes of their constituent fields are overlaid as black lines. Individual populations are drawn as in Fig. 2(b); intermediate state populations are omitted for clarity of presentation.

intruder state. Assuming Lorentzian envelopes, for n_d subpulses the ansatz for the avoided-crossing related, approximately cd correction field $E_{\mathrm{cdac}}(t)$ becomes

$$E_{\mathrm{cdac}}(t) = \sum_{i=1}^{n_d} \frac{A_i}{\gamma_i^2 + (t-\tau_i)^2} \cos(\omega_i t + \varphi_i), \tag{4}$$

with individual adjustable centers τ_i, amplitudes A_i, widths γ_i, carrier frequencies ω_i, and phases φ_i of the subpulses. Initially, the subpulses are centered at the crossings of the quasienergy states, so that $\tau_i = \tau_{di}$, and we set $\omega_i = \omega_{45}$ so as to ascertain strong coupling between target state and intruder state. Although these parameters are allowed to vary during the optimization, it turns out that they drift only marginally away from these input values.

Before discussing correction fields obtained with this approach, we note that other simple pulse forms, e.g., Gaussian ones, perform similar to Lorentzian pulses, but do show a somewhat inferior overall performance. In Fig. 3, we show some representative results for correction fields placed at avoided crossings. The following observations can be made. (1) There are only small differences between the correction fields with two pulses placed at the outer crossing points $\tau_{d\,1}$ and $\tau_{d\,2}$, and with four pulses placed at all four avoided crossings. (2) The correction fields successfully restore the 3-PT to the target state. (3) They do not fully restore the smooth population dynamics of unperturbed π-pulse excitation. In particular, there remains a noticeable amount of intermediate intruder population. (4) The fields in Figs. 3(a) and 3(b) are obtained with low weight of the penalty term $\lambda_{\mathrm{int}} I_{\mathrm{int}}$ ($\lambda_{\mathrm{int}}=2$). The intermediate intruder population can be well reduced by using larger values of λ_{int}, but only at the expense of the final target population.

Thus operationally our approach does provide control fields suppressing leaking to background states. However, they do not remove all transitional intruder population, as puristic cd corrections would do. We can now attempt to improve the Lorentzian correction fields by optimal control. In such runs, we observe two different types of behavior. On the one hand, enforcing complete suppression of intermediate intruder state population is a straightforward exercise, readily accomplished by the use of sufficiently large values of $\lambda_{\mathrm{int}} (>100)$. However, the results indicate that such success invariably is connected with global changes of the correction fields and with a radical change in the mechanism of excitation. We will discuss this case in Sec. III C. Conversely, invoking the constraint on the intermediate intruder population only mildly, keeping $\lambda_{\mathrm{int}} < 5$ so that $\lambda_{\mathrm{int}} I_{\mathrm{int}}$ contributes less to the objective function than the term involving the final populations, the local structure of the correction fields is retained, but there are only marginal improvements to the analytical fields shown in Fig. 3. It turns out to be hardly possible to quench the transient intruder population that way.

B. Population-branching related correction fields

If information on the dressed states are not available, the occurrence of diabatic perturbations has to be inferred indirectly. From Fig. 2(b), phenomenologically the onset of diabatic dynamics is indicated by the emergence of intruder state population. The cd principle, establishing adiabatic behavior at all times, then demands that by adding a correction field, all such population should be suppressed as it arises, or, to put it more pragmatically, should be driven back to the ladder states immediately. Noting that the steep and smooth rise of intruder population occurs in the time interval τ_{int} lasting from about 4.2 to 7.5 ps, this is the interval where the cd correction should be put into operation.

In view of the extended time interval over which the population-branching related, approximately cd trial correction field denoted E_{cdpb} will have to act, in order to adapt properly to the varying population dynamics it is likely to require increased flexibility. It is hence assumed to be a shaped pulse,

$$E_{\mathrm{cdpb}}(t) = A_p(t)\cos(\omega_p t + \varphi_p), \tag{5}$$

with carrier frequency ω_p, phase φ_p, and an unspecified envelope function tending to zero outside τ_{int}. For convenience in the parameter optimization, we approximate $A_p(t)$ as a sum of Lorentzian envelope functions,

$$A_p(t) = \sum_{i=1}^{n} \frac{s_i A_i}{\gamma_i^2 + (t-\tau_i)^2}. \tag{6}$$

The variables s_i are +1 or −1. Like all the other parameters in Eq. (6), including n, they are treated as adjustable optimization parameters.

Because of the anharmonicity of the system, $\omega_{45} = (\varepsilon_4 - \varepsilon_5)/\hbar$ is well separated from the three-photon resonance

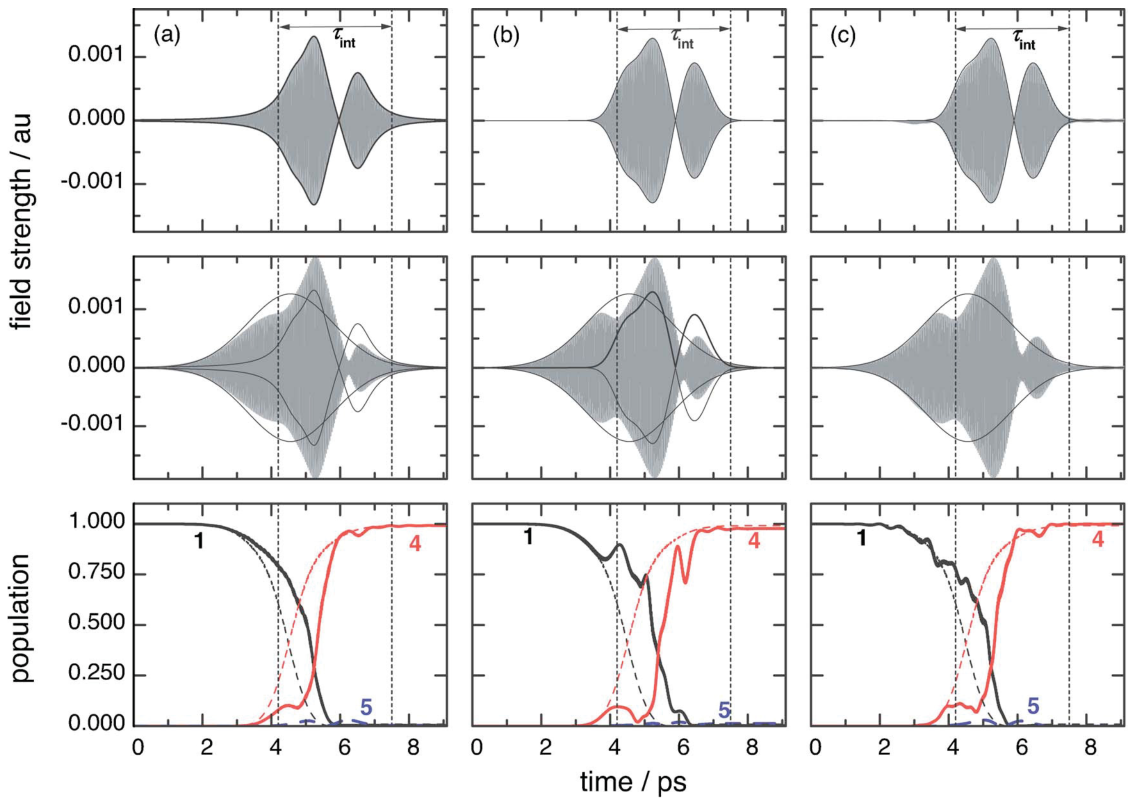

FIG. 4. Total control fields, correction fields, and associated population dynamics in the model five-level system for population-branching related correction fields. Column (a): the best analytically represented counterdiabatic control field E_{cdpb} obtained as a superposition of three Lorentzians put into the interval τ_{int} (see text). Column (b): similar to (a), but for a superposition of three Gaussians. Column (c): control field obtained by careful optimal control improvement of (b) (see text). The extension of τ_{int} is indicated by short-dashed vertical lines. All other graph properties are as in Fig. 3.

frequency ω_r, and hence $\omega_p = \omega_{45}$ is again an obvious first guess for pumping the 1-PT $|5\rangle \rightarrow |4\rangle$ without repopulating the ladder states. Using this starting value together with $n = 3$, we arrive at the control field E_{cdpb} shown in Fig. 4(a). This correction restores the target population close to 100% and quenches the intermediate intruder population to a very large extent, in fact, almost quantitatively.

The residual intruder population averages to less than 0.002, with peak values below 0.03. As for the fields derived in Sec. III A, the complete removal of this residual population, which in the present system is very small, can be enforced by optimal control with sufficiently large values of λ_{int}. Although only minute changes in the population dynamics would be required, this strategy is only successful if the control fields are changed drastically and globally. The corresponding transfer mechanism is the same one already found for enforced optimization of avoided crossing related control fields (Sec. III A), and will be described in the following subsection.

Note that in order to represent E_{cdpb} we have also used other simple pulse forms, in particular, Gaussians. Such control fields give rise to similar but somewhat inferior results than the ones obtained for sums of Lorentzians. The consistency of our approach is demonstrated by the fact that subjecting such "best" sum-of-Gaussian fields to mildly constrained optimal control leads to correction fields closely matching the best Lorentzian combination E_{cdpb} described above and shown in Fig. 4(a). The complete example is illustrated in Fig. 4. The optimal control cycle mainly adds more pronounced tails to the Gaussian fields, indicating that the cd correction requires a sufficiently slow decay of the field amplitude.

Comparing the approximately cd fields obtained from the avoided-crossing related method in Fig. 3 with those from the population-branching related ones in Fig. 4, we see that on a purely operational level, both methods are successful in mending the leaking resonance, populating the target state quantitatively and suppressing background state population partially (E_{cdac}) to effectively completely (E_{cdpb}). The correction fields returned by the population-branching related method obey the constraint of intermediate intruder state suppression very well and look to be closer to true cd correction fields.

C. Enforced removal of transient intruder state population

As described in the two previous subsections, the complete removal of intermediate intruder population by "brute-force" optimal control is invariably connected with *global* changes of the control field. These changes affect all pulse stages, even those where no diabatic perturbations are occurring in the first place, implying an associated switch to a drastically different transfer mechanism. In Fig. 5, both the population dynamics and the Fourier spectra of such brute-force optimized control fields, which otherwise fulfill the specifications of maximizing $P_{tar}(T)$ and removing $P_{int}(t)$ completely, reveal that 1-PTs between the states along the

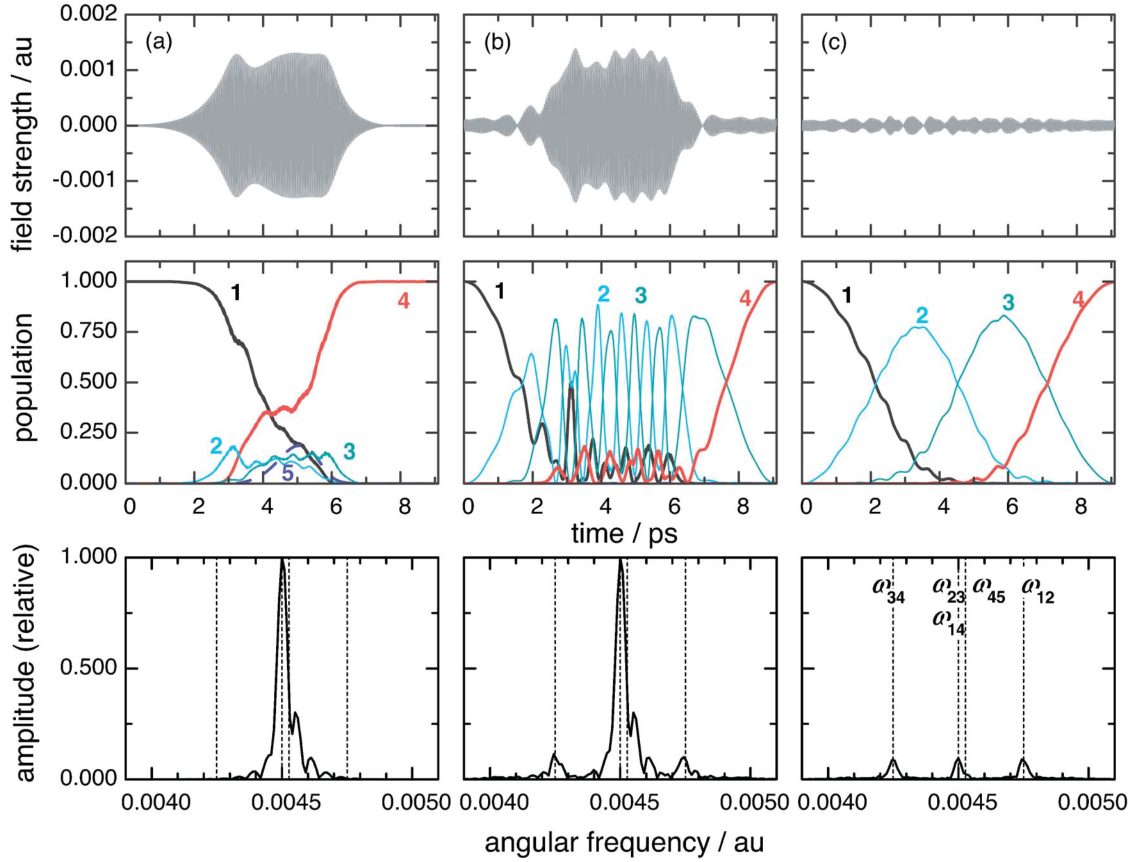

FIG. 5. Control fields obtained by brute-force optimal control, and corresponding Fourier spectra and population dynamics. The short-dashed vertical lines at 0.004 25, 0.004 50, and 0.004 75 a.u. shown in the panels in the middle row indicate the zero-order 1-PT frequencies ω_{34}, ω_{23}, and ω_{12} along the anharmonic ladder. The 3-PT frequency ω_{14} coincides with ω_{23}. The lines near 0.004 527 a.u. indicate the target-intruder transition frequency ω_{45}. Column (a): E_{cdpb} from Fig. 4(a) used as input field. Column (b): control field obtained from (a) by optimal control with strong reduction of $P_{\mathrm{int}}(t)$ ($\lambda_{\mathrm{int}} > 100$, variable in several iterations). Column (c): control field obtained from (b) with strong fluence reduction ($\lambda_{\mathrm{fl}} > 100$, variable in several iterations). Other graph properties are as in Fig. 3.

anharmonic ladder are now dominating the mechanism.

Since the initial fields drive 3-PTs and carry much higher intensities than those required for simple π-pulse 1-PTs, control fields obtained from optimal control consist of intertwined multi π pulses giving rise to strongly oscillatory population dynamics from repeated upwards and downwards 1-PTs involving the states $|1\rangle$–$|4\rangle$. Reoptimizing such control fields under a severe constraint on the fluence ($\lambda_{\mathrm{fl}} > 100$), all optimal control runs are ultimately driven towards a control field consisting of three separate consecutive π pulses driving sequentially the 1-PTs $|1\rangle \rightarrow |2\rangle \rightarrow |3\rangle \rightarrow |4\rangle$ along the anharmonic ladder. Note that after the first few cycles these control fields are practically identical irrespective of the startup field.

By construction of our simplistic model 5LS, the unperturbed sequential 1-PT to the target state is available as an obvious mechanism of excitation. In general, in more complex systems this route will be less readily accessible. Anyway, a switch to this mechanism does not correspond to a cd correction, the idea behind the cd principle being not the spotting of a deviation around, but the removal of a perturbation.

IV. SUMMARY AND CONCLUSIONS

In this paper we took a look at the adaptation of the cd paradigm[5–7] as a practical control strategy for molecular population transfer processes. We gave a reinterpretation of the cd principle as a tool using a time-local control strategy to avoid undesirable branching in the field-induced population dynamics. By construction, our control fields are only approximately counterdiabatic. That means that the actual overall mechanism to some degree will still include nonadiabatic transitions. The optimization step of our method guarantees that their contributions are properly controlled by interference; however, this part of the mechanism will not become transparent.

Our pragmatic implementation of the cd principle responds to the phenomenological consequences of diabatic perturbations rather than addressing the perturbations themselves. In this sense it is a useful control strategy on the operational level, relying on suitably constrained optimization rather than theoretical inversion. The approach, building at least in principle on observable properties, may thus be amenable to closed loop implementations of optimal control.[23–25] Time-local suppression of undesirable branching may be a readily available building block in feedback control techniques.

An application of our methods has been made to the control of background state population in resonance leaking. Within a five-level model system with parameters mimicking bend excitation in HCN, which by construction shows strong resonance leaking for a 3PT, the objective of quenching background population is readily fulfilled by our strategy. A control field consisting of optimally adjusted Lorentzian pulses placed at the crossing points of quasienergy correlation curves suppresses background population very efficiently, although the adiabatic mechanism of a direct resonant multiphoton transition is not fully restored (avoided-crossing related cd). In our principal method of population-branching related cd, control suppressing transient intruder state population near quantitatively can be achieved by fields consisting of few Lorentzian pulses or other simple pulse forms. Final touches by optimal control theory with suitably defined penalty functions can further improve these control fields. For the model system investigated in this paper, such improvements are hardly necessary, and full control is obtained using simple pulse forms, while in more complex systems improving analytical correction fields by optimal control may be a more important issue. In addition, our phenomenological implementation points to distinct relations between cd control and local optimal control,[26] and thus for a more versatile variant of this strategy it will be appropriate to employ local optimal control algorithms. Work on the application of such control strategies to realistic molecular *N*-level systems is currently in progress.

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