PHYSICAL REVIEW LETTERS

Quantum-Control Spectroscopy with Exact State Selectivity

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A method of exact state-selective spectroscopy is introduced, based on quantum control through four specific short laser pulses. The exact conditions for the two pairs of ultrafast pulses are set by the feedback control for selective excitation to one specific resonance state while the other state is destructively interfered as the shadow pair, leading to a state-selective spectrum.

Laser control of atomic and molecular processes has recently emerged as an important topic of science and technology [1]. This is basically because the inventions of the short pulse laser and pulse-shaping techniques have enabled the utilization of laser field coherence for effective control. From a theoretical point of view, control is a problem of finding an external field necessary to achieve the desired results based on knowledge of the system. From an experimental point of view, on the other hand, the optimal external field for control can be found even without previous knowledge of the system, if the fitness for optimization can be obtained directly from experimental results. The idea of feedback control proposed by Rabitz and co-workers [2] has been experimentally realized by many groups [3–5] utilizing computer programmed pulse shapers [6,7] with learning algorithms. The optimal field experimentally obtained through feedback control should contain information about the system that may allow us to obtain spectroscopic data that would be hard to obtain by conventional methods of spectroscopy. In this Letter, we introduce a new spectroscopic method that utilizes laser coherence with feedback control to realize exact state selectivity. This is valid for both time-resolved spectroscopy and the spectroscopy of short-lived resonance states. Since state selection and energy selection are different concepts, we find that state selection in a short time is possible even when the energy uncertainty is much greater than the energy spacing between the states. In our method, optimal conditions for a pulse train to achieve zero total excitation probability are searched for by feedback control scheme. It is proved that the obtained parameters provide the conditions for a pulse train to achieve ultrafast state-selective pumping. This leads to separate signals from individual (resonance) excited states. This does not break the uncertainty principle, because it does not require measurements of the selectivity to find the conditions for selective pumping. Conventional spectroscopy requires the analysis of a mixture of signals from the states within the energy broadening due to the finite lifetimes of resonance states. Our new method of spectroscopy, on the other hand, relieves us from the difficulty in the analysis and is expected to open new possibilities in spectroscopy, provid-

ing detailed knowledge of various kinds of resonance states or ultrafast dynamical processes. Such knowledge may be regarded as experimentally impossible to obtain thus far.

The key to our spectroscopic method is to find a pulse train to achieve state-selective pumping, which leads to state-selective spectroscopy. State-selective pumping is achieved by a pulse train constructed by the combination of *shadow pairs*. We define a shadow pair as a pair of laser pulses designed to suppress the excitation to a selected closely lying resonance state and to allow transitions to the other states. The conditions for a shadow pair leads to the position and width of the resonance state to be suppressed. It is a very difficult task, however, to find the shadow pairs by feedback control because we cannot obtain the selection ratio from the spectroscopic signal, especially in the case of overlapping resonance. Instead of using shadow pairs, we search for a *dark pulse train* that is designed to achieve vanishing total excitation probability, since the total excitation probability can easily be measured. As is intuitively understood, a dark pulse train can be constructed by combination of shadow pairs. We prove below that a dark pulse train with specific constraints can be constructed *only* by combining shadow pairs. Consequently, the search for a dark pulse train by feedback control yields a condition for shadow pairs that allows state-selective spectroscopy. In a quite different context, a set of laser pairs has been considered to provide coherent control over computer feedback to accomplish the phase-space cooling of atoms [8].

As a simple example, let us take the nondegenerate three-state system A, B, C, whose eigenenergies are E_A, E_B, and E_C, respectively. When an excited state X ($X = B, C$) decays in a finite lifetime, the eigenenergy has the imaginary part $E_X = \varepsilon_X + i\Gamma_X/2$. Here we assume that the decay process does not involve the other two states. From the fact that the time propagation of the probability amplitude of the state X is given by $e^{iE_X t}$, it is easily seen that the population decays exponentially due to the imaginary part of E_X.

Our spectroscopy requires us to find a dark pulse train composed of four pulses with the common central frequency ω and temporal profile $F(t)$ of the electric field given by

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$$E(t) = \sum_{i=1}^{4} A_i F(t - \tau_i) e^{i(\omega t + \sigma_i)}, \qquad (1)$$

where A_i, τ_i, and σ_i are the peak amplitude, irradiation time, and the initial phase of the ith pulse, respectively. Assuming that the bandwidth of each pulse is broad enough to excite both excited states B and C and that the system linearly responds to the irradiation, the probability amplitude of the excited state X ($X = B, C$) at time t (after the irradiation of the pulse train) is given by

$$c_X(t) = \sum_{i=1}^{4} C_{X,i}(t). \qquad (2)$$

Here $C_{X,i}(t)$ represents the transition amplitude of the excited state X created by the irradiation of the ith pulse, given by

$$C_{X,i}(t) = \alpha_X A_i e^{-iE_X(t-\tau_i)} e^{-i(\omega \tau_i + \sigma_i)} e^{-iE_A \tau_i}, \qquad (3)$$

where the initial time is 0, and α_X is a constant depending on the transition dipole moment and the temporal profile $F(t)$. Here and in the following, units have been chosen such that $\hbar = 1$, unless otherwise stated. The three exponential factors in Eq. (3) respectively represent the time propagation on state A before irradiation, the additional phase due to the irradiation of the ith pulse, and the time propagation on the state X after irradiation. The pulse train given by Eq. (1) is a dark pulse train if and only if

$$c_B(t) = c_C(t) = 0. \qquad (4)$$

We demand the constraints on the pulse train in such a way that the time delay, the initial phase difference, and the ratio of the peak intensity between the first and second (third) pulses are the same as those between the third (second) and fourth pulses:

$$\tau_2 - \tau_1 = \tau_4 - \tau_3 = \Delta\tau_1, \qquad (5)$$

$$\sigma_2 - \sigma_1 = \sigma_4 - \sigma_3 = \delta_1, \qquad (6)$$

$$A_2/A_1 = A_4/A_3 = r_1, \qquad (7)$$

$$\tau_3 - \tau_1 = \tau_4 - \tau_2 = \Delta\tau_2, \qquad (8)$$

$$\sigma_3 - \sigma_1 = \sigma_4 - \sigma_2 = \delta_2, \qquad (9)$$

and

$$A_3/A_1 = A_4/A_2 = r_2. \qquad (10)$$

The four parameters δ_1, δ_2, r_1, and r_2 are determined with fixed $\Delta\tau_1$ and $\Delta\tau_2$ by the feedback control method to achieve the vanishing total excitation probability. Since the total excitation probability does not have any saddle point as a function of the four parameters except for the real minima, the optimization of the parameters can be achieved without any difficulty.

From the constraint equations (5)–(10), we derive that

$$c_{x,3}(t) + c_{x,4}(t) = (c_{x,1}(t) + c_{x,2}(t)) \, c_{x,3}(t)/c_{x,1}(t). \qquad (11)$$

This enables us to factorize Eq. (2) as

$$c_X(t) = (C_{X,1}(t) + C_{X,2}(t))(C_{X,1}(t) + C_{X,3}(t))/C_{X,1}(t). \qquad (12)$$

The condition equation (4) demands either

$$C_{B,1}(t) + C_{B,2}(t) = 0 \quad \text{and} \quad C_{C,1}(t) + C_{C,3}(t) = 0, \qquad (13)$$

$$C_{B,1}(t) + C_{B,3}(t) = 0 \quad \text{and} \quad C_{C,1}(t) + C_{C,2}(t) = 0, \qquad (14)$$

$$C_{B,1}(t) + C_{B,2}(t) = 0 \quad \text{and} \quad C_{C,1}(t) + C_{C,2}(t) = 0, \qquad (15)$$

or

$$C_{B,1}(t) + C_{B,3}(t) = 0 \quad \text{and} \quad C_{C,1}(t) + C_{C,3}(t) = 0. \qquad (16)$$

The condition equations (15) and (16) are satisfied when a pair of pulses is simultaneously the shadow pair for both the excited states. This situation takes place only when the time delay $\Delta\tau_i$ and the energy gap between the excited states ΔE satisfy the relation $\Delta E \Delta\tau_i = 2n\pi$ ($n = 1, 2, \ldots$). If we set the time delay to be shorter than that, that is,

$$\Delta E \Delta\tau_i < 2\pi, \qquad (17)$$

it is made sure that the shadow pulse for one state achieves excitation to the other state with nonzero probability. This leads to state-selective pumping. We thus conclude that if the constrained pulse train given by Eq. (1) is a dark pulse train and if the condition equation (17) is satisfied, either Eq. (13) or Eq. (14) is satisfied as well. This means that the pair of the first and second pulses constitutes a shadow pair for one state, while the pair of the first and third pulses is a shadow pair for the other state. The obtained shadow pairs can be used for ultrafast state-selective pumping, leading to both time-resolved and energy-resolved state-selective spectroscopy. Furthermore, the four parameters obtained by the feedback provide the positions and widths of both states B and C:

$$\varepsilon_X - E_A = \omega + [(2n + 1)\pi + \delta_i]/\Delta\tau_i, \qquad (18)$$

and

$$\Gamma_X = 2\ln(r_i)/\Delta\tau_i, \qquad (19)$$

where $(X, i) = (B, 1)$, $(b, 2)$, $(c, 1)$, or $(c, 2)$.

This method can be extended directly to multilevel problems. In the case of an $(N + 1)$ system with N resonance states and one initial state, irradiating pulse trains of 2^N pulses enable us to find $2N$ optimal parameters for the

achievement of vanishing total excitation probability. From the optimal parameters, we obtain the positions and widths of the resonance states and can construct a pulse train of 2^{N-1} pulses to excite to only one of the resonance states by the combination of the shadow pairs.

We take an example of a three-state system whose eigenenergies are given by

$$E_A = 0 \; [\text{cm}^{-1}], \tag{20}$$

$$E_B = 10\,000 - 25i \; [\text{cm}^{-1}], \tag{21}$$

and

$$E_C = 10\,021 - 27i \; [\text{cm}^{-1}]. \tag{22}$$

Here the widths of the excited states and the energy gap are of the same order, which might be regarded as a model of various kinds of physical systems with overlapping resonances, e.g., the Auger states, predissociative states of a molecule, and short-lived resonance states with isotope shifts.

We solve the Schrödinger equation to obtain the total excitation probability after irradiating the pulse train with $\Delta\tau_1 = 300$ fs and $\Delta\tau_2 = 330$ fs. The duration time and the carrier frequency of each pulse are set to 86 fs and 9990 cm^{-1}, respectively. The parameters are optimized in order to minimize the total excitation probability. Since there is no local minimum, it may be possible to employ simple methods such as the downhill simplex method or Powell's method to find the parameters to achieve the vanishing excitation probability. Here we take a much simpler way by using the variable transformation given by

$$a = (\delta_1 + \delta_2)/2, \tag{23}$$

$$b = (\delta_1 - \delta_2)/2, \tag{24}$$

$$c = (r_1 + r_2)/2, \tag{25}$$

and

$$d = (r_1 - r_2)/2. \tag{26}$$

By taking the initial conditions $b = 0$, $c = 1$, and $d = 0$, we start optimizing each variable independently in the order of $a \rightarrow c \rightarrow b \rightarrow d \rightarrow a \rightarrow \cdots$. Since it may be difficult to adjust the parameters precisely in real experiments, we vary the parameters up to only three digits.

Table I shows the selection ratios achieved by the shadow pairs obtained after each optimization loop. The *darkness* of the pulse train defined as the total excitation probability divided by the transition probability induced by irradiating only the first pulse of the train is also shown in Table I. In our spectroscopy, it is necessary to distinguish a sufficiently small signal from the noise and background signals in order to obtain a better dark pulse. As shown in Table I, the fourth loop achieves a darkness of about 0.002, providing shadow pairs with excellent selection ratios

TABLE I. The selection ratios achieved by shadow pairs obtained after each optimization loop and the darkness of the pulse train. The darkness is the ratio of transition probabilities attained by the pulse train to the probability by the first pulse of the train.

No. of loops	$|c_B|^2/|c_C|^2$	$|c_C|^2/|c_B|^2$	Darkness
1	0.102	0.078	0.0673
2	0.0565	0.0325	0.0323
3	0.002 38	0.003 15	0.004 15
4	0.000 471	0.000 301	0.002 14
Exact	0	0	0

($\sim 10^{-4}$). This means that such an accurate state-selective pumping is attainable if the S/N ratio is greater than 500, which is not difficult to realize in today's experimental facilities [9]. It should be noted that the time delays are set to around 300 fs, and the corresponding energy uncertainty is about 50 cm^{-1}, which is more than twice that of the energy gap between the excited states. Even faster and more accurate selective pumping is possible with a greater S/N ratio and a more precise adjustment of the parameters.

To show the effectiveness of Eqs. (18) and (19), we plot the decay signal from each resonance state using the
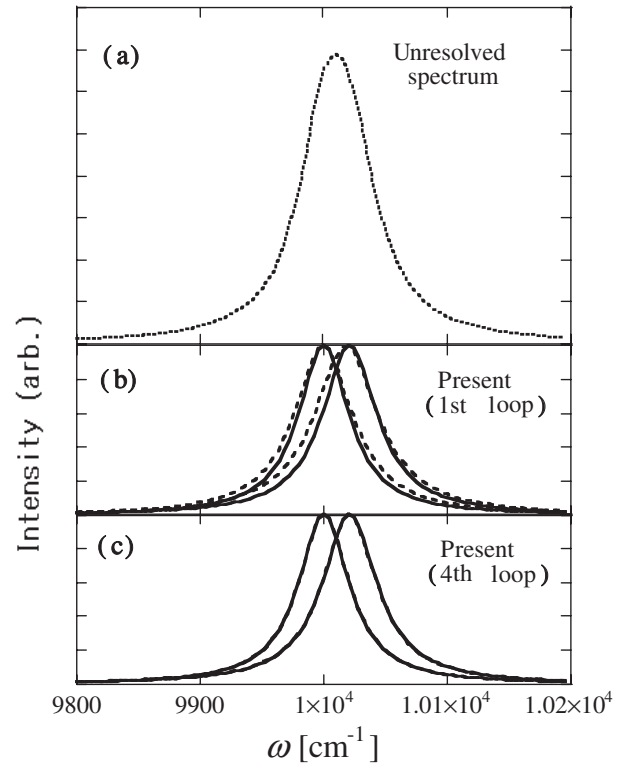

FIG. 1. The dotted line in (a) shows the sum of the spectra from the excited states. The solid lines in (b) and (c) show the exact Lorentzian spectrum from each excited state. Dashed lines show the present results of the Lorentzian spectrum with the parameters obtained by the (b) first and (c) fourth optimization loops.

obtained positions and widths in Fig. 1. Figure 1(a) shows the sum of the Lorentzian curves of the excited states. This is what conventional spectroscopy normally yields (or the interference effects may be included in some cases). Figures 1(b) and 1(c) show the *separated* Lorentzian signal with the parameters obtained, respectively, after the first and fourth loops by the present spectroscopy, together with the curves with the exact positions and widths. Even a crude optimization of the first loop roughly reproduces the separated signals. Further optimization can refine the results. As shown in Fig. 1(c), the parameters obtained after the fourth loop provide decay signals almost indistinguishable from the exact ones, thus demonstrating the power of our method.

The present idea of state-selective spectroscopy may be widely applicable to various types of decay processes. Examples are the Auger process, the predissociation of molecules, or the natural emission of photons. In these examples, a dark train is searched for by measuring Auger electrons, dissociation products, or fluorescence after the irradiation of the pulse train. The dark pulse train provides the positions, widths, and shadow pairs for the excited resonance state. The ultrafast and accurate state selectivity attained by precise pulse shaping drastically improves the conventional methods of ultrafast spectroscopy and the spectroscopy of short-lived resonance states, elucidating what the conventional methods cannot.

Since its invention, the laser has been regarded as a powerful tool for spectroscopy by virtue of its ability to provide precise measurements through its monochromatic nature and intensity. Coherence is also a great feature of the laser and is expected to usher in a new world of spectroscopy, especially together with the technique of pulse shaping. One may employ multidimensional spectroscopy [10]

to utilize pulse-shaping techniques, but this requires the analysis of parameters, which is tedious when there are large numbers of parameters. With feedback spectroscopy, on the other hand, many parameters are analyzed automatically through the optimization procedure. As is shown in this Letter, the appropriate setting of the optimization and constraints of the optimal pulse provides detailed information that is hard to obtain by conventional spectroscopy.

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