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Coherent control of wavepacket dynamics by locally designed external field

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Abstract

A new coherent control theory for manipulating quantum mechanical dynamics is proposed. The control field is designed locally (in time domain) so as to realize monotonous increase of the overlap between currently evolving wavefunction and the time-dependent target state, which will eventually reach to a desired quantum state under field-free condition. The present theory is applied to one-dimensional harmonic oscillator and Morse potential systems.

1. Introduction

Coherent control of chemical reaction, or wavepacket dynamics in terms of quantum mechanics, has been intensively studied in recent years [1–15]. Although there have been various types of control theories proposed so far, the most frequently used approach is the application of the optimal control theory (OCT) to the quantum system [16–24]. The OCT based theories which can essentially deal with global optimization problems in time domain, provide us a flexible and general way to design the optimal control field. However, significant drawback of such theories is lying in the fact that it often requires computationally intensive iterative procedure. This is closely related to the nature of the problem, that is, obtaining the globally optimal function turns out to be the 'two-point boundary value problems'.

On the other hand, various local optimization procedures have been also proposed. Because of its practical applicability, the control theories of this type have been applied to many molecular systems [25–35]. In this approach, the control field $E(t)$ is obtained as a function of time-dependent system variables. The explicit expression of $E(t)$ is determined differently in various local control theories depending on the viewpoint towards the concept 'local optimum'. One of the clear pictures is that one determines the control field so as to realize monotonous increase of the performance index $y(t)$, which is defined to express how much the present quantum state is content with the desired physical goal. An intuitive and typical choice for $y(t)$ is to take the

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overlap between the currently evolving wavefunction and the target state. In most of the applications of local control theories, the target state is taken to be a time-invariant quantum state, such as one of the molecular eigenstates. This kind of local approach has been successfully applied to selective excitation, wavepacket dynamics control and so on [32–35]. However, once one takes a non-stationary quantum state as a target state, it turns out to be difficult to design the control field under the local control picture. The widely used local control theory proposed by Kosloff et al. [17] stands on the requirement that the target operator commutes with the system Hamiltonian, whereas the projection operator for the non-stationary state, or the target operator, does not. Another type of the local control theory based on the linear time invariant (LTI) system [27,28,30] seems to be free from such physical restriction. However, the LTI-based local control theory requires the quadratic form of the performance index with respect to system variables $\mathbf{x}(t)$, i.e. $y(t) = \mathbf{x}(t) \cdot \mathbf{Q} \cdot \mathbf{x}(t)$, where $\mathbf{Q}$ is square positive real matrix. Projection operator for arbitrary non-stationary state is not necessarily expressed by 'positive' matrix because of the existence of off-diagonal elements, which makes it difficult to choose $\mathbf{Q}$ matrix for the definition of appropriate performance index.

Such limitation narrows the applicability of the local coherent control theories, for the desired quantum state is not necessarily one of the system eigenstates. Since flexibility in the choice of the target state is one of the key features for manipulating the wavepacket dynamics, we propose a new local control theory for designing the control field that makes possible to drive the wavepacket to a desired general quantum state, or an arbitrary non-stationary state. For this purpose, we introduce a new performance index that enables us to target non-stationary states. In Section 2, theoretical aspect of the present method is described together with brief summary of the former local control theory. In Section 3, the present theory is applied to various one-dimensional model systems and its usefulness is discussed.

2. Theoretical

In this section, we briefly summarize the basic concept of the local control theory, which is originally proposed by Kosloff et al. [17]. The time evolution of the quantum mechanical state $|\psi(t)\rangle$ under the external field $E(t)$ is governed by the time-dependent Schrödinger equation

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = -\frac{\mathrm{i}}{\hbar}[\hat{H} - \hat{\mu}E(t)]|\psi(t)\rangle, \tag{1}$$

where $\hat{H}$ and $\hat{\mu}$ denote the system Hamiltonian and the dipole moment operator, respectively. To obtain the local control field, one needs locally (in time domain) defined performance index. In most of the local control theories, the performance index $y(t)$ is given as an expectation value of the projection operator $\hat{W} \equiv |w\rangle\langle w|$ as

$$y(t) = \langle\psi(t)|\hat{W}|\psi(t)\rangle = |\langle w|\psi(t)\rangle|^2, \tag{2}$$

where $|w\rangle$ denotes the target quantum state. Note that the projection operator introduced here is time-independent and the t-dependence of $y(t)$ is brought through the wavepacket dynamics $|\psi(t)\rangle$.

By differentiating Eq. (2), time-derivative of the performance index is given as

$$\frac{\mathrm{d}}{\mathrm{d}t}y(t) = -\frac{\mathrm{i}}{\hbar}\langle\psi(t)|[\hat{W},\hat{H}]|\psi(t)\rangle + \frac{\mathrm{i}}{\hbar}\langle\psi(t)|[\hat{W},\hat{\mu}]|\psi(t)\rangle E(t). \tag{3}$$

The first term of Eq. (3) governs the wavepacket evolution under field-free condition, while the second term contributes to the dynamics explicitly driven by the external field. We call these two terms 'field-free' and 'field-driven' terms, respectively.

Under the condition where the target operator commutes with the system Hamiltonian, that is, $[\hat{W},\hat{H}] = 0$, the 'field-free' term in Eq. (3) vanishes and one obtains

$$\frac{\mathrm{d}}{\mathrm{d}t}y(t) = \frac{\mathrm{i}}{\hbar}\langle\psi(t)|[\hat{W},\hat{\mu}]|\psi(t)\rangle E(t) = -\frac{2}{\hbar}\mathrm{Im}[\langle\psi(t)|\hat{W}\hat{\mu}|\psi(t)\rangle]E(t). \tag{4}$$

By defining the external field with the amplitude parameter $A_0(>0)$ as

$$E(t) = -A_0 \mathrm{Im}[\langle\psi(t)|\hat{W}\hat{\mu}|\psi(t)\rangle]\hbar/2, \quad (5)$$

one can realize the condition, $\dot{y}(t) = A_0[E(t)]^2 \geqslant 0$ that brings the monotonous increase of $y(t)$. This feature guarantees that the propagating wavepacket always approaches to the target state. A typical example satisfying the above condition is the case in which one of the system eigenstates is chosen as a target state. However, it should be noticed that the required condition, $[\hat{W}, \hat{H}] = 0$, is not necessarily satisfied in general cases. For example, in the case that a non-stationary state is taken to be the target state, $\hat{W}$ does not commute with the system Hamiltonian, and monotonously increasing condition of $y(t)$ cannot be realized by the local control field given as Eq. (5).

Now, we introduce a new time-dependent target operator $\hat{W}(t) \equiv |w(t)\rangle\langle w(t)|$, which brings the performance index $y(t)$ given as

$$y(t) = \langle\psi(t)|\hat{W}(t)|\psi(t)\rangle = |\langle w(t)|\psi(t)\rangle|^2. \quad (6)$$

Note that the projection operator has its own time-dependence in this case, whereas $\hat{W}$ in Eq. (2) is time-independent. Here, $|w(t)\rangle$ denotes the target state propagating under field-free condition as

$$\frac{\mathrm{d}}{\mathrm{d}t}|w(t)\rangle = -\frac{\mathrm{i}}{\hbar}\hat{H}|w(t)\rangle, \quad (7)$$

with the final condition, $|w(t_\mathrm{f})\rangle = |v\rangle$, where $|v\rangle$ denotes the desired quantum state that we will call 'objective state' hereafter.

Time-derivative of $y(t)$ can be obtained by differentiating Eq. (6) as

$$\frac{\mathrm{d}}{\mathrm{d}t}y(t) = -\frac{2}{\hbar}\mathrm{Im}[\langle\psi(t)|\hat{W}(t)\hat{\mu}|\psi(t)\rangle]E(t). \quad (8)$$

Here, the following differential equation with respect to the overlap $\langle\psi(t)|w(t)\rangle$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle\psi(t)|w(t)\rangle &= \frac{\mathrm{i}}{\hbar}\langle\psi(t)|[\hat{H} - \hat{\mu}E(t)]|w(t)\rangle \\ &\quad - \frac{\mathrm{i}}{\hbar}\langle\psi(t)|\hat{H}|w(t)\rangle \\ &= -\frac{\mathrm{i}}{\hbar}\langle\psi(t)|\hat{\mu}|w(t)\rangle E(t), \end{aligned} \quad (9)$$

and the complex conjugate of Eq. (9) are used in the derivation of Eq. (8). Since there is no 'field-free' term found in Eq. (8), one can achieve the monotonous increase of the performance index by simply defining $E(t)$ as

$$E(t) = -A_0 \mathrm{Im}[\langle\psi(t)|\hat{W}(t)\hat{\mu}|\psi(t)\rangle]\hbar/2, \quad (10)$$

which leads to the condition $\dot{y}(t) = A_0[E(t)]^2 \geqslant 0$.

3. Results and discussion

As a demonstration, we first apply the present theory to the wavepacket dynamics control of the one-dimensional harmonic oscillator system. The system Hamiltonian is given in dimensionless form as

$$\hat{H} = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{x^2}{2}, \quad (11)$$

whereas eigenvalues are analytically given as $E_n = n + 1/2$ $(n = 0, 1, \ldots)$. Note that dimensionless time and system energy are used in the following discussions. The system energy is measured by the unit frequency ω while the unit time is given as $1/\omega$. The control field is also expressed in dimensionless quantity $f(t)$, which is related to the realistic field $E(t)$ through the relation $E(t) = \hbar\omega f(t)/ql$, where l and q denote the unit length and the unit electric charge, respectively.

Eigenstates from $n = 0$ to 30 have been used to span the Hilbert space as basis functions. Ground state is chosen to be the initial state, while the Gaussian wavepacket created by displacing the ground state by 2.5 is taken to be the objective state. Final time t_f is set to 500. Mathematically speaking, there is no restriction nor proper guideline for the setting of t_f. From a physical viewpoint we set the final time within the time scale in which the molecular eigenfrequencies can be perceived well enough and yet the created vibrational coherence is retained.

Shown in Fig. 1a is the time-dependence of the obtained control field. The field contains only one frequency component 2π that corresponds to the transition energy between the eigenstates, that is 1.0. It is seen that $y(t)$ increases monotonously as expected and it finally reaches 0.99 at t_f. For further investigation, we introduce the quantity $z(t)$ defined as

$$z(t) = |\langle v|\psi(t)\rangle|^2. \quad (12)$$

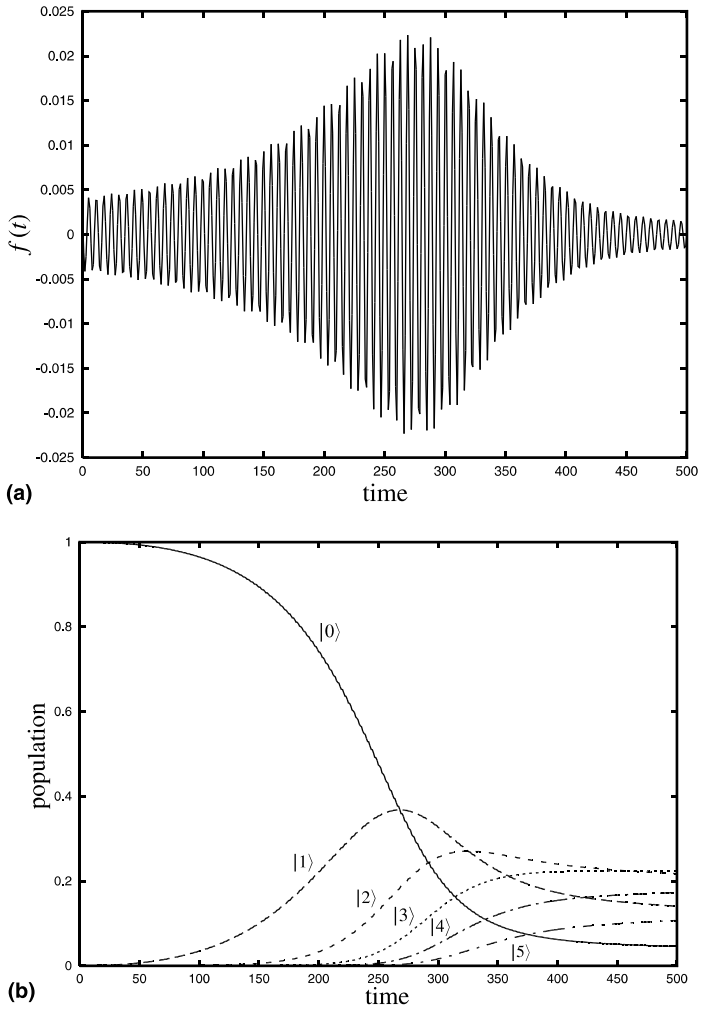

Fig. 1. (a) Time dependence of the control field designed for the objective state prepared by displacing the ground state by 2.5. (b) Time dependence of population distribution under the control field.

As clearly seen from the definition, $z(t)$ corresponds to the amount of overlap between the current wavepacket $|\psi(t)\rangle$ and the objective state $|v\rangle$. In contrast with the behavior of $y(t)$, $z(t)$ heavily oscillates reflecting the wavepacket motion in the coordinate space. The wavepacket coherently stimulated by the external field moves back and forth along the potential curve retaining its Gaussian shape. Thus, as the wavepacket approaches to the region (at around $x = 2.5$ in the present case) where the objective state is located, $z(t)$ increases, and decreases as the wavepacket moves away from that region. Note that the current wavepacket always follows the appropriate moving target that finally leads to the desired objective state $|v\rangle$. Shown in Fig. 1(b) is the population dynamics under the control field. At the final time, the population is adequately distributed over the eigenstates required to expand the objective state. Notice that the present method makes it possible to create not only the desired population distribution but also arbitrary phase relations between the eigenstates. We also design the control field which translates the

Gaussian wavepacket initially located at $x = 2.5$ (the objective state of the previous case) to the Gaussian packet located at $x = 3.0$ at $t_f = 1000$. In the obtained control field, only one frequency component 2π is found, which reflects the fact that all the transition frequencies are equal for the harmonic oscillator system. At the final time, $y(t_f) = 0.92$ is obtained. Notice that both the initial and objective states are linear combinations of the eigenstates in the present case, with which former local control theories are not capable to handle. Additional control fields for pulling apart the center of the Gaussian from the equilibrium position can be obtained similarly.

Next, we apply the present method to the Morse oscillator system, which has a variety of transition frequencies because of its anharmonicity. The potential function is given as

$$V(x) = D(1 - \exp[-\beta(x - 5)])^2, \tag{13}$$

where $D = 10$ and $\beta = 0.2$. We consider two different paths for controlling the wavepacket dynamics as shown in Fig. 2. The first one, which we call path A, is for designing the control field via transitions between 'non-stationary' states or Gaussian wavepackets: $|a\rangle \rightarrow |b\rangle \rightarrow |c\rangle \rightarrow |d\rangle$ (See Fig. 2). The second path is for creating highly excited and localized wavepacket $|d\rangle$ starting from the excited eigenstate $|e\rangle$, which we call path B.

First, we consider the path A. As a first step ($|a\rangle \rightarrow |b\rangle$), the initial state $|a\rangle$ is taken to be the ground state while the objective state $|b\rangle$ at this

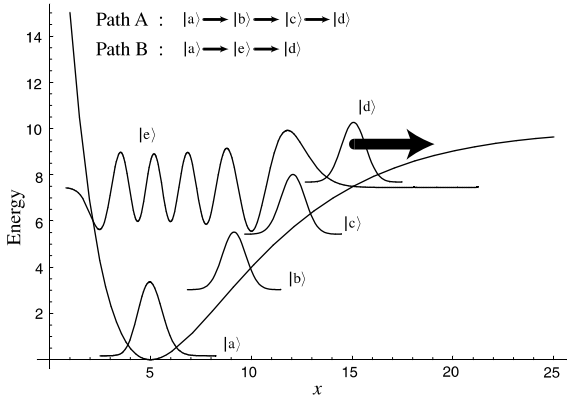

Fig. 2. Two different paths for controlling the wavepacket dynamics on Morse potential.

stage is given as the Gaussian wavepacket $G(x) = \exp[-(x - x_0)^2/2])$ with $x_0 = 9.0$. Shown in Fig. 3 is the time-dependence of the obtained control field. Compared with the harmonic oscillator case, the control field looks complicated, which suggests that various transitions with different frequencies are involved in the excitation process. Although the wavepackets at $t = 350$ and $t = 500$ are delocalized over the potential well, the properly controlled phase condition between the eigenstates recreates the localized wavepacket at the final time $t_f = 1500$. The final value of the performance index, $y(t_f) = 0.99$, denotes that the dynamics is well controlled. The localized wavepacket $|b\rangle$ obtained by the field shown in Fig. 3 can be further transported to the state $|c\rangle$, by applying the additional control field designed similarly as the first step. We take the Gaussian wavepacket with $x_0 = 12.0$ as the objective state $|c\rangle$ for the process $|b\rangle \rightarrow |c\rangle$ and the final yield $y(t_f) = 0.97$ is obtained. To demonstrate the applicability to the dissociation dynamics control, we choose the Gaussian wavepacket with positive momentum as $|d\rangle$ for the final step of path A: $|c\rangle \rightarrow |d\rangle$. Here, the Gaussian packet $|d\rangle$ is taken to be $G(x) = \exp[-(x - x_0)^2/2 + ikx]$ with $x_0 = 15.0$ and $k = 2.0$. Under the designed control field, $y(t_f) = 0.89$ is obtained. To confirm the dissociative dynamics of the objective Gaussian, we calculate the time evolution of the wavepacket generated by the control field under field-free condition. Because of the positive momentum that $|d\rangle$ possesses, the wavepacket moves towards dissociation as t increases, which implies that dissociation dynamics can be effectively promoted by the present method.

Finally, we show the results corresponding to the path B process. Since the energy levels of lower eigenstates are rather sparse compared with those of highly excited eigenstates, one can achieve the selective excitation from the ground state $|a\rangle$ to the highly excited eigenstate $|e\rangle$ using former local control theory [25–27,33]. However, it turns out to be difficult to control the dynamics via eigenstates as nearly degenerate highly excited eigenstates are involved in the excitation process. This is mainly caused by the fact that the selectivity is disturbed due to the dense energy levels. Thus, we focus on

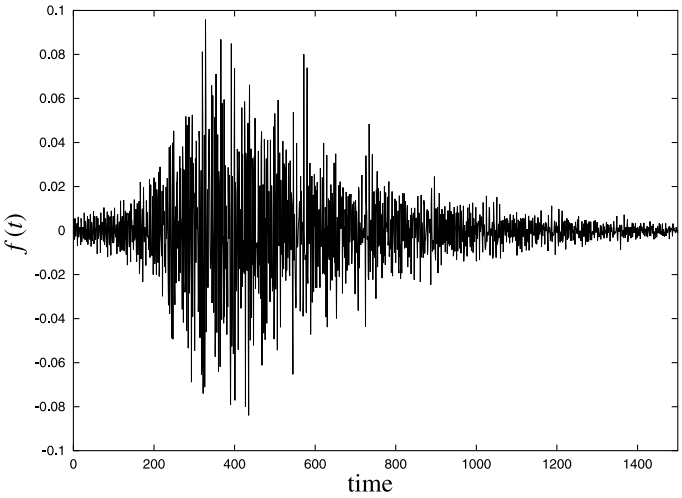

Fig. 3. Time dependence of the control field designed for the Gaussian objective state with $x_0 = 9.0$.

designing the control field which creates the localized wavepacket $|\mathrm{d}\rangle$ from the excited eigenstate $|\mathrm{e}\rangle$. Here, initial state is taken to be $n = 9$ excited eigenstate while Gaussian parameters for $|\mathrm{d}\rangle$ are chosen as $x_0 = 15.0$ and $k = 0$. Shown in Fig. 4 is the time-dependence of the obtained control field. It is seen that the control field consists of roughly four time stages, $t = 0$–150, $t = 150$–300, $t = 300$–450, and > 450. At the final time, the population is distributed over the eigenstates $n = 9$–12 which are required to expand the state $|\mathrm{d}\rangle$. The final value of the performance index is 0.98. To investigate the frequency component of the control field, we carried out the windowed Fourier analysis. The Blackman window is used for introducing the time-resolution 127 and corresponding frequency resolution 0.049. It is found that the obtained laser field contains four main frequency components as expected from the profile in Fig. 4. The peak frequency of the first pulse 0.49 corresponds to the

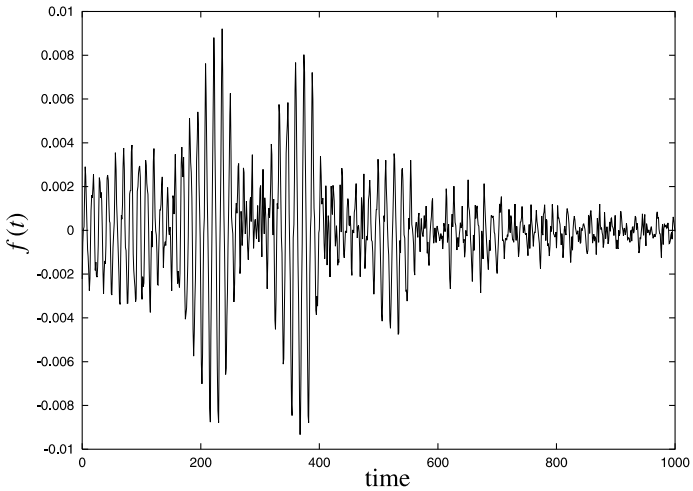

Fig. 4. Time dependence of the control field designed for creating the Gaussian wavepacket with $x_0 = 15.0$ from the initial state, $n = 9$ excited eigenstate.

transition energy between $n = 9$ and 10 eigenstates. Peak frequencies, 0.45, 0.44, 0.41, of the successive three pulses which are responsible for the sequential population transfer, roughly coincide to the transition energies corresponding to $n = 10 \leftrightarrow 11$, $n = 11 \leftrightarrow 12$ and $n = 12 \leftrightarrow 13$.

4. Summary

We propose a new local control theory for designing the external field which makes it possible to manipulate the wavepacket dynamics. In the present theory, the performance index is given as the overlap between the current wavepacket and the moving target state, which eventually becomes the desired objective state at the final time t_f under field-free condition. The local control field is designed so that the performance index increases monotonously. The present theory significantly widens the applicability of the local control theory, that is, one can use non-stationary quantum states for both initial and objective states. Since the present method can handle arbitrary quantum systems as long as the system eigenstates are known, various applications to the molecular reaction control are expected. The application of the present method to the dissociation dynamics control under the existence of the intramolecular energy redistribution is now in progress.

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