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Quantum control of chemical reaction dynamics in a classical way

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A simplified approach to quantum control of chemical reaction dynamics based on a classical, local control theory was developed. The amplitude of the control pulse is proportional to the linear momentum of the reaction system within the dipole approximation for the system-radiation field interaction. The kinetic energy of the system is the controlling parameter. That is, the reaction is controlled by accelerating the representative point on a potential energy surface before crossing over a potential barrier and then by decelerating it to the target after passing over the potential barrier. The classical treatment was extended to control of wave packet dynamics by replacing the classical momentum by a quantum mechanically averaged momentum on the basis of the Ehrenfest theorem. The present method was applied to a quantum system of a simple one-dimensional, double-well potential for checking its validity. A restriction of the applicability of the simplified method was also discussed. An isomerization of HCN was treated as a model system for wave packet control of a two-dimensional reaction. © 2000 American Institute of Physics. [S0021-9606(00)01033-3]

I. INTRODUCTION

In recent years, there has been considerable efforts made in theoretical treatments of quantum control of chemical reaction dynamics.¹⁻⁷ Various treatments based on optimal or local control theory and on perturbative or nonperturbative methods have been developed for designing laser pulses to manipulate nuclear wave packets to the desired target under consideration.⁸⁻³⁴

In our previous studies, we developed a nonperturbative, quantum mechanical feedback control theory based on a local control method.^{24,33,34} In that treatment, the time-development of reaction dynamics was divided into short time stages in which the system can be considered to follow the equation of motion of a time-invariant system. The control theory is free from the laser intensities used and is applicable to reaction dynamics in strong laser field cases as well as weak field cases. For the quantum control of reactions in the ground electronic state, a sequence of optical transitions between the relevant quantum states was utilized in order for the reaction to proceed.^{24,33} This procedure was well applicable to simple systems such as a multiphoton dissociation of HF in the ground state, but may experience a difficulty in controlling reactions in multidimensional systems. In order to overcome such a difficulty, it is important to develop a control theory based on classical mechanics rather than quantum mechanics.^{10,14,17,28,29}

From the general viewpoint of chemical reaction dynamics, the process of the reaction is described in terms of a representative point that moves from a reactant to a product over a transition region.³⁵⁻³⁷ It is natural to consider a reaction in quantum control in a similar way, i.e., quantum control is viewed as a representative point moving on the reaction coordinate in nonstationary laser fields. That is, quantum control is treated in a classical way.

Another theoretical viewpoint is that the target operator (performance index) for the local control scheme has to com-

mute with the system Hamiltonian.³⁴ In usual cases in which the population of the system is taken as the target, there is no problem because the population operator commutes with the system Hamiltonian. The nuclear kinetic energy of a representative point, on the other hand, can not be taken as the performance index in a quantum system. However, the kinetic energy can be considered to be a characteristic quantity controlling chemical reactions in the ordinary reaction dynamics on the basis of chemical intuition; an efficient yield of chemical reactions under consideration is obtained by increasing kinetic energy along its reaction coordinate to cross over the transition state region. From these points of view, it is interesting to consider an optimization procedure based on the classical treatment, in which a representative point of reaction obeys the Hamilton's equation of motion in classical mechanics.

In this paper, we present a classical, local control theory for controlling reaction dynamics of multidimensional systems. The theory is based on a classical mechanical, feedback control method within a local optimization treatment presented in a previous paper.^{24,33} The classical treatment was extended to control wave packet dynamics by replacing the classical momentum by a quantum mechanically averaged momentum on the basis of the Ehrenfest theorem. That is, the controlled field is derived from the Hamilton's equation of motion under the constraint of a smaller amount of laser energy. The dynamics, on the other hand, is evaluated by solving the time-dependent Schrödinger equation.

There have been several studies on classical optimal control developed mainly by Rabitz's group.^{14,17,28,29} The main problem encountered in classical optimal control is first how to take into account an ensemble of N trajectories and secondly how to keep close to quantum mechanics. Regarding the first problem, an optimization approach to a classical system with m degrees of freedom involves $2mN$ time-dependent Lagrange multipliers for the propagation of the ensemble of N trajectories. Its procedure needs much com-

putational time for a multidimensional system, and the solution was shown to be unstable in some cases. Botina, Rabitz, and Rahman presented a new classical treatment with $2m$ Lagrange multipliers.²⁸ In their treatment, the average trajectory is controlled under the constraint that the mean phase space trajectories are preserved. In our treatment, on the other hand, time development of Lagrange multipliers is no longer needed for the control of the ensemble of N trajectories since we can use the Riccati equation to control the linear time-invariant (LTI) system within short time approximation.

Regarding the second problem, in general, the optimal control method for a classical system is not always expected to control a quantum system. One of the solutions for the second problem is to keep classical trajectories close together by introducing a variance term in the cost functional.^{14,29} The resulting field is expected to control the corresponding quantum system to some extent, because the ensemble of classical trajectories tends to spread more easily than the quantum wave packet in the case of existing chaos or other pure classical phenomena. Another solution is to evaluate quantum/classical differences in the cost functional explicitly.¹⁷ On the other hand, in our treatment, an ensemble average of linear momentum was replaced by a quantum mechanical average at each short time stage; in other words, we corrected the classical trajectory to a quantum wave packet at each time. Therefore, our treatment is applicable to a quantum system as long as it behaves a wave packet.

In the next section, after introducing a local feedback control treatment, a classical mechanical, local control theory is presented. In Sec. III, the theory is applied first to a simple one-dimensional system to check the applicability of our theory. We show that the present theory can be applied not only to classical systems but also to some quantum reaction systems. Finally, we apply the theory to two-dimensional reaction dynamics of HCN isomerization.

II. THEORY

A. Local feedback control of a linear time-invariant system

Consider a reaction system in an external control field. The equation of motion of the system is given by

$$\frac{d}{dt}\mathbf{x}(t) = f(\mathbf{x}(t), \mathbf{u}(t), t). \quad (1)$$

Here, $\mathbf{x}(t)$ is the n -dimensional system variable vector, and $\mathbf{u}(t)$ is the m -dimensional input vector that is an arbitrary external field to control the system. $\mathbf{x}(t)$ corresponds to wave functions and $\mathbf{u}(t)$ corresponds to laser fields in the case of quantum systems. An optimal input vector is determined by minimizing a performance index J during the time interval from t_0 to t_f ,

$$J = \frac{1}{2}\mathbf{x}(t_f)^T\Phi\mathbf{x}(t_f) + \frac{1}{2}\int_{t_0}^{t_f} [\mathbf{u}(t)^T\mathbf{R}(t)\mathbf{u}(t) + \mathbf{x}(t)^T\mathbf{Q}(t)\mathbf{x}(t)]dt. \quad (2)$$

Here, Φ and \mathbf{Q} are $n \times n$ real matrices, and \mathbf{R} is an $m \times m$ real matrix. Control parameter matrices Φ , \mathbf{R} and \mathbf{Q} are

related to the final status of the system at time t_f , the field intensity, and the path within the control time $t_0 - t_f$, respectively. Equation (2) is an expression for a global control since J is minimized within a period of time between t_0 and t_f .

Consider a LTI system³⁸ whose n -dimensional system variable vector $\mathbf{x}(t)$ satisfies

$$\frac{d}{dt}\mathbf{x}(t) = \mathbf{A}\mathbf{x}(t) + \mathbf{B}\mathbf{u}(t), \quad (3)$$

where \mathbf{A} and \mathbf{B} are time-independent matrices, and $\mathbf{u}(t)$ is the m -dimensional input vector. The optimal input vector minimizing performance index J is given as

$$\mathbf{u}(t) = -\mathbf{R}^{-1}\mathbf{B}^T\mathbf{P}(t)\mathbf{x}(t). \quad (4)$$

Here, $\mathbf{P}(t)$ is a time-dependent, $n \times n$ symmetric positive definite matrix that obeys the so-called Riccati equation,³⁹

$$\frac{d\mathbf{P}(t)}{dt} = -\mathbf{A}^T\mathbf{P}(t) - \mathbf{P}(t)\mathbf{A} + \mathbf{P}(t)\mathbf{B}\mathbf{R}^{-1}\mathbf{B}^T\mathbf{P}(t) - \mathbf{Q}, \quad (5)$$

under the final condition

$$\mathbf{P}(t_f) = \Phi. \quad (6)$$

In Eq. (4), $\mathbf{R}^{-1}\mathbf{B}^T\mathbf{P}(t)$ is called the feedback gain matrix. Equation (4) is a general expression for global optimization of a LTI system.

Even in the case in which the system of interest is not a LTI system, we can use the LTI optimization procedure as described above by taking a short time limit.²⁴ We divide the total control period $t_0 - t_f$ into short time steps. In the i th short time step, we rewrite the equations of motion of the system through Taylor expansion around a certain point $(\mathbf{x}_0^{(i)}, \mathbf{u}_0^{(i)})$ to the 1st order as

$$\frac{d}{dt}(\Delta\mathbf{x}^{(i)}) = \left. \frac{\partial f}{\partial \mathbf{x}} \right|_{\substack{\mathbf{x}=\mathbf{x}_0^{(i)} \\ \mathbf{u}=\mathbf{u}_0^{(i)}}} \Delta\mathbf{x}^{(i)} + \left. \frac{\partial f}{\partial \mathbf{u}} \right|_{\substack{\mathbf{x}=\mathbf{x}_0^{(i)} \\ \mathbf{u}=\mathbf{u}_0^{(i)}}} \Delta\mathbf{u}^{(i)}. \quad (7)$$

Here, $\Delta\mathbf{x}$ and $\Delta\mathbf{u}$ are differences from a certain point $(\mathbf{x}_0^{(i)}, \mathbf{u}_0^{(i)})$

$$\begin{cases} \mathbf{x}^{(i)}(t) = \mathbf{x}_0^{(i)} + \Delta\mathbf{x}^{(i)}(t) \\ \mathbf{u}^{(i)}(t) = \mathbf{u}_0^{(i)} + \Delta\mathbf{u}^{(i)}(t) \end{cases} \quad (8)$$

Equation (7) has the same form of the LTI system, and we obtain an expression for the control input vector for the system from Eq. (4) as

$$\Delta\mathbf{u}^{(i)}(t) = -\mathbf{R}^{(i)-1}(t)\mathbf{B}^{(i)T}\mathbf{P}^{(i)}(t)\Delta\mathbf{x}^{(i)}(t). \quad (9)$$

Notice that $\mathbf{P}^{(i)}(t)$ should not be so far from $\mathbf{P}^{(i)}(t_f) = \Phi^{(i)}$ within the short time limit, and we therefore set $\mathbf{P}^{(i)}(t) \rightarrow \mathbf{P}^{(i)}(t_f)$. As a result of this replacement, the local control input vector at the i th short time step is described in a feedback form as

$$\Delta\mathbf{u}^{(i)} = -\mathbf{R}^{(i)-1}\mathbf{B}^{(i)T}\Phi^{(i)}\Delta\mathbf{x}^{(i)}. \quad (10)$$

By carrying out the short time control procedure repeatedly, we can control the reaction system. This is called local feedback control.

B. Classical local control theory

Now consider an n -dimensional particle motion in a time-dependent external field whose dynamics is given by classical Hamilton's equations of motion,

$$\begin{cases} \frac{d}{dt}q_i = \frac{\partial H}{\partial p_i} \\ \frac{d}{dt}p_i = -\frac{\partial H}{\partial q_i}, \end{cases} \quad (i=1, \dots, n). \quad (11)$$

Here, $H=H(\mathbf{q}, \mathbf{p}, t)$, the total Hamiltonian, is expressed as

$$H(\mathbf{q}, \mathbf{p}, t) = \frac{\mathbf{p}^2}{2M} + V(\mathbf{q}) - \boldsymbol{\mu}(\mathbf{q}) \cdot \mathbf{E}(t), \quad (12)$$

where dipole approximation for the particle-external field interaction is assumed. M , $\mathbf{q}(t)$, and $\mathbf{p}(t)$ denote particle mass, position, and momentum, respectively. $V(\mathbf{q})$, $\boldsymbol{\mu}(\mathbf{q})$ and $\mathbf{E}(t)$ are the potential, the dipole moment of the system, and the external field, respectively.

We define system variable vector $\mathbf{x}(t)$ and input vector $\mathbf{u}(t)$ as

$$\mathbf{x}(t) = \begin{bmatrix} \mathbf{q}(t) \\ \mathbf{p}(t) \end{bmatrix} \quad (13)$$

and

$$\mathbf{u}(t) = \mathbf{E}(t). \quad (14)$$

Within a short time approximation shown in Sec. II A, the equations of motion at the i th repetition at time t are rewritten by a difference $(\Delta \mathbf{x}_0^{(i)}, \Delta \mathbf{u}_0^{(i)})$ from a point $(\mathbf{x}_0^{(i)}, \mathbf{u}_0^{(i)})$ as

$$\begin{aligned} \frac{d}{dt}(\Delta \mathbf{q}^{(i)}) &= \frac{\Delta \mathbf{p}^{(i)}}{M}, \\ \frac{d}{dt}(\Delta \mathbf{p}^{(i)}) &= \left(-\frac{\partial^2}{\partial \mathbf{q}^2} V - [\boldsymbol{\mu} \mathbf{E}] \right) \bigg|_{\substack{\mathbf{q}=\mathbf{q}_0^{(i)} \\ \mathbf{p}=\mathbf{p}_0^{(i)} \\ \mathbf{E}=\mathbf{E}_0^{(i)}}} \Delta \mathbf{q}^{(i)} \\ &\quad + \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{q}} \right) \bigg|_{\substack{\mathbf{q}=\mathbf{q}_0^{(i)} \\ \mathbf{p}=\mathbf{p}_0^{(i)} \\ \mathbf{E}=\mathbf{E}_0^{(i)}}} \Delta \mathbf{E}^{(i)}. \end{aligned} \quad (15)$$

Then, the local control field is expressed as Eq. (10) with

$$\mathbf{B}^{(i)} = \begin{bmatrix} 0 & \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{q}} \right) \bigg|_{\substack{\mathbf{q}=\mathbf{q}_0^{(i)} \\ \mathbf{p}=\mathbf{p}_0^{(i)} \\ \mathbf{E}=\mathbf{E}_0^{(i)}}} \end{bmatrix}^T. \quad (16)$$

We set Φ , \mathbf{Q} , and \mathbf{R} matrices as

$$\Phi^{(i)} = \mathbf{Q}^{(i)} = \begin{bmatrix} \mathbf{f}_{\mathbf{q}\mathbf{q}}^{(i)} & \mathbf{f}_{\mathbf{q}\mathbf{p}}^{(i)} \\ \mathbf{f}_{\mathbf{p}\mathbf{q}}^{(i)} & \mathbf{f}_{\mathbf{p}\mathbf{p}}^{(i)} \end{bmatrix} \quad (17)$$

and

$$\mathbf{R}^{(i)} = \begin{bmatrix} r_1^{(i)} & & 0 \\ & \ddots & \\ 0 & & r_m^{(i)} \end{bmatrix}, \quad (18)$$

respectively. Here, Φ is required to be a symmetric positive definite matrix according to the final condition. This requirement is satisfied if off-diagonal elements between \mathbf{p} and \mathbf{q} , $\mathbf{f}_{\mathbf{q}\mathbf{p}}^{(i)}$ and $\mathbf{f}_{\mathbf{p}\mathbf{q}}^{(i)}$ are set to zero. In this case, the local control field is expressed as

$$\Delta \mathbf{u}^{(i)} = -\mathbf{R}^{(i)-1} \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{q}} \right) \bigg|_{\mathbf{q}=\mathbf{q}_0^{(i)}} \mathbf{f}_{\mathbf{p}\mathbf{p}}^{(i)} \Delta \mathbf{p}^{(i)}. \quad (19)$$

The performance index at the i th short time step is expressed as

$$\begin{aligned} J^{(i)} &= \frac{1}{2} \Delta \mathbf{p}^{(i)}(t_f^{(i)})^T \mathbf{f}_{\mathbf{p}\mathbf{p}}^{(i)} \Delta \mathbf{p}^{(i)}(t_f^{(i)}) \\ &\quad + \int_{t_0^{(i)}}^{t_f^{(i)}} dt \left[\Delta \mathbf{u}^{(i)}(t)^T \mathbf{R}^{(i)} \Delta \mathbf{u}^{(i)}(t) \right. \\ &\quad \left. + \frac{1}{2} \Delta \mathbf{p}^{(i)}(t)^T \mathbf{f}_{\mathbf{p}\mathbf{p}}^{(i)} \Delta \mathbf{p}^{(i)}(t) \right]. \end{aligned} \quad (20)$$

To control the system, we would like to know how the diagonal matrix element $\mathbf{f}_{\mathbf{p}\mathbf{p}}^{(i)}$ plays a role in the system. Notice that \mathbf{x}_0 and \mathbf{u}_0 can be chosen arbitrary. In this paper, we set $\mathbf{x}_0 = (\mathbf{q}(t), \mathbf{0})$ and $\mathbf{u}_0 = \mathbf{0}$, so that $\Delta \mathbf{q} = \mathbf{0}$ and $\Delta \mathbf{p} = \mathbf{p}$. Then, Eq. (20) is rewritten as

$$\begin{aligned} J^{(i)} &= \frac{1}{2} \mathbf{p}^{(i)}(t_f^{(i)})^T \mathbf{f}_{\mathbf{p}\mathbf{p}}^{(i)} \mathbf{p}^{(i)}(t_f^{(i)}) \\ &\quad + \int_{t_0^{(i)}}^{t_f^{(i)}} dt \left[\mathbf{u}^{(i)}(t)^T \mathbf{R}^{(i)} \mathbf{u}^{(i)}(t) + \frac{1}{2} \mathbf{p}^{(i)T}(t) \mathbf{f}_{\mathbf{p}\mathbf{p}}^{(i)} \mathbf{p}^{(i)}(t) \right] \end{aligned} \quad (21)$$

with

$$\mathbf{u}^{(i)} = -\mathbf{R}^{(i)-1} \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{q}} \right) \bigg|_{\mathbf{q}=\mathbf{q}_0^{(i)}} \mathbf{f}_{\mathbf{p}\mathbf{p}}^{(i)} \mathbf{p}^{(i)}. \quad (22)$$

Equation (21) shows that the control parameter $\mathbf{f}_{\mathbf{p}\mathbf{p}}$ is a multiplier to the kinetic energy. This means that our control is carried out through changing the kinetic energy of the representative point of the reaction system. The control fields minimize the performance index J given by Eq. (21). The control fields promote the kinetic motion of the system in the case in which J becomes smaller and, on the other hand, suppress the kinetic motion in the case in which J becomes larger. For example, if f_{pp} has a negative value, then the control field energizes the system. On the other hand, if f_{pp} has a positive value, then the control field decreases the kinetic energy of the system.

Notice that our local control scheme consists of a sequence of many short time steps. Because control parameters are defined at each step, we can control the kinetic energy of the particle as a function of time, position, momentum, or other physical properties of the system.

So far, we restricted ourselves to local control of a trajectory of a representative point starting with an initial value of \mathbf{p} and that of \mathbf{q} . In other words, we did not consider a distribution of initial conditions. We now consider two kinds

of initial conditions and three kinds of the expressions for the control field assuming that all of the particles are controlled by the same field at time t .

1. $\mathbf{p}=\mathbf{p}(t_0)$ and $\mathbf{q}=\mathbf{q}(t_0)$ at $t=t_0$

In this one particle case, the control field at the i th time stage is simply given by Eq. (22).

2. \mathbf{p} and \mathbf{q} have a distribution of conditions

In this case, two types of control field are constructed. The first type of control field is given by using both classical ensemble averages of the momentum $\langle \mathbf{p} \rangle_{\text{en}}$ and coordinate $\langle \mathbf{q} \rangle_{\text{en}}$ at each step,

$$\mathbf{u}^{(i)} = \mathbf{u}_{\mathbf{q}=\langle \mathbf{q}^{(i)} \rangle_{\text{en}}} = -\mathbf{R}^{(i)-1} \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{q}} \right) \Bigg|_{\mathbf{q}=\langle \mathbf{q}^{(i)} \rangle_{\text{en}}} \mathbf{f}_{\mathbf{pp}}^{(i)} \Bigg|_{\mathbf{p}=\langle \mathbf{p}^{(i)} \rangle_{\text{en}}} \langle \mathbf{p}^{(i)} \rangle_{\text{en}}. \quad (23)$$

$\langle \rangle_{\text{en}}$ denotes the ensemble average over the trajectories. The second type of control field is given as

$$\mathbf{u}^{(i)} = \langle \mathbf{u}^{(i)} \rangle_{\text{en}} = -\mathbf{R}^{(i)-1} \left\langle \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{q}} \right) \Bigg|_{\mathbf{q}=\mathbf{q}^{(i)}} \mathbf{f}_{\mathbf{pp}}^{(i)} \Bigg|_{\mathbf{p}=\mathbf{p}^{(i)}} \mathbf{p}^{(i)} \right\rangle_{\text{en}}. \quad (24)$$

That is, the control field is created by averaging the fields for the trajectories at each step.

C. Extension to wave packet dynamics

The fields, derived in the preceding section, applied to a classical system do not always control the quantum system because of spreading and/or bifurcation or other pure quantum behaviors of nuclear wave packets. Therefore, we need to extend the classical local feedback control method derived above to a quantum system whose wave function $|\Psi(t)\rangle$ satisfies

$$i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = (\hat{H}_0 - \boldsymbol{\mu} \cdot \mathbf{E}(t)) |\Psi(t)\rangle, \quad (25)$$

where \hat{H}_0 is the system Hamiltonian.

The basic idea for extending to the quantum control is appropriate selection of the representative points in the phase space of the system. The simplest method is just to use the quantum averaged position $\langle \mathbf{q} \rangle$ and momentum $\langle \mathbf{p} \rangle$ for the nuclear wave packet on the basis of the Ehrenfest theorem. Explicitly, this should be applicable to a system of a harmonic potential. However, it is expected that the simplest method is effective as long as the wave packets are not so separated, as shown in the next section. Another method is to use a quantum phase space distribution function such as Wigner⁴⁰ or Husimi distribution function.^{41,42} Such a method is expected to be applicable to a quantum system even in case in which the wave packet splits, but its computational task would be too great to obtain such a distribution function at each local control step. For this reason, we adopted the former method. In this case, the control field for a quantum system at the i th short time step is expressed as

$$\mathbf{u}^{(i)} = -\mathbf{R}^{(i)-1} \left(\frac{\partial \boldsymbol{\mu}}{\partial \mathbf{q}} \right) \Bigg|_{\mathbf{q}=\langle \mathbf{q}^{(i)} \rangle} \mathbf{f}_{\mathbf{pp}}^{(i)} \Bigg|_{\mathbf{p}=\langle \mathbf{p}^{(i)} \rangle} \langle \mathbf{p} \rangle^{(i)}. \quad (26)$$

Here, $\langle \rangle$ denotes the quantum expectation value of the system.

In our treatment, time propagation of the quantum system is required. This causes computational difficulties in a large system with many degrees of freedom. One possibility for such a system is the approach using a Gaussian wave packet representation of wave function.^{43,44} In this approach, wave function is represented as a sum of Gaussian wave packets located in phase space. In our methodology, we could say that these Gaussian wave packets are one of the selections for the representative points of the system. And of course, our local feedback theory can be applied to the purely classical system. This wide applicability of our theory is based on the locally controlled property, that is, correction of the field parameters \mathbf{p} and \mathbf{q} to the target system at each time step.

III. APPLICATIONS AND DISCUSSION

For checking the present local control method, we first apply this method to a one-dimensional double-well quantum system. Next, we apply the local control method to control of isomerization reaction of HCN as an example of a two-dimensional quantum system.

A. A double-well system

In many chemical reactions, the representative point moves along the reaction path over the barrier into products. One of the simplest models for these types of reaction is a double-well system.

In this section, we apply the local feedback method derived in the preceding section to a one-dimensional double-well system where potential is expressed by

$$V(q) = aq^4 - bq^2 + cq^3 \quad (27)$$

as a function of the reaction coordinate q . Here, it was assumed that $a = 9.22 \times 10^5 \text{ cm}^{-1} \text{ \AA}^{-4}$, $b = 3.79 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$, and $c = 1.59 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-3}$. The system mass was assumed to be $M = 99.3 \text{ amu}$. Figure 1(a) shows the potential function $V(q)$ whose two minima are denoted by A and B, $|0\rangle$ and $|5\rangle$ are the eigenstates of A and B, respectively. This system has 42 eigenstates below the potential barrier. For the interaction between the system and external fields, we used

$$\mu(q) = \mu_0 + \mu_1 q \quad (28)$$

as a dipole moment function. Here $\mu_0 = 0.716 \text{ \AA} e$ and $\mu_1 = 0.310 e$.

Consider a control of a reaction from A to B. Now we set the initial state to a ground state $|0\rangle$ of the system and the control target is set to be the lowest position B in the target well shown in Fig. 1(a). To achieve a control, we need to set the control parameter f_{pp} appropriately. Recalling that f_{pp} is a parameter for controlling kinetic energy, f_{pp} should be a continuum function of position, which has negative values in the initial well to energize the system and positive values in

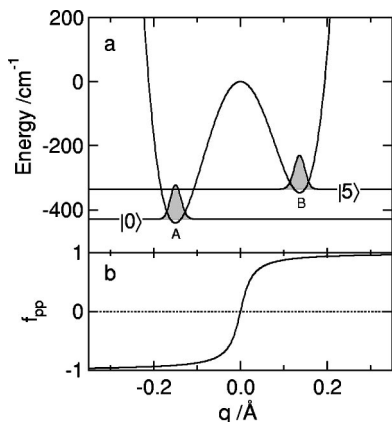


FIG. 1. (a) Potential of a one-dimensional double-well model in Eq. (27). $|0\rangle$ and $|5\rangle$ are the eigenstates of the two minima A and B, respectively. (b) Control parameter f_{pp} as a function of the coordinate whose form is given by Eq. (29).

the target well to decrease the kinetic energy. Since the control procedure is robust for a form of $f_{pp}(q)$, we adopted an analytical form of f_{pp} as

$$f_{pp}(q) = \frac{2}{\pi} \tan^{-1}(sq), \quad (29)$$

where $s = 50 \text{ \AA}^{-1}$. Figure 1(b) shows f_{pp} as a function of q .

Figure 2(a) shows the time evolution of the controlled wave packets in a phase space. Here the laser intensity parameter r was set to $r = 2930$ and the wave packet dynamics

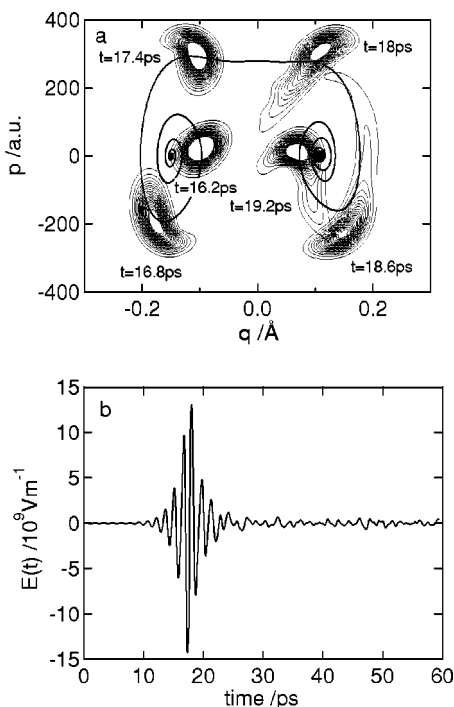


FIG. 2. Controlled wave packet dynamics in the phase space by using the field expression Eq. (26). We set the initial state to a ground state $|0\rangle$ shown in Fig. 1 and the laser intensity parameter r was set to $r = 2930$. The solid line shows the trajectory of quantum expectation values of position $\langle q \rangle$ and momentum $\langle p \rangle$, and contours represent wave packets expressed in Husimi representation. (b) Obtained control field for this quantum wave packet dynamics.

was computed by the symplectic integrator (SI)-FFT scheme⁴⁵ under the control field expressed in Eq. (26). The solid line describes the trajectory of the quantum averaged position $\langle q \rangle$ and momentum $\langle p \rangle$. The contours in Fig. 2(a) represent the wave packets expressed in the Husimi representation,

$$\rho_H(q,p) = (2\pi\hbar)^{-1} |\langle \phi_{qp} | \Psi \rangle|^2 \quad (30)$$

at the time denoted by its side. Here ϕ_{qp} denotes the minimal wave packet given by

$$\phi_{qp}(x) = (2\pi(\Delta q)^2)^{-1/4} \exp\left[\frac{i}{\hbar} px - \frac{(x-q)^2}{4(\Delta q)^2}\right], \quad (31)$$

with an uncertainty of coordinate space Δq with $\Delta q = (\hbar/2) \times 0.04$ a.u. Figure 2(b) shows the control field obtained by using Eq. (26).

We can see from Fig. 2 that the quantum 1D double-well system is really controlled by using the local feedback method described in the preceding section. Figure 2(a) shows that the system moves from the initial well to the target well, keeping a localized character of the wave packet in phase space, and its trajectory of $\langle q \rangle - \langle p \rangle$ is not so far from the center of the wave packet, especially in the initial well. After crossing the barrier, the system begins to spread to some extent because of a branching by the barrier, but the spreading is small enough to control the system as a wave packet. In fact, the trajectory of $\langle q \rangle - \langle p \rangle$ evaluated by using the Ehrenfest theory closely resembles that of the classical one, and the control field shown in Fig. 2(b) has a similar structure to the control field applied to the classical system.

Consider a special case in which the system moves toward the top of the barrier with zero momentum. Figure 3 shows the controlled wave packet dynamics and control field in that case. Here the laser intensity parameter r was set to $r = 3050$. Figures 3(a) and 3(b) show the controlled wave packet dynamics prior to crossing over the reaction barrier and after stopping at the barrier, respectively. In Figs. 3(a) and 3(b), the solid line describes the trajectory of the quantum expectation values of position $\langle q \rangle$ and momentum $\langle p \rangle$ until $t = 30$ ps. The contours represent the system expressed in Husimi representation defined by Eq. (30) at the time denoted by its side. Just after the wave packet reaches at the top of the barrier, the high energy components of the wave packet proceed to the target well, and, on the other hand, the low energy component of the wave packet turns back to the initial well. Therefore, as shown in Fig. 3(b), the wave packet splits into two parts. This causes the system to become uncontrollable. After splitting, the wave packet spreads out into both wells, and then the averaged position $\langle q \rangle$ and the averaged momentum $\langle p \rangle$ are no longer appropriate for the representative point of the system. In fact, such a system cannot be controlled by using the simplest local feedback expression for pulses given in Eq. (26) as shown in Fig. 3(c).

B. Isomerization of HCN

Consider control of the isomerization of HCN to HNC by using two perpendicular polarized laser pulses as control fields. We adopt a two-dimensional model in which the car-

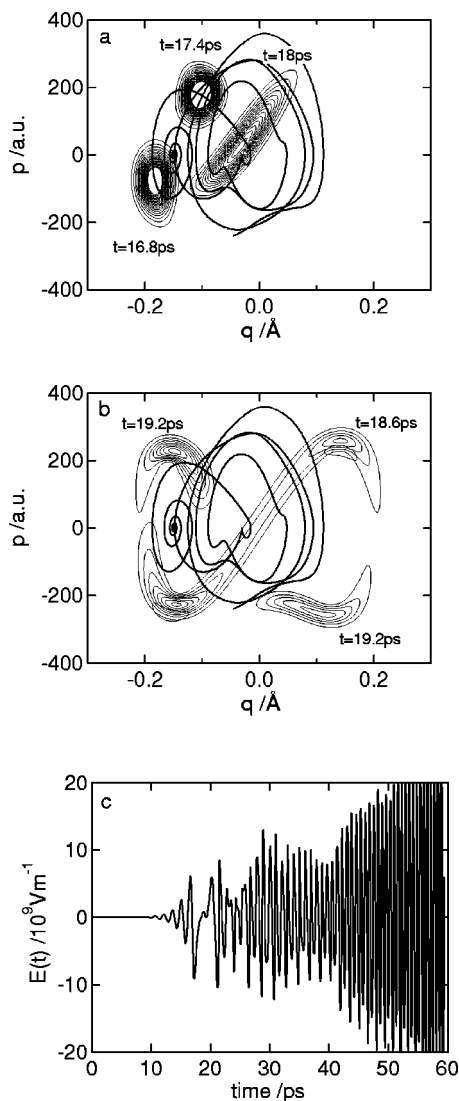


FIG. 3. Controlled wave packet dynamics in the phase space, and corresponding control field with $r=3050$. (a) and (b) show the dynamics before and after reaction barrier crossing, respectively. The solid line shows the trajectory of the quantum expectation value of position $\langle q \rangle$ and contours represent wave packet expressed in Husimi representation. (c) Corresponding control field.

bon and nitrogen atom positions are fixed and the hydrogen atom moves on the x - y plane. The potential energy surface and the dipole moment function of the reaction system were calculated by the GAMESS *ab initio* program.⁴⁶ The system has two minima, which correspond to the two isomers HCN and HNC. The potential energy surface and the adopted control parameter f_{pp} are shown in Fig. 4. In this figure, the contour around H represents the vibrational ground state of HCN. We used the same function as the control parameter f_{pp} for the x -polarized field E_x and the y -polarized field E_y . For simplicity, we adopt the form of f_{pp} as

$$f_{pp}(q_x, q_y) = f_{pp}(q_x) = \frac{2}{\pi} \tan^{-1}(s(q_x - q_b)), \quad (32)$$

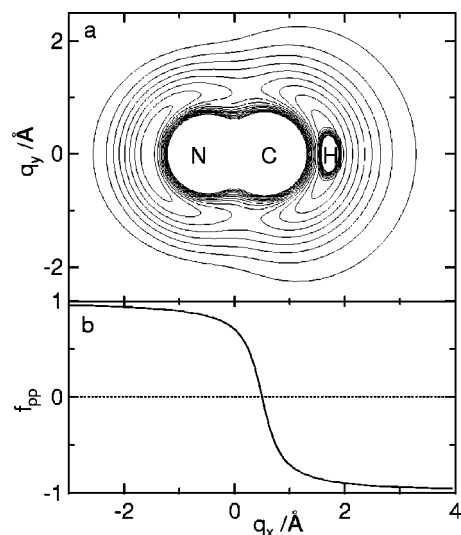


FIG. 4. (a) Potential energy surface of HCN molecule. The contour around H represents vibrational ground state of HCN. (b) Control parameter f_{pp} as a function of the x coordinate.

where $s=4 \text{ \AA}^{-1}$ and $q_b=0.5 \text{ \AA}$. The intensity parameters for E_x and E_y were chosen to be $r_x=3030$ and $r_y=556$, respectively.

Figures 5(a) and 5(b) show the time development of the wave packets of the controlled isomerization reaction. The contours with time t describe the wave packet at that time and the dashed line denotes the trajectory of the quantum averaged position $\langle \mathbf{q} \rangle$ of the wave packet. We can see that the trajectory runs along the reaction path and that the wave packet moves on that trajectory except for the final part of the reaction. This small difference between the trajectory $\langle \mathbf{q} \rangle$

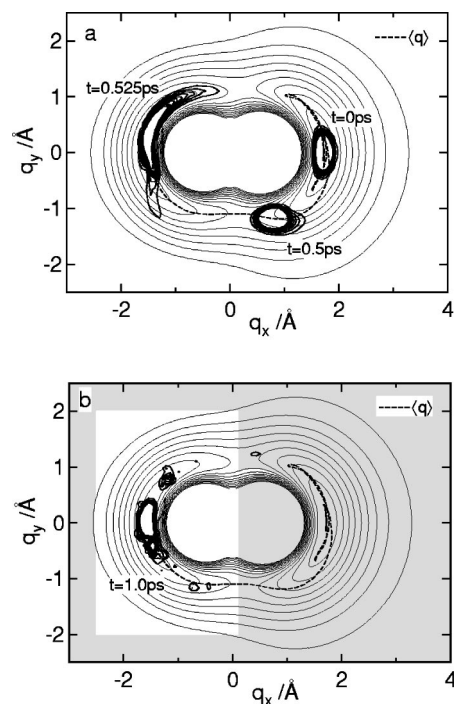


FIG. 5. Controlled wave packet dynamics (a) under two linearly polarized control fields, and (b) after. The dashed line shows the trajectory of $\langle \mathbf{q} \rangle$.

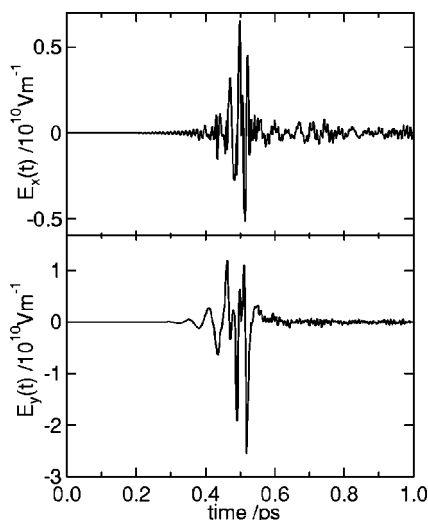


FIG. 6. Two linearly polarized control fields E_x for the x -direction and E_y for the y -direction.

and the center of each wave packet indicates the validity of our simplified treatment with Eq. (26) for controlling the isomerization of HCN. At the end of the control pulses shown in Fig. 5(b), the system was localized at the bottom of HNC with a little distribution that excited bending vibration. This remaining part is the origin of the differences between the trajectory of $\langle \mathbf{q} \rangle$ and the wave packet at the final part of the control.

Figure 6 shows the control fields for this isomerization. The upper figure represents the x -polarized field E_x and the lower one represents the y -polarized field E_y . In Figs. 5 and 6, E_y mainly controls the wave packet except for the period in which the system just moves over the reaction barrier. This is because control fields are obtained in proportion to the momentum expressed by Eq. (26). From the point of view of transition moment of the quantum system, C–H stretching motion is excited faster than C–H bending motion. However, since the potential energy curve slopes gently in the C–H bending direction, the wave packet easily moves toward this bending direction. In the early stage, the C–H stretching motion was excited by the E_x field first, but once the wave packet began to move in the C–H bending direction, this motion was much more quickly enhanced by the positive feedback of the E_y control field. On the top of the isomerization barrier, the E_x control field is enhanced for the same reason as that mentioned above. After going over the barrier, the wave packet spreads a little, and then the correspondence between the wave packet and the classical particle breaks down to some extent. That is one of the reasons why the control pulses are so complicated after the barrier crossing. At the end of control, most of the wave packet settles down to HNC [Fig. 5(b)].

Figure 7 shows the time-dependent isomerization probability defined by

$$P_{\text{iso}}(t) = \int_{-0.25}^0 dx \int_{-2}^2 dy |\Psi(x, y, t)|^2. \quad (33)$$

The integrated region is shown by a white rectangle in Fig.

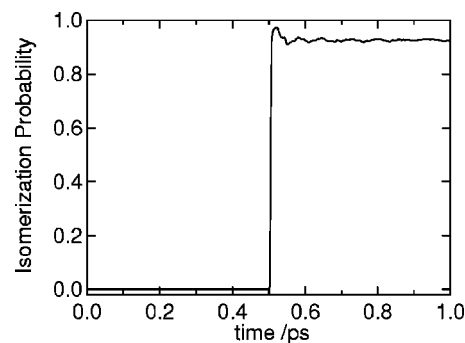


FIG. 7. Isomerization probability as a function of time.

5(b). About 92% of the wave packet is localized in that region at the end of the control pulses. It should be noted that there is no oscillatory behavior in isomerization probability after the control pulses come to an end. This indicates that the wave packet remains localized in the product region of HNC.

Figure 8 shows the expectation value of the molecular Hamiltonian along the reaction coordinate defined in the previous paper.³³ A dotted line represents the dissociation threshold of HCN \rightarrow H + CN. The wave packet absorbed energies while oscillating in the initial well. It should be noted that the energy absorbed by the system is sufficiently lower than the dissociation energy even around the transition state region. Namely, the dissociation is not induced by the controlled pulses shown in Fig. 6. Once the wave packet comes to the region in the target well, the system is stabilized to HNC by stimulated emission by controlled pulses.

Let us now make a comparison between the present method and other methods proposed so far. Accuracy and computational times in control methods depend on control objectives adopted, the reaction system under consideration, approximations used, etc. There have been several kinds of control objectives in quantum optimal control theory of chemical reaction. One of the objectives is a population of target states, and control theories with this object have been widely investigated and applied to one- or two-dimensional systems. It should be noted that there is computational difficulty inherent in this objective in the case of large systems. That is how to obtain reliable eigenstates of the reaction

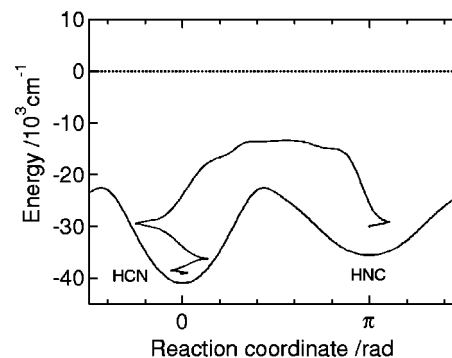


FIG. 8. The trajectory of the energy along the reaction coordinate under the control fields shown in Fig. 6. Around the point with 0 rad, the system is HCN, and HNC with π rad.

system of interest, and further one needs to find which are the target states and which are not out of a number of eigenstates.

Another objective is molecular geometry, in other words, position and momentum of wave packet. For this objective, matrix diagonalization of large dimensions described above is not necessary. This type of control has been achieved by considering density matrix,¹⁹ phase space representation¹⁸ like Wigner representation, δ -target^{27,30} or position tracking.⁴⁷⁻⁴⁹ However, the direct treatment of phase space, which involves density matrix calculation or phase space representation, requires additional heavily computational tasks. Therefore, approximations in weak field regimes such as the time-dependent Hartree approximation⁵⁰ and a linearized δ -target approximation^{27,30} have been introduced. The linearized δ -target approach is quite efficient if one wants for the system to be localized at a position at desired time τ . However, it does not specify its momentum. Then the system cannot be stabilized in a target well. Position tracking is a different kind of optimal control. This algorithm requires explicit target tracks of the objectives. It is useful if one has already known physically reasonable tracks.⁴⁹

A local track generation, developed by Chen *et al.*,⁴⁹ is similar to our local control methods. They employed an analogy to a classical particle in the quantum regime, and determined the objective track locally by using the system expectation value at each time. Even in this local track generation, one needs to obtain an explicit tracking path before its short time evolution. It means that in principle, one can control the system along the desired path. However, one must know the detailed information on the system in order to determine the path. On the other hand, our local feedback method is different from tracking, and control parameters such as f_{pp} are easily obtained

Our local feedback control method is one of the approximation methods to treat phase space in quantum mechanical dynamics. It should be noted that this control method is applicable to systems under intense field conditions as well as under weak field ones. We have treated phase space within classical mechanics, and then extended it to a quantum system on the basis of the Ehrenfest theorem. That is, we adopt the quantum expectation value of position $\langle \mathbf{q} \rangle$ and momentum $\langle \mathbf{p} \rangle$ as a representative point. In this simplified treatment, quantum-classical correspondence keeps automatically by compensation at each short time step. The conditions under the treatment works and when it fails can be qualitatively seen from Figs. 2 and 3. More generally, when wave packets act as a single packet in the phase space, they correspond to a classical particle and then our classical local feedback method works well. On the other hand, when wave packets bifurcate and split into two or more parts, our method cannot handle them since the correspondence between the wave packets and the classical particle breaks down.

IV. CONCLUSIONS

We have developed a simple method for quantum control of chemical reaction dynamics based on a classical local control theory. The principle of the control is to manipulate a

representative point on reaction coordinates by accelerating and/or decelerating its momentum by control fields. In the ordinal quantum mechanical local control theory, the target, such as population, should commute with the system Hamiltonian, while in the classical control theory, the control target is the momentum or kinetic energy. Our method was applied to a system with a one-dimensional double-well potential to check its applicability. It was shown that our simple method is applicable to nuclear wave packet control by using a quantum mechanically averaged nuclear momentum on the basis of the Ehrenfest theorem. A limitation of wave packet control by the present method was discussed. Isomerization of HCN to HNC was controlled in a two-dimensional model with $\sim 90\%$ yields. In conclusion, this shows the usefulness of our simplified method for reaction control.

It should be noted that in our treatment, a control equation itself does not need to be obtained from the exact system equation under a local control treatment. We can use other system equations that approximate desired control objectives, instead of the whole target system. This feature might be efficient for a system with more complicated dynamics.

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