

Pulse-shaping algorithm of a coherent matter-wave-controlling reaction dynamics

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A pulse-shaping algorithm for a matter wave with the purpose of controlling a binary reaction has been designed. The scheme is illustrated for an Eley-Rideal reaction where an impinging matter-wave atom recombines with an adsorbed atom on a metal surface. The wave function of the impinging atom is shaped such that the desorbing molecule leaves the surface in a specific vibrational state.

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A binary chemical reaction can be coherently controlled by means of interference of matter waves. A coherent source of matter waves could originate from an output coupler of a Bose-Einstein condensate (BEC) [1–4]. A two-pulse scenario for such a control scheme has been previously explored and termed 2PACC spectroscopy [5,6]. The control knobs in the 2PACC model were limited to the time delay between the matter-wave pulses and their phase difference. It was demonstrated that the control achieved a significant enhancement of the probability of creating a gas phase molecule in an Eley-Rideal reaction. The main drawback of the 2PACC scheme was that the desorbing molecules possessed a broad distribution of vibrational states. The present study demonstrates that additional control on the incoming matter wave can create a specific final vibrational state.

To achieve this target, the task is to figure out the optimal shape of the incoming wave packet. An iterative computation scheme is developed for this task which is in analogy to the optimal control theory of optical pulse shaping [7–10]. Equally important is the development of experimental schemes able to shape such a wave packet.

As in earlier studies [5,6], the control target is the Eley-Rideal bimolecular reaction where an impinging atom recombines with an adsorbed atom on a metal surface to form a diatomic molecule,



The source of atom Y is a matter wave, which in the presented model consists of either hydrogen or alkali-metal atoms. The matter wave of Y is directed to a cold Cu(111) surface with low coverage chemisorbed hydrogen atoms. When the wave function of Y overlaps with that of the adsorbed atom, interaction is expected, leading to a recombination that forms the YH molecule. If the newly formed molecule has sufficient kinetic energy, it will eventually desorb from the surface. By shaping the wave function, the vibrational state of the desorbing molecules becomes controlled by constructive or destructive quantum interferences. Since the reactant atom on the surface has a random phase, the relative phase between the desorbing molecule and the im-

pinging matter-wave atom is not known. This means that the desorbing molecules will not form a BEC of molecules. A possible control scheme to form a BEC of molecules can be done by recombining the two impinging phase-related coherent matter waves on a surface [11].

The wave function of the system is described by a vector,

$$\Psi(r, Z, t) = \begin{pmatrix} \Psi_R(r, Z, t) \\ \Psi_P(r, Z, t) \end{pmatrix}, \quad (2)$$

where the reactant and product channels are denoted by the index $\{R, P\}$. The two degrees of freedom are the intramolecular distance between the two atoms (r) and the distance from the surface to the center-of-mass motion of the molecule (Z). We assume a collinear arrangement of two atoms relative to the surface. The impinging atom is located at $z_y = Z + r(m_h/M)$, whereas the location of the adsorbed atom is at $z_h = Z - r(m_y/M)$. The total mass of the system is given by $M = m_h + m_y$.

The dynamics of the Eley-Rideal reaction was followed by solving the time-dependent two-channel Schrödinger equation. The pulse-shaping algorithm is based on propagating the wave function forward and backward in time. The Chebychev propagation method [12] was employed allowing the propagation of the wave function in both directions of time.

The task is to find the initial wave packet on the reactive channel which will lead to desorption of the molecule in the v th vibrational state. The scheme is based on reversing the reaction, e.g., starting from a product wave function representing the desorbing molecule in the v th vibrational state. This wave function is propagated backwards in time to find the reactive wave function leading to the desired final condition. The scheme is illustrated for an Eley-Rideal reaction in which an impinging lithium atom recombines with an adsorbed hydrogen atom. A trial wave function on the product channel has been constructed. Far enough from the surface, the internal and external degrees of freedom are uncoupled. Thus the trial wave packet can be expressed as a product of the v th molecular vibrational eigenstate, $\chi_v(r)$ ($v = \{0, 1, \dots\}$), and a Gaussian wave function, $g(Z)$,

$$\Psi_{\text{trial}}(r, Z) = \begin{pmatrix} 0 \\ \chi_v(r)g(Z) \end{pmatrix}. \quad (3)$$

The wave function used for control is the wave function of a lithium matter-wave source. The target is to desorb a lithium

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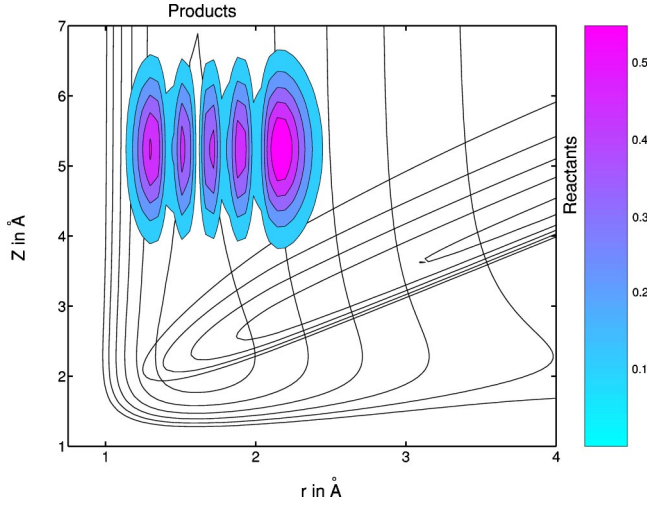


FIG. 1. (Color online) To illustrate the pulse-shaping algorithm, we consider the Eley-Rideal reaction of the impinging lithium recombines with a chemisorbed hydrogen atom on a Cu(111) surface. The above wave function has been used as the target trial wave function for obtaining the wave function of the matter wave, causing the molecule to desorb in the fifth vibrational state ($v=4$). The contour values of the potential-energy surfaces are -3 , -2.5 , -2 , -1.5 , -1 , and -0.5 eV.

hydride molecule in the fifth vibrational state ($v=4$). A target trial wave function has been constructed according to Eq. (3) and is shown in Fig. 1. An iterative scheme is used for inversion, i.e., finding the condition for the wave packet on the reactant channel leading to desorption of the molecules in the v th vibrational state.

(i) *Backward propagation.* A trial wave function $\Psi_{\text{trial}}(r, Z)$ is propagated backward in time. As the molecule approaches the surface, population is transferred to the reactant channel through the nonadiabatic coupling. The part of the wave packet that is transferred to the reactant channel corresponds to a molecular dissociation. That is, one atom is

chemisorbed on the surface and the other desorbs to the gas phase. After a preassigned time the propagation is stopped, leading to the wave function $\Psi_1 = (\phi_R^b, \phi_P^b)$. Figure 2 (left) shows a wave packet in the reactant channel after termination of the backward time propagation.

(ii) *Selection.* Part of the backward-propagating wave function, Ψ_1 , is selected consisting of a wave function outside the interaction region. In Fig. 2 (left), the wave function before selection is shown. The part of the wave function which is inside the box has been selected. The selected wave function, ϕ_R^{select} , can be decomposed into

$$\phi_R^{\text{select}}(z_H, z_{\text{Li}}) = \sum_{i=0} \zeta_i^{\text{H}}(z_H) \zeta_i^{\text{Li}}(z_{\text{Li}}), \quad (4)$$

where ζ_i^{H} is the vibrational eigenstate of the hydrogen-surface bond. The wave function of the impinging atom, ζ_i^{Li} , is given by

$$\zeta_i^{\text{Li}}(z_{\text{Li}}) = \int [\zeta_i^{\text{H}}(z_H)] * \phi_R^{\text{select}}(z_H, z_{\text{Li}}) dz_H. \quad (5)$$

We assume that the Cu(111) surface is cold (~ 1 K), therefore the chemisorbed atom should be in the lowest vibrational state, e.g., $i=0$. At this temperature, the population at any vibrational excited state is below 10^{-20} . The wave function representing the reactive channel is given by $\Psi_2 = (\zeta_0^{\text{H}}(z_H) \zeta_0^{\text{Li}}(z_{\text{Li}}), 0)$. The size and location of the box are chosen such that the energy of the selected and normalized wave packet is close to the energy of the trial wave packet.

(iii) *Forward propagation.* The selected wave function, Ψ_2 , is propagated forward in time through the nonadiabatic coupling between two potential-energy surfaces. The newly formed molecules desorb, leading to the wave function $\Psi_3 = (\phi_R^f, \phi_P^f)$.

(iv) *Projection.* The overlap between the forward-propagated wave function, Ψ_3 , and the trial wave function is evaluated as a function of the center of mass,

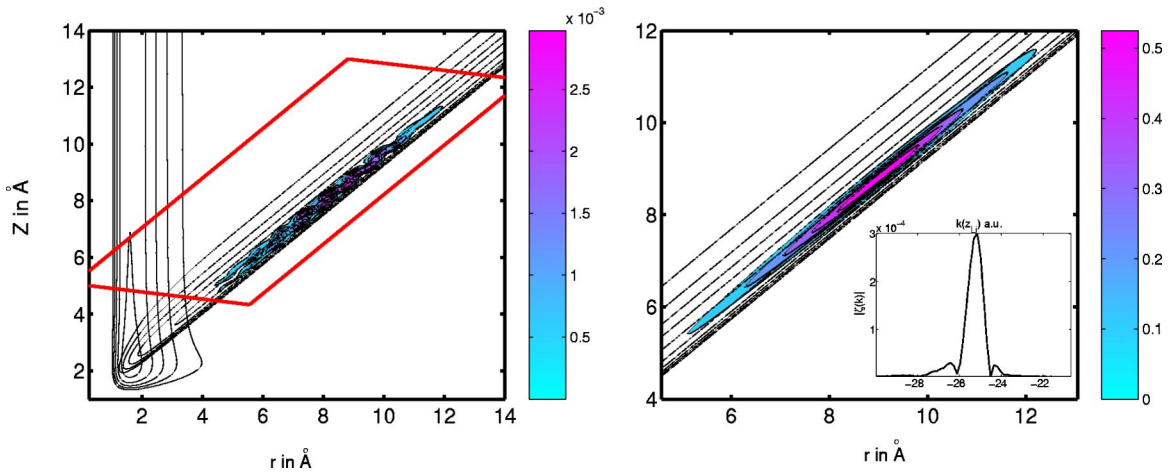


FIG. 2. (Color online) Above, the selection step of the pulse-shaping scheme is illustrated. A wave function on the reactant channel, ϕ_R^b , is shown after termination of the backward time propagation (left). The wave packet of the box has been selected for the decomposition of the wave function [Eq. (4)]. On the right part, the renormalized decomposed wave function, $\zeta_0^{\text{Li}}(z_{\text{Li}}) \zeta_0^{\text{H}}(z_{\text{H}})$, is shown. This represents the initial wave function of the matter-wave atom, and the chemisorbed atom in the lowest vibrational state is shown. This wave packet is used for forward propagation. In the inset, the momentum components of the wave function of the matter wave atom, $\zeta_0^{\text{Li}}(z_{\text{Li}})$, are displayed.

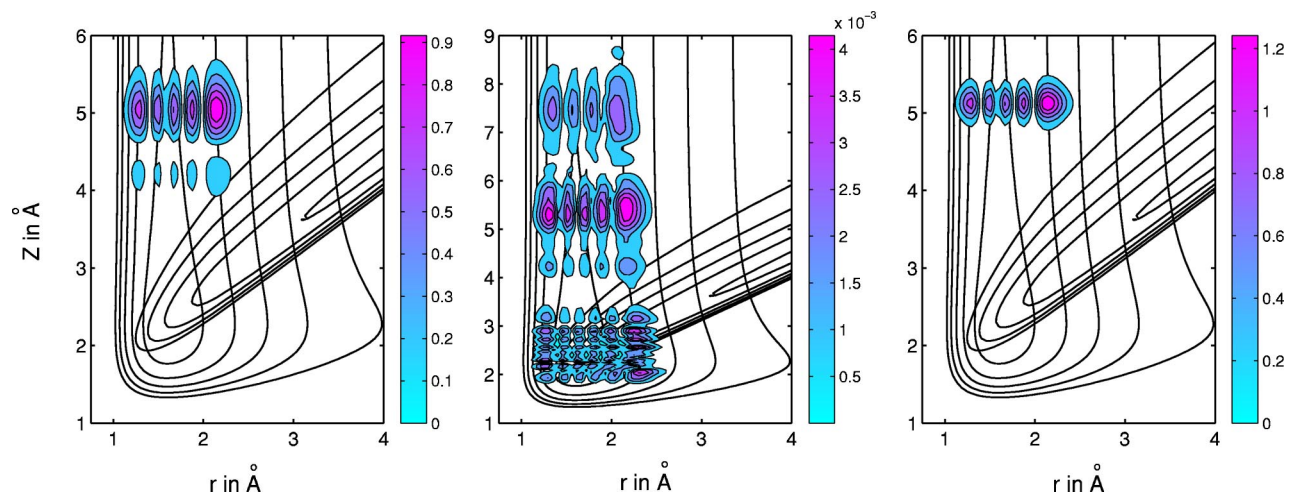


FIG. 3. (Color online) Above, the projection step of the pulse-shaping scheme is illustrated. The trial wave function before the projection is showed on the left. The wave function on the product channel, ϕ_R^f , after termination of forward time propagation is shown in the center. The trial wave function after projection is shown on the right.

$$c_n(Z) = \int [\Psi_{\text{trial}}(r, Z)]^* \Psi_3(r, Z) dr. \quad (6)$$

A new trial wave function is created,

$$\Psi_{\text{Proj}}(r, Z) = \begin{pmatrix} 0 \\ c_n(Z)f(Z)\chi_n(r) \end{pmatrix}. \quad (7)$$

In the first iteration, $f(Z)$ is $g(Z)$. This new wave function is renormalized and it is used as a new trial wave function in step (i), $\Psi_{\text{trial}} = \Psi_{\text{proj}}$. The projection of the forward-propagated wave packet is illustrated in Fig. 3

The above pulse-shaping scheme is repeated a number of times. It is important that the energy of the total system is conserved after either the selection stage or projection of the total wave function. The pulse-shaping algorithm is stopped when a satisfactory yield in the desired vibrational state has been reached. The ultimate goal is that all the flux of the desorbing molecules is probed into the particular vibrational state. In order to improve the convergence of the algorithm, the number of grid points has been enlarged (1024×1024) and the grid spacing has been reduced ($dr=dZ=0.05$ a.u.) compared to the earlier 2PACC calculations [6]. The potential-energy surfaces are given in Ref. [6], where the nonadiabatic coupling term was increased to $\beta=0.1$ eV. The backward propagation is stopped when the nonadiabatic population transfer is negligible. The size and location of the box used for selecting the wave packet in step (ii) vary from iteration to iteration in order to keep the reactive wave packet inside the box. The forward propagation is terminated when the overlap between the trial wave function and the propagated wave function is maximized.

Starting from the trial wave function of Fig. 1, the pulse-shaping scheme was used to obtain the optimal wave packet in the reactant channel, leading to desorption of the molecule in the fifth vibrational state. Figure 4 shows the accumulated flux of desorbing molecules as a function of the iteration number. State-resolving the accumulated flux enables us to calculate the percentage of desorbing molecules in the fourth

and fifth vibrational states (see Fig. 4). A monotonic increase of the yield in $v=4$ is observed.

The reactant wave function is shown in Fig. 2 (right). The momentum representation is obtained by performing a Fourier transform of the one-dimensional matter wave, ξ_0^{Li} . The momentum components are shown in the inset of Fig. 2 (right). Several momentum components can be observed which are needed for creating the necessary constructive quantum interference in the fifth vibrational state and destructive in all the other vibrational states. This momentum spread is obtainable within proposed manipulation of the matter wave [13]. The multipulsed matter wave confirms previous studies, which showed that control is obtained by destructive or constructive quantum interferences of the matter with itself.

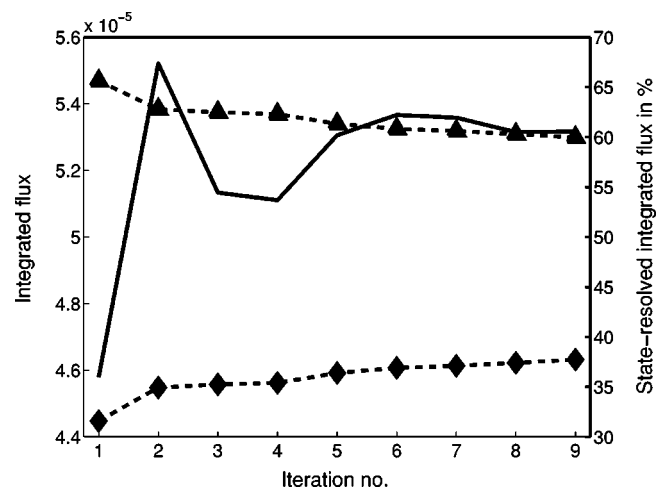


FIG. 4. The accumulated flux (solid line) is shown as a function of the iteration number. The percentage of the accumulated flux in the fourth and fifth vibrational state have been computed as a function of the iteration number. The fourth and fifth vibrational states are shown with triangles and diamond, respectively.

For experimental realization, the source of the matter waves, the BEC condensate, has to be positioned very close to a surface. Such a device has been developed in the so-called atom chips [14–17] or surface microtraps [18,19]. In the atom chips, for example, the BEC has been placed a few hundred microns above a metal surface [16].

The experimental realization of the control scheme depends on the ability to shape matter waves. Four-wave mixing [20] of matter waves has been demonstrated which can control different momentum components of the matter waves. A more comprehensive solution could follow ideas

from optical pulse shaping. A matter-wave diffraction grid has been demonstrated [21–23]. A setup of two diffraction grids and a phase-shift device would constitute the ultimate matter-wave pulse shaper. Such a device would make the suggested control scheme realizable.

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