The Journal of Chemical Physics

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Cite as: J. Chem. Phys. **115**, 3590 (2001); https://doi.org/10.1063/1.1389306
Submitted: 16 May 2001 • Accepted: 12 June 2001 • Published Online: 10 August 2001

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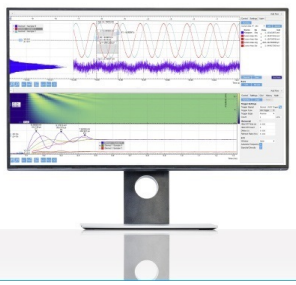

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Coherent control of quantum chaotic diffusion: Diatomic molecules in a pulsed microwave field

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(Received 16 May 2001; accepted 12 June 2001)

Extensive phase control of quantum chaotic diffusion is demonstrated for diatomic molecules periodically kicked with microwave pulses. In particular, both complete suppression of chaotic diffusion as well as its enhancement can be achieved by varying the phase of the initial superposition state. The origin of this control in deviations from random matrix theory is also discussed. The results should motivate experiments that are relevant to both coherent control and to quantum chaos. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1389306]

I. INTRODUCTION

Interference is at the heart of quantum mechanics. The observation that quantum interference and hence molecular dynamics can be altered via experimentally controllable parameters motivated the rapidly developing field of coherent control (CC) of molecular processes.[1] The essence of several scenarios of CC of molecular processes consists of three steps: (1) create a superposition state composed of several basis states; (2) control the relative phases of these basis states; and (3) subject the molecular system to external fields that yield multiple coherent pathways to the same target state. Successful control results when the cross section of particular target states can be extensively and selectively altered by changing the relative phases in the second step. Studies of this kind include, for example, our original bichromatic control scenarios,[2] two-pulse control schemes applied to various problems,[3] and the CC of molecular scattering.[4]

Traditional studies in coherent control typically deal with integrable systems where very few energy levels are involved in the dynamics. By contrast, the majority of real molecular systems is complex: the quantum dynamics may involve many energy levels and the underlying classical dynamics may be strongly chaotic. For this reason, consideration of control for chaotic systems is of general interest and importance.

Classical chaotic systems display intrinsic stochasticity that is generated by the dynamics itself.[5] Thus, even without external noise, a classical chaotic system ''loses its memory'' of the initial state exponentially fast. Considering the quantum-classical correspondence principle in quantized chaotic systems,[6] it is expected that various manifestations of classical chaos should occur in the quantum dynamics when the relevant actions are much larger than Planck's constant.[7] With this perspective, there are those who intuitively believe that quantum phases embedded in initial states should play a minor role in classically chaotic systems, and that controlling quantized chaotic dynamics in the semiclassical regime could be just as difficult as controlling classical Hamiltonian chaos.[8] This is in fact the case. However, coherent control over quantum chaotic dynamics far from the classical limit, as demonstrated below, should be feasible.

Recently, we computationally demonstrated that extensive phase control of quantum chaotic diffusion is achievable[9] using the delta-kicked planetary rotor (DKPR) model[10] in the quantum regime. In particular, preparing a simple superposition state comprising two basis states allowed for a wide range of control over the ensuing diffusive dynamics. Further, the control was found to persist in the presence of weak decoherence, and diminished, as expected, with increasing decoherence strength. This result opened an interesting direction for coherent control, overlapping with fields such as quantum chaos and chaos control.

In this paper, we consider quantum chaotic diffusion in diatomic molecules in pulsed microwave fields in an effort to extend our studies to realistic systems and in order to motivate experimental coherent control studies of quantum chaotic diffusion. Indeed, experimental studies of microwave-pulse-kicked diatomic molecules appear feasible today and may be easier to realize than, for example, atomic physics approaches discussed in Ref. 9 (e.g., kicked atoms in a single quantum well, or ultracold atoms in a periodic standing wave of near-resonant light).

This paper is organized as follows. In Sec. II, we briefly introduce the DKPR model. In Sec. III, we consider both the classical dynamics and quantum dynamics in detail for diatomic systems kicked by periodic microwave pulses. In Sec. IV, we present representative results, followed by discussions on the mechanism of phase control. Conclusions and a summary comprise Sec. V.

II. THE DELTA-KICKED PLANETARY ROTOR

Before considering molecular systems, it is beneficial to introduce the DKPR model, a paradigm of both classical and quantum chaos, that will be compared to the kicked diatom. The DKPR Hamiltonian is given by

$$H(\hat{L},\theta)=\frac{\hat{L}^2}{2I}+\lambda\cos(\theta)\sum_n \delta(t/T-n), \tag{1}$$

where $\hat{L}=-i\hbar(\partial/\partial\theta)$ is the angular momentum operator, θ is the conjugate angle, I is the moment of inertia, λ is the

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strength of the kicking field, and T is the time interval between kicks. The Hilbert space is spanned by the angular momentum eigenstates $\exp(im\theta)/\sqrt{2\pi}$ $(m=0,\pm1,\pm2,...)$. The quantum time evolution operator $\hat{M}$ between two kicks is given by[10]

$$\hat{M}=\exp\left[i\frac{\tau}{4}\frac{\partial^2}{\partial\theta^2}\right]\exp[-ik\cos(\theta)]\exp\left[i\frac{\tau}{4}\frac{\partial^2}{\partial\theta^2}\right], \tag{2}$$

where $\tau\equiv\hbar T/I$ and $k\equiv\lambda T/\hbar$ are dimensionless parameters. The parameter τ plays the role of the effective Planck constant of the system. If we fix the value of the product $k\tau$ and decrease the value of τ, the system approaches the classical limit. This classical limit is given by the standard map,[10] which, when expressed in terms of dimensionless variables θ and the scaled classical angular momentum $\tilde{L}=L\tau/\hbar$, takes the following form:

$$\begin{aligned}\theta_N&=\theta_{N-1}+(\tilde{L}_N+\tilde{L}_{N-1})/2,\\ \tilde{L}_N&=\tilde{L}_{N-1}+(k\tau)\sin(\theta_{N-1}+\tilde{L}_{N-1}/2).\end{aligned} \tag{3}$$

As is seen from Eq. (3), the classical dynamics depends only on the product $k\tau$. When $k\tau>0.9716$, the last Kolmogorov–Arnold–Moser (KAM) invariant curve vanishes and chaotic trajectories can diffuse into the entire unbounded phase space. The scaled mean energy $\langle\tilde{L}^2/2\rangle$ of classical ensembles then displays unrestricted diffusive growth, whose approximate diffusion constant can be evaluated analytically. By contrast, the quantum DKPR displays ''quantum localization.''[11] That is, energy absorption is restricted; the external field only excites a finite number of unperturbed energy levels that is related to the classical diffusion constant.[12] Thus, there is a marked difference between the classical and quantum dynamics manifest in qualitatively different energy absorption behavior.

Recently,[9] we found that the extent of quantum chaotic diffusion can be actively controlled by manipulating the initial-state coherence. Specifically, we considered the dynamics resulting from an initial superposition state comprising two basis states $\exp(im\theta)/\sqrt{2\pi}$ and $\exp(in\theta)/\sqrt{2\pi}$. By varying the relative phase between the two basis states, we were able to change the quantum diffusion from almost-completely suppressed to much enhanced with the latter behavior much closer to classical diffusion. Thus, quantum chaotic dynamics in the DKPR is both vulnerable to decoherence effects[13] and sensitive to initial-state coherence effects. The DKPR model is experimentally achievable via atom optics,[14] but the control experiment in such a system would be difficult. In addition, the system is somewhat contrived. To this end we examine microwave absorption in diatomics, which provides an alternative realistic system for consideration.

III. MICROWAVE KICKED DIATOMIC MOLECULES

The proposal to use microwave kicked diatomic molecules as a molecular analog of the DKPR was advanced more than a decade ago.[15] In particular, with the vibrational degree of freedom frozen, the Hamiltonian for the rotational motion of diatomic molecules subject to periodic microwave pulses resembles that of the DKPR. That is, if the orientation of a diatomic molecule is described by two angles θ and ϕ,[16] then the corresponding Hamiltonian is

$$\hat{H}=\frac{\hat{J}^2}{2I}+\mu E_0\cos(\theta)\sum_n\Delta\left(\frac{t}{T}-n\right), \tag{4}$$

where $\hat{J}$ is the angular momentum operator in three dimensions

$$\hat{J}^2=-\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left[\sin(\theta)\frac{\partial}{\partial\theta}\right]+\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right], \tag{5}$$

μ is the molecular electric dipole moment, E_0 is the amplitude of the driving field whose polarization direction defines the z direction, I is the moment of inertia of the molecule about an axis perpendicular to the symmetry axis, and $\Delta(t/T-n)$ is the pulse shape function simulating the delta kicking in the DKPR model. Microwave pulses may be realized by an array of phase-locked microwave generators and, following Blümel *et al.*,[15] we assume Δ takes the form

$$\Delta\left(\frac{t}{T}-n\right)=1+2\sum_{m=1}^{m=7}\cos\left[2m\pi\left(\frac{t}{T}-n-1/2\right)\right]. \tag{6}$$

The kicked CsI molecule appears to be an excellent candidate for experimental studies of chaotic rotational excitation by microwave pulses[15] since: (1) it has a large dipole moment, thus dramatically increasing the molecule–field coupling strength; and (2) the excitation energy of the first vibrational energy level in CsI corresponds to that of the 71st rotational energy level, so that vibrational excitation and rotation–vibration coupling can generally be neglected. Blümel *et al.* also estimated[15,16] that for CsI, $\tau\equiv\hbar T/I=1.0$ translates into a driving frequency of $T^{-1}\approx9$ GHz, and that $k\equiv\mu E_0T/\hbar=5.0$ translates into the relatively moderate field amplitude $E_0\approx1$ kV/cm.

Since the projection of the angular momentum onto the z direction is a constant, we choose it to be zero. As a result, the second term in Eq. (5) gives zero contribution, and the kicked diatomic molecule has only one relevant degree of freedom (θ). Nonetheless, there still remain several important differences between the DKPR model and the kicked diatomic systems. First, the kicking microwave field can only approximate the delta kicks. Second, θ ranges from 0 to 2π in the DKPR model, whereas it ranges from 0 to π for a three-dimensional rotor. Third, the Hilbert space for the kicked molecule case is spanned by the basis states $|j,0\rangle$, where 0 denotes the zero projection of the angular momentum onto the z axis, and j is the rotational quantum number; in the DKPR model rotational quantum numbers m can be both positive and negative, representing two possible directions of the angular momentum of the planetary rotor. Fourth, in the DKPR model, the matrix elements of the coupling potential $\cos(\theta)$ are given by

$$\langle m|\cos(\theta)|m'\rangle=\tfrac{1}{2}(\delta_{m',m-1}+\delta_{m',m+1}), \tag{7}$$

while in the kicked molecule case, we have

$$\langle j,0|\cos(\theta)|j',0\rangle=C_j\delta_{j',j-1}+C_{j+1}\delta_{j',j+1}, \tag{8}$$

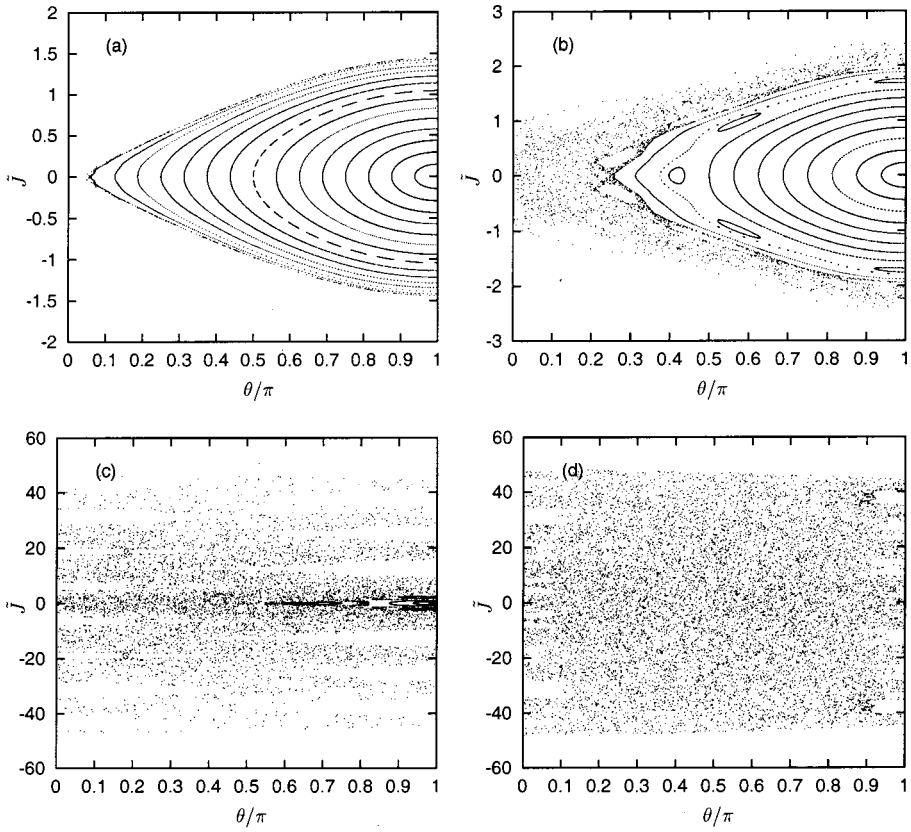

FIG. 1. The Poincaré surfaces of section for the classical dynamics of the kicked diatomic molecule (see Sec. III). $\tilde{J}$ is the scaled angular momentum in dimensionless units. Results are obtained by numerical integration of 15 different initial trajectories with $\tilde{J}(0)=0$ and $\theta(0)=l\pi/16$, $l=1,2,...,15$, for time equal to 720 kicks. (a) $k\tau=0.5$. (b) $k\tau=1.0$. (c) $k\tau=2.5$. (d) $k\tau=5.0$. Apparently, the classical dynamics is predominantly chaotic when $k\tau\geqslant 5.0$.

where

$$C_j \equiv \frac{j}{\sqrt{(2j-1)(2j+1)}}. \tag{9}$$

Given these differences, it is necessary to independently establish conditions for phase control of quantum diffusion in kicked diatomic systems.

A. Classical dynamics

With the vibrational degree of freedom frozen and the projection of the angular momentum onto the polarization vector of the driving field being zero, the classical Hamiltonian H_{cl} for diatomic molecules kicked by microwave pulses is given by

$$H_{cl}=\frac{I\dot{\theta}^2}{2}+\mu E_0\cos(\theta)\sum_n \Delta\left(\frac{t}{T}-n\right). \tag{10}$$

The classical equation of motion for θ is then

$$I\frac{d^2}{dt^2}\theta=\mu E_0\sin(\theta)\sum_n \Delta\left(\frac{t}{T}-n\right). \tag{11}$$

If we define $\xi\equiv t/T$, $\tilde{J}\equiv\dot{\theta}T$, the above equation can be re-expressed as two canonical equations in $\tilde{J}$ and θ

$$\begin{aligned}\frac{d\theta}{d\xi}&=\tilde{J},\\ \frac{d\tilde{J}}{d\xi}&=(k\tau)\sin(\theta)\sum_n \Delta(\xi-n).\end{aligned} \tag{12}$$

Clearly, $\tilde{J}$ is the counterpart of $\tilde{L}$ in the DKPR model [see Eq. (3)], and the classical dynamics depends only on the product of k and τ. Note also that the quantum counterpart of $\tilde{J}^2$ is $j(j+1)\tau^2$, where j is the rotational quantum number.

Figure 1 displays the Poincaré surfaces of section for $k\tau=0.5$, 1.0, 2.5, and 5.0. The results are obtained by numerical integration of 15 different initial trajectories with $\tilde{J}(0)=0$ and $\theta(0)=l\pi/16$, $l=1,2,...,15$, for time equal to 720 kicks. It is clear from Fig. 1 that when $k\tau\geqslant 5.0$, the classical dynamics is predominately chaotic in the entire $\tilde{J}$ region. We focus below on quantum dynamics in this $k\tau$ regime.

B. Quantum dynamics

To solve for the time-evolving wave function $|\psi(t)\rangle$ for the kicked molecule, we first expand the wave function in the Hilbert space basis

$$|\psi(t)\rangle=\sum_j A_j(t)|j,0\rangle. \tag{13}$$

Substituting this expansion into the time-dependent Schrödinger equation and using Eq. (8), we have

$$\begin{aligned}i\hbar\frac{dA_j(t)}{dt}=&\frac{j(j+1)\hbar^2}{2I}A_j(t)+\mu E_0\sum_n \Delta\left(\frac{t}{T}-n\right)\\ &\times(C_jA_{j-1}(t)+C_{j+1}A_{j+1}(t)).\end{aligned} \tag{14}$$

The dynamical equations can be further simplified by working with an interaction picture.[16] Specifically, let $B_j(t)=A_j(t)\exp[i\hbar j(j+1)t/(2I)]$; we finally get

$$i\frac{dB_j(\xi)}{d\xi}=k\sum_n \Delta(\xi-n)\{\exp[i\tau j\xi]C_jB_{j-1}(\xi) + \exp[-i\tau(j+1)\xi]C_{j+1}B_{j+1}(\xi)\}. \quad (15)$$

Clearly, in contrast to classical dynamics, the quantum dynamics of the kicked molecule depends on two parameters, τ and k. Thus, by decreasing the magnitude of τ with $k\tau$ fixed, we can arbitrarily decrease the quantum effects due to the quantization of angular momentum while keeping the underlying classical dynamics unaffected.

The coupled equations of motion for the expansion coefficients $B_j(t)$ can be readily solved using the fourth-order Runger–Kutta method, with a time step of $10^{-4}T$, and with the number of basis states chosen to be $500/\tau$. With these choices, convergence of the results was excellent.

IV. PHASE CONTROL OF QUANTUM CHAOTIC DIFFUSION IN KICKED MOLECULES

As clearly seen from Eqs. (4) and (6), the Hamiltonian of the system considered here is strictly periodic with time. Hence, the time-evolution operator $\hat{F}$ associated with one period T is of particular interest and will prove useful in the analysis of the results. The formal solution for $\hat{F}$ can be written, with the help of the time-ordering operator Γ, as

$$\hat{F}=\Gamma\left[\exp\left\{\frac{-i}{\hbar}\int_0^T dt'\,\hat{H}(t')\right\}\right], \quad (16)$$

where

$$\Gamma[\hat{C}(t)\hat{D}(t')]=\hat{C}(t)\hat{D}(t'), \quad \text{if } t>t',$$
$$\Gamma[\hat{C}(t)\hat{D}(t')]=\hat{D}(t')\hat{C}(t), \quad \text{if } t<t'. \quad (17)$$

Although it is not possible to give an explicit form of $\hat{F}$ in the kicked molecule case, the existence of this formal solution yields a stroboscopic description of the dynamics

$$|\psi(nT)\rangle=\hat{F}^{n-1}|\psi((n-1)T)\rangle=\hat{F}^n|\psi(0)\rangle. \quad (18)$$

More importantly, as we will see below, eigenfunctions and eigenphases of the quantum map operator $\hat{F}$ help provide clear insights on how chaotic rotational excitations may be controlled by manipulating quantum phase in the initial state.

A. Formal dynamics and initial-state coherence effects

Consider now an initial superposition state prepared as

$$|\psi(0)\rangle=\cos(\alpha)|j_1,0\rangle+\sin(\alpha)\exp(-i\beta)|j_2,0\rangle. \quad (19)$$

Here, we use only two basis states (more basis states can be considered, providing more adjustable parameters for control). After the molecule is kicked N times, the quantum state evolves to $\hat{F}^N|\psi(0)\rangle$. In order to compare quantum results for our case with that for the DKPR model and the classical limit, we define the dimensionless rotational energy $\tilde{E}\equiv\Sigma_j P_j j(j+1)\tau^2/2$, where $P_j=|B_j|^2$ is the occupation probability of the $|j,0\rangle$ state. The classical limit of $\tilde{E}$ is given by $\langle\tilde{J}^2/2\rangle$. $\hat{F}$ can be formally diagonalized by a unitary transformation

$$\langle j_a,0|\hat{F}|j_b,0\rangle=\sum_{j_c}\exp(-i\phi_{j_c})U^*_{j_c,j_a}U_{j_c,j_b}, \quad (20)$$

where $U_{j_c,j_a}\equiv\langle j_c,0|\hat{U}|j_a,0\rangle(j_a=0,1,2,...)$ is the eigenvector with eigenphase ϕ_{j_c}. Moreover, since the basis states $|j,0\rangle$ are time-reversal invariant, one can prove that the matrix elements U_{j_c,j_b} can be chosen as real numbers,[7] i.e.,

$$U^*_{j_c,j_a}=U_{j_c,j_a}, \quad j_a,j_c=0,1,2,\ldots. \quad (21)$$

Further, evaluating $\tilde{E}$ at $t=NT$ with Eqs. (19), (20), and (21) gives

$$\frac{2\tilde{E}}{\tau^2}=\langle\psi(0)|\hat{F}^{-N}\frac{\hat{J}^2}{\hbar^2}\hat{F}^N|\psi(0)\rangle$$
$$=\cos^2(\alpha)\sum_{jj_aj_b} j(j+1)U_{j_aj_1}U_{j_bj}U_{j_aj}U_{j_bj_1}$$
$$\times e^{iN(\phi_{j_a}-\phi_{j_b})}+\sin^2(\alpha)\sum_{jj_aj_b} j(j+1)$$
$$\times U_{j_aj_2}U_{j_bj}U_{j_aj}U_{j_bj_2}e^{iN(\phi_{j_a}-\phi_{j_b})}+\tfrac{1}{2}\sin(2\alpha)$$
$$\times\Bigg(e^{-i\beta}\sum_{jj_aj_b} j(j+1)U_{j_aj_1}U_{j_bj_2}U_{j_aj}U_{j_bj}$$
$$\times e^{iN(\phi_{j_a}-\phi_{j_b})}+\text{c.c.}\Bigg). \quad (22)$$

Evidently, the first two terms are incoherent since they do not depend on the value of β. They represent quantum dynamics associated with each of the states $|j_1,0\rangle$ and $|j_2,0\rangle$ independently. The last two terms represent interference effects due to initial-state coherence between $|j_1,0\rangle$ and $|j_2,0\rangle$. Below we show that quantum diffusion over the energy space can be extensively controlled by manipulating the initial quantum phase described by β, which corresponds to manipulating the interference term in Eq. (22).

B. Phase control results

In Fig. 2 we present two representative examples [$\tau=1.0$, $k=5.0$ in Fig. 2(a) and $\tau=1.2$, $k=4.8$ in Fig. 2(b)] to illustrate phase control of quantum chaotic diffusion in kicked diatomic molecules. In both examples the underlying classical dynamics of rotational excitation is strongly chaotic, as shown in Fig. 1. We choose $j_1=1$ and $j_2=2$ to create the initial superposition state $(|1,0\rangle\pm|2,0\rangle)/\sqrt{2}$, i.e., $\alpha=\pi/4$ and $\beta=0$, π in Eq. (19) (reasons for choosing β to be 0 or π will be explained in subsection C). As seen in Fig. 2, the phase control is striking. For both examples, $(|1,0\rangle-|2,0\rangle)/\sqrt{2}$ results in almost no diffusion over the energy space whereas $(|1,0\rangle+|2,0\rangle)/\sqrt{2}$ shows extraordinarily fast diffusion (even faster than the semiclassical diffusion shown in Fig. 5 later below) before it essentially stops at $t\approx 10T$. Note (1) that this huge difference is achieved solely by changing the initial relative phase between the two participating states $|1,0\rangle$ and $|2,0\rangle$ in the initial superposition state, and (2) that by contrast, each of $|1,0\rangle$ or $|2,0\rangle$ individually

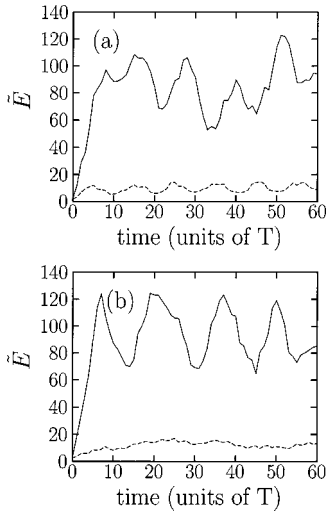

FIG. 2. The dimensionless rotational energy of the kicked diatomic molecule $\tilde{E}=\Sigma_j P_j j(j+1)\tau^2/2$ vs time (in units of T). Solid line and dashed lines are for the initial states $(|1,0\rangle+|2,0\rangle)/\sqrt{2}$ and $(|1,0\rangle-|2,0\rangle)/\sqrt{2}$, respectively. (a) $\tau=1.0$, $k=5.0$. (b) $\tau=1.2$, $k=4.8$.

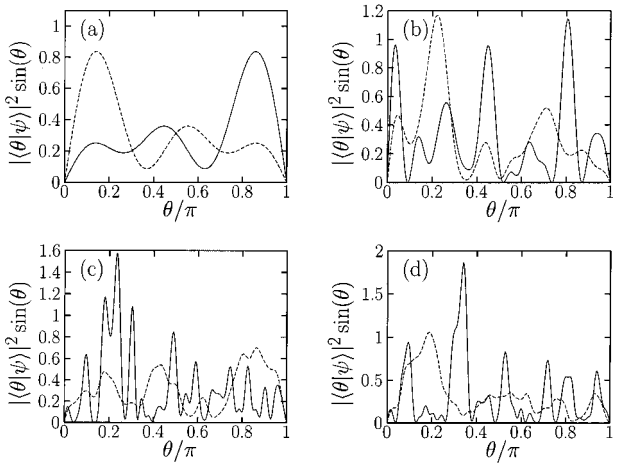

FIG. 4. $|\langle\theta|\psi(nT)\rangle|^2\sin(\theta)$ vs θ/π for (a) $n=0$; (b) $n=2$; (c) $n=10$; and (d) $n=20$. Solid and dashed lines are for the initial states $(|1,0\rangle+|2,0\rangle)/\sqrt{2}$ and $(|1,0\rangle-|2,0\rangle)/\sqrt{2}$, respectively. $\tau=1.0$, $k=5.0$.

would give very similar diffusion behavior lying between the solid and dashed lines in Fig. 2. In effect, the two participating states $|1,0\rangle$ and $|2,0\rangle$ can either constructively or destructively interfere with each other, even though the underlying classical dynamics is strongly chaotic. Details of the respective wave functions at $t=60T$ are shown in Fig. 3 in terms of the occupation probability P_j versus j. In both Fig. 3(a) and Fig. 3(b), one sees vividly that changing β from 0 to π alters the occupation probability of many states by almost an order of magnitude. This further demonstrates the role of the initial quantum phase embedded in the initial nonclassical states in chaotic molecular processes.

In an effort to gain insight into the nature of this control we examined the evolving wave functions $|\psi(nT)\rangle$ in the θ representation. Figure 4 displays $|\langle\theta|\psi(nT)\rangle|^2\sin(\theta)$ versus θ/π for $n=0$, 2, 10, and 20, for the case of $\tau=1.0$ $k=5.0$ and

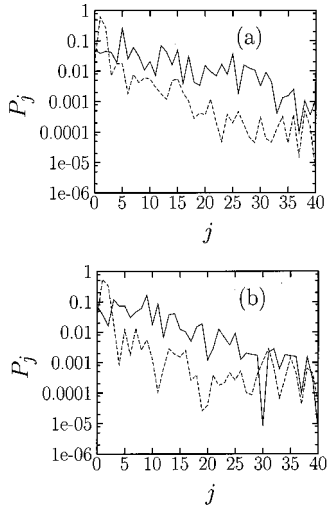

FIG. 3. The occupation probability P_j vs the rotational quantum number j at $t=60T$. Solid line and dashed lines are for the initial states $(|1,0\rangle+|2,0\rangle)/\sqrt{2}$ and $(|1,0\rangle-|2,0\rangle)/\sqrt{2}$, respectively. (a) $\tau=1.0$, $k=5.0$. (b) $\tau=1.2$, $k=4.8$.

for $\psi(0)\rangle=(|1,0\rangle+|2,0\rangle)/\sqrt{2}$ or $(|1,0\rangle-|2,0\rangle)/\sqrt{2}$. Note that due to wave function normalization $\int_0^\pi|\langle\theta|\psi(nT)\rangle|^2\sin(\theta)d\theta=1$. At $t=0$ [Fig. 4(a)], the relative phase between the basis states $|1,0\rangle$ and $|2,0\rangle$ is manifest as a difference in molecular orientation. In particular, for the initial state $(|1,0\rangle-|2,0\rangle)/\sqrt{2}$, the highest of the three significant peaks of $|\langle\theta|\psi(0T)\rangle|^2\sin(\theta)$ is located at $\theta_0\approx0.15\pi$, whereas for $|\psi(0)\rangle=(|1,0\rangle+|2,0\rangle)/\sqrt{2})$ the peak is at $\pi-\theta_0\approx0.85\pi$. However, since the kicking force is proportional to $\sin(\theta)$ and since $\sin(\theta_0)=\sin(\pi-\theta_0)$, such orientation effects cannot be the direct origin of our phase control. Indeed, after only two kicks [Fig. 4(b)], it becomes very hard to see any significant difference between the two evolving wave functions in the θ representation, although their energy absorption behavior afterwards [see Fig. 2(a)] continues to be completely different. Also of interest is the comparison in Fig. 4(c) and Fig. 4(d) at times $t=10T$ and $20T$ [at these times the energy absorption shown in Fig. 2(a) has stopped]. We find that, in the suppressed diffusion cases, the wave function displays fairly smooth behavior over the entire range of θ, whereas in the enhanced diffusion cases the magnitude of the wave function drastically oscillates with θ. However, the wave functions in Fig. 4(c) and Fig. 4(d) for both the suppressed and the enhanced cases show similar behavior on the average. Hence, the θ dependence of the wave function sheds little light on the origins of the observed control. Indeed, gaining insight into the origins of the control is difficult insofar as it is a nonresonant multiphoton absorption process.

To further demonstrate that our phase control results are quantal in nature, we show (Fig. 5) the dynamics after reducing the effective Planck constant τ by 50 times, while keeping $k\tau$ constant. As further discussed below, when the system is closer to the semiclassical limit, one expects the extent of phase control to decrease. This is confirmed in Fig. 5. For both the case of $\tau=0.02$ and $k=250$ in Fig. 5(a) and the case of $\tau=0.024$ and $k=240$ in Fig. 5(b), the energy diffusion shows only slight dependence on β. In essence, phase control disappears. We therefore confirm the expectation that quan-

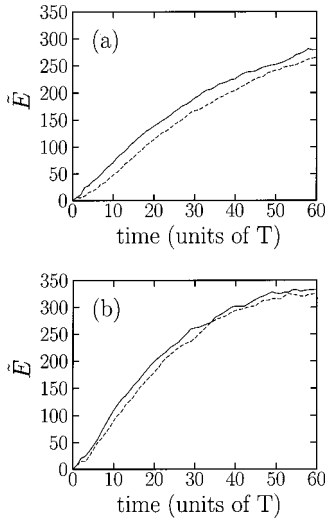

FIG. 5. As in Fig. 2 except that the effective Planck constant τ is 50 times smaller. (a) $\tau=0.02$, $k=250$. (b) $\tau=0.024$, $k=240$.

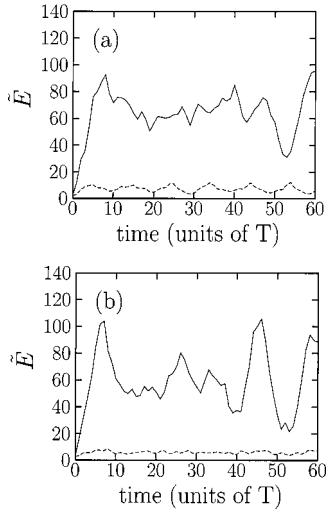

FIG. 6. As in Fig. 2 except that the pulse shape function is given by Eq. (23).

tum chaotic dynamics in the classical limit is insensitive to initial-state coherence.

We have also examined the stability of the results in Fig. 2 for τ far from resonance. We have checked that control in Fig. 2(a) [Fig. 2(b)] remains essentially the same when τ is changed from 1.01 to 1.0 to 0.99, or from 1.21 to 1.20 to 1.19. This insensitivity may be important for experimental studies, suggesting that extensive control of quantum diffusion should be robust to small fluctuations of the frequency of the periodic kicking field. It should be noted that for periodically kicked systems, the dynamics can be very sensitive to the exact value of τ. For example, when $\tau=p\pi/q$, where p,q are integers, the free evolution of the kicked system is in resonance with the kicking field, and the corresponding quantum diffusion can be extremely fast.[7,10] Indeed, when the resonance condition is satisfied, the spectrum of the system assumes a completely different form (for example, in the DKPR model, the spectrum is continuous at resonance). Here, we have examined cases of τ far from resonance since the uncontrolled dynamics for the case of resonant τ is still poorly understood. Nevertheless, we note that the possible range of quantum diffusion rates due to phase control, as shown in Fig. 2, is comparable to, or even larger than, that induced by quantum resonances in kicked diatomic systems. For τ near-or on resonance, we also observed extensive phase control in many cases (e.g., for $\tau=\pi/2$, $k=4.5$; or $\tau=2\pi/5$, $k=5.0$). However, due to the sensitivity of the dynamics to τ, the phase control for τ near-or on resonance is also very sensitive to τ.

Finally, we examine the pulse-shape dependence of our phase control. Our previous calculations have used the microwave pulse given by Eq. (6), which needs seven consecutive harmonically related microwave frequencies. Although this case is indeed very close to delta-kicked dynamics, it is challenging experimentally since one has to phase lock so many different microwave fields. Fortunately, we found that similar phase control can be observed using only three consecutive harmonically related microwave fields. Figure 6 displays the somewhat less extensive phase control results, where the pulse shape function $\Delta(t/T-n)$ in Eq. (4) is replaced by

$$\Delta'\left(\frac{t}{T}-n\right)=1+2\sum_{m=1}^{m=3}\cos\left[2m\pi\left(\frac{t}{T}-n-1/2\right)\right]. \qquad (23)$$

It is clear that the main characteristics of the phase control results in Fig. 2 are also observed in Fig. 6. Thus, utilizing Eq. (23) should significantly reduce technical difficulties in experimental studies of phase control of quantum chaotic diffusion.

C. Discussion

The results obtained for CsI are similar to those in the DKPR model,[9] despite the fact that there are several differences between the DKPR model and the kicked molecule case. This suggests that the mechanism for phase control of microwave kicked diatomics may be the same as that for the DKPR model. Below, we discuss the fact that phase control is based upon, and is a manifestation of, strong statistical deviations from random matrix theory (RMT).

One of the main results of the study of quantum chaos is that statistical properties of eigenfunctions and eigenvalues of the quantum map operator $\hat{F}$ (or the Hamiltonian operator for conservative systems) tend to be well described by RMT if the underlying classical dynamics is chaotic.[7] Indeed, statistical behavior close to RMT predictions is regarded as a clear signature of classical chaos. In particular, RMT claims that eigenvector components of $\hat{F}$ are random and obey universal statistical laws. However, in the case of the DKPR model and the kicked diatoms, deviations from RMT are observed in the suppressed quantum diffusion.[10] Here, we demonstrate that quantum control is another strong manifestation of the deviation from RMT.

We first note that Eq. (22) can be further simplified, for relatively large N, by making a fairly good approximation. That is, the factor $e^{iN(\phi_{j_a}-\phi_{j_b})}$ tends to oscillate so rapidly that essentially only those terms with $j_a=j_b$ contribute in the sum over j_a and j_b. We then obtain

$$\frac{2\tilde{E}}{\tau^2} = \cos^2(\alpha)\sum_j j(j+1)\sum_{j_a} |U_{j_a j}|^2 |U_{j_a j_1}|^2 + \sin^2(\alpha)\sum_j j(j+1)\sum_{j_a} |U_{j_a j}|^2 |U_{j_a j_2}|^2 + \sin(2\alpha)\cos(\beta)\sum_j j(j+1) \times \sum_{j_a} |U_{j_a j}|^2 U_{j_a j_1} U_{j_a j_2}. \quad (24)$$

Evidently, the last term in Eq. (24) arising from quantum interference is proportional to $\cos(\beta)$, and would be most effective when $\beta=0$ or $\beta=\pi$. This explains our previous choice of $\beta=0$, π for the demonstration of extensive phase control.

Consider then RMT applied to the statistics of the eigenvectors U_{j_c,j_b} in Eq. (24). Suppose the effective dimension of the Hilbert space is $D\propto 1/\tau$, τ being the effective Planck constant. We then assume that $U_{j_a j}$, $U_{j_a j_1}$, and $U_{j_a j_2}$ are independent random numbers with mean value 0 and variance $1/D$, in accord with RMT. With this statistical description, we are now ready to compare the magnitudes of the interference term and the incoherent terms in Eq. (24). Consider first the interference term. As an approximation, $\Sigma_{j_a}|U_{j_a j}|^2 U_{j_a j_1} U_{j_a j_2} \approx 1/D\Sigma_{j_a}(U_{j_a j_1} U_{j_a j_2})$, where high-order correlations between $|U_{j_a j}|^2$ and $U_{j_a j_1} U_{j_a j_2}$ are neglected. Note that the ensemble average of $U_{j_a j_1} U_{j_a j_2}$ $(j_1 \neq j_2)$ is zero. Hence, the standard deviation of $1/D\Sigma_{j_a}(U_{j_a j_1} U_{j_a j_2})$ is given by $1/\sqrt{D}$ times the standard deviation of $U_{j_a j_1} U_{j_a j_2}$ (which is of the order of $1/D$). It follows that the standard deviation of $\Sigma_{j_a}(U_{j_a j_1} U_{j_a j_2})$ from zero is of the order of $1/\sqrt{D}$. On the other hand, for the incoherent terms, say, the first term, $\Sigma_{j_a}|U_{j j_a}|^2 |U_{j_a j_1}|^2 \approx 1/D\Sigma_{j_a}|U_{j_a j_1}|^2 = 1/D$. Thus, according to RMT, the interference term is zero statistically, and the magnitude of the fluctuation of the interference term is $1/\sqrt{D}$ times smaller than that of the incoherent term. That is, RMT predicts that phase control of quantum diffusion is bound to fail. Further, since D scales with $1/\tau$, the magnitude of the fluctuations of the quantum interference term in Eq. (24) scales with $\tau^{1/2}$. As we approach the classical limit by decreasing the effective Planck constant τ, initial-state coherent effects and thus phase control necessarily vanish.

Thus, our control results imply that RMT is not a good statistical description when the periodically kicked molecular system is not close to the semiclassical limit. Just as in the DKPR model, when quantum effects are large, the $\hat{F}$ matrix and thus the $\hat{U}$ matrix are banded matrices[17] in the representation of angular momentum eigenstates. This band structure causes strong statistical deviations from RMT expectations. In particular, in the sum $\Sigma_{j_a}|U_{j j_a}|^2 U_{j_a j_1} U_{j_a j_2}$, only those terms with $|j-j_a|$ less than the band width of the $\hat{U}$ matrix (or the localization length of the eigenvector U_{j,j_a}) will contribute, i.e., the number of contributing terms in the sum will be much less than D, the effective dimension of the Hilbert space. This directly leads to enhanced fluctuations of $\Sigma_{j_a}|U_{j j_a}|^2 U_{j_a j_1} U_{j_a j_2}$, i.e., the interference term in Eq. (24) can be comparable to the first two incoherent terms. As a result, extensive phase control of quantum chaotic diffusion becomes possible.

Based on the observation that statistical deviations from RMT are responsible for control, in Ref. 9 we quantitatively obtained a necessary condition for extensive phase control. Specifically, in the DKPR model we require $k<50/\kappa$ or $\tau > \kappa^2/50$ for control. The essence of this condition is evident. That is, larger quantum effects induce more phase control. It is thus very natural to conjecture that this condition could also apply to the model of periodically kicked molecules. Indeed, (1) under this condition, for numerous cases of varying α, β, k, and τ, we have obtained extensive phase control results similar to those in Fig. 2, and (2) outside that domain, phase control is not extensive in general.

V. CONCLUSION AND SUMMARY

The results of this paper should impact strongly on two research areas, that of quantum chaos and that of coherent control. The focus of traditional studies in quantum chaos is quantum-classical correspondence, i.e., the conditions under which quantum and classical dynamics agree, and how this agreement breaks down with time as a result of quantum interference effects. In order to understand interference effects, most studies have used classical initial states and have avoided using nonclassical initial states. As such, the literature of quantum chaos rarely considers initial-state coherence effects. Rather, people often take the semiclassical view that the classical chaotic dynamics leads to a randomization of the phase in quantum evolution, and that the quantum dynamics is insensitive to the form of the initial condition.[18] By contrast, studies in coherent control[1] emphasize the significance of quantum phases, both in the initial state and the ensuing dynamics.

Our study clearly demonstrates the importance of initial-state coherence in quantized chaotic dynamics. Specifically, we have demonstrated that initial-state coherence can dramatically alter the dynamics of quantum diffusion when the system is far from the semiclassical limit. This sensitivity is lost as the system approaches the classical limit. This phase control is based on, and is a manifestation of, strong statistical deviations from RMT. Further, it is distinct from other studies of control in diatomic excitation,[19,20] which can essentially be described classically.[21]

Having shown theoretically that initial-state coherence can be used to control chaotic rotational excitation of diatomic molecules, the only issue remaining is the experimental preparation of initial superposition states such as $(|1,0\rangle \pm |2,0\rangle)/\sqrt{2}$, or, more generally, the generation of rotational coherence before the periodic kicking field is turned on. We note that stimulated Raman adiabatic passage (STIRAP)[22] provides a natural choice for such superposition state preparation. In particular, in the tripod-STIRAP scheme,[23] an additional laser couples the intermediate level (through which the initial and final state are radiatively connected via the pump and Stokes laser) with another unpopu-

lated state. Depending on the overlap in time of the interaction of the additional laser with that of the pump and Stokes laser, any coherent superposition of the initial and final state can be created.

In summary, the general principle of coherent control has been successfully applied to chaotic rotational excitation of diatomic molecules. Corresponding experimental studies on the kicked *CsI* system are of interest to both areas of quantum chaos and coherent control.

ACKNOWLEDGMENTS

The authors thank the U.S. Office of Naval Research and Photonics Research Ontario for support of this research.

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