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Time evolution in a driven quantum system: Excitation through bands of states

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Time-evolution patterns for energy absorption in a driven Hénon-Heiles Hamiltonian with and without extra off-diagonal random-coupling terms are reported. The time dependence of the average number of photons absorbed is quite different for these two systems, being fluence dependent for the latter. Similarities are found between the dynamics of the driven system with random coupling and a four-mode molecular model which interacts with a quantum monochromatic field. Comparison is made between the presently found mechanism of excitation and the diffusive energy growth due to externally induced chaos found in the kicked-rotor or in microwave ionization of the hydrogen atom.

I. INTRODUCTION

Recently, there has been renewed interest in the details of the dynamics of multiphoton excitation (MPE) of molecular vibrational modes by an intense laser.[1,2] Earlier experimental studies revealed most cases that the energy absorbed by the molecule depended strongly on the fluence of the applied field (i.e., the total energy in the laser pulse) rather than on the laser intensity.[3] Such system behavior may be simulated by the rate equations approach, valid in the limit of a very high density of states (quasicontinuum approximation). The classical studies of Ackerhalt, Milonni, and Galbraith[1] showed that even for systems for which the rate equations approach breaks down, the dynamics of the driven system may become chaotic. One then observes the diffusive, linear-in-time (for fixed intensity) growth of the absorbed energy producing the fluence-type absorption.[1] Similar diffusive energy growth has been extensively discussed in studies of the kicked-rotator[4] or microwave ionization of the hydrogen atom.[5]

The molecular model treated by Ackerhalt *et al.* consisted of an anharmonic oscillator coupled linearly to a set of harmonic oscillators (so-called background modes) and driven by the laser field. This classical model neglects possible quantum correlations. Their influence has been investigated in detail by Brunet *et al.*,[6] who considered a fully quantized version of the above-described model. The authors have found that quantum correlations tend to prevent unlimited excitation of the system and did not observe the diffusive energy growth in the quantum model with two background modes. Interestingly, for a similar quantum model with large number of background modes, the linear (on average) absorbed energy growth has been observed by the same group.[2] The dynamics of the system remained however, regular, the origin of the linear growth being due to the complex sharing of the absorbed energy between the pump and background modes.

Although the physical nature of the linear energy absorption growth in both classical[1] and quantum[6] versions of the model is quite different, both versions lead to a strong redistribution of the absorbed energy between different modes. In the extreme excitation process when the molecule becomes photodissociated, this redistribution of energy would lead to products that would have mixed-mode character.

The other possibility, i.e., mode-selective excitation, has also been frequently suggested.[7] In this picture, the laser excites the molecule through the ladder of states belonging to one vibrational mode; in photodissociation the molecule would fragment into a pattern of vibrational states being the natural extension of the mode sequence appropriate to the climbed ladder. This picture runs into difficulties when one considers that anharmonicities in the molecular potential will detune the ladder from the laser frequency for higher excitations. Moreover, nonlinear coupling in the molecular potential will normally produce strong mixing of different modes, which could destroy the ladder.

These difficulties may be overcome by using for excitation the special ladders of "extreme motion" states as suggested by Hose and Taylor[8] for a model two-dimensional system. These states are only weakly coupled to other modes; as such they persist into high-energy regions and are only slightly perturbed. Indeed, using the Floquet approach, Wyatt *et al.*[9] have verified that highly selective excitation along the ladder of so-called Q I states in the model Hénon-Heiles system may be obtained. Later, Hose and Taylor argued[10] that in polyatomic molecules the extreme motion states lead to highly nonuniform distribution of oscillator strengths in the high-density-of-states region in a similar way to resonances in the scattering continua.

The aim of the present paper is to show that mode-selective photoexcitation and the fluence dependence of the absorption are not mutually exclusive as it may seem at first. To this end, we discuss the dynamics of the driven Hénon-Heiles-like potential. The advantage of this model lies in the fact that the Hénon-Heiles potential has been extensively studied in the past and therefore an almost complete understanding of the "molecular" dynamics is at hand. This provides us with an additional insight, absent in the earlier studies of Ackerhalt *et al.*[1] That in turn will allow us to shed some light onto the role played by the driving field and the origin of the linear energy growth.

In Sec. II, we define and discuss the molecular model (modified Hénon-Heiles potential) and study the properties of the energy levels. The dynamical studies, i.e., the time dependence of the MPE process, are reported in Sec. III. Finally, in Sec. IV the discussion of the results and conclusions is presented.

II. HAMILTONIAN AND EIGENSPECTRUM ANALYSIS

The quantum-mechanical Hénon-Heiles Hamiltonian in dimensionless units ($\hbar\omega=1$) is

$$H=-\frac{l}{2}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right]+\frac{1}{2}(x^2+y^2)+\lambda\left[xy^2-\frac{x^3}{3}\right], \tag{1}$$

$$=-\frac{1}{2}\left[\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right]+\frac{1}{2}r^2-\frac{\lambda r^3}{3}\cos 3\theta , \tag{2}$$

where $\lambda=0.08$. The dissociation energy, $D=1/6\lambda^2=26.04$, is much higher than in the former study[9] where $\lambda=0.118$ and $D=13.33$. Neither in Cartesian (1) nor in polar (2) coordinates is this Hamiltonian separable. According to Hose and Taylor,[7,8] the quantum condition for a state to be regular (localized) is that the square of its overlap (the weight) with an eigenstate of any two-dimensional separable Hamiltonian H^0 is larger than 0.5. A regular state is labeled Q I (Q II) according to the polar (Cartesian) nature of the separable Hamiltonian H^0 that meets the above condition.[10] Delocalized, chaotic states are labeled N. At low energy all of the states of this Hamiltonian are regular (Q I, Q II, or both), while at high energies most of them are not. In the present case,[11] there are 374 quasibound states and 250 energy levels below the dissociation energy. Of these states, 45 are of type Q I, 28 are of type Q II, and 188 are of type N. Eleven states are simultaneously Q I and Q II. The classical critical energy, which marks the onset for chaotic motion at higher energies, is $E_c=17.15$.[8] Both the quantum Hose and Taylor (HT) criterion and the semiclassical quantization techniques[12] lead to the same conclusions as to the nature of states. In fact, the HT criterion has been thought of as a quantum equivalent to the classical Kol'ogorov-Arnold-Moser theorem.[10]

An efficient means to determine the nature of quantum states is the natural expansion analysis. Among all products of one-particle basis functions $f(u)g(v)$, the so-called natural orbitals provide the most localized representation of a nonseparable two-dimension wave function in the u,v coordinates. Coordinates u,v are arbitrary and in our case may refer to either Cartesian or polar coordinates. If the variational eigenfunctions are given by

$$\Psi(u,v)=\sum_{i,j=1}^{N} C_{ij}f_i(u)g_j(v) , \tag{3}$$

then the natural expansion proceeds by diagonalizing the matrices **A** and **B**

$$A_{nm}=\sum_{i=1}^{N} C_{ni}^{*}C_{mi}, \quad B_{nm}=\sum_{i=1}^{N} C_{in}^{*}C_{im} . \tag{4}$$

The natural orbitals for the two modes are then given by

$$m_l(u)=\sum_{i=1}^{N} f_i(u)P_{il}, \quad n_l(v)=\sum_{i=1}^{N} g_i(v)Q_{il} , \tag{5}$$

where **P** and **Q** are the eigenvector matrices of **A** and **B** respectively. Finally, the natural expansion of this eigenfunction is

$$\Psi(u,v)=\sum_{l=1}^{N} d_l m_l(u)n_l(v) . \tag{6}$$

If for instance no natural weight $(d_l)^2$ is larger than 0.5 in polar coordinates, then the state can be said not to be Q I, irrespective of the initial $f(r)g(\theta)$ basis chosen for the analysis. For a similar analysis, we refer to a previous study of the two-dimensional Cartesian or polar Pullen-Edmonds Hamiltonian.[13]

The square of the largest natural expansion coefficients (referred to as weights) of the Hénon-Heiles (HH) bound states in polar coordinates is plotted in Fig. 1(a) in the energy interval which is to be considered in the dynamical calculation below. According to the HT criterion, only those states whose weight exceeds 0.5 are regular Q I states. The energy separation between successive Q I states is nearly constant and therefore the resulting Q I ladder is a favorable route to initiate a multiphoton absorption process.[8,9] However, although the energy spacing increases, the ladder structure persists up to the dissociation limit and the maximum weight gradually becomes smaller than 0.5. This means that along this ladder the discrimination between regular and chaotic states, as would result from the strict application of the HT criterion, is somewhat arbitrary.

It is physically more realistic for polyatomic molecules that the regular ladder merges into a quasicontinuum of highly mode-mixed states (i.e., with small natural coefficients in either the Cartesian or polar basis) before dissociation occurs. In order to simulate such a configuration we added off-diagonal random-coupling terms to the original HH Hamiltonian. For simplicity (if not for concreteness) we have chosen a uniform coupling scheme $\epsilon_{ij}=\epsilon(1-\delta_{ij})$, where ϵ is a random number in the interval [0,0.2]. Results of the natural expansion analysis in polar coordinates are shown in Fig. 1(b). The ladder structure is partially destroyed although some pseudoregular states (i.e., with a weight of ~ 0.2 for instance) project above the mode-mixed background.

We now turn to the dynamics of these two quantum models in the presence of an external fied. The time-dependent Hamiltonian describing the interaction with a monochromatic field in the semiclassical dipole approximation is

$$H(t)=H-\mu E_0\cos(\omega t)\ , \tag{7}$$

where H is the HH quantum Hamiltonian in Eqs. (1) and (2), including eventually the random-coupling terms, μ is the dipole function, E_0 and ω are laser parameters. In this study $\mu=x$, so that only even states in y are retained. With this restriction, there are 195 energy levels below the dissociation energy. The first 115 energy levels are kept for the dynamical calculation, to a maximum energy of $E=20$. It is thus a pure bound-state problem since the dissociation channel is artificially closed. As such, the rebound of amplitude will cause artifical interferences with the still-climbing part of the wave packet. However, this artifact does not affect the early time dynamics, our main matter of concern in this study.

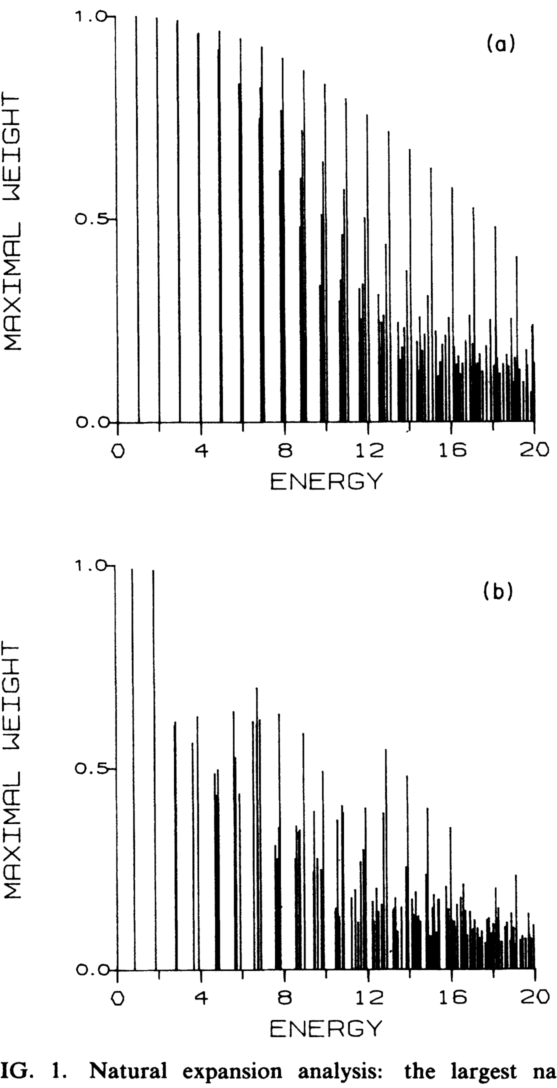


FIG. 1. Natural expansion analysis: the largest natural weight in polar coordinates is plotted vs the eigenvalue of each state. (a) HH Hamiltonian; (b) random off-diagonal coupling terms added.

Periodicity of the total Hamiltonian in Eq. (7) with respect to time calls for use of Floquet methods to compute the quantum propagator. Development and applications of Floquet theory for quantum molecular systems in an oscillating field have been described already in much detail (Ref. 14 and references therein) and we refer to these earlier works instead of again presenting the relevant equations.

III. DYNAMICAL STUDIES

A. Hénon-Heiles system

In the following dynamical studies the laser parameters are $E_0=0.1$ and $\omega=1$, so that the laser is nearly resonant with the low-energy Q I ladder spacing. In Fig. 2(a) the number of photons absorbed versus time for the driven regular HH Hamiltonian is shown. The initial condition is that the wave function at time zero is the molecular ground state. About ten photons are absorbed smoothly during the first 30 optical cycles before recurrences occur due to the spurious interference effects mentioned above. Indeed, the build-up of probability in level 115 reaches a maximum after 30 optical cycles. Larger calculations including as many as 200 and 250 levels have also been performed. With 200 levels (all even y states up to the dissociation limit), 13 photons are absorbed after 35 optical cycles, while 15 photons are absorbed after 40 cycles if 50 additional states are included. These states form a discretized approximation to the continuum since they lie above the dissociation energy.

In order to understand the underlying dynamics, we computed instantaneous transition probabilities from the ground state to all of the molecular excited states. The results are displayed as stick diagrams showing the transition probabilities versus the eigenvalue of the state at various times after turning on the laser field. At time zero, the probability for the system to be in the first (initial) state is one and zero elsewhere. For the regular HH quantum system, two such diagrams are shown after 10 and 19 optical cycles in Fig. 3(a) and 3(b), respectively.

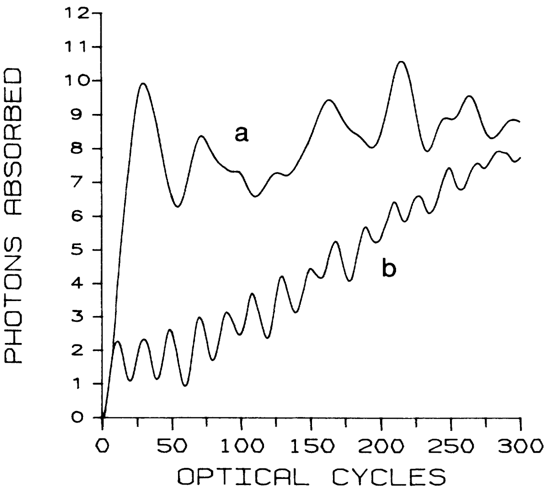
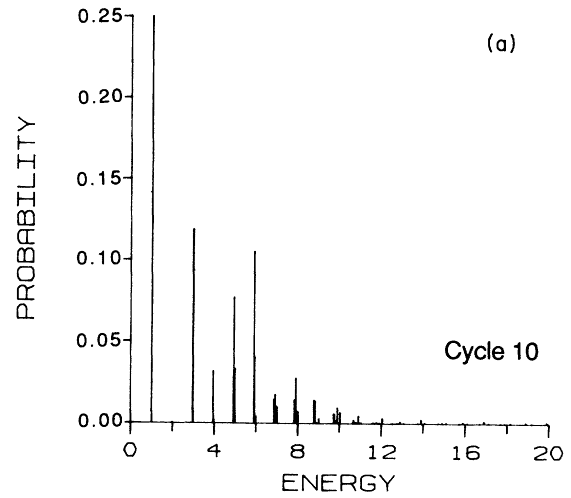


FIG. 2. Number of photons absorbed vs time. (a) HH Hamiltonian; (b) random off-diagonal coupling terms added.



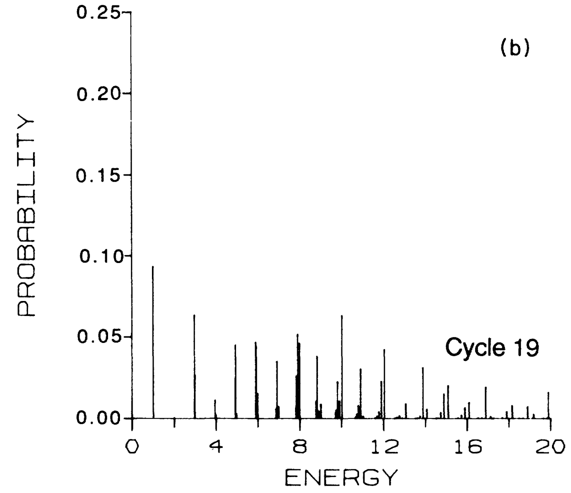


FIG. 3. Instantaneous transition probability stick spectra for the driven HH Hamiltonian at two times. (a) Ten optical cycles; (b) 19 cycles.

The wave packet quickly expands through the high-energy region and reaches the top states after about 20 optical cycles. A close inspection shows that the larger the natural weight of a state (i.e., the more localized the wave function), the higher the transition probability. Implications of results such as this for mode-selective multiple-photon absorption in real systems have been described elsewhere.[7,8]

As noticed before and depicted in Fig. 1(a), as the energy increases there is no sudden interruption in the Q I ladder but rather a smooth decay of the maximum weights. It has been suggested previously in many-mode molecules that the destruction of Q I is gradual and does not lead immediately to N states that are completely delocalized.[7] For systems with many degrees of freedom, the Q states might progressively transform into Q bands as the energy increases. These bands are groups of nonuniform N states that fulfill the HT criterion *as a whole.* As suggested in Ref. 7, these bands would then form a ladder with thick rungs for multiphoton absorption. Our analysis of the excitation process somewhat supports this picture for the two-coupled mode HH system. However, rather than a clustering of states projecting above the uniform background of fully mixed-mode states, we find a superposition of two distinct ladders that constitute two routes concurrently followed during the excitation process. The coupling with additional modes, if present in more complex systems, would lead to additional ladders whose rungs would cluster to form Q bands.

A close inspection of Fig. 1(a) shows that each of the highest peaks is preceded by a growing number of smaller peaks as the energy increases. The highest of these secondary peaks can be viewed as forming the rungs of a second ladder. Although states of both ladders are Q I at low energy, the weight of the smaller peaks decay rapidly and above $E=12$, they form an N ladder that coexists with the original Q I ladder. The original Q I states themselves fall into the N class above $E=17$; this is where their largest weight becomes less than 0.5. It is perhaps surprising that the energy spacing between the N ladder runs is more regular than between the Q I's. As a result, the Q I ladder rungs are progressively shifted forward in energy from their N ladder-rung parents as the total energy of the system increases [see Fig. 1(a)].

A close inspection of state-to-state probabilities shows that the initial wave packet splits while climbing the Q I ladder so that two routes are concurrently followed in the multiple-photon excitation process. However, because the eigenfunctions of the N state ladder are less localized than the original Q I states, the flow of probability along this second path is less important. This scenario is illustrated in Fig. 3(b), where the largest transition probability peaks, carried by states of the Q I ladder [compare with Fig. 1(a)], are paired with a secondary peak carried by neighboring states of the N ladder. Note also that a few smaller peaks are grouped around each pair (this is particularly noticeable near $E=8$, 10, and 12). These are due to surrounding N states that have a non-negligible natural weight. As a result, there is a clustering of several transition probability peaks close to the energy of a dominant mode-localized state. This occurrence illustrates the concept of Q bands that form thick ladder rungs for multiple-photon excitation.[7]

B. Random-coupling system

Adding random-coupling terms to the molecular-Hamiltonian does not affect the absorption process during the very first cycles, as seen in Fig. 2(b). Later, the molecular system starts absorbing energy while still Rabi-oscillating until saturation occurs after 300 optical cycles. With random-coupling terms included in the Hamiltonian, the molecular energy shows linear (on the average) diffusive-type growth. By comparison with the regular case, not as many photons are absorbed but more importantly the time evolution patterns are markedly different.

Stick spectra of time-dependent transition probabilities are shown in Fig. 4 for optical cycles 20, 30, 157, and 168. Cycles 20 and 157 (30 and 168) correspond to local

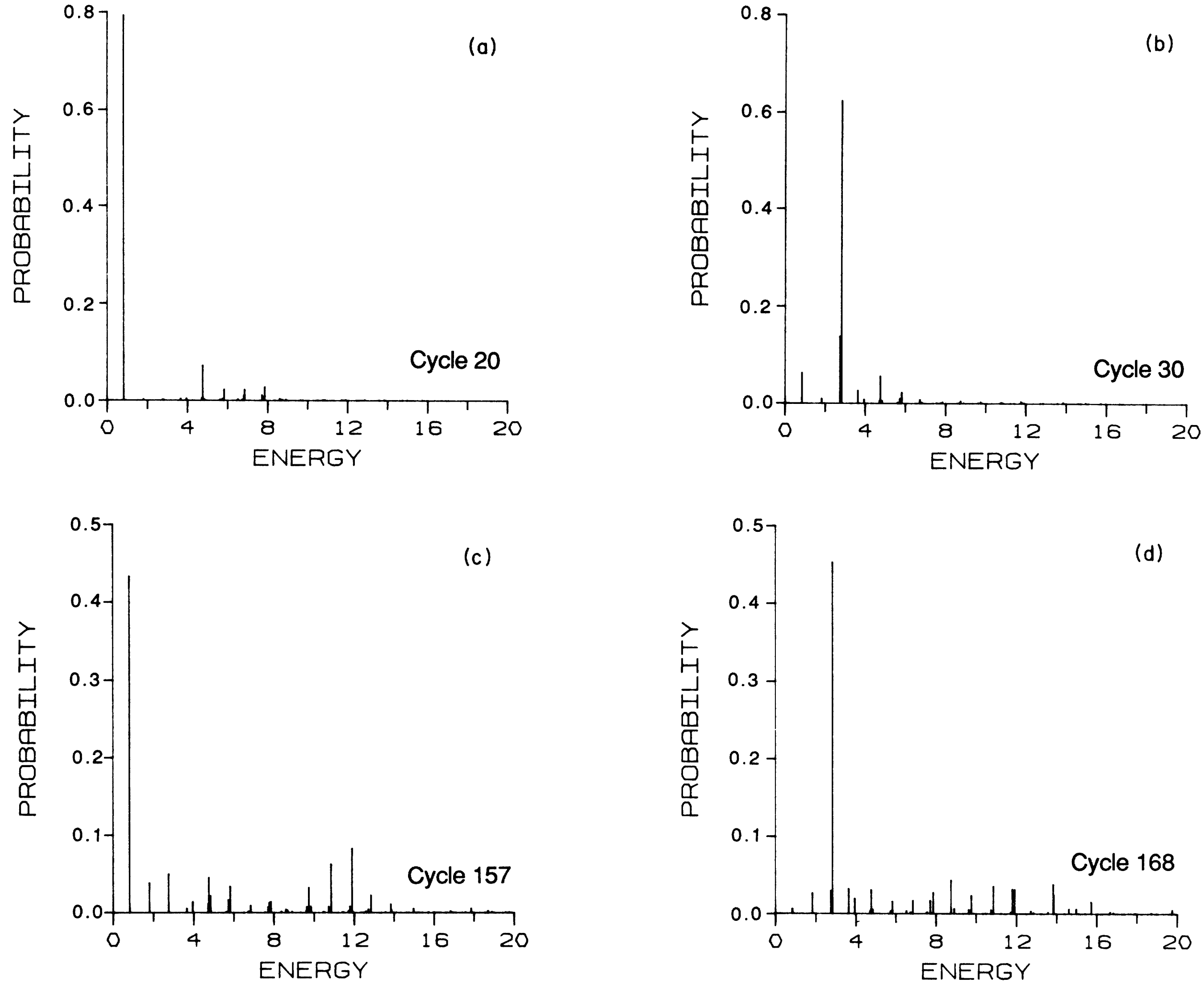


FIG. 4. Instantaneous transition probability stick spectra for the driven HH Hamiltonian with random-coupling terms at four times. (a) Twenty optical cycles; (b) 30 cycles; (c) 157 cycles; (d) 168 cycles.

minima (local maxima) of the Rabi oscillations at two different stages of the absorption process. The origin of Rabi oscillations is clearly depicted in Figs. 4(a) and 4(b): a large fraction of the wave packet oscillates between states 1 and 4. These two states alternately carry most of the probability at minima (state 1) and maxima (state 4) of the oscillations. The wave packet remains very narrow (in energy space) and does not expand over many excited states as with the regular HH Hamiltonian. This breathing process between state 1 and state 4 is still dominant (yet somewhat attenuated) after 157 and 168 optical cycles, as see in Figs. 4(c) and 4(d). Non-negligible transition probability is now carried by excited states and this "leaking" of transition probability is responsible for the gradual absorption of photons shown in Fig. 2(b). Nevertheless, the excitation of the wave packet only significantly involves the first 60 molecular states. The highest excited states are not reached before cycle 250 and therefore the artificial truncation of the basis set is not felt by the system before that time. By comparing Figs. 4(c) and 4(d) with Fig. 1(b), it is clear that states carrying the highest probability are the ones with the largest natural weight. Therefore, the absorption is selective, as in the nonrandom case.

In conclusion, the addition of random couplings to the original HH Hamiltonian has a strong localizing effect on the ascending wave packet that entails a delayed multiple-photon absorption mechanism. The dynamics can be compared to that of the rising tide; the influx and ebb of the wave are superimposed on a much slower progressive motion that results in the gradual rise of long ocean waves.

IV. DISCUSSION

We wish to relate this study to a former one on a laser-driven multimode quantum model.[2] In that model, a quantum monochromatic laser field interacts with an anharmonic molecular pump mode, which in turn is linearly coupled to a harmonic background mode. This background mode it itself the extremity of a chain of three linearly coupled harmonic oscillators. The Hamil-

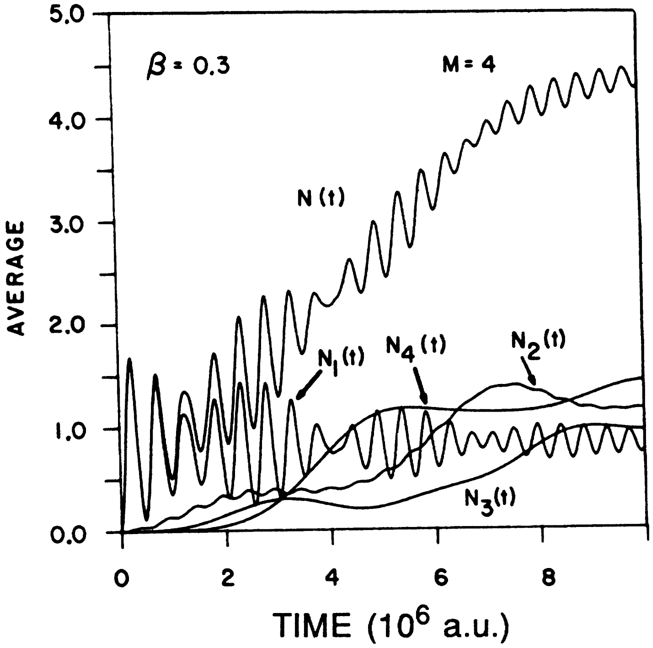


FIG. 5. Total number of photons absorbed, $N(t)$, in a four-degree-of-freedom molecular-quantum model and the average degree of excitation in all molecular modes (from Ref. 2).

tonian for this four-molecular-mode system interacting with the one-mode laser field is

$$\begin{aligned} H=&\omega_0 a^\dagger a-\chi(a^\dagger a)^2+\sum_{i=1}^{3}\omega_i b_i^\dagger b_i+\beta(a^\dagger b_1+ab_1^\dagger)\\ &+\beta\sum_{i=1}^{3}(b_i^\dagger b_{i+1}+b_i b_{i+1}^\dagger)\\ &+\Omega c^\dagger c+\epsilon(a+a^\dagger)(c+c^\dagger)\ , \end{aligned} \tag{8}$$

where $a^\dagger(a)$, $b_i^\dagger(b_i)$, and $c^\dagger(c)$ are the creation (annihilation) operators for the pump, background, and field modes, respectively. The mode frequencies are equal, $\omega_0=\omega_i=\Omega=1000\ \mathrm{cm}^{-1}$, the pump-mode anharmonicity is $\chi=1\ \mathrm{cm}^{-1}$, the molecular intermode coupling strength is $\beta=0.3\ \mathrm{cm}^{-1}$, and the laser-molecule coupling strength is $\epsilon=1.646\ \mathrm{cm}^{-1}$. The fourth and fifth terms in the Hamiltonian are intramolecular one-quantum exchange terms while the last term describes the interaction of the pump mode with the quantum field. The basis set consists of products of five harmonic-oscillator functions for each of the four molecular models dressed by three field states ($5^4\times 3=1875$ states). The total number of photons absorbed versus time $N(t)$ and the average degree of excitation in all molecular modes are shown in Fig. 5: $N_1(t)$ refers to the pump mode; $N_2(t)$, $N_3(t)$, and $N_4(t)$ refer to the three background modes.

The similarity between curve $N(t)$ in Fig. 5 and Fig. 2(b) is striking. In both cases, $N(t)$ executes a few Rabi oscillations and then shows average linear energy absorption with superimposed Rabi oscillations. In the four-model molecular case, the growth-saturation curves of the four molecular modes yield, when added together, the linear (on the average) total excitation curve, $N(t)$. The present study shows that a similar effect (linear average energy growth) is obtained by adding random-coupling terms to a two-dimensional Hamiltonian.

Perhaps more importantly, we are able to trace the nature of the linear energy growth to the character of the molecular Hamiltonian. When the important states, along which the excitation process occurs, are dominantly regular (and highly localized) the absorption process is coherent and the excitation proceeds along a highly selective ladder, as already found earlier.[9] The addition of random-coupling terms does not increase the average density of states but leads to a more highly mode-mixed Hamiltonian with a much less pronounced and more delocalized ladder. According to the HT (Ref. 10) criterion, the states of this Hamiltonian are mostly of the N type (chaotic) in the high-energy region. In this case a linear absorbed energy growth is observed. We have thus traced the liner, seemingly diffusive, energy growth to the chaotic nature of the molecular system alone. The external laser field, although strong, probes only this molecular chaos, indicating it by means of the linear energy growth.

This conclusion was reached due to our detailed analysis of the molecular part of the Hamiltonian. It would be interesting to see whether a similar analysis performed for the other common model of multiphoton excitation[1,2,6] leads to a similar conclusion.

Lastly, let us correlate this work with other studies of similar linear energy growth, such as investigations of the dynamics of the kicked rotor[4] or the microwave ionization of the hydrogen atom.[6] The latter systems are profoundly different from the one discussed here, since the molecular (atomic), time-independent part of the Hamiltonian is integrable and fully regular in the quantum case. The origin of the classical chaotic behavior is in these systems entirely due to the coupling with the external driving field. Quantum mechanically, the kicked rotor behaves in the regular way; the diffusive energy growth is suppressed due to the analog of Anderson localization.[15,16] In our study, the laser frequency is rather high (it is resonant with the first allowed transition in the low-density-of-states region) and indeed the wave packet in the "random-coupling case" remains localized. The packet stays mostly on a few Q states and leaks amplitude up the energy ladder. One would have imagined from the analogy to classical diffusive energy growth that the center of the packet, which spreads in time over more and more states, moves itself up in energy. In this sense we observe a "quantum limitation." In the pure Hénon-Heiles potential, the partial delocalization of the wavepacket is perfectly regular and is related to a typical ladder climbing pattern and not related to chaotic behavior.

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