Quantum Dynamics for Driven Weakly Bound Electrons near the Threshold for Classical Chaos

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The absorption of energy by highly excited electrically polarized hydrogen atoms in intense microwave fields is studied experimentally, and theoretically in terms of a one-dimensional quantum model. The quantum calculations reveal a sudden onset of basis-set instability that correlates well with the threshold for classical chaos.

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Recent classical calculations[1-4] of the response of weakly bound electrons to an ac electric field show a rapid transition from regular to irregular orbits as the ratio of the strengths of the external and internal fields is increased. These calculations correlate well with experiments[5-7] which examine the onset of ionization of highly excited states of hydrogen atoms ($30 \leq n \leq 75$) interacting with microwave fields. This correspondence suggests that there may be a close analogy between quantum dynamics and nonlinear classical dynamics in the limit of large n and large photon absorption number k, and that effects similar to classical chaos may be found in the results of quantum calculations.

The nature of this analogy needs to be examined carefully, since the Schrödinger equation is linear. For example, some classical systems when in their chaotic regimes display stochastic diffusion in energy or momentum space. On the other hand, Hogg and Huberman[8] have shown that for any time-periodic Hamiltonian, a bounded quantum system will reassemble itself infinitely often in the course of time, implying that no strict quantum stochasticity is possible. Several authors have examined the periodically kicked rotator[9-11] and have shown that quantum interference effects suppress diffusive flow through phase space, leaving primarily quasiperiodic (regular) motion.

It has been reemphasized[11] that results for a bounded system do not necessarily apply to problems in which the unperturbed spectrum has a continuous component. However, in the driven-bound-electron problem, quantum interference effects do lead to very large reductions in the rates of multiphoton transitions,[12] and quantum inhibition of diffusive motion in energy space has been clearly demonstrated through the calculations reported by Shepelyansky[13] and by Casati, Chirikov, and Shepelyansky.[14]

In this Letter, we report the results of quantum calculations on the behavior of Rydberg states of hydrogen in microwaves that provide evidence for a correspondence between classical and quantum dynamics for one-dimensional unbounded systems, and that are compared with new experimental results on n-changing processes involving selected extreme Stark states.

Since the quantum treatment of unbounded systems involves serious technical difficulties, it is especially helpful to study simple one-dimensional systems. Two models are available that retain the accumulation point in the bound-state spectrum at the border of the continuum. The first is the surface-state electron model[3] in which an electron near a perfect reflecting surface interacts with its image charge. The second is the stretched hydrogen atom (SHA) model[12,13] in which the highly excited atom is constrained to the states at the edge of the Stark manifold. In terms of parabolic quantum numbers (n,n_1,n_2,m), these are the states for which m and n_1 are zero. As $n \to \infty$, the two models become equivalent, and for $n \geq 30$, they are essentially the same. Through experimental field-ionization studies it has been shown[15] that if atoms are selectively excited to one such state, through the imposition of a dc field that separates the Stark levels, and if the microwave and dc fields are aligned, then the microwave-produced atoms have $n_1 = 0$ or 1. Theoretically the n_1 value should be zero except at very narrow resonant frequency regions, as electric dipole transitions among the highly excited states are more rapid by a factor of 10^{+3} when n_1 remains zero.[12,13]

To facilitate the comparison with the experimental measurements on n-changing interactions, the quantum solution is obtained by expansion of the time-dependent wave function in terms of a basis set of unperturbed SHA eigenstates. The Schrödinger equation then leads to a set of coupled differential equations for the expansion coefficients $c_n(t)$:

$$i\dot{c}_n(t) = E_n c_n + F \sin(\omega t + \phi) \sum_{n'} z_{nn'} c_{n'}(t), \qquad (1)$$

in which E_n is the energy of the nth state, allowing for the dc Stark shift; F, ω, and ϕ are the strength, frequency, and phase of the microwave field. The dipole matrix elements $z_{nn'}$ are proportional to n^2, and for the coupling of neighboring n levels are well approximated by $0.32n^2$.[13] These equations were solved by the fourth-order Runge-Kutta method, with the atom in state n_0 at $t=0$.

Because of the periodicity of the perturbing potential, it is only necessary to solve these equations for one cycle of the microwave field. The subsequent motion can be determined from the repeated operation of the one-cycle time evolution operator, $T(\phi)$, defined so that

$$c(\tau)=T(\phi)c(0), \tag{2}$$

where τ $(=2\pi/\omega)$ is the period of the microwave radiation. Within our finite basis set, T is represented by a matrix $T_{nn'}(\phi)$, and the repeated operation involves only matrix multiplication.

The unitary operator T provides a quantum map whose eigenvalues and eigenvectors can be used to characterize the motion. The spectral properties of this Floquet operator are also those of Howland's quasienergy operator.[16] Its eigenvalues can be expressed as $\exp(i\alpha^{(j)})$ and its eigenvectors as $a_n^{(j)}$. The structure of these eigenvectors obtained by projection onto the unperturbed states is especially interesting in the region near the onset of classical chaos. In Fig. 1, we show these projections obtained with $\phi=0$, $F=9.1$ V/cm, $\omega=7.11$ GHz, and a dc field of 8.0 V/cm. The basis set contained 21 states, with n ranging from 55 to 75. Ten eigenvectors are almost completely dominated by a single SHA hydrogenic state, accounting for at least 98% of the state population. Five eigenvectors have strong mixing between two or three neighboring levels. The remaining six provide strong coupling among a group of states that extends up to the highest n value included in the basis set. When the calculation is repeated with a higher upper limit to the basis set, the eigenvectors in the first two groups remain essentially unchanged, whereas those in the third group are very sensitive to such changes. A calculation with 41 basis states shows that there is strong mixing between the level $n=69$ and all higher levels in the basis set (up to 95).

This eigenvector structure for $\phi=0$ indicates the extent of state mixing produced by an integral number of sinelike cycles of the external field. Levels with $n\leqslant 64$ are mixed only with their nearest neighbors, and then only weakly. Levels with $65\leqslant n\leqslant 68$ are mixed with several neighboring states, whereas those with $n\geqslant 69$ are very susceptible to n-changing interactions and are, in a sense, delocalized. In general, the specific values of n delineating the three zones have been found to vary with the value of the phase ϕ by 6 ± 1 units, indicating an important dependence on initial conditions.

By our expanding any given initial state in terms of these eigenvectors, it can be easily confirmed that, within a calculation with a fixed basis set, the energy is bounded and the solution must be quasiperiodic, in agreement with the Hogg-Huberman theorem.[8] On the other hand, it is also clear that for initial states $n\geqslant 69$, no quantum calculation with a finite basis set can give any accurate results for the long-time behavior. Thus for such states, the physical usefulness of the theorem is limited.

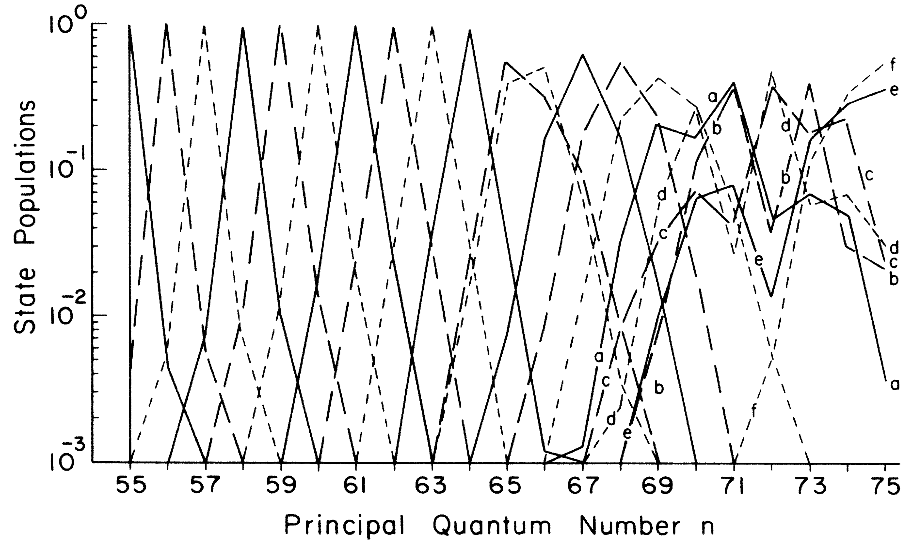

FIG. 1. An example of the unperturbed-state composition of 21 time-evolution eigenstates. To aid the eye, straight-line segments of different types connect the values defined at the discrete quantum numbers. A curve for one eigenstate has a fixed segment type and ends with a point of population 10^{-3}, larger than the calculated value. Three different zones of behavior can be seen, the regular zone 1 on the left, the transition zone 2, and the irregular zone 3 on the right. Letters are used to indicate the six vectors of type 3; the remaining fifteen eigenvectors are localized with substantial coefficients from only a few free-atom states.

Classical calculations have been performed for the parameter values of Fig. 1 by Jensen.[17] These indicate that the highest regular orbit (last Kolmogorov-Arnol'd-Moser surface) lies at $n=68$ and that the range of n values for which the orbits are partly regular and partly chaotic is 66 through 68. There is thus a close quantitative similarity between the classical and quantum regimes. This similarity persists as the zone-boundary values change over a range $n=55$ to 70 with changes in the microwave frequency and the two external fields. Further investigation of this correspondence and of the relationship between our three zones and Berry's three regimes of semiclassical theory[18] would be worthwhile.

Let us now turn to the comparison between theory and new n-changing experiments that probe the irregular zone. The experimental techniques that we use have been described previously.[15,19] In our experiments there is great control of the substate population, and nearly one-dimensional behavior is achieved.[15] The exciting laser beam is collinear with the atomic beam. A series of recent supplementary experiments proved that at least 99.5% of the $n_0=63$ atoms were laser excited before entering the microwave waveguide region. Principal tests were a direct field-ionization prequenching experiment showing at least 65% excitation before the waveguide when the microwaves were off, and a negative search for low-order microwave-sideband laser-excitation resonances,[20] which placed a bound on laser excitation within the waveguide with the microwaves on. Theoretically we find that the small possible fractions of atoms formed within the microwaves do not contribute to the n-changing probabilities disproportionately to their size.

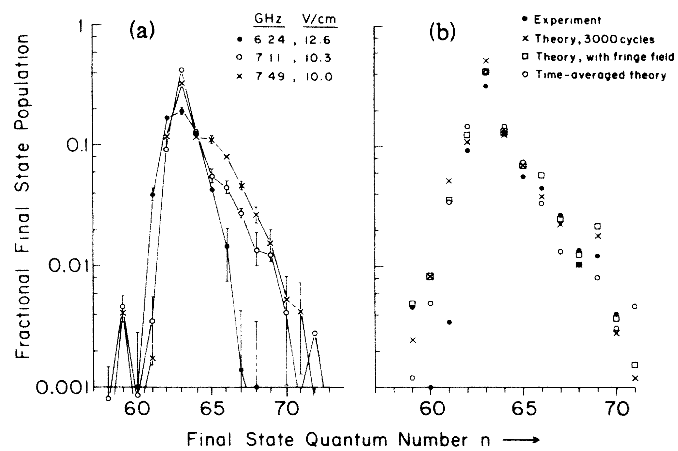

FIG. 2. (a) Experimental final-state population distributions for $n_0=63$ electrically polarized atoms driven by a linearly polarized microwave electric field. The polarizing static field strength is 8.0 V/cm. (b) A comparison of theoretical calculations with experimental data at 7.11 GHz. Filled circles: experimental points; crosses: 41-state theory for 3000 field oscillations averaged over values of the phase $\phi=0$, $\pi/2$, π, and $-\pi/2$; squares: 41-state theory for 3000 oscillations after 100 oscillations of fringe field development; open circles: 16-state theory averaged between 1 and 3000 oscillations and over eleven values of ϕ.

In Fig. 2(a) we show experimental populations of various n levels after the atom beam has emerged from a waveguide of length 70 cm, having been excited into an extreme Stark state with $n_0=63$. The microwave interaction time was approximately 3000 cycles. Results are given for three frequencies,[21] with field strengths that are about half those required to place the initial state within the irregular zone 3 for $\phi=0$, and about those required for $\phi=\pi/2$.

In Fig. 2(b) the experimental results at 7.11 GHz are compared with the predictions of the 1D SHA model. The computed populations correspond to evolution through an integral number of cycles N. Some results are shown for (1) $N=3000$; (2) $N=3000$ with sine-squared switching-on of the field over 100 cycles; and (3) laser excitation within the microwaves, where one averages over all values of N between 1 and 3000. The first two cases used the basis set $n=55$ through 95, and the last, $n=58$ through 73.

From the figure we see that the extent of energy transfer is described well by the quantum calculations. The calculated populations do not critically depend on the field switching. Although transitions do occur within the fringe field, these do not affect the 3000-cycle final probabilities very much. Also, the N-averaged results are dominated by the larger N values, so that laser excitation inside and outside the microwaves give qualitatively similar results.

Note that the computed populations for levels in the irregular zone above $n=69$ may be inaccurate, because of basis-set instability. In particular, the rise in population near $n=72$ in Fig. 2(b) is entirely due to the proximity of the upper limit on the basis set at $n=73$. The low-n discrepancies in Fig. 2(b) provide the incentive to seek improvements in both theory and experiments, while the general level of agreement gives confidence that the simple 1D model is a good theoretical starting point. This is particularly true since an early apparent discrepancy in the ionization threshold[3] can now be understood as arising from the uncharacteristic choice $\phi=0$.

When starting the atom below the region of classical chaos, our experiments relate to zone 2 and the edges of zones 1 and 3. Yet the fields are strong enough so that traditional two-state multiphoton pictures are no longer sufficient. In Fig. 3, we present an experimental frequency scan of the probability of transitions from $n=63$ to 62 at a field near 10 V/cm. While the field-saturated four-photon resonance near 6.26 GHz is clearly visible, there is an almost flat background, corresponding to a field-saturated 10% population in

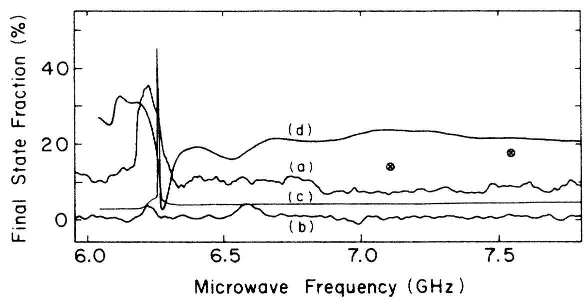

FIG. 3. The $n=62$ final-state population fraction as a function of microwave frequency for a microwave field strength near 10 V/cm. Curve a, experimental data at 9 ± 1 V/cm, frequency independent within errors except in the resonance region near 6.26 GHz; curve b, experimental background to be subtracted from curve a, containing n-changing populations to $n=61$ and below. The quantum theory curves at 10 V/cm are for no field switching and for values of the initial phase of, curve c, 0 and, curve d, $\pi/2$; crosses are theory averaged over eleven values of this phase.

state $n=62$ at all frequencies. The quantum calculations lead to a similar result, but do overestimate this nonresonant probabilty somewhat. Experimentally this background is also flat at lower fields, below saturation. The origin of the background theoretically involves important coherent nonresonant contributions from at least four states, two states on either side of the initally prepared state. The Fano-type profile in Fig. 3 for the $\phi=\pi/2$ case indicates that the background is acting as a separate n-changing quasicontinuum process that couples coherently with the resonant n-changing process. The fact that these resonant and nonresonant n-changing probabilities are both saturated with microwave field strength is part of the explanation of the theoretically predicted quantum "freezing" at long times[14] of the n-changing population distributions for our values of the parameters.

We have identified a quantum phenomenon that appears to be the equivalent of classical chaos, but we have not yet determined the extent to which quantum dynamics in our irregular zone 3 can be described as stochastic diffusion in phase space. We believe that this question will not be resolved until quantum theory properly includes the continuum.

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[1]J. G. Leopold and I. C. Percival, Phys. Rev. Lett. **41**, 944 (1978), and J. Phys. B **12**, 709 (1979).

[2]D. A. Jones, J. G. Leopold, and I. C. Percival, J. Phys. B **13**, 31 (1980).

[3]R. V. Jensen, Phys. Rev. A **30**, 386 (1984), and Phys. Rev. Lett. **54**, 2057 (1985).

[4]J. G. Leopold and D. Richards, J. Phys. B **18**, 3369 (1985).

[5]J. E. Bayfield and P. M. Koch, Phys. Rev. Lett. **33**, 258 (1974).

[6]J. E. Bayfield, L. D. Gardner, and P. M. Koch, Phys. Rev. Lett. **39**, 76 (1977).

[7]K. A. H. van Leeuwen, S. Renwick, J. B. Bowlin, P. M. Koch, R. V. Jensen, O. Rath, D. Richards, and J. G. Leopold, Phys. Rev. Lett. **55**, 2231 (1985).

[8]T. Hogg and B. A. Huberman, Phys. Rev. Lett. **48**, 711 (1982).

[9]G. Casati, B. V. Chirikov, F. M. Izrailev, and J. Ford, in *Stochastic Behavior in Classical and Quantum Hamiltonian Systems,* edited by G. Casati and J. Ford, Lecture Notes in Physics Vol. 93 (Springer, New York, 1979), pp. 333–352.

[10]S. Fishman, D. R. Grempel, and R. E. Prange, Phys. Rev. Lett. **49**, 509 (1982).

[11]D. R. Grempel, R. E. Prange, and S. Fishman, Phys. Rev. A **29**, 1639 (1984).

[12]J. N. Bardsley and B. Sundaram, Phys. Rev. A **32**, 689 (1985).

[13]D. L. Shepelyansky, in *Chaotic Behavior in Quantum Systems,* edited by G. Casati (Plenum, New York, 1985), pp. 187–204.

[14]G. Casati, B. V. Chirikov, and D. L. Shepelyansky, Phys. Rev. Lett. **53**, 2525 (1984).

[15]J. E. Bayfield and L. A. Pinnaduwage, Phys. Rev. Lett. **54**, 313 (1985).

[16]K. Yajima, J. Math. Soc. Jpn. **29**, 729 (1977).

[17]R. V. Jensen, private communication.

[18]M. V. Berry, Philos. Trans. Roy. Soc. London, Ser. A **287**, 237 (1977), and J. Phys. A **10**, 2083 (1977).

[19]J. E. Bayfield and L. A. Pinnaduwage, J. Phys. B **18**, L49 (1985).

[20]J. E. Bayfield, L. D. Gardner, Y. Z. Gulkok, and S. D. Sharma, Phys. Rev. A **24**, 138 (1981).

[21]Frequencies in this paper are for the atom's reference frame, obtained by correction of the laboratory-frame values for the Doppler shift of 40–50 MHz. References 5, 6, 15, 19, and 20 give unshifted values.