PHYSICAL REVIEW LETTERS

VOLUME 49 — 8 NOVEMBER 1982 — NUMBER 19

Stochastic Ionization of Surface-State Electrons

Roderick V. Jensen
Mason Laboratory, Yale University, New Haven, Connecticut 06520
(Received 23 July 1982)

A classical analysis is presented of the microwave perturbation of electrons bound to the surface of liquid helium by their image charge. Since the classical dynamics can exhibit chaotic behavior, this one-dimensional quantum system provides a novel system for the experimental investigation of quantum stochasticity. Analytic estimates for the classical thresholds and rates for stochastic excitation and ionization are determined as functions of microwave field amplitude and frequency. The frequencies and powers required to study stochasticity in the quantum regime are readily available.

PACS numbers: 03.65.Bz, 03.20.-i

Recently, deterministic classical systems with chaotic dynamics have been the subject of extensive research; however, little progress has been made on the profound question of whether the chaotic dynamics persist in a quantum mechanical description of these systems. This problem is important for a wide range of applications such as the calculation of the vibrational and rotational spectra of polyatomic molecules and the determination of the response of atoms and molecules to time-dependent electromagnetic fields.[1] Both the n-body problems and the driven oscillators correspond to nonintegrable, classical systems which exhibit chaotic behavior.

Numerical studies[2] of systems which exhibit chaotic behavior in the classical limit suggest that the quantum dynamics are also stochastic (mixing). However, for time-dependent Hamiltonians with discrete quasi-energy spectra[3] the quantum dynamics are always quasiperiodic and never chaotic. The question of whether a quantum system can be stochastic must, ultimately, be answered by experimental investigations of real physical systems. The purpose of this Letter is to suggest a realistic experiment to study the quantum dynamics of a time-dependent system which exhibits classical stochasticity.

The experiments of Bayfield and Koch[4] on microwave ionization and excitation of highly excited hydrogen atoms (principal quantum number $n \sim 50$) provide the strongest evidence for stochastic behavior in a quantum system. Because of the large n values, the electron can be treated semiclassically. For sufficiently high microwave power, ionization results when a chaotic, classical trajectory diffuses over the ionization threshold. Monte Carlo studies[5] of the classical trajectories of an electron in combined Coulomb and microwave fields give ionization rates which are in excellent agreement with experiment.

Unfortunately, Bayfield and Koch were unable to probe the quantum regime (low n) because of the high orbital frequencies and binding energies of the electron in the hydrogen atom. Moreover, further analytic study of the classical, semiclassical, and quantum behavior of this system has been complicated by the three-dimensional character of the electron dynamics.

A simpler and more accessible quantum system for experimental study is provided by surface-state electrons (SSE) which are weakly bound to the surface of liquid helium by their image charge. Spectroscopic studies by Grimes *et al.*[6] found that the energy levels of the SSE are given by the hydrogenic formula $E_n = -Z^2\mathcal{R}/n^2$, $n = 1, 2, 3, \ldots$, where $\mathcal{R} = 13.6$ eV. These energy levels result from a one-dimensional quantum mechanical treatment of the SSE which assumes an attracting $1/x$ potential due to the image charge and a repulsive barrier at the surface due to Pauli exclusion. Since liquid helium is a poor dielectric the effective charge is very small, $Z \sim 7\times10^{-3}$. Consequently, the binding energies and the characteristic frequencies are four orders of magnitude smaller than those for a hydrogen atom.

The experiment that I propose is a study of the dynamics of a SSE in a microwave field. The remainder of this paper consists of analytic estimates of the classical threshold for stochastic ionization and excitation of the SSE as functions of microwave amplitude and frequency. These results, which are based on the resonance overlap criterion for onset of global stochasticity, should be valid for large quantum numbers n. Moreover, if the chaotic dynamics persist for low n, this calculation suggests that the microwave frequencies and powers required to probe the quantum regime are readily available. More detailed semiclassical and quantum (time-dependent perturbation theory) treatments of this system will be considered in future work for comparison with the experimental results which will, hopefully, be forthcoming.

First, we consider the integrable dynamics of a classical electron in a one-dimensional $1/x$ potential with a repulsive barrier at the origin. The equations of motion for this system are generated by the Hamiltonian

$$H_0(x,p) = p^2/2m_e + \begin{cases} -Ze^2/x, & x>0, \\ \infty, & x\le 0. \end{cases} \tag{1}$$

A bound electron with fixed energy $-E_0$ bounces back and forth in the potential well between $x=0$ and $x = a_0 = Ze^2/E_0$ with angular frequency $\omega_0 = (8Ze^2/m_e a^3)^{1/2}$.

A canonical transformation[7] to action-angle variables reduces the unperturbed dynamics to straight-line trajectories in action-angle space,

$$I = \tfrac{1}{4}\sqrt{a}\,, \tag{2}$$

$$\theta = \begin{cases} 2\{\sin^{-1}[(x/a)^{1/2}] - [(x/a)(1-x/a)]^{1/2}\}, & p \ge 0, \\ 2\pi - 2\{\sin^{-1}[(x/a)^{1/2}] - [(x/a)(1-x/a)]^{1/2}\}, & p<0, \end{cases} \tag{3}$$

where a is the maximum excursion of the electron in units of a_0. The new Hamiltonian is $H_0(I) = -1/128I^2$ which gives a constant angular velocity $\Omega_0(I) = dH_0/dI = 1/64I^3$.

Since the microwave wavelengths are long compared with the maximum excursion, a, of the SSE from the liquid-helium surface, we can neglect the spatial variation of the perturbing electric fields. Therefore, in dimensionless variables the perturbed potential due to a microwave field with amplitude E and frequency ω is $V(x,t) = \epsilon x \cos(\Omega t)$, where $\Omega = \omega/\omega_0$ and $\epsilon = a_0^2 E/8Ze$.

For sufficiently small electric fields the Kolmogorov-Arnold-Moser (KAM) theorem[7] guarantees that most of the straight-line trajectories in action-angle space will be only slightly distorted by the perturbation. If we expand the perturbation in a double Fourier series[8] in θ and t, the perturbed Hamiltonian can be written as

$$H(I,\theta,t) = H_0(I) + \sum_{m,n} V_{mn} \exp[-i(m\theta + n\Omega t)]. \tag{4}$$

The maximum distortion of the orbits will occur at the resonant frequencies and actions which are determined by the relation[8]

$$m\Omega_0(I) + n\Omega = 0. \tag{5}$$

For small perturbations the Hamiltonian can be approximated in the vicinity of each resonance by the Hamiltonian of a pendulum, and the electron trajectories near the resonances are confined in narrow island chains in action-angle space. The electrons gain and lose energy as they ride the perturbation but no net change in the energy occurs. The island chains corresponding to the three lowest resonances are shown in Fig. 1.

As the perturbation increases the islands grow wider in action. When the islands are sufficiently large the electron can diffuse in action (or energy) by wandering from one island chain to another. Roughly speaking, this occurs when the islands generated at the resonances overlap, and the orbit of the electron is so distorted by one resonance that its oscillation frequency becomes resonant with another resonance. This "resonance overlap criterion" has been the subject of extensive numerical investigations[8] which indicate that it provides a good estimate for the onset of stochasticity.

The widths of the islands are determined by the corresponding Fourier amplitudes, V_{mn}, of the perturbation. Following Ref. 8 we estimate the island widths by approximating the Hamiltonian in the vicinity of the resonance by the Hamiltonian for a pendulum. The island width corresponds to the width of the trapping (libration) region[8]:

$$W_{mn} = 2\left(\frac{8V_{mn}(I)}{d\Omega_0/dI}\right)^{1/2}\Bigg|_{I_{mn}}, \tag{6}$$

where $I_{mn} = 0.25(m/n\Omega)^{1/3}$ is the resonant action defined by Eq. (5).

The Fourier components, V_{mn}, of the oscillating microwave potential are given by

$$V_m(I) = (\epsilon/4\pi)\int_0^{2\pi} d\theta\, e^{im\theta} x(\theta, I), \tag{7}$$

where $n = \pm 1$. To evaluate the integral in Eq. (7) we use Eq. (3) to change the variable of integration from θ to x. This gives

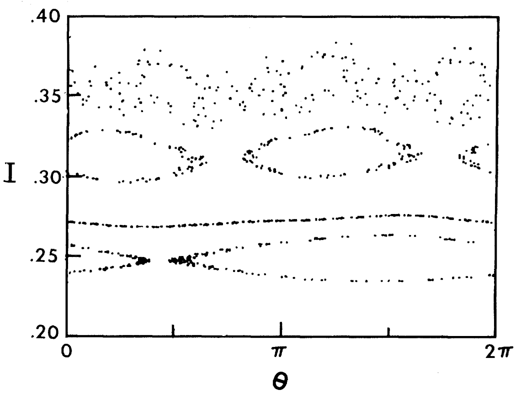

FIG. 1. Island chains for the $m = 1, 2, 3$ resonances for a perturbation with $\Omega = 1$ and $\epsilon = 0.003\,75$. The $m = 3$ islands already exhibit large stochastic regions. Also shown is a confining KAM surface between the $m = 1$ and $m = 2$ resonances.

$$V_m(I) = (\epsilon a/\pi)\int_0^1 dz\, z^{3/2}(1-z)^{-1/2}\cos(2m\{\sin^{-1}(z^{1/2}) - [z(1-z)]^{1/2}\}) \sim (0.26/\pi)\epsilon a m^{-3/2}, \tag{8}$$

where $z = x/a$. Then the width of the mth resonance is

$$W_m \sim 0.47\epsilon^{1/2} m^{1/4}/\Omega. \tag{9}$$

The zero-order islands overlap when the ratio of the island width to separation is greater than 1,

$$1 < 0.5(W_{m+1} + W_m)/\delta_m \sim 5.6\epsilon^{1/2} m^{11/12}/\Omega^{2/3}, \quad m \gg 1, \tag{10}$$

where the separation of the resonances is

$$\delta_m = I_{m+1} - I_m = 0.25[(m+1)^{1/3} - m^{1/3}]/\Omega^{1/3} \sim 1/12\Omega^{1/3} m^{2/3}, \quad m \gg 1. \tag{11}$$

Equation (10) determines the critical microwave field required for excitation from one classical resonance to another,

$$\epsilon_c > 0.032\Omega^{4/3} m^{-22/12}. \tag{12}$$

Since the island overlap, Eq. (10), increases with m, once the microwave field exceeds the threshold for stochastic diffusion for electrons with action I_m then these electrons can diffuse to larger actions (or energies) until they ionize.

When the islands overlap, the classical excitation rate can be estimated with random-walk arguments. A quasilinear[9] treatment of the distribution of trajectories in action-angle space leads to a Fokker-Planck–type diffusion equation. An estimate[10] of the characteristic diffusion rate for an electron to random walk from the m to the $m+1$ resonance is given by

$$\nu_m \sim 44\epsilon^2 m^{8/3}/\Omega^{5/3}, \quad m \gg 1. \tag{13}$$

Since Eq. (13) is a rapidly increasing function of m it provides a convenient order-of-magnitude estimate for the stochastic ionization rate.

These analytic estimates for the stochasticity threshold, Eq. (12), and the excitation rate, Eq. (13), have been verified by numerical integrations of the perturbed equations of motion. For small electric fields the electrons remain confined near their initial action (see Fig. 1); however, as the field is increased above the threshold, the trajectories span several resonances indicating the breakup of confining KAM surfaces.[7] The numerical results for both the stochastic threshold and excitation rate agree well with the analytic predictions as shown in Fig. 2.

If we normalize the present predictions with respect to the quantum mechanical ground-state energy of the SSE in the experiment of Grimes *et al.*,[6] $-E_0 = -Z^2\mathfrak{R} = 6.7\times10^{-4}$ eV, we can assess the feasibility of the proposed experiment. The maximum excursion and oscillation frequency of the corresponding classical electron are $a_0 = 1.51\times10^{-6}$ cm and $\nu_0 = \omega_0/2\pi = 320$ GHz, and the bind-

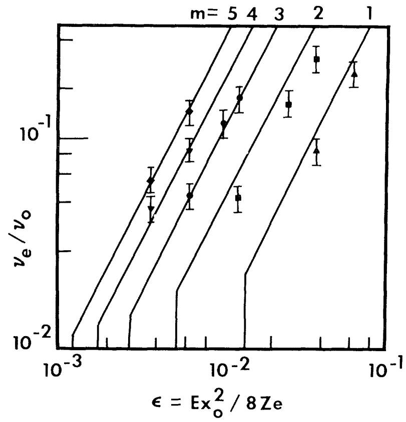

FIG. 2. Theoretical, Eq. (13), and numerical excitation rates from the m to $m+1$ resonances plotted as a function of the dimensionless electric field strength, ϵ, for the first five resonances with $\Omega = 1$. The five different symbols for the numerical data points correspond to the different values of m. The error bars represent an estimate of statistical errors in the Monte Carlo calculations. No excitations were observed, numerically, for $\epsilon < \epsilon_c$ as predicted by Eq. (10).

ing electric field at maximum excursion is $E_0 = Ze/a_0^2 = 450$ V/cm. Therefore, in real units the predictions for the threshold microwave fields and frequencies and the subsequent diffusion rates are

$$E = \epsilon \times 3600 \text{ V/cm}, \tag{14}$$

$$\omega/2\pi = \Omega \times 320 \text{ GHz}, \tag{15}$$

$$\nu_e = \nu_m \times 320 \text{ GHz}. \tag{16}$$

For microwave frequencies ~320 GHz, $\Omega \sim 1$, a field of $E \sim 115$ V/cm is required to *classically* excite a SSE at a rate $\nu_e \sim 14$ GHz. Moreover, since the nth quantum level is approximated by the mth classical resonance with $m = n^3\Omega$, the power threshold for stochastic ionization decreases significantly for SSE's in excited states. If the classical stochasticity persists for this driven, quantum oscillator, experimentalists should observe both enhanced linewidths and measurable ionization rates which increase with microwave power.

The author thanks Dr. P. Koch for suggesting this problem and Dr. I. Bernstein for useful discussions. This work was supported by the U. S. Department of Energy under Contract No. DE-AC02-77ET-53053.

[1]Special issue on laser chemistry, Physics Today 33, No. 11, 27–59 (1980).

[2]G. M. Zaslavskii, Phys. Rep. 80C, 157 (1981).

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

[4]J. E. Bayfield and P. M. Koch, Phys. Rev. Lett. 33, 258 (1974); J. E. Bayfield, L. D. Gardner, and P. M. Koch, Phys. Rev. Lett. 39, 76 (1977).

[5]J. G. Leopold and I. C. Percival, J. Phys. B 12, 709 (1979).

[6]C. C. Grimes, T. R. Brown, M. L. Burns, and C. L. Zipfel, Phys. Rev. B 13, 140 (1976).

[7]V. I. Arnold, *Mathematical Methods of Classical Mechanics* (Springer, New York, 1978).

[8]B. V. Chirikov, Phys. Rep. 52C, 263 (1979).

[9]G. M. Zaslavskii and N. N. Filonenko, Zh. Eksp. Teor. Fiz. 54, 1590 (1968) [Sov. Phys. JETP 25, 851 (1968)].

[10]R. V. Jensen and I. B. Bernstein, to be published.