Long-Period Orbits in the Stark Spectrum of Lithium

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We report observation of the signature of very-long-period orbits in the Stark spectrum of lithium in a regime of classical chaos. We identify recurrences associated with the orbits parallel to the electric field, including those beyond the 100th return of the primitive orbit. We also identify recurrences due to scattering of an incoming wave from one orbit into another by the alkali-metal core.

Periodic-orbit theory provides an important link between quantum theory and classical dynamics in regimes of disorderly (chaotic) motion [1]. The closely related closed-orbit theory [2,3] predicts the photoabsorption spectrum of a system from knowledge of its closed classical orbits. Long-period orbits are of particular interest because they determine the resolution the theory can achieve, and because they play a crucial role in determining how well the theory's predictions converge to the true quantum spectrum. However, long-period orbits are difficult to study experimentally and theoretically. Consequently, the limits of periodic-orbit theory are not well understood. We report here an experimental study of the spectrum of lithium in an electric field that reveals the signature of very-long-period closed orbits in a regime of disorderly motion.

An important result of periodic-orbit theory is the Gutzwiller trace formula, an expression for the level density that is obtained from the trace of the semiclassical Green's function [1]:

$$g_c(E) = \sum_k T_k \sum_{n=1}^{\infty} \frac{1}{2\sinh(\chi_{nk}/2)} e^{i(nS_k - \alpha_{nk}\pi/2)} \quad (1)$$

(atomic units). The index k distinguishes the primitive periodic orbits: the shortest period orbits for a given set of initial conditions. T_k is the period and S_k is the action of a periodic orbit. Each primitive orbit retraces itself, leading to new orbits with periods nT_k and actions nS_k, where n is an integer. Hence, every repetition of a periodic orbit is another periodic orbit. The quantity χ_{nk} is related to the stability of an orbit, and α_{nk} is the orbit's Maslov index.

Spectroscopic experiments measure transition probabilities, not level densities. Delos and co-workers have made contact between periodic-orbit theory and experiment in a formulation known as closed-orbit theory [2,3]. This theory, which is similar to the trace formula in derivation, yields the oscillator strength as a function of energy. Only orbits that begin and end at the nucleus are important in closed-orbit theory. Physically, these are associated with the outgoing waves that are generated when a tightly bound electron is excited to a high-lying state.

According to closed-orbit theory, the average oscillator strength density is given by a smooth background plus an oscillatory sum of the form [3]

$$Df(E, F) = \sum_k \sum_{n=1}^{\infty} A_{nk} \sin(nS_k - \alpha_{nk}\pi/2 - \phi_{nk}), \quad (2)$$

where E is the energy and F is the electric field. A_{nk}—the recurrence amplitude of a closed orbit—contains information about the stability of the orbit, its initial and final directions, and the matrix element of the dipole operator between the initial state and a zero-energy Coulomb wave. α_{nk} is the Maslov index, and ϕ_{nk} is an additional phase that depends on details of the orbit.

Computing a spectrum with resolution ΔE requires summing over all closed orbits of the system with periods up to $2\pi\hbar/\Delta E$. For low resolution, where only short-period orbits need to be considered, the theory has enjoyed considerable success [2,4,5]. However, extending the theory to high resolution presents a formidable challenge. Not only does the number of periodic orbits proliferate exponentially with period or action for chaotic systems, long-period orbits are difficult to compute because they become increasingly unstable and sensitive to numerical details [1].

We have studied the Stark spectrum of lithium, a system that is similar to hydrogen except for one crucial difference: the classical motion of lithium displays a transition to chaos, whereas the motion of hydrogen is always orderly. The classical dynamics of hydrogen in an electric field follows a simple scaling law. Its Hamiltonian ($H = p^2/2 - 1/r + Fz$, atomic units) can be rescaled using the substitutions $r = F^{-1/2}\tilde{r}$ and $p = F^{1/4}\tilde{p}$, so that $\tilde{H} = F^{-1/2}H$ has no explicit dependence on the field. As a result, the classical dynamics depends only on the scaled energy $\epsilon = EF^{-1/2}$, not on E and F separately. This classical scaling is a good approximation for lithium.

The scaled action of a given closed orbit, $\tilde{S}_k = F^{-1/4}S_k$, depends only on ϵ. If the spectrum is recorded while the field and energy are varied simultaneously so as to keep ϵ constant, the classical dynamics remains constant [6]. This approach has been used on several

systems [6–8]. An orbit's scaled action and recurrence strength can be obtained directly from the Fourier transform of the spectrum. This Fourier transform is called the recurrence spectrum because, in principle, each peak is located at the scaled action of a periodic orbit, and the height of each peak is proportional to that orbit's recurrence strength. We have applied this approach to the lithium Stark spectrum with higher accuracy than previously achieved in such studies, making it possible to search for high-action closed orbits.

In applying these ideas to lithium, an essential point is that the potential of lithium differs significantly from $1/r$ only near the nucleus where the electron penetrates the core charge of the lithium ion. We have modeled this classically by adding a short range potential to the hydrogenic Hamiltonian, chosen to give the proper quantum defects. Within these constraints, a variety of model potentials yields essentially the same classical behavior. In particular, as the scaled energy is increased, lithium shows a transition from regular to chaotic motion at about $\epsilon = -16$.

This behavior is shown in Fig. 1, which displays two Poincaré surfaces of section. Below $\epsilon = -16$ the trajectories form well-defined curves, each curve being a slice through a two-dimensional torus in four-dimensional phase space. Regular trajectories are confined to these tori. At $\epsilon = -16$, some of the tori have been destroyed, indicating the onset of chaos. At $\epsilon = -3$, the motion is chaotic throughout most of phase space, though small regular regions remain.

We have carried out laser spectroscopy on an atomic beam of lithium in an applied electric field. One laser excites the $2S \rightarrow 3S$ two-photon transition. A second laser excites the atoms to $m = 0$ Rydberg states in the vicinity of $n = 45$. The excited atoms are detected by electric field ionization. A spectrum at $\epsilon = -3.000(2)$ (the number in parentheses is the estimated error in the last digit) was obtained by scanning the laser from -65 to -50 cm^{-1} relative to the zero field ionization limit, while the scaled field, $w = F^{-1/4}$, was scanned between 100 and 120 (atomic units). The absolute error in w is estimated to be $\delta w \approx 0.025$. The recurrence spectrum (Fig. 2) was obtained by Fourier transforming the scaled-energy spectrum plotted with respect to w. The recurrence spectrum is expected to be accurate for $\bar{S}_{max} \leq \pi/\delta w \approx 100$ [9].

To verify our methods, the experimental recurrence spectrum at $\epsilon = -3.000$ is compared with a recurrence spectrum obtained from quantum computations [10] in Fig. 2. Agreement is generally good, although there are some discrepancies which we believe arise from experimental noise and neglect of the continuum in the computations.

Closed orbits parallel to the field play an important role in the spectrum. These form two classes: "uphill" orbits, directed toward the cathode, and "downhill" orbits,
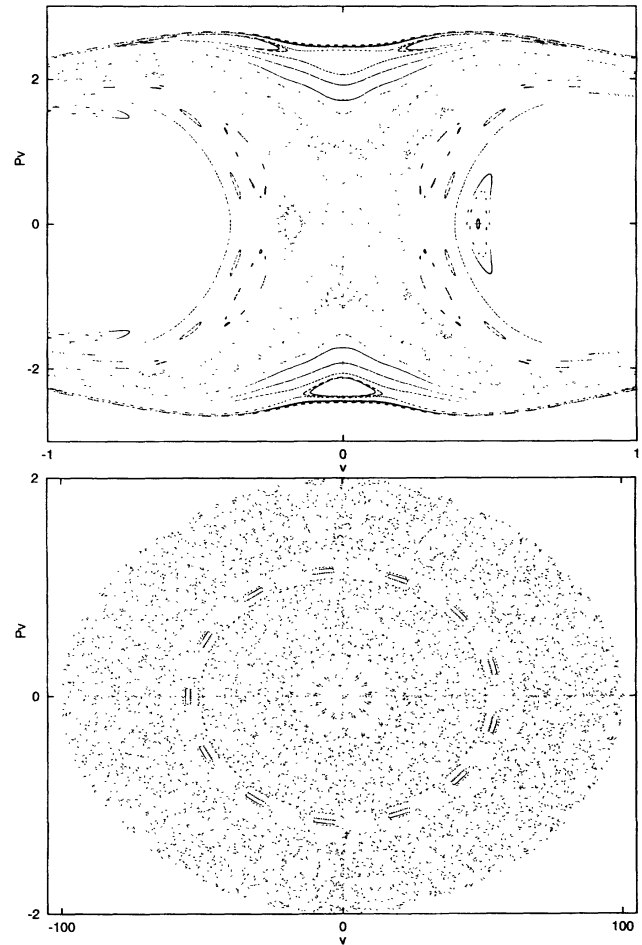

FIG. 1. Poincaré surfaces of section in semiparabolic coordinates ($u = (r + z)^{1/2}$, $v = (r - z)^{1/2}$) for lithium $m = 0$. Top: Early stages of the breakup of tori are visible in the region near the core at $\epsilon = -16$. Bottom: Most of the phase space is chaotic for $\epsilon = -3$, and the near-ergodic orbits are excluded from small regions by remaining tori.

directed toward the anode. For $\epsilon = -3.000(2)$, the first return of the uphill orbit has a scaled action $\bar{S}_1^u = 0.3915$, and the first return of the downhill orbit has $\bar{S}_1^d = 0.4285$. As a result, the recurrence spectrum is expected to have peaks at $\bar{S}_n^u = 0.3915n$ and $\bar{S}_n^d = 0.4285n$. In Fig. 3 most of the prominent peaks for $\bar{S} \leq 10$ are identified as corresponding to repetitions of the parallel orbits.

Gao and Delos [3] have studied the Stark problem for hydrogen and have found that every repetition of the parallel orbits gives rise to new orbits by a series of bifurcations of these main orbits. The scaled action of a newly created orbit is close to the scaled action of the parent orbit. With respect to the behavior of alkali-metal atoms, Eichmann et al. [8] showed that the recurrence spectra of hydrogen and sodium are similar for $\bar{S} < 6$. We have found that lithium is similar to hydrogen
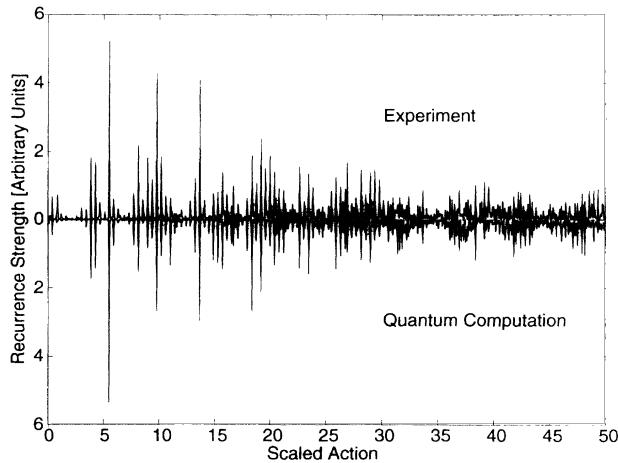
FIG. 2. Lithium recurrence spectrum for $\epsilon = -3.000(2)$. A mirror plot is used for comparison of the experimental spectrum (top) with the results of a quantum computation (bottom). The computed spectrum has been normalized to provide comparable heights.

FIG. 4. Comparison of experimental recurrence spectrum for lithium (top) with computed recurrence spectrum for hydrogen (bottom). Peaks a at $\tilde{S} = 9.792(3)$ and b at $\tilde{S} = 13.658(4)$ are due to core scattering, as described in the text.

for $\tilde{S} < 8$ [11]. However, as shown in Fig. 4, we find significant differences for $\tilde{S} > 8$. The existence of extra peaks in the lithium spectrum as the action is increased is consistent with the proliferation of closed orbits in chaotic systems.

For high action, the parallel orbits continue to display a strong signature in the spectrum. We have identified recurrences near the 100th return of the uphill parallel orbit (Fig. 5). This illustrates the power of closed-orbit theory to associate spectral features with long-period

orbits. Not all repetitions are visible in the recurrence spectrum because their recurrence strengths may be weak or the repetitions may be masked by other peaks. (In Fig. 5, the $n = 102$ and $n = 108$ repetitions of the uphill orbit are missing.) Furthermore, numerous additional peaks are visible in the spectrum. We believe that some of these extra peaks are repetitions of the downhill orbit, but their recurrence strengths in the range of Fig. 5 are generally too weak to permit a definite association.

A number of processes could generate the unidentified peaks in Fig. 5. In hydrogen, one expects peaks at repetitions of the orbits which bifurcate from the parallel orbits. These orbits have scaled actions slightly different from the repetitions of the parallel orbit and may be
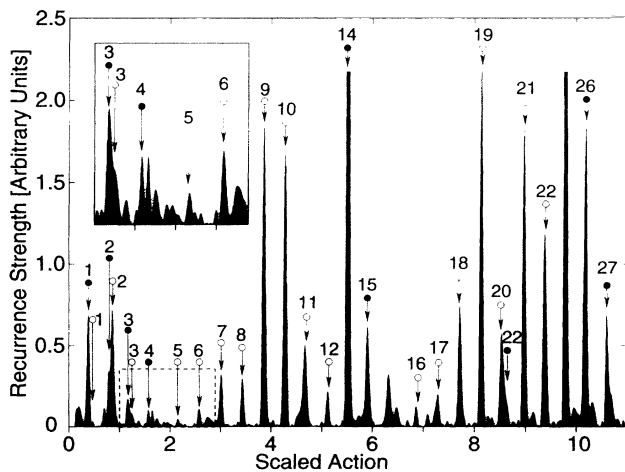

FIG. 3. Blowup of experimental data in Fig. 2. Recurrences corresponding to the parallel orbits are marked with arrows. Filled circles: uphill orbits. Open circles: downhill orbits. The number specifies the number of repetitions of the primitive orbit. The truncated peak at $\tilde{S} = 5.5$ has strength 5.2. The truncated peak at $\tilde{S} = 9.8$ has strength 4.3. The inset shows detail near $\tilde{S} = 2$.
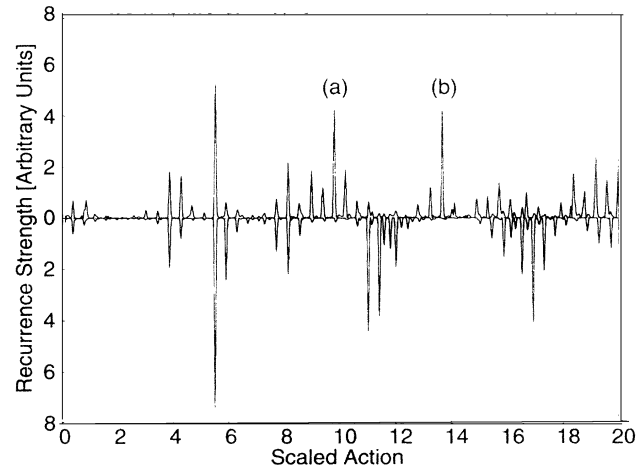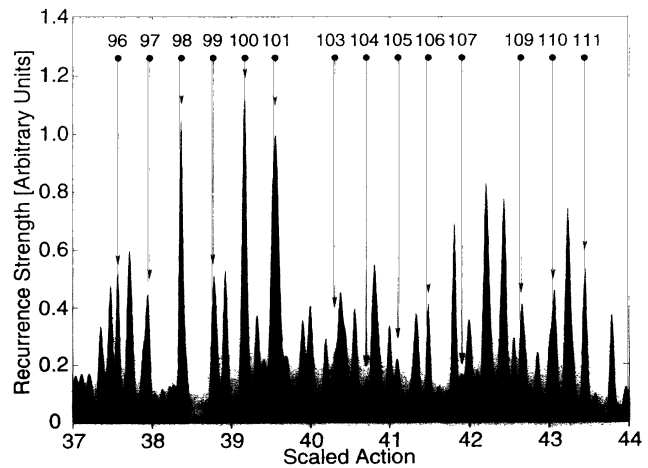

FIG. 5. Blowup of Fig. 2 at large action. Peaks identified with uphill parallel orbits are marked with arrows, as in Fig. 3.

resolved at high action. However, the recurrences due to these orbits have not yet been calculated.

As pointed out by Gao and Delos [12], core effects can be understood by considering scattering from one hydrogenic orbit into another by the alkali-metal core. This effect gives additional recurrences at the sum of actions of combinations of closed orbits [13]. Core-scattered recurrences can be large whenever the amplitudes of their components are large. For example, in Fig. 4, the recurrence at peak a, $\tilde{S} = 9.792(3)$, is located at $\tilde{S}_{10}^d + \tilde{S}_{14}^u = 9.792(3)$ [14], indicating that it can be understood as the core scattered sum of these two recurrences. Similarly, the recurrence at peak b, $\tilde{S} = 13.658(4)$, is located near $\tilde{S}_9^d + \tilde{S}_{10}^d + \tilde{S}_{14}^u = 13.654(4)$ and $\tilde{S}_{19}^d + \tilde{S}_{14}^u = 13.652(4)$ [15]. However, other recurrences that are found in lithium but not in hydrogen cannot be reliably identified using this scheme. Thus, it is uncertain how far this approach can be applied to compute the high-action recurrences we observe. Nonetheless, the possibility of describing a chaotic system in terms of a related separable system by closed-orbit theory is compelling: It would allow one to compute the closed orbits of an orderly classical system—eliminating the problem of the proliferation of orbits and the difficulties locating long-period orbits—and introduce the core-induced chaos quantum mechanically.

In summary, the high resolution of our experiment demonstrates the validity of closed-orbit theory at much higher actions than in previous work and provides experimental evidence for core scattering. The lithium Stark problem in the regime studied here seems well suited to probing the limits of periodic-orbit theory.

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[9] The unit of action here is the same as used in [8], but differs by a factor of 2π from that used in [3,5,12].

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[11] We have labeled the recurrences according to the repetition of the parallel orbit. Eichmann *et al.* [8] associated low-action recurrences with the first return of orbits with various initial angles. Inspection of their Table I reveals that most of the classical orbits they report have scaled actions that are integer multiples of parallel orbits. The two approaches are similar because most of the recurrences at small action include contributions from a given repetition of a parallel orbit and an orbit which bifurcated from that repetition.

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[13] See also D. Delande, K. T. Taylor, M. H. Halley, T. van der Veldt, W. Vassen, and W. Hogervorst, J. Phys. B (to be published).

[14] The experimental values of S_{10}^d and S_{14}^u are used here. They differ slightly from $10S_1^d$ and $14S_1^u$ because of other orbits with slightly different actions which lie within the peaks. These differences are small compared with the linewidths.

[15] The observed recurrence amplitude is the coherent sum over all orbits with action within the experimental linewidth. Other orbits have actions within these core scattered peaks, but their amplitude in hydrogen is small. Consequently, they are not expected to be important in lithium.
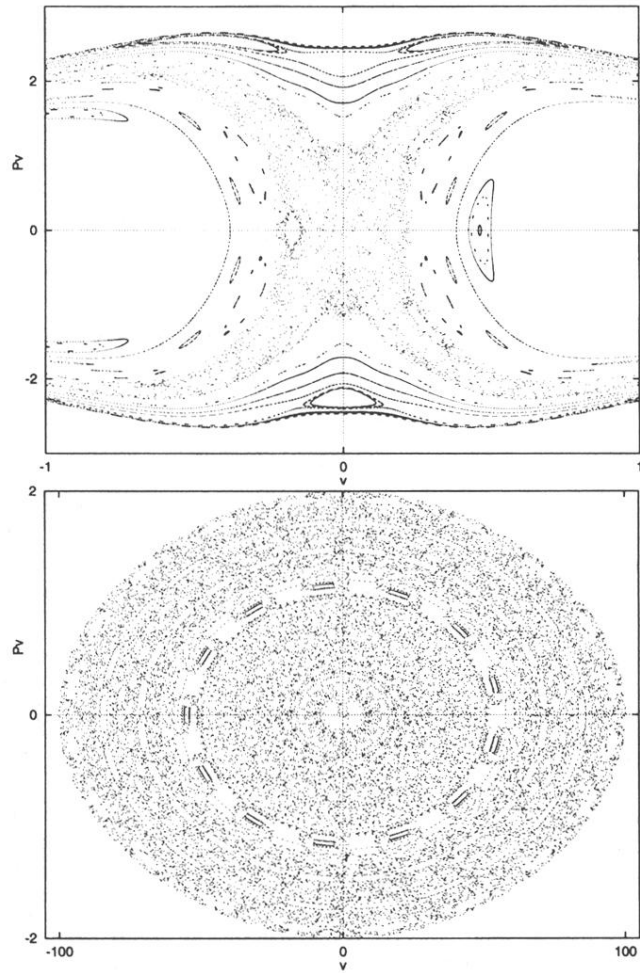
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