Quantum Chaos and Statistical Properties of Energy Levels: Numerical Study of the Hydrogen Atom in a Magnetic Field

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The transition to chaos in "the hydrogen atom in a magnetic field" is numerically studied and shown to lead to well-defined signature on the energy-level fluctuations. Upon an increase in the energy, the calculated statistics evolve from Poisson to Gaussian orthogonal ensemble according to the regular or chaotic character of the classical motion. Several methods are employed to test the generic nature of these distributions.

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During the last few years, the quantum analog of classical chaos has been the subject of numerous investigations. An important question is, how does classical chaos express itself in the quantum spectrum (and eigenstates)?

Chaotic two-dimensional billiards have been numerically studied. The energy-level fluctuations are in good agreement with the predictions of the Gaussian orthogonal ensemble (GOE) of random matrices.[1] Bohigas, Giannoni, and Schmit conjectured that this phenomenon was generic for all chaotic systems.[2] The results of Seligman, Verbaarschot, and Zirnbauer on a family of two-dimensional oscillators supported this conjecture.[3]

In this Letter, we numerically study the classical dynamics and the quantum spectrum of the hydrogen atom in a magnetic field. The classical dynamics exhibits a smooth transition from regular to completely chaotic motion.[4] Using group-theoretical techniques, we are able to compute a very large number of energy levels both in the regular regime and in the chaotic regime. This allows the most accurate comparison ever done with the theoretical predictions. We believe that the hydrogen atom in a magnetic field is the first system which allows both accurate numerical predictions (as done in this Letter; see also Wintgen and Friedrich[5]) and experimental investigations.

The nonrelativistic Hamiltonian of the hydrogen atom in a magnetic field is (in atomic units)

$$H=\frac{p^2}{2}-\frac{1}{r}+\frac{\gamma}{2}L_z+\frac{\gamma^2}{8}(x^2+y^2). \tag{1}$$

$\gamma=B/B_c$ is the reduced magnetic field ($B_c=m^2|q|^3/(4\pi\epsilon_0)^2\hbar^3\simeq 2.35\times 10^5$ T). The z component of the angular moment L_z and parity are constants of the motion. We limit our discussion to $L_z=0$, even-parity states. Similar conclusions can be reached from a study of $L_z=3$, odd-parity states.

Upon introduction of the "semiparabolic" coordinates

$$\mu=(r+z)^{1/2},\qquad \nu=(r-z)^{1/2}, \tag{2}$$

the Schrödinger equation for the energy E is

$$\{F(\mu,-2E)+F(\nu,-2E)+(\gamma^2/8)\mu^2\nu^2(\mu^2+\nu^2)-2\}|\Psi\rangle=0, \tag{3}$$

with

$$F(\mu,-2E)=-\frac{1}{2}\left(\frac{\partial^2}{\partial\mu^2}+\frac{1}{\mu}\frac{\partial}{\partial\mu}\right)-E\mu^2. \tag{4}$$

$F(\mu,-2E)$ is the Hamiltonian of a two-dimensional oscillator with frequency $\omega=(-2E)^{1/2}$ and $L_z=0$ written in polar coordinates.

Equation (3) establishes the equivalence between the hydrogen atom in a magnetic field and a system of oscillators coupled by the anharmonic term $\mu^2\times\nu^2(\mu^2+\nu^2)$. This equivalence has group-theoretical implications which are important for obtaining the dynamical symmetries of the system.[6]

In order to avoid the variation of the frequency of the oscillators with E, we define the "dilated" semiparabolic coordinates

$$u=(-2E)^{1/4}\mu,\qquad v=(-2E)^{1/4}\nu. \tag{5}$$

If we set $\lambda=\gamma^2/(-2E)^2$ and $\epsilon=1/(-2E)^{1/2}$, the eigenvalue for the coupled oscillators system takes the form

$$H_0|\Psi\rangle=2\epsilon|\Psi\rangle, \tag{6}$$

with

$$H_0 = F(u,1) + F(v,1) + (\lambda/8)u^2v^2(u^2+v^2). \quad (7)$$

In order for the comparison between classical and quantum behaviors to be meaningful, we first focus on the classical dynamics. The hydrogen atom in a magnetic field and the coupled-oscillators system in (7) share the same trajectories in phase space. The classical form for H_0 is[7]

$$H_0 = \tfrac{1}{2}p_u^2 + \tfrac{1}{2}p_v^2 + \tfrac{1}{2}u^2 + \tfrac{1}{2}v^2 + \tfrac{1}{8}\lambda u^2v^2(u^2+v^2) = 2\epsilon, \quad (8)$$

which obeys the scaling law

$$(u,v,p_u,p_v) \rightarrow (\alpha u, \alpha v, \alpha p_u, \alpha p_v),$$
$$\epsilon \rightarrow \alpha^2\epsilon, \quad (9)$$
$$\lambda \rightarrow \lambda/\alpha^4.$$

Hence, the classical dynamics depends only on one parameter,

$$\beta = \lambda\epsilon^2 = \gamma^2/(-2E)^3. \quad (10)$$

By numerical integration of the equations of motion associated with (7), Poincaré surfaces of section have been built. We project out of phase space the $p_v = 0$ plane and plot the "energy" $(p_u^2 + u^2)$ of the u oscillator versus its phase $\tan^{-1}(p_u/u)$. Figure 1 shows two selected surfaces of sections taken at $\beta = 0.8$ and 70. At very low β, the motion is fully regular. Around $\beta = 0.8$ some chaos appears [a very small chaotic region is hardly visible on Fig. 1(a)].

The fixed point at the center of the figure corresponds to the trajectories $u = v$, i.e., $z = 0$ for the atomic problem. It is associated with a trajectory in the plane perpendicular to the magnetic field. The stability of this trajectory can be studied by the usual linearization technique.[8] It is stable up to $\beta = 60.638$, where the fixed point transforms into a hyperbolic one which remains unstable up to $\beta \rightarrow \infty$.

Above $\beta = 60.638$ the phase space is fully chaotic [see Fig. 1(b)] except for very small regions, e.g., those located near $u = 0$ or $v = 0$ (their relative sizes are smaller than 10^{-4} which makes them negligible). Our analysis is in overall agreement with previous studies.[4]

The present system has some advantages over the oscillator system studied in Ref. 3. Actually the size of the chaotic volume in phase space increases with the parameter β and there is only one *convex chaotic region* with non-negligible volume. This is associated with the way in which the Coulomb dynamical symmetry is broken by the magnetic field.[6]

The next step is to calculate the quantum spectrum

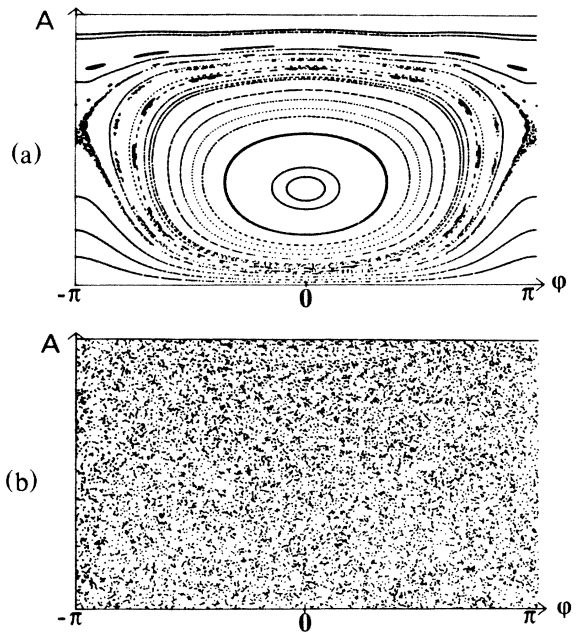

FIG. 1. Poincaré surface of section for the hydrogen atom in a magnetic field (or for the equivalent oscillator problem). We draw the energy of the u oscillator $A = p_u^2 + u^2$ vs its phase $\phi = \tan^{-1}(p_u/u)$ (section is defined by $p_v = 0$). (a) Section showing the low-field regular regime ($\beta = 0.8$). (b) Section showing the high-field chaotic regime ($\beta = 70$).

for our system. In zero field ($\gamma = \lambda = 0$), H_0 is the Hamiltonian of a pair of uncoupled oscillators. One readily deduces the usual Coulomb spectrum

$$E = -1/2\epsilon^2 = -1/2(n_u + n_v + 1)^2 \quad (11)$$

(n_u, n_v non-negative integers). For finite λ, we calculate the eigenvalues of H_0 by performing a diagonalization in a truncated oscillator basis. The matrix elements of the coupling $u^2v^2(u^2+v^2)$ can be easily calculated by use of group-theoretical techniques.[6]

The matrix representing H_0 in an oscillator basis has a band structure which allows efficient truncation and numerical diagonalization. One obtains the different eigenvalues ϵ for a given λ. This gives the spectrum *for the oscillator problem.*[5]

The convergence of the eigenvalues can be checked by variation of the size of the basis or by variation of the frequency of the oscillator basis (upon which the band structure of the matrix remains stable).[3] We used matrices of dimension up to 3025. All the eigenvalues used in the statistics presented below have an accuracy of better than 1% of the mean spacing.

In order to obtain the energy-level statistics *for the real physical problem,* we also calculated the spectrum for the hydrogen problem; that is, for fixed γ (instead of fixed λ). This can be done with Eq. (3) rewritten

as

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial\mu^2}+\frac{1}{\mu}\frac{\partial}{\partial\mu}+\frac{\partial^2}{\partial\nu^2}+\frac{1}{\nu}\frac{\partial}{\partial\nu}\right)+\frac{\gamma^2}{8}\mu^2\nu^2(\mu^2+\nu^2)-2\right]|\Psi\rangle=E(\mu^2+\nu^2)|\Psi\rangle. \quad (12)$$

This equation represents a generalized eigenvalue problem [of the type $(A-\lambda B)|\Psi\rangle=0$] for the energy E. In an oscillator basis, both A and B operators have a band structure. Using the Crawford algorithm,[9] we numerically calculated the different energies E for fixed values of γ (in a way analogous to that in Ref. 6 and Clark and Taylor[10]).

We now turn to the results concerning the energy-level fluctuations and first consider the nearest-neighbor spacing distribution for both the oscillator problem (eigenvalues ϵ for fixed λ) and the hydrogen problem (eigenvalues E for fixed γ). The mean spacing can be determined either by means of a semiclassical approximation or equivalently by fitting of the numerical results with a smooth curve. The results are insensitive to the fitting.

In the regular regime, as expected, we find a Poissonian distribution of spacings for both the oscillator problem and the hydrogen problem. This is associated with the existence of an approximate symmetry in this regime.[11] This is illustrated in Fig. 2 showing spacing distributions obtained for the oscillator problem and the *real physical system* (hydrogen atom in a magnetic field). The statistical significance is increased by the superposition of several spectra for different values of λ or γ. These distributions are clearly of Poissonian type, characterized by the existence of many small spacings. This is the manifestation of an underlying dynamical symmetry valid in the low-field limit which makes the different energy levels nearly cross.[11]

However, we tested the agreement with the Poissonian distribution by performing a χ^2 test on the first twenty classes of the histogram (each of width 0.1 of the mean spacing) and a Kolmogorov-Smirnov test on the distribution (that is, testing the maximum distance between the integrated distribution and the theoretical one) and found signficant deviations. This is due to the degeneracy of the zero-field energy levels, and can be understood by use of the semiclassical arguments of Berry.[12]

The spacing distributions in the chaotic regime are displayed in Fig. 3. They are clearly of Wigner type and exhibit the well-known phenomena of level repulsion (very little number of small spacings). This is the manifestation of the destruction of the dynamical symmetry and the onset of chaos which makes all the energy levels anticross. No significant deviation from the Wigner distribution is found, by either χ^2 or Kolmogorov-Smirnov tests. Because of the large number of energy-level spacings involved in the distribution of Fig. 3(a) (2958 level spacings), we have obtained, to our knowledge, the most accurate comparison with the Wigner distribution ever obtained. The correlation coefficients between two adjacent spacings are $C=-0.28\pm0.02$ (for the oscillator system) and $C=-0.31\pm0.03$ (for the hydrogen in a magnetic field), in good agreement with the GOE prediction

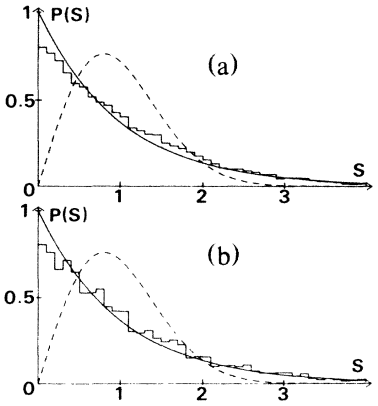

FIG. 2. Nearest-neighbor spacing histogram in the regular regime ($0.4>\beta>0.8$) together with the Poisson (solid line) and Wigner (dashed line) distributions. (a) 9095 energy-level spacings of the oscillator problem (16 spectra superimposed, λ ranging from 9.2×10^{-5} to 1.22×10^{-4}). (b) 4047 energy-level spacings of the *real physical problem* (hydrogen atom in a magnetic field) (16 spectra superimposed, γ ranging from 1.5×10^{-6} to 1.8×10^{-6}).

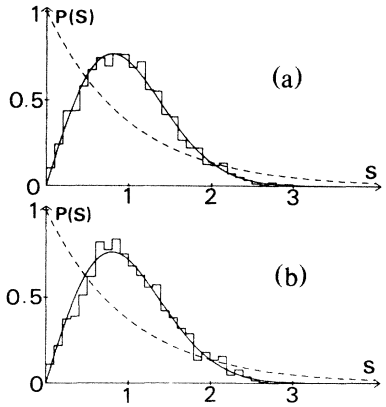

FIG. 3. Nearest-neighbor spacing histogram in the chaotic regime ($\beta>60.638$) together with the Wigner (solid line) and Poisson (dashed line) distributions. (a) 2958 energy-level spacings of the oscillator problem (15 spectra superimposed λ ranging from 3.5×10^{-2} to 7×10^{-2}). (b) 1294 energy-level spacings of the *real physical problem* (27 spectra superimposed, γ ranging from 3×10^{-5} to 2×10^{-4}).

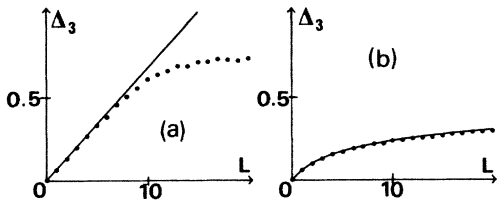

FIG. 4. Δ_3 statistics of the spectrum (spectral rigidity). (a) Oscillator system in the regular regime. The solid line is the Poisson prediction. (b) Real physical problem (hydrogen in a magnetic field) in the chaotic regime. The solid line is the GOE prediction.

$C = -0.27$.

Finally, a further test has been performed: We calculate the so-called "spectral rigidity," that is, the Δ_3 statistic measuring the long-range correlation of the spectrum.[1,3] Figure 4(a) shows the Δ_3 statistics obtained in the regular regime for the real physical problem (hydrogen atom in a magnetic field). Agreement with the Poisson prediction $\Delta_3(L) = L/15$ is excellent up to $L = 10$ where a saturation effect appears, in agreement with the prediction of Berry.[12] Figure 4(b) displays the Δ_3 statistics in the chaotic regime for the oscillator system [sample as in Fig. 3(b)]. Again, agreement with the GOE predictions[1] is excellent. This proves that, in the chaotic regime, the spectrum is surprisingly more rigid than in the regular one [the GOE asymptotic prediction (large L) is $\Delta_3(L) \simeq (1/\pi^2)\ln L$].[1]

In conclusion, through the numerical study of the energy-level fluctuations in the problem of a hydrogen atom in a magnetic field, we have demonstrated that the transition to chaos in the classical problem is associated with a profound change in the statistics. In the regular regime, the agreement with the Poisson model is good, while in the chaotic regime predictions from the GOE model based on random-matrix theory agree excellently with our results, both for the coupled-oscillators system and the real atomic system. This supports the conjecture of Bohigas, Giannoni, and Schmit[2] on the universality of energy-level fluctuations and suggests that the hydrogen atom in a magnetic field may serve as an ideal system for an experimental study of quantum chaos.

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