

Scaled-Energy Spectroscopy and Its Relation with Periodic Orbits

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We show that the use of scaled variables in data recording leads to a simple but powerful parametrization of complicated spectra. In the case of the atomic Stark effect the parametrization is complete for all experimentally resolved states and emphasizes the similarities between different atoms, e.g., sodium and hydrogen. Theoretically, the parametrization is linked, in a natural way, to the classical periodic orbits of the system. We found excellent agreement between measurements, calculated quantum spectra, and classical calculations.

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Experimental progress over the last decade has enabled the spectroscopy of highly excited states of atomic, molecular, and nuclear systems. Thereby, interest has shifted from many-body problems, typically associated with ground-state systems, towards questions concerning the mutual interaction of only few particles and their behavior in external fields. From a theoretical point of view such systems are frequently intractable by exact quantum calculations because the Schrödinger equation is multidimensional and nonseparable. In addition, highly excited systems have a vastly increased level density of their spectra even if only a few particles are effectively involved. This, if not concealed by experimental resolution, often prohibits a traditional level-by-level analysis of experimental results.

As a consequence, research on highly excited systems must concentrate on finding small numbers of parameters which describe the whole spectrum or, at least, major portions of it. One approach consists in identifying groups of energy levels which are treated as one single entity ("channel"), even though each group may cover the whole energy range of the spectrum and may consist of a large or even an infinite number of levels. This approach originates from scattering theory and has proven to be extremely successful for various systems, like highly excited hydrogen atoms¹ (single-channel systems), one-electron-excited atoms or molecules with a structured core^{2,3} (multichannel systems), or even excited hydrogenic and nonhydrogenic atoms in external fields.^{4,5}

An alternative parametrization of complex spectra starts from the investigation of common properties of *all* levels lying within a given energy region of the spectrum. The approach is based on a semiclassical approximation of Feynman's path-integral formalism. This parametrization is linked, in a natural way, to the periodic orbits of the classical system. Recently, it has been applied successfully to the spectra⁶ and the photo cross sections^{7,8} of a hydrogen atom in a uniform magnetic field.

The power of this method is most evident when applied to spectra which were recorded as functions of *scaled variables*. Experimental spectra of this kind cannot usually be generated from existing data, since their

recording requires the simultaneous variation of several parameters, e.g., the energy and the external field strength. The functional dependence of the parameters follows from inherent scaling properties of the classical Hamiltonian. In the present Letter we shall demonstrate that experimental spectra, when recorded as a function of scaled variables, can be reproduced by a limited number of Fourier components, even if no regularity whatsoever is visible on a linear energy scale. The relevant Fourier components remain constant over the entire range of the spectrum; they can be completely predicted from the calculation of the periodic orbits of the corresponding classical system. It turns out that they mostly retain their relevance even if the scaling properties are only approximately fulfilled, or if the spectrum is slightly distorted because of the finite experimental resolution. These modifications affect only a subset of the parameters in certain domains of the Fourier spectrum, while others, representing the more important general structure of the spectrum, remain unaffected.

The atomic Stark effect provides a perfect example for a demonstration of the method. Both for hydrogen and nonhydrogenic one-electron atoms the Stark effect is well understood, and a variety of methods exist to calculate quantum mechanical level densities.⁹ Furthermore, the equations of motion are separable for hydrogen and can largely be simplified by taking into account classical scaling laws. On the one hand, this allowed us to calculate quantum mechanically the spectrum of hydrogen in external fields to any desired accuracy, as a function of scaled energies (for convenience we shall restrict the discussion to such energies below the classical field ionization threshold where the finite width of the Stark states is negligible, although the theory does not impose such restrictions). On the other hand, all periodic orbits could be found by integration of the classical equations of motion. The calculations revealed the rigorous correspondence between quantum spectroscopy in scaled variables and classical periodic orbits. For comparison with experiment we have then recorded experimental Stark spectra in sodium as functions of (hydrogenic) scaled variables. The parametrization of these spectra

was compared with that of the synthetic hydrogen spectra and turned out to be nearly identical over a large range of the parameter space, demonstrating the power of this method in a practical example. Moreover, the Stark-effect studies allowed us to investigate the influence of small scaling-law violations (as they occur in sodium, as opposed to hydrogen) and of finite experimental resolution in practical applications.

The theoretical basis of the method has been developed by Gutzwiller¹⁰ and others.¹¹ In essence, the level density is expressed as the trace of the semiclassical Green's function, which is a sum over all classical periodic orbits. The theory simplifies considerably if the classical system is integrable or obeys scaling laws. In the present case both simplifications apply. It has been shown that the theory then yields the same results as the direct semiclassical Einstein-Brillouin-Keller quantization method.¹²

The Hamiltonian for a hydrogen atom in an electric field parallel to the z axis reads (in atomic units)

$$H = p^2/2 - 1/r + \Phi z, \quad (1)$$

where Φ measures the electric field in units of $F_0 = 5.14 \times 10^9$ V/cm. For one-electron Rydberg atoms other than hydrogen the Hamiltonian has to be modified near the origin; in the following, the theoretical treatment is for hydrogen. The Hamiltonian (1) obeys the scaling law

$$H(p, r; \Phi) = \Phi^{1/2} H(\Phi^{-1/4} p, \Phi^{1/2} r; \Phi = 1).$$

According to this scaling law we investigate spectra with fixed values of the scaled energy $\epsilon = E\Phi^{-1/2}$. These spectra are studied as functions of $\Phi^{-1/4}$ ($\Phi^{-1/4}$ is inversely proportional to the de Broglie wavelength). The connection between the scaled-energy spectroscopy [which probes the level density $n(\Phi)$] and its Fourier transform (FT) derives from the relation¹²

$$n(\Phi^{-1/4}) = \Phi^{-1/2} \bar{n} + \sum_r A_r \sum_{j=1}^{\infty} \frac{\cos(j\{\Phi^{-1/4} S_r - \alpha_r \pi/2\})}{j^{1/2}}. \quad (2)$$

In (2) the summation is over all primitive periodic orbits r having actions S_r and Maslov indices α_r , and all repetitions j of a primitive orbit. Each periodic orbit r generates an oscillatory contribution to the mean level density $\Phi^{-1/2} \bar{n}$. Thus, the Fourier transform of the spectrum (2) with respect to $\Phi^{-1/4}$ consists of discrete peaks at the classical actions S_r of the periodic orbits. The advantage of using scaled variables is that the actions S_r (and amplitudes A_r) are independent of energy and field strength. As a consequence, the FT of any part of the spectrum remains the same, as long as the ratio $E\Phi^{-1/2}$ is kept constant.

We have performed quantum and classical calculations for hydrogen using semiparabolic coordinates,

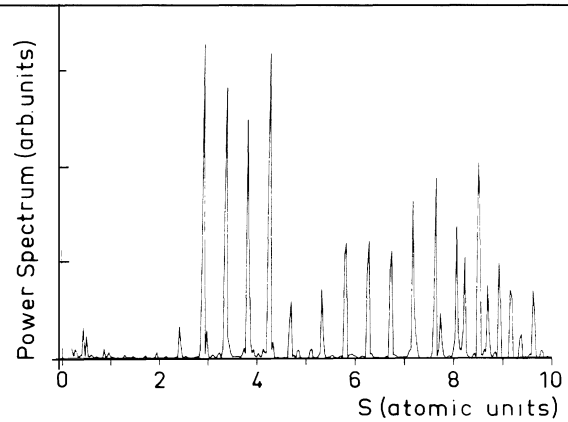


FIG. 1. Power spectrum of the calculated hydrogenic level density in the $m=2$ subspace for $E\Phi^{-1/2} = -2.5$.

which regularize the Coulomb singularity. The numerical techniques used to calculate large-scale quantum spectra for fixed scaled energies are described in Ref. 8. Classical periodic orbits were found by numerical integration of the Hamilton-Jacobi equations. The periodic orbits form continuous families of topologically equivalent orbits, which are confined on the same torus in phase space.¹³ One member of each family is an orbit which passes through the origin. Hence, it is sufficient to find only those orbits which start and end at the origin. Most of the periodic orbits found are rather complicated, with several loops around the Coulomb center. Calculations (and measurements) presented here are for $\epsilon = E\Phi^{-1/2} = -2.5$, which is lower than, but close to the classical escape threshold $\epsilon_{\text{esc}} = -2$.

The FT of the calculated quantum level density (between levels 150 and 350) of hydrogen is shown in Fig. 1 for $m=2$. For other m subspaces the results are nearly identical, because the scaled z component $\tilde{m} = \Phi^{1/4} m$ of the angular momentum always becomes negligibly small for high excitations. Each peak appearing in the figure can be related to a periodic orbit and vice versa: For each periodic orbit with scaled action S_r , a peak in the FT is present at $S = S_r$. This isomorphism clearly reveals the complete decomposition of the quantum mechanical level density in terms of the classical periodic orbits. The actions S_r of all (primitive) periodic orbits up to $S=8$ are listed in Table I.

We note that in an experimental situation one measures the distribution of the oscillator strength rather than the level density. The positions of the peaks in the corresponding FT remain the same but their heights are weighted by a factor which depends merely on the geometry of the transition involved.⁸ For direct comparison with experiment we have also calculated oscillator strength distributions and their FT's, which will be discussed below.

For the measurements we used an apparatus, presented elsewhere,¹⁴ which was modified as described below to be suitable for the present experiments. A collimated

TABLE I. Scaled period, actions, and initial angles in the ρ - z plane for all primitive orbits with actions $S < 8$ ($m=0$). For an orbit obeying a symmetry with respect to the $\rho = \phi$ axis, only half the period and action is relevant and tabulated (Ref. 10).

Orbit	Initial angle (degrees)	Period	Action
1	0	0.070	0.425
2	180	0.139	0.484
3	176.6	0.695	2.418
4	128.5	0.714	2.895
5	103.5	0.732	3.357
6	80.5	0.747	3.807
7	55.2	0.762	4.247
8	11.1	0.776	4.677
9	144.4	1.410	5.318
10	115.4	1.446	6.255
11	112.0	1.479	7.166
12	151.1	2.105	7.737

thermal beam of Na atoms passed through a pair of field plates, 0.8 cm apart, where the static voltage and also the field ionization pulse were applied. Two collinear, pulsed tunable dye-laser beams intersected the atomic beam at right angles. The first dye laser selected one of the fine-structure transitions, either $3s_{1/2}$ - $3p_{1/2}$ or $3s_{1/2}$ - $3p_{3/2}$, leaving the intermediate state in a $|m_l| = 0, 1$ mixed magnetic state. The second dye laser was scanned in the energy range around 414 nm. The bandwidth of the lasers (0.5 cm^{-1}) did not allow observation of a fully resolved Stark-state spectrum in the strong n -mixing regime, where the experiments were performed. With the second laser polarized linearly and parallel to the electric field axis, the selection rule $\Delta m_l = 0$ restricted the final states to belong to $|m_l| = 0, 1$ subspaces, whereas linear polarization perpendicular to the electric field axis additionally excited $|m_l| = 2$ magnetic substates. The spectra were recorded by scanning the second laser and the field strength simultaneously under computer control, thereby keeping the ratio $\epsilon = E\Phi^{-1/2}$ constant. Absolute energy calibration was obtained by comparison with a well-known zero-field state, e.g., Na $18d$. The excited Rydberg states were field ionized and detected with a multichannel-plate detector. The signals were digitized and stored in a computer for further evaluation.

A typical experimental scaled-energy spectrum is shown in Fig. 2. It represents the observed oscillator strength distribution in sodium along the line $E(\Phi) = 1.25E_{\text{esc}}$, where $E_{\text{esc}} = -2\Phi$ is the classical saddle-point energy for field ionization. No obvious regularity can be seen or expected, since states ranging from $n \approx 17$ up to $n \approx 26$ contribute with their overlapping Stark manifolds to the structures in this energy region, yielding a total of about 120 Stark states of different intensity.

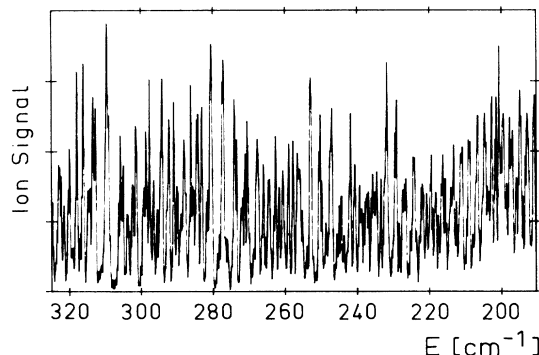


FIG. 2. Experimental scaled-energy spectrum for sodium at $E\Phi^{-1/2} = -2.5$. The spectrum covers the energy range from 325 to 190 cm^{-1} below the zero-field ionization limit. During the scan the field was varied from 1.8 to 0.6 kV/cm to keep the scaled energy constant.

The effect of spin-orbit splitting of the intermediate $3p$ state on the oscillator strengths must be kept in mind when comparing the sodium experiments with calculations for hydrogen. The spectrum shown in Fig. 2 and its FT in Fig. 3(a) contain final states from the subspaces $|m_l| = 0, 1, 2$, with the $|m_l| = 2$ states giving the dominant contribution.¹⁵ For direct comparison, the FT of the calculated hydrogenic oscillator strengths from the $2p(m_l = 1)$ state into the $m_l = 2$ Rydberg states is shown in Fig. 3(b). One finds remarkable agreement between the calculations for hydrogen and the measurements on sodium. In particular, a close inspection of Figs. 3(a) and 3(b) gives complete agreement between the theoretical and the experimental peak positions within the experimental errors. When considering the peak heights, the theoretical FT in Fig. 3(b) fits well the part of the experimental FT for $S < 6$. The deviation of the peak heights for $S \geq 6$ is due to the fine experimental resolution, as discussed below.

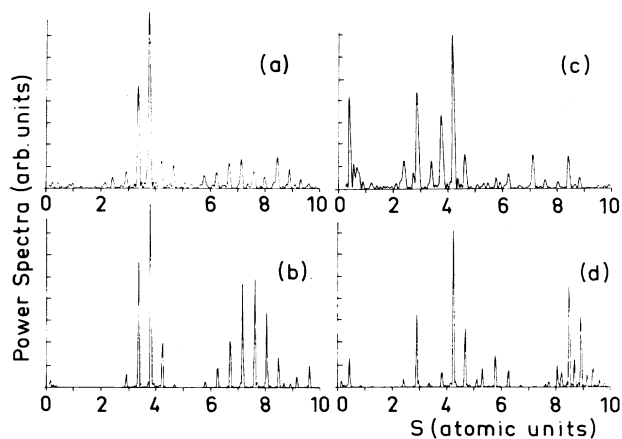


FIG. 3. Power spectra of (a),(c) measured sodium photo cross sections and (b),(d) calculated hydrogen oscillator strength distributions, obtained for fixed scaled energy $E\Phi^{-1/2} = -2.5$.

In Fig. 3(c) $m_l=0$ and $|m_l|=1$ states contribute to the experimental cross sections and hence to the FT. The spectrum should be compared qualitatively with Fig. 3(d), which shows the FT of $\Delta m=0$ oscillator strengths from the initial hydrogen $2p(m_l=1)$ state. Compared to Figs. 3(a) and 3(b) the agreement in the peak heights is not so close because the $m_l=0$ states, not contained in the theoretical spectra, contribute significantly to the experimental spectra in Fig. 3(c). But even with such simplified LS -coupling calculations one obtains qualitative agreement in the peak heights and, more importantly, again quantitative agreement in the peak positions.

The close overall agreement between calculations for the hydrogen and the sodium experiments may be surprising, but is consistent with general properties of highly excited atoms. Since the excited electron spends most of the time outside the ionic core, one expects the general structure of the spectrum to be the same as for a point core. In fact, it is known⁹ that the effect of the nonhydrogenic core on the Stark spectra consists mainly in avoided instead of exact level crossings. Spectroscopically, this amounts to small fluctuations in the energy positions of the levels with respect to hydrogen. These small fluctuations appear only in the "high-frequency" part of the Fourier spectrum (at large values of S), but do not affect the general structure of the spectrum. Similarly, finite experimental resolution affects only the high-frequency part by suppressing it exponentially. This is observed as a decrease of peak heights in the Fourier-transformed spectrum above $S \geq 6$, which was mentioned above.

In summary, we have shown that scaled-energy spectroscopy provides a powerful way of interpreting complicated spectra. Although it requires slightly more elaborate experimental techniques in data recording, it allows for compact and comprehensive parametrizations even in cases which exhibit no apparent regularity in the distribution of oscillator strengths. Theoretically, the parameters are closely linked to the classical periodic orbits of the system. A classical periodic orbit generates oscillatory contributions to physical observables such as the photo cross section. These are *collective* properties of all states of the quantum spectrum and should not be confused with a "semiclassical quantization scheme" to obtain single quantum states from classical periodic orbits. A very good agreement between measured sodium spectra, calculated hydrogen spectra, and classical periodic orbit theory is obtained. Finite experimental resolution and nonhydrogenic deviations for sodium do not show up in the low-frequency part of the Fourier transform, which parametrizes the global structures of the spectrum. Hence, the use of scaled-energy spectroscopy is of considerable value also in those cases where the scaling properties are only approximate.

The spectroscopy of periodic orbits might have far-reaching applications in all areas of physics, where complex systems are to be quantized. In particular, for sys-

tems which seem to be intractable by quantum calculations the method provides the possibility of understanding at least major parts of a spectrum. More interestingly, it represents a semiclassical scheme to parametrize (and to calculate!) smoothed fluctuations of physical observables like the level density or cross sections. Such fluctuations often exhibit properties which can be simulated by random matrices and seem, at first sight, unpredictable.¹⁶ The present results, however, show that observed fluctuations, although very complex, may be far from random. It is conceivable that this aspect has received too little attention in areas of physics (e.g., nuclear physics) where complex spectra were successfully described by random-matrix theories (see also Bohigas and Weidenmüller¹⁷).

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¹M. J. Seaton, Mon. Not. Roy. Astron. Soc. **118**, 507 (1958).

²M. J. Seaton, Rep. Prog. Phys. **46**, 167 (1983).

³C. H. Greene and Ch. Jungen, Adv. At. Mol. Phys. **21**, 51 (1985).

⁴U. Fano, Phys. Rev. A **24**, 619 (1981).

⁵D. A. Harmin, Phys. Rev. A **26**, 2656 (1982).

⁶D. Wintgen, Phys. Rev. Lett. **58**, 1589 (1987).

⁷J. Main, G. Wiebusch, A. Holle, and K. H. Welge, Phys. Rev. Lett. **57**, 2789 (1986).

⁸D. Wintgen and H. Friedrich, Phys. Rev. A **36**, 131 (1987).

⁹For reviews see D. Kleppner, M. G. Littman, and M. L. Zimmerman, in *Rydberg States of Atoms and Molecules*, edited by R. F. Stebbings and F. B. Dunning (Cambridge Univ. Press, London, 1983), p. 73; *Atomic Excitation and Recombination in External Fields*, edited by M. H. Nayfeh and C. W. Clark (Gordon and Breach, London, 1985).

¹⁰M. C. Gutzwiller, Physica (Amsterdam) **5D**, 183 (1982), and references therein.

¹¹For a review see M. V. Berry, in *Chaotic Behavior of Deterministic Systems*, edited by G. Iooss *et al.* (North-Holland, Amsterdam, 1983), p. 171.

¹²M. V. Berry and M. Tabor, J. Phys. A **10**, 371 (1977).

¹³This is a specific property of integrable systems only. A whole (continuous) family is treated as a single orbit; see Ref. 12.

¹⁴W. Sandner, U. Eichmann, V. Lange, and M. Völkel, J. Phys. B **19**, 51 (1986).

¹⁵See, e.g., H. A. Bethe and E. A. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977), Eqs. 60.11 and 60.12 (note that the second laser was polarized perpendicular to the field).

¹⁶O. Bohigas, M. J. Giannoni, and C. Schmit, in *Quantum Chaos and Statistical Nuclear Physics*, edited by T. H. Seligman and H. Nishioka, Lecture Notes in Physics Vol. 263 (Springer-Verlag, Berlin, 1986), p. 18.

¹⁷O. Bohigas and H. Weidenmüller, Ann. Rev. Nucl. Part. Sci. (to be published).