J. Phys. B: At. Mol. Opt. Phys. 22 (1989) 2985-2990. Printed in the UK

Spectral rigidity in atomic uranium

Sudeshna Sinha† and Ramakrishna Ramaswamy‡

† Chemical Physics Group, TIFR, Bombay 400 005, India
‡ School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110 067, India

Received 30 March 1989, in final form 24 April 1989

Abstract. We study the level statistics of parity-selected electronic states of atomic uranium (including autoionisation levels), obtained from recent photoionisation experiments. The spacings distribution which reflects short-range structure appears to be Poisson but spectral *fluctuation* measures reveal rigidity, and are consistent with a superposition of GOE sequences as is typically seen in nuclear spectra.

There is accumulating evidence that the energy eigenvalue statistics of quantum systems have universal fluctuation patterns. The universality classes are presumed to be determined by the underlying classical dynamics (Berry 1987, Eckhardt 1988). When this dynamics is chaotic, for example, the level correlation properties are modelled by random matrix ensembles like the GOE, GUE and the GSE (Brody *et al* 1981, Mehta 1967). Experimentally, GOE-type fluctuations are seen in compound-nucleus resonances (Haq *et al* 1982, Bohigas *et al* 1985), rare-earth atomic spectra (Rosenzweig and Porter 1960, Camarda and Georgopoulos 1983), as well as in spectra of molecules such as Na_2 (Lombardi *et al* 1988), NO_2 (Zimmerman *et al* 1988, Haller *et al* 1983), acetylene (Sundberg *et al* 1985, Pique *et al* 1987) and methanol (Ferretti *et al* 1987). Systems with regular underlying classical motion are in a different universality class, with uncorrelated level spacings which follow a Poisson distribution (Berry and Tabor 1977). This has been observed experimentally in lithium Rydberg spectra (Welch *et al* 1989).

In this paper we analyse the electronic energy levels of ^{238}U using techniques deriving from the study of complex systems (Brody *et al* 1981) as well as from the analysis of chaotic systems (Bohigas *et al* 1984, Berry 1987, Yukawa and Ishikawa 1988).

The data used here were recently obtained by multiphoton ionisation spectroscopy (Mago *et al* 1987a, b, 1988, Suri *et al* 1987, Bajaj *et al* 1988, Manohar *et al* 1989). The experimental set-up consists of two pulsed tunable dye lasers focused to spatially overlap onto an atomic beam of uranium in a quadrupole mass analyser. One laser excites uranium atoms from the ground state to an intermediate level and the other is scanned to record resonances. Over 800 levels have been located and partially assigned (see below). *Spectral universality* becomes evident in the semiclassical limit and the data we examine are particularly suitable in this respect as they correspond to a high-energy portion of the spectrum where the level density is high.

Statistical measures for the analysis of spectra (Brody *et al* 1981, Mehta 1967, Porter 1965, Yukawa and Ishikawa 1988) are applied after unfolding, i.e. eliminating the smooth secular trend $\overline{N(\varepsilon)}$ which is the integrated density of states for the energy

0953-4075/89/192985+06$02.50

sequence. Here we unfold by a fit to a polynomial function, $\overline{N(\varepsilon)} = \Sigma\, a_i \varepsilon^i$ with fitting parameters a_i (Haller *et al* 1983). The average level spacing of $E_1, E_2, \ldots, E_N$ is then 1 over the entire energy interval.

In complex atoms such as ^{238}U, the spin–orbit (LS) coupling terms are of the same magnitude as the electrostatic attraction. Thus L_i and S_i are not separately conserved and only the total angular momentum J and parity π are good quantum numbers. In order to study level statistics, the energy states need to be properly desymmetrised—here it implies that the data must be both J and π selected (Porter 1965). The present photoionisation experiments allow π selection but the J assignment is uncertain to within 1 quantum. The four sets of states analysed here are 214 (odd) levels in energy region 34 000–37 000 cm^{-1}, 138 (odd) levels in energy region 37 540–38 420 cm^{-1}, 261 (odd) levels in energy region 39 900–41 600 cm^{-1}, and 221 even-parity *autoionisation* resonances in the range 50 590–51 560 cm^{-1}. In these energy intervals, the fraction of levels missing is expected to be small (Chakraborti 1988), and this aids in proper data analysis.

The nearest-neighbour spacing distribution (NNSD) for the four data sets is shown in figure 1. In all cases, this distribution is apparently Poisson, but this observation is not entirely definitive since some deviation (from $\exp(-s)$, the broken curves in figure 1) is also evident. It is thus necessary to compute more sensitive probes which examine long-range correlations in the data.

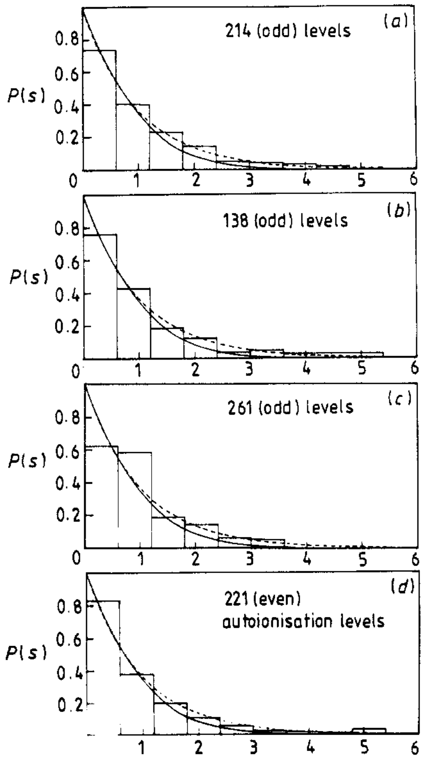

Figure 1. Histogram of experimentally observed spacing distributions. The broken curve is the Poisson and the full curve the prediction of a superposition of GOE distributions for the four data sets analysed.

We calculate Δ which is the average least-squares deviation of the integrated density of states of the unfolded levels, $N(E)$, from the best straight line fitting it (Dyson and Mehta 1963)

$$\begin{aligned}\Delta(2L) &= \left\langle (\tfrac{1}{2}L) \min_{A,\,B} \int_{-L}^{L} [N(E)-AE-B]^2\,\mathrm{d}E \right\rangle \\ &= \left\langle (\tfrac{1}{2}L) \int_{-L}^{L} [N(E)]^2\,\mathrm{d}E - (\tfrac{1}{4}L^2)\left[\int_{-L}^{L} N(E)\,\mathrm{d}E\right]^2 \right. \\ &\quad \left. - (\tfrac{3}{4}L^4)\left(\int_{-L}^{L} E\,N(E)\,\mathrm{d}E\right)^2 \right\rangle \end{aligned} \tag{1}$$

In terms of the ordered eigenvalues $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n$, lying in the interval $[-L, L]$, we get (Bohigas and Giannoni 1975)

$$\begin{aligned}\Delta(2L) &= \left\langle (n^2/16) - (\tfrac{1}{4}L^2)\left(\sum_{p=1}^{n} \varepsilon_p\right)^2 + (\tfrac{3}{8}L^2)\left(\sum_{p=1}^{n} \varepsilon_p^2\right) \right. \\ &\quad \left. - (\tfrac{3}{16}L^4)\left(\sum_{p=1}^{n} \varepsilon_p^2\right)^2 + (\tfrac{1}{2}L)\left(\sum_{p=1}^{n} (n-2p+1)\varepsilon_p\right) \right\rangle \end{aligned} \tag{2}$$

We also compute the average number variance, $\Sigma^2(L) = \langle (n-L)^2 \rangle$ where n is the number of levels in the interval L. The GOE values for all these statistics are well known (Brody *et al* 1981, Mehta 1967)

$$P_{GOE}(S) = (\pi S/2)\exp(-\pi S^2/4) \tag{3a}$$

$$\Delta_{\mathrm{GOE}}(L) = \log L/\pi^2 - 0.006\,95\ldots \qquad (\text{for } L > 10) \tag{3b}$$

$$\Sigma^2_{\mathrm{GOE}}(L) = 2\Sigma^2_2(L) + (1/\pi^2)[\mathrm{Si}(\pi L)]^2 - 1/\pi\,\mathrm{Si}(\pi L) \tag{3c}$$

with

$$\Sigma^2_2(L) = (1/\pi^2)[\log(2\pi L) + \gamma + 1 - \cos(2\pi L) - \mathrm{Ci}(2\pi L)] + L[1 - (2/\pi)\,\mathrm{Si}(2\pi L)].$$

A major problem with the present data is incomplete J assignment, and consequently, rather than seeing a single GOE, we should expect to observe a *superposition* of appropriately weighted GOE distributions. The number of superposed GOE is determined by the number of sequences in the data with relative weight given by the empirically determined fractional density. In this case, the pertinent expressions for the fluctuation statistics become (Brody *et al* 1981)

$$\bar{\Delta}(L) = \sum_{i=1} \Delta_{\mathrm{GOE}}(f_i L) \tag{4a}$$

and

$$\bar{\Sigma}^2(L) = \sum_{i=1} \Sigma^2_{\mathrm{GOE}}(f_i L) \tag{4b}$$

where f_i are the relevant fractions. It is evident from equations (4) that these values can be *significantly* different from the Poissonian value $\Sigma^2_{\mathrm{p}}(L) = L$, and $\Delta_{\mathrm{p}}(L) = L/15$, if the number of GOE superposed is not too large. On the other hand, the NNSD function of N superposed GOE begins to look quite Poissonian, even when N is around 3 or 4, since for mixed sequences, the NNSD is given by (Rosenzweig and Porter 1960)

$$P^N(s)=\prod_{k=1}^{N} D(f_k x)\{\Sigma_i^N f_i^2 P(f_i x)/D(f_i x) + [\Sigma_i^N f_i R(f_i x)/D(f_i x)]^2-\Sigma_i^N[f_i R(f_i x)/D(f_i x)]^2\} \tag{4c}$$

($P(x)$ is the NNSD function normalised to unity). For superposed GOE distributions (with $P(x)$ given by equation (3a))

$$R(x)=\int_0^\infty P(y+x)\,\mathrm{d}y=\exp(-\tfrac{1}{4}\pi x^2)$$

and

$$D(x)=1-(2/\pi)^{1/2}\int_0^{x(\pi/2)^{1/2}}\exp(-y^2/2)\,\mathrm{d}y.$$

Near the origin, when $D(0)=R(0)=1$ and $P(0)=0$, equation (3) reduces to $P^N(0)=1-\Sigma_{i=1}^N f_i^2$ which for large N is almost 1. The detection of a superposition of a number of GOE in NNSD is then difficult, if not impossible, whereas $\bar{\Delta}$ and $\bar{\Sigma}^2$, which reflect long-range rigidity, are much more discerning and sensitive probes. This is amply demonstrated in our analysis: the full curves in figure 1(a–d) are the results from equation (4c) and this is clearly a more accurate representation of the NNSD.

As the density of states is very high, some levels may be missing at random, and this can be problematic in the case of autoionisation resonances when as much as 20% may be missing. If the fraction of missing levels is f_m, then $\bar{\Delta}$ and $\bar{\Sigma}^2$ become (Mukamel *et al* 1984)

$$\bar{\bar{\Delta}}(L)=(f_m L/15)+(1-f_m)^2\bar{\Delta}(L/(1-f_m)) \tag{5a}$$

and

$$\bar{\bar{\Sigma}}^2(L)=(f_m L)+(1-f_m)^2\bar{\Sigma}^2(L/(1-f_m)) \tag{5b}$$

Results presented in figures 2 and 3 for the fluctuation measures make it clear that these, for the first three data sets at least, match extremely well with the theoretical curves for superposition of weighted GOE, obtained via equations (4–5). We thus have *clear experimental evidence* for level repulsion in atomic uranium. For the autoionisation data, agreement is poorer although the fluctuations are markedly different from Poisson. (In addition to missing levels there possibly are spurious assignments as well.)

Given that even simple dynamical models of atomic systems show widespread chaotic motions (Gutzwiller 1971), it seems reasonable to expect that the classical dynamics of a complex 92-electron atom at high energies must be dominated by chaos. The present study then supports evidence that quantum levels of such systems show the universal random-matrix fluctuations.

In summary, NNSD, Δ and Σ^2 statistics of parity-selected high-energy sequences of atomic uranium have been analysed. Our main observation is that all spectral *fluctuation* measures are fully consistent with those of superposed GOE and are thus similar to those of nuclear level data (Haq *et al* 1982, Bohigas *et al* 1985).

Our study highlights the inadequacy of examining the NNSD alone, which can be misleading as the short-range structure of superposed GOE and Poisson have little difference (equation (4c)). However, probes of long-range correlations, the Δ and Σ^2

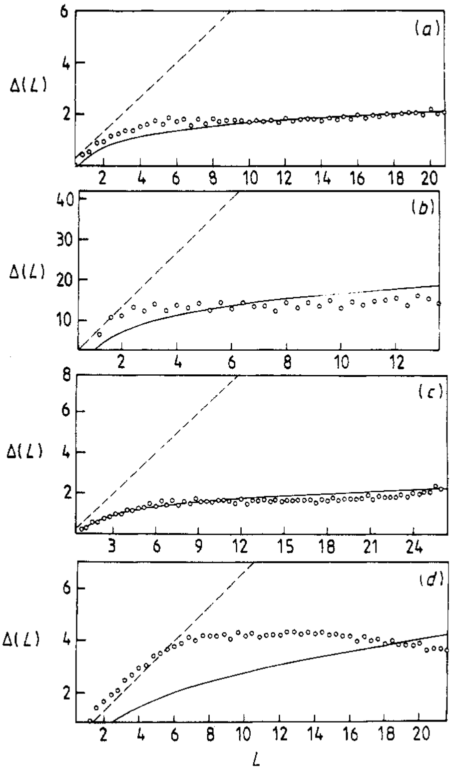

Figure 2. As in figure 1 for the $\bar{\Delta}$ statistic; the experimentally observed $\bar{\Delta}$ are denoted by open circles.

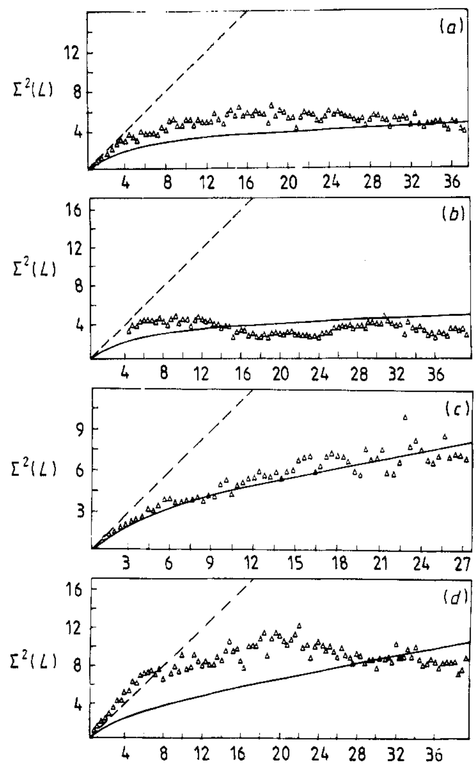

Figure 3. As in figure 1 for the Σ^2 statistic; the experimentally observed Σ^2 are denoted by open triangles.

statistics conclusively demonstrate *rigidity* and we are thus able to unambiguously identify the GOE nature of the present data. Such analysis is of considerable importance in treating *typical* experimental data.

Acknowledgments

We are most grateful to P K Chakraborti for kindly supplying us with unpublished data on uranium and explaining details of the experiments, to M V Berry and M C Gutzwiller for discussions and to A Pandey for generous advice and helpful comments and suggestions.

References

Bajaj P N, Manohar K G, Suri B M, Dasgupta K, Talukdar R, Chakraborti P K and Rao P R K 1988 *Appl. Phys.* B **45** 554–8
Berry M V 1987 *Proc. R. Soc.* A **413** 183–98
Berry M V and Tabor M 1977 *Proc. R. Soc.* A **356** 375–94
Bohigas O and Gianonni M J 1975 *Ann. Phys., NY* **89** 393–422
Bohigas O, Giannoni M J and Schmit C 1984 *Phys. Rev. Lett.* **52** 1–4

Bohigas O, Haq R U and Pandey A 1985 *Phys. Rev. Lett.* **54** 1645–8

Brody T A, Flores J, French J B, Mello P A, Pandey A and Wong S S M 1981 *Rev. Mod. Phys.* **53** 385–479

Camarda H S and Georgopoulos P D 1983 *Phys. Rev. Lett.* **54** 492–4

Chakraborti P K 1988 Private communication

Dyson F J and Mehta M L 1963 *J. Math. Phys.* **4** 701–12

Eckhardt B 1988 *Phys. Rep.* **163** 207–97

Gutzwiller M C 1971 *J. Math. Phys.* **12** 343–58

Ferretti A, Moruzzi G and Rahman N K 1987 *Phys. Rev.* A **36** 3736–42

Haller E, Koppel H and Cederbaum L S 1983 *Chem. Phys. Lett.* **101** 215–20

Haq R U, Pandey A and Bohigas O 1982 *Phys. Rev. Lett.* **48** 1086–9

Lombardi M, Labastie P, Bordas M C and Broyer M 1988 *J. Chem. Phys.* **89** 3479–90

Mago V K, Lal B, Ray A K, Rao P R K and Sharma S D 1987a *J. Phys. B: At. Mol. Phys.* **20** 6531–9

Mago V K, Lal B, Ray A K, Kapoor R, Sharma S D and Rao P R K 1987b *J. Phys. B: At. Mol. Phys.* **20** 6021–30

Mago V K, Ray A K, Lal B and Rao P R K 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 955

Manohar K G, Bajaj P N, Suri B M, Talukdar R, Dasgupta K, Chakraborti P K and Rao P R K 1989 *Appl. Phys.* B **48** 525–30

Mehta M L 1967 *Random Matrices and the Statistical Theory of Energy Levels* (New York: Academic)

Mukamel S, Sue J and Pandey A 1984 *Chem. Phys. Lett.* **105** 134–8

Pique J P, Chen V, Field R W and Kinsey J L 1987 *Phys. Rev. Lett.* **58** 475–9

Porter C E 1965 *Statistical Theories of Spectra: Fluctuations* (New York: Academic)

Rosenzweig N and Porter C E 1960 *Phys. Rev.* **120** 1698–714

Sundberg R L, Abramson E, Kinsey J L and Field R W 1985 *J. Chem. Phys.* **83** 466–75

Suri B M, Dasgupta K, Bajaj P N, Manohar K G, Talukdar R, Chakraborti P K and Rao P R K 1987 *J. Opt. Soc. Am* B **4** 1835–6

Welch G R, Kash M M, Iu C, Hsu L and Kleppner D 1989 *Phys. Rev. Lett.* **62** 893–6

Yukawa T and Ishikawa T 1988 KEK Preprint-88-70 KEK-TH-213

Zimmermann T, Koppel H, Cederbaum L S, Persch G and Demtroder W 1988 *Phys. Rev. Lett.* **61** 3–6