Statistical Behavior of Atomic Energy Levels: Agreement with Random-Matrix Theory

H. S. Camarda and P. D. Georgopulos
The Pennsylvania State University, Delaware County Campus, Media, Pennsylvania 19063

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The statistical behavior of complex atomic spectra of neutral and ionized rare-earth atoms has been examined. The authors found eight sets of atomic spectra of sufficient quality and statistics to compare with the predictions of random-matrix theory. Good agreement between theory and experiment was found for the covariance of adjacent spacings, $\mathrm{Cov}(S_i, S_{i+1})$, and the Δ_3 statistic.

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The statistical properties of the energy levels of highly excited nuclei are well described by Wigner's Gaussian orthogonal ensemble (GOE).[1] The GOE (also known as random-matrix theory) is applicable to physical systems which are time-reversal invariant, and also rotationally invariant if the total spin of the system is half integer, and is represented by an ensemble of real symmetric matrices whose matrix elements obey certain statistical laws. The eigenvalues of the matrices associated with the GOE exhibit a definite statistical behavior, and it is this predicted behavior of energy-level fluctuations, as well as other predictions, which is compared with experimentally observed levels. In principle the GOE is applicable to any complicated physical system with the requisite symmetries regardless of the underlying interaction, e.g., nuclear or electromagnetic. To date, the validity of random-matrix-theory level-fluctuation predictions has been tested almost exclusively with nuclear data, as is evidenced by a recent review[2] and a Letter.[3] Neutron resonance data collected by the Columbia group[4,5] has played a particularly prominent role.

Highly excited atoms with complex spectra should also be suitable systems for description by the GOE. Early work by Rosenzweig and Porter[6] on atomic spectra demonstrated that adjacent levels characterized by the *same* quantum numbers repelled each other and that the experimental adjacent-level spacing distribution was in good agreement with the Wigner spacing distribution, $P(x)dx = \frac{1}{2}\pi x \exp(-\frac{1}{4}\pi x^2)dx$, $x = S/\langle D\rangle$. The Wigner spacing distribution accurately reflects *one* of the predictions of the GOE. It implies that adjacent levels E_i and E_{i+1} are correlated and not distributed at random; otherwise a Poisson adjacent-level spacing distribution would apply. Of further interest is whether or not atomic spectra are in accord with other predictions of the GOE, e.g., are levels E_i, E_{i+2}, E_i, E_{i+3}, etc., correlated as has been found in the nuclear case.[4] We present evidence below that atomic spectra exist which are in good agreement with the full energy-level-fluctuation predictions of GOE. To the best of our knowledge this is the first time such complete evidence has been presented. The atomic spectra which mirror the nuclear data in that only total spin and parity are good quantum numbers appear to lie in the third long period of the periodic table.[6] These atoms are relatively heavy and one might expect that neither the residual electron interaction nor the spin-orbit interaction dominates. Consequently, the atom cannot be characterized by either LS or jj coupling, and only total spin and parity J^π are expected to be good quantum numbers. (The predictions of GOE considered below apply to sequences of levels with the same J^π.)

A compilation of atomic energy levels of neutral and ionized atoms in the rare-earth region (lanthanum through lutetium) has become available within the past few years.[7] These data, which form the basis of our analysis, lie in the beginning of the third long period of the periodic table. We have applied two statistical tests to the data: (1)

$$\mathrm{Cov}(S_i, S_{i+1}) = \frac{\sum_i (S_i - \langle S_i\rangle)(S_{i+1} - \langle S_{i+1}\rangle)}{[\sum_i (S_i - \langle S_i\rangle)^2 \sum_i (S_{i+1} - \langle S_{i+1}\rangle)^2]^{1/2}}.$$

The covariance of adjacent spacings is sensitive to correlations between levels E_i and E_{i+2} and is predicted by GOE theory to have the value of -0.27.[4,8] (2) The Dyson-Mehta Δ_3 statistic,[9] where

$$\langle \Delta_3\rangle = \min(A, B)(\Delta E)^{-1}\int_E^{E+\Delta E}[N(E) - AE - B]^2 dE.$$

$N(E)$ is a staircase plot of n consecutive energy levels and the Δ_3 statistic is a measure of the fluctuations of $N(E)$ from a best-fitting straight-line, under the assumption of a constant level

density. For the GOE $\langle\Delta_3\rangle = 1/\pi^2(\ln n - 0.0687)$, with a standard deviation of 0.11 independent of the number of levels n. This test is sensitive to both long- and short-range correlations between levels. For levels which obey the Wigner spacing distribution but which are otherwise uncorrelated (hereafter referred to as UW levels), $\langle\Delta_3\rangle = n/(55 - 210/n)$ with a standard deviation of $n/86$.[10]

It is important that these tests be applied to high-quality data. Missing, spurious, or misassigned levels introduce "noise" and dilute the information that can be extracted. In the nuclear case the widths of the excited states are usually available, and a well-defined procedure for assessing the quality of the data can be carried out.[4] Atomic widths are generally not available. The atomic states differ from the nuclear states because they are bound and represent states at a lower excitation energy. Over a span of 30 atomic levels a significant change in level density is apparent. The change in level density must be unfolded before the Δ_3 statistic is applied.

The criteria we have used to select the atomic data are as follows: (1) there should be a statistically significant number of levels ($\gtrsim 25$) of a given J^π; (2) the levels should obey the Wigner nearest-neighbor spacing distribution; (3) the energy levels should represent complicated states. As a signature of the last criterion we look at regions of excitation where the cumulative number of levels N versus excitation energy E (in units of inverse centimeters, 8000 $\text{cm}^{-1} \cong 1$ eV) can be fitted by $N(E) = \int (dN/dE)dE$, where dN/dE is given by the simple thermodynamic expression $dN/dE = \rho_0 \exp(a\sqrt{E})$. ρ_0 and a are constants found from fitting the data.

An example of this is shown in Fig. 1 for $\frac{9}{2}^-$ levels of neutral terbium (Tb I). The staircase plot represents the experimental data. The smooth curve was generated with the thermodynamic expression for $N(E)$ by using values of $\rho_0 = 1.75\times10^{-6}$ and $a = 5.2\times10^{-2}$ and represents the data well between $E = 19\,450$ and $27\,581$ cm^{-1}. It signifies that few if any levels are being missed in this region of excitation. Consequently, the 45 levels in this energy region should be a good test case for comparison of theory with experiment. The analytical fit to this data enabled us to transform the exponentially increasing level density to a constant level density, as is shown in Fig. 2. The staircase plot fluctuates about the straight line drawn through the data, and it is to these fluctuations that the Δ_3 statistic is sensitive. The experimental and GOE predicted values of Δ_3 for the 45 Tb I $\frac{9}{2}^-$ levels are given on the plot. It is on the unfolded data of all acceptable spectra that the statistical tests were made. We examined the rare-earth data in the recent compilation[7] and found that the following spectra satisfied criteria (1), (2), and (3): Nd I (4^-, 6^-), Nd II ($\frac{7}{2}^-$, $\frac{11}{2}^-$, $\frac{13}{2}^-$, $\frac{15}{2}^-$), Sm II (3^-), and Tb I ($\frac{9}{2}^-$). In Fig. 3 is plotted the nearest-neighbor spacing distribution for the levels considered. It con-

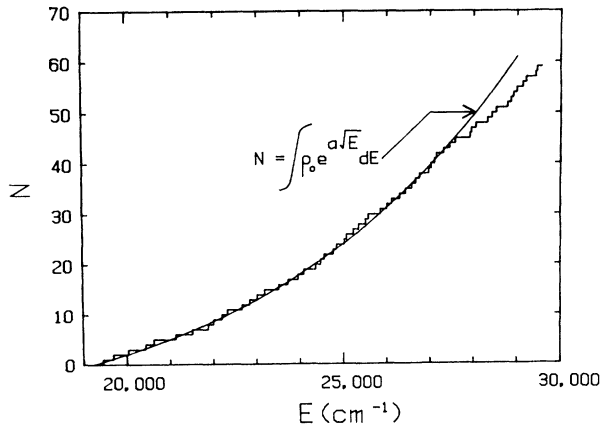

FIG. 1. A staircase plot of the cumulative number of levels N vs excitation energy E (in units of cm^{-1}) above the ground state for the $9/2^-$ levels of Tb I. The smooth curve resulted from fitting the data with a simple thermodynamic model of $N(E)$ (see text).

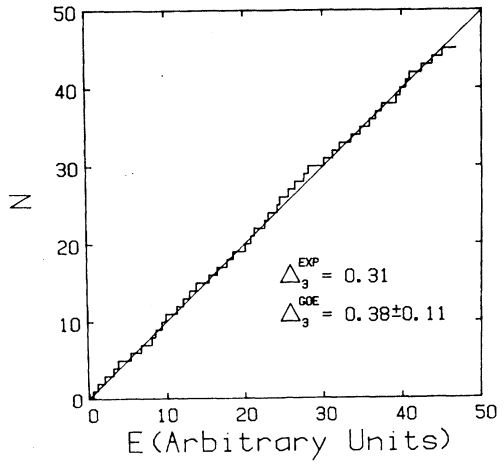

FIG. 2. A staircase plot of the cumulative number of levels N vs E (arbitrary units) for Tb I $9/2^-$ levels with the variation in level density unfolded. The Δ_3 statistic is sensitive to the fluctuations of $N(E)$ about the straight line drawn through the data. The agreement between the experimental and random-matrix theory predicted values of Δ_3 is good.

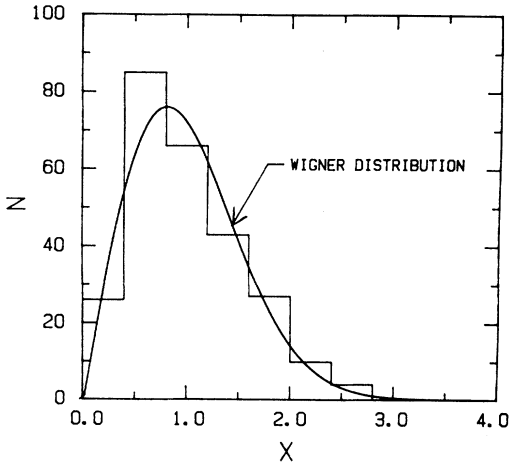

FIG. 3. Combined adjacent-level spacing distribution of eight sets of atomic energy levels. The smooth curve represents the Wigner distribution which accurately reflects a prediction of random-matrix theory.

sists of eight individual spacing distributions each plotted with respect to the "normalizing variable" $x = S/\langle D\rangle$ ($\langle D\rangle$ is the average spacing for a given set of levels) which were then combined into one histogram. As can be seen from Fig. 3 these data are in good agreement with the Wigner spacing distribution and at the very least exhibit adjacent-level repulsion.

Table I summarizes our results when statistical tests (1) and (2) were applied to the individual atomic spectra. The fifth column of Table I lists the values of $\mathrm{Cov}(S_i, S_{i+1})$ found experimentally along with its uncertainty. Although a few individual values of $\mathrm{Cov}(S_i, S_{i+1})$ are within one standard deviation of zero (the expected result if only adjacent levels are correlated), the average value of $\mathrm{Cov}(S_i, S_{i+1})$ for our eight samples is -0.23 with a standard deviation 0.054. This is within one standard deviation of the GOE prediction of -0.27 and more than four standard deviations from zero. The agreement with the GOE is good. Listed in the last three columns of Table I are values of the Δ_3 statistic found experimentally, predicted by GOE, and expected for UW levels. Agreement between the expected GOE Δ_3 values and those found experimentally is quite good. The expected Δ_3 values of the UW levels differ "greatly" from the experimental values, but their individual uncertainty is large. It is significant, however, that all experimental Δ_3 values lie below the expected UW values. We construct the statistic $\Delta = \sum_i \Delta_{3i}$ and find that $\Delta^{\mathrm{exp}} = 2.98$, $\Delta^{\mathrm{GOE}} = 2.77 \pm 0.31$, and $\Delta^{\mathrm{UW}} = 5.51 \pm 1.12$. Δ^{exp} is less than one standard deviation from the GOE value and more than two standard deviations from the UW prediction.

We believe that these results represent strong evidence that under appropriate conditions the GOE accurately describes the statistical behavior of atomic energy levels. This implies that there exist both short- and long-range correlations between levels. The degree of agreement found between GOE theory and the atomic data is typical of that found for most neutron resonance data.[2,5]

While this agreement is interesting in and of itself, it has other implications. For example, it should be possible to apply concepts based on nuclear reactions to gain information about the behavior of the widths of the atomic states. Since the atomic states examined above are bound, the widths of the states are determined by photon emission to lower-lying states. This is similar

TABLE I. Results of the statistical tests applied to the atomic spectra satisfying criteria (1), (2), and (3) as described in the text. For the GOE the expected value of $\mathrm{Cov}(S_i, S_{i+1})$ is -0.27. The expected values of Δ_3 for GOE and UW levels are also presented.

Atoms [a]	J^π	No. of levels	ΔE(cm^{-1})	$\mathrm{Cov}(S_i, S_{i+1})$	Δ_3^{exp}	Δ_3^{GOE}	Δ_3^{UW}
Nd I	4^-	35	16059–23562	-0.13 ± 0.13	0.39	0.35 ± 0.11	0.71 ± 0.41
Nd I	6^-	38	15220–23324	-0.28 ± 0.14	0.45	0.36	0.77 ± 0.44
Nd II	$7/2^-$	34	20830–27805	-0.21 ± 0.13	0.30	0.35	0.70 ± 0.40
Nd II	$13/2^-$	28	23802–29813	-0.23 ± 0.17	0.37	0.33	0.59 ± 0.33
Nd II	$15/2^-$	32	24547–32905	-0.34 ± 0.18	0.39	0.34	0.66 ± 0.37
Sm II	$3/2^-$	26	26484–32492	-0.14 ± 0.17	0.37	0.32	0.55 ± 0.30
Sm II	$9/2^-$	31	25336–31352	-0.27 ± 0.17	0.40	0.34	0.64 ± 0.36
Tb I	$9/2^-$	45	19450–27581	-0.22 ± 0.13	0.31	0.38	0.89 ± 0.52

[a] The symbols I and II refer to neutral and singly ionized atoms.

to neutron capture in which a compound-nuclear state decays via gamma emission to many low-lying states.[11] Agreement of nuclear spectra with GOE theory implies that the capturing state is very complex and, as a result, the total capture width Γ_γ is assumed to be a statistically independent sum of partial widths Γ_{γ_i} to low-lying states, $\Gamma_\gamma = \sum_i \Gamma_{\gamma i}$. Application of the central limit theorem of statistics to the sum leads to a Gaussian distribution for Γ_γ which is relatively narrow. Similar considerations should apply to the bound states of atoms, especially as the excitation energy increases.

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Propagation of Ultrashort Optical Pulses in Degenerate Laser Amplifiers

I. R. Gabitov

L. D. Landau Institute for Theoretical Physics, Moscow V334, U. S. S. R.

and

S. V. Manakov

L. D. Landau Institute for Theoretical Physics, Moscow V334, U. S. S. R., and Department of Mathematics, University of Manchester Institute of Science and Technology, Manchester M601QD, United Kingdom

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The shape and area of the output from physically realizable amplifiers of inverted $Q(2)$-degenerate two-level atoms are calculated analytically. The $(4\pi-\delta)$- or δ-pulse output is made up from a sequence of $\pm 4\pi$ double-humped pulses followed by $\pm(4\pi-2\delta)$ pulses, where $\delta = 2\cos^{-1}(-\frac{1}{3})$.

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The output from very long systems of initially inverted nondegenerate two-level atoms has already been described analytically[1,2] and was shown to be a π pulse made up of alternating $\pm 2\pi$ pulses. The calculations made use of the complete integrability of the Maxwell-Bloch (MB) envelope and phase equations which apply to both nondegenerate attenuators and amplifiers with suitable changes of sign. This integrability meant that they could be solved by the inverse scattering method[3] in both cases. Results for the attenuator are well known,[4] but the analysis[1,2] was the first consistent application of the method to amplifiers in the sharp-line limit.[5,6] In the degenerate cases, the MB equations are not integrable[7] and so the inverse method cannot be used. We show in this Letter, nevertheless, how the output from an inverted two-level atomic medium can be calculated whether or not the atomic transition is degenerate.

