"Repulsion of Energy Levels" in Complex Atomic Spectra*

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It is shown that "repulsion of energy levels" of the same symmetry type occurs in complex atomic spectra. Thus, for the elements Hf, Ta, W, Re, Os, and Ir, for which the spin-dependent forces are relatively strong, the spacings between neighboring odd-parity levels of the same J value follow the Wigner distribution (approximately). For the elements Sc, Ti, V, Cr, Mn, Fe, Co, and Ni, for which the spin-dependent forces are relatively weak, a similar distribution is obtained for the odd-parity levels having fixed values for S, L, and J. (When the quantum numbers S and L are disregarded, the same levels give rise to a distribution of spacings which is approximated by a random superposition of a number of appropriately weighted Wigner distributions.) For the elements Y, Zr, Nb, Mo, Ru, Rh, and Pd, for which the spin-dependent forces are of intermediate strength, the empirical distribution of spacings between the odd levels of the same J value has a character which is intermediate between the Wigner and exponential distributions. All of these observations are explained in terms of a statistical model for the Hamiltonian matrix in the S, L, J, π representation. Quantitative results are obtained for a relatively simple form of the model which depends on only two parameters, viz., the dimensionality N and the ratio μ of the dispersions of the normal distributions for the off-diagonal and diagonal matrix elements. The transition from the exponential to the Wigner distribution occurs, roughly speaking, in the range of $N\mu^2$ from 0 to 1. The results of this work suggest that an empirical study of the distribution of the spacing between the energy levels of a complex quantum system may be capable of pointing to the existence of constants of the motion beyond those which are already known.

I. INTRODUCTION

THE purpose of this paper is to present the experimental evidence for, and the theoretical interpretation of, the "repulsion" of energy levels in complex atomic spectra. This study is a direct outgrowth of the discovery, made in recent years, that the distribution of the spacing between the adjacent levels of a highly excited nucleus follows definite laws, the existence of which were first surmised by Wigner[1,2] and by Landau and Smorodinsky[3] on the basis of a statistical hypothesis for the many-body Hamiltonian. The consequences of that hypothesis, which we have developed quantitatively and reported previously,[4-6] are in good agreement with the results obtained in the scattering of slow neutrons.[7-11] The rule, as proposed by Wigner for highly excited nuclei, may be stated in two parts as follows.

1. The spacing between adjacent levels having the same spin and parity is distributed (relative to the mean spacing) according to a frequency function which is given to a good approximation by the distribution

$$p(x) = \tfrac{1}{2}\pi x \exp(-\tfrac{1}{4}\pi x^2), \quad x = \frac{S}{D} = \frac{\text{spacing}}{\text{mean spacing}}. \quad (1)$$

The function (1) is plotted as curve a in Fig. 1. The most characteristic features of this distribution are that the probability of a zero spacing vanishes, that the maximum occurs in the neighborhood of the mean, and that the tail is relatively short. This should be compared with what one gets on the basis of the incorrect supposition that the levels occur in a completely random way (Poisson process on the energy axis). That assumption leads to an exponential, also shown in Fig. 1 (curve b), which has its greatest value at $x=0$. The deficiency of small spacings in the Wigner distribution, as compared with the exponential distribution, is the phenomenon of the "repulsion of levels."

2. The second part of the rule states that levels of different spin or parity are not in any way correlated in position. This has the consequence that if one is dealing with a sequence of levels which is a superposition of sets of different spin (or parity), the resulting distribu-

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[1] E. P. Wigner, Gatlinburg Conference on Neutron Physics by Time-of-Flight, Oak Ridge National Laboratory Report ORNL-2309, 1957 (unpublished), p. 59.

[2] E. P. Wigner, Proceedings of the International Conference on Neutron Interactions with the Nucleus, Columbia University Report CU-175 (TID-7547), 1957 (unpublished), p. 49.

[3] L. Landau and Ya. Smorodinsky, *Lectures on the Theory of the Atomic Nucleus* (State Technical-Theoretical Literature Press, Moscow, 1955) [translation: Consultants Bureau, Inc., New York, 1958, p. 55.]

[4] S. Blumberg and C. E. Porter, Phys. Rev. 110, 786 (1958).

[5] N. Rosenzweig, Phys. Rev. Letters 1, 101 (1958).

[6] C. E. Porter and N. Rosenzweig, Suomalaisen Tiedeakatemian Toimituksia A VI, No. 44 (1960).

[7] I. I. Gurevich and M. I. Pevsner, Physica 22, 1132 (1956), see also Nuclear Phys. 2, 575 (1957). References to earlier experimental data are cited in reference 6.

[8] J. A. Harvey and D. J. Hughes, Phys. Rev. 109, 471 (1958).

[9] J. L. Rosen, Ph.D. thesis, Columbia University, New York, New York, 1959 (unpublished); also J. L. Rosen et al., Phys. Rev. 118, 687 (1960).

[10] S. Desjardins, Ph.D. thesis, Columbia University, New York, New York, 1959 (unpublished).

[11] P. A. Moldauer, Bull. Am. Phys. Soc. 4, 319 (1959).

tion of spacings has a character which is intermediate between the Wigner distribution and the exponential distribution. For example, the broken line in Fig. 1 (curve c) gives the calculated result for the random superposition of two independent systems of levels which have the same mean spacing.[12] If a large number of unrelated systems of levels are superposed, the exponential will be approached, under certain conditions. (The problem of superposing any number of sequences is considered in the Appendix.)

We have previously reported in a preliminary way[13] that a similar repulsion phenomenon occurs in the spectra of many complex atoms. In this paper, we present the empirical evidence in detail for the different regions of the periodic table and we also attempt to interpret the results in terms of the theoretical ideas given in reference 6. In this connection it will be necessary to modify the random matrix hypothesis to take account of the enormous range in strength of the spin-dependent forces in atomic spectra.

It seems worthwhile to summarize at this point some of the differences, which are relevant in this work, between the typical atomic spectrum in the range of excitation energy of a few ev and the spectrum of a heavy nucleus excited to about 7 Mev. (1) Even the most complex atomic spectrum is so simple compared with the nuclear spectrum, that it is by no means a foregone conclusion that the atomic spectra are sufficiently complex for the statistical properties to show up. In fact, we seem to have the interesting situation that the statistical properties begin to appear only in the more complex spectra. (2) Related to the first point is the fact that the density of energy levels in a highly excited nucleus is virtually constant over an energy
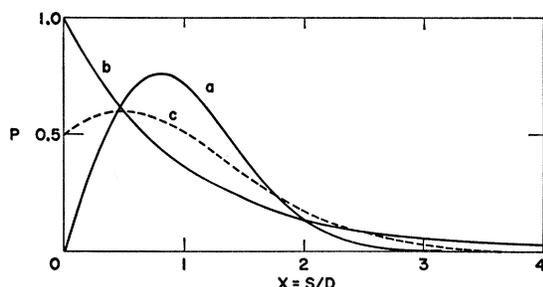

FIG. 1. Illustration of the "repulsion of energy levels." The Wigner distribution of nearest-neighbor spacings, curve a, for which the frequency of a small spacing is relatively low, represents a high degree of repulsion. This should be compared with the exponential distribution, curve b, which is obtained if the energy levels occur completely at random. Curve c, which results from the random superposition of two sequences, each governed by the Wigner distribution of the same density, is characterized by a degree of repulsion which is intermediate between the extremes of a and b.

interval which contains hundreds of levels. In the atomic case the density of levels typically changes by a factor of 2 or 3 in the interval which contains two or three hundred levels. It therefore is necessary to consider the problem of defining a "local" mean spacing. (3) It is well known that in many cases the spin-dependent forces are relatively small compared to the central forces (Russel-Saunders case). This results in the spin and orbital angular momenta being constants of the motion to a good approximation. One is therefore led to consider the role which these additional (approximate) quantum numbers play in the phenomenon of repulsion of energy levels.

This paper is divided into four major sections as follows. Sections II, III, and IV are devoted mainly to an examination of the voluminous experimental material. In Sec. II we shall treat one example, viz., the spectrum Hf I, in greater detail than will be practical for the other elements. By means of the example we shall define the method of analysis to be used throughout the paper. In Sec. III we take up a comparative survey of the odd-parity levels in three regions of the periodic table. In Sec. IV a similar study is made of the even-parity levels. In Sec. V we discuss the results of the preceding sections in terms of a statistical model for the Hamiltonian matrix.

II. STATISTICAL PROPERTIES OF THE ENERGY LEVELS OF Hf I

1. General Remarks about Atomic Energy Levels

It is natural to ask to what extent the statistical rules observed for the quasi-stationary states of compound nuclei are applicable to the discrete states of other quantum systems. In this connection it will be remembered that the experimental data on atomic energy levels, having been assiduously deduced from the analysis of optical spectra by many workers over a period of decades, are very extensive and of very high quality.[14] For virtually all of the known atomic energy levels, parity and total angular momentum are given with almost complete reliability. In many of the cases in which it is meaningful to do so, assignments of the spin and orbital angular momentum (S and L, respectively) have also been made. It is therefore a relatively straightforward matter to make an empirical study of the distribution of the spacing between neighboring energy levels of the same symmetry type.

In deciding what spectra to examine first, we were guided by two considerations. On the one hand, one expects that the repulsion phenomenon, if it occurs at all in the atomic domain, will be characteristic of the "complex" spectra arising from the interaction of many,

[12] A. M. Lane, Oak Ridge National Laboratory Report ORNL-2309, 1957 (unpublished), p. 121. The problem of superposing two independent sequences was first considered in reference 7.

[13] N. Rosenzweig and C. E. Porter, Bull. Am. Phys. Soc. 4, 353 (1959). Reference 6 contains a preliminary report for some of the elements of the third long period.

[14] Charlotte E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C.), Vol. I, June 15, 1949; Vol. II, August 15, 1952; Vol. III, May 1, 1958. This admirable compilation of experimental data, without which our task would have been very much more difficult, will hereafter be referred to as AEL.

TABLE I. Positions of energy levels of Hf I (expressed in cm^{-1}) which are not listed in AEL, grouped according to parity and J value. The even-parity levels are entered in the top section, the odd-parity levels in the bottom section of the table.

0	1	2	3	4	5	6
25 444	46 101	45 666	47 112	31 575	27 019	26 944
	47 309	47 345	47 897	45 388	47 769	
	51 091	47 955	48 746	46 678	49 181	
		48 459	49 347	48 221	51 930	
		48 552	49 660			
		48 906	50 680			
		48 991	51 847			
		49 404				
		49 999				
		51 508				
27 232	47 092	10 509	42 396	41 175	44 537	25 462
48 985	48 259	42 076	44 049	42 454		
		44 504	44 464	43 795		
		45 848	45 522	46 290		
		47 345	46 218	48 236		
		50 084	48 648	52 581		
			50 355	53 064		
			50 584			

or at least a few, electrons. On the other hand, the only spectra useful for studying the distribution of spacing between nearest neighbors are those for which a reasonably complete and sufficiently large set of levels is available. It seems that both requirements are fulfilled to an adequate extent in the regions of the periodic table in which the outermost s and d orbits compete energetically in the formation of the ground state and the low-lying excited states.[15] This results in the particularly rich, and yet in many cases thoroughly analyzed, structure of odd-parity levels arising mainly from the overlapping configurations $d^n p$ and $d^{n-1} s p$. Spectra of this type occur in three periods,[16] namely between $_{21}$Sc and $_{28}$Ni, between $_{39}$Y and $_{46}$Rh, and between $_{72}$Hf and $_{77}$Ir. We shall focus our attention in this paper entirely on the spectra of these three groups of elements. We shall begin our survey by describing the distributions of interest and the methods of obtaining them, using the spectrum of Hf I as an example.

2. The Energy Levels of Neutral Hf

In addition to the 217 levels of Hf I which are listed in AEL, 57 additional levels are known from a preliminary unpublished analysis by Meggers.[17] For the purpose of fully documenting the basis of our computation we have listed these additional levels of Hf I in Table I. Thus, there are altogether 274 known levels of Hf I ranging in energy from 0 to about 52 000 cm^{-1} above the ground state. The ionization potential of Hf I is estimated to be approximately 56 500 cm^{-1}. The distri-

[15] The spectra of the elements in the rare earth region are even more complex, but they are not known to an extent which would make them useful in our study.
[16] Presumably some of the recently discovered, or still to be discovered, elements of atomic number greater than 100 have spectra that are similar to those considered in this work.
[17] This was kindly drawn to our attention by Dr. R. E. Trees.

bution of these 274 levels with respect to parity and J value is shown in Table II.

Before attempting to find out what are the rules (if any) which govern the fluctuation of individual spacings about their mean value—which is the principal objective of the empirical part of this work—it is necessary to show that it is possible to define the mean spacing as a function of excitation energy. For this purpose we define the monotonically increasing step function $T(E)$ as being equal to the number of observed energy levels having energy $\leqslant E$. Figure 2 is a plot of $T(E)$ for the levels of Hf I. It is seen that the variation of $T(E)$ with energy is sufficiently regular that it is possible to define an increasing *continuous* function $T^*(E)$ which will represent $T(E)$ fairly accurately. Therefore, it makes sense to speak of the density of levels at energy E, it being given by $dT^*(E)/dE$ evaluated at energy E. The "local" mean spacing $D(E)$ is given by the reciprocal of the density, i.e.,

$$\frac{1}{D(E)} = \frac{d}{dE} T^*(E). \tag{2}$$

In the formation of the empirical distribution of spacings relative to the mean, it is evidently necessary to determine the value of D which is appropriate for each individual spacing. We shall circumvent the complicated step of obtaining an analytical form for $D(E)$ according to the scheme described above, by inferring an appropriate value of D directly from the experimentally observed spacings as follows. The energy levels will be divided into adjacent groups of k levels. We compute the average value of the $k-1$ spacings and use it as the mean spacing for each of the $k-1$ spacings in the group. In terms of Eq. (2), this amounts to the approximation

$$\frac{1}{D} \approx \frac{T(E_k) - T(E_1)}{E_k - E_1} = \frac{k-1}{E_k - E_1}, \tag{3}$$

where E_1 and E_k are the least and greatest values of the energy levels in a group of k levels.

Insofar as possible one wants to choose k large enough to determine the mean spacing with adequate accuracy, but not so large that the energy dependence of this quantity destroys the validity of the procedure. This point will be pursued somewhat further in the Appendix

TABLE II. Distribution of the known energy levels of Hf I with respect to parity and J value.

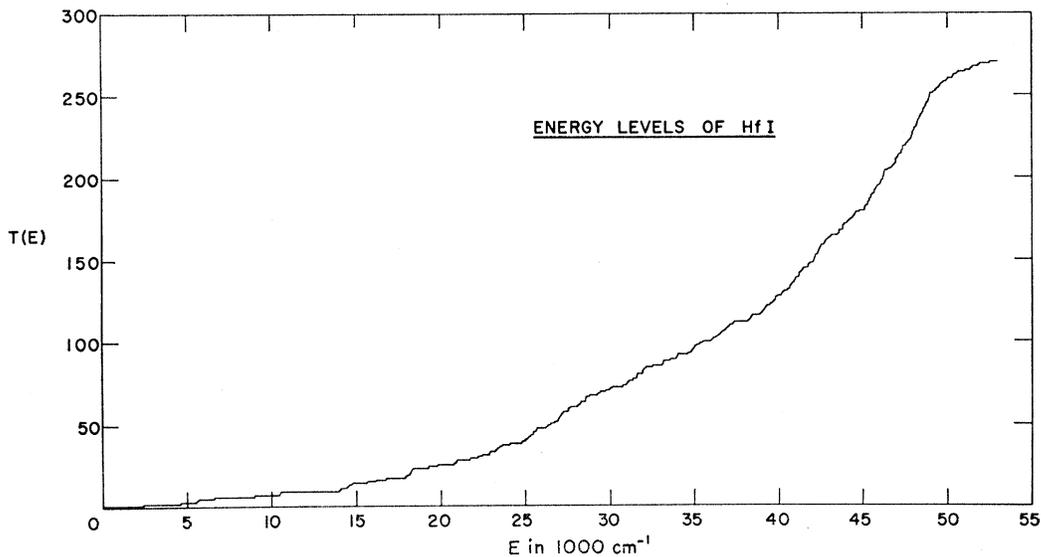| J	Odd	Even
0	5	3
1	25	22
2	35	45
3	37	37
4	22	22
5	7	9
6	1	1

FIG. 2. A plot of $T(E)$ vs E for Hf I. $T(E)$ is the number of levels of energy less than or equal to E, the excitation energy above the ground state expressed in units of 1000 cm^{-1}. $T(E)$ is seen to increase smoothly with E, tending to show that it makes sense to speak of "local" density of levels.

where the dependence of the most important empirical results of this work are studied as a function of k. It turns out that the main qualitative features of these results are largely independent of k for a certain range of values of k. The lower end of this range contains $k=7$ which we adopt, somewhat arbitrarily, as the value which is used in all the computations, unless otherwise stated.[18]

3. Repulsion of Odd-Parity Levels Having the Same J Value

In the region of the periodic table which contains the element Hf the spin-dependent forces seem to be of the same order of magnitude as the residual electrostatic interaction. The situation is therefore very similar to the nuclear case since the total angular momentum J and parity π are the only general constants of the motion that arise from such well-known symmetry properties of the Hamiltonian as invariance under rotation and reflection. We are therefore interested in obtaining the distribution of the spacing between adjacent levels having odd parity and the same J value.

In order to obtain the desired empirical distribution, the odd-parity levels were separated into sequences consisting of the levels of a definite J value (seven sequences altogether corresponding to the seven values of J which occur). A set of spacings was obtained separately for each sequence, the reduction to unit

mean also being accomplished separately for each J sequence. As each of the sets was relatively small, the spacings were combined to yield a single distribution, in order to reduce statistical fluctuations. The resulting histogram is shown in Fig. 3. The repulsion of the levels is quite evident, the histogram reflecting a distribution rather similar to the Wigner distribution (solid curve in Fig. 3).

4. Superposition of J Sequences

Having shown that the odd-parity levels of Hf I obey the first part of the rule stated in the Introduction, we shall now produce some evidence that the same levels are also in accord with the second part of the rule, which states that levels of different J value are not correlated in position. This lack of correlation may be exhibited, for example, by considering the distribution of the
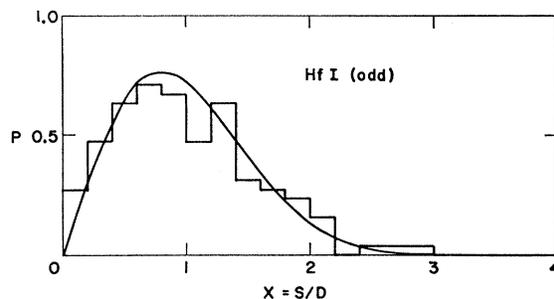

FIG. 3. Plot of the empirical distribution of nearest-neighbor spacings for the odd-parity levels of neutral Hf. The mean spacing D used in the construction of the histogram is defined by Eq. (3). To obtain this figure, separate histograms for $J=0, 1, 2, 3, 4, 5,$ and 6 were constructed and then combined. The Wigner distribution, represented by the continuous curve, is in excellent qualitative agreement with the empirical distribution.

[18] Unless the total number of spacings happens to be an integral multiple of 6, there will be a few spacings left over. Unless stated otherwise, these "remainders" are included in our distributions, the mean being computed on the basis of less than six spacings in these cases. We shall draw attention to the few cases where this treatment of the remainders makes a significant difference in the results.

spacings in the sequence consisting of *all* the odd-parity levels, no attention being paid to angular momentum classification. Qualitatively, it is easily seen that a random superposition of two or more unrelated sequences leads to an increase in the number of very small spacings (as before, every spacing must be divided by the now much smaller mean spacing of the combined system of levels!). In the combined system of levels there will be a nonvanishing probability that a level of one sequence will be followed by a level of a different sequence. Since these two levels are assumed to be not correlated in any way, there will be a nonvanishing probability (per unit interval) that the spacing between them is zero. Thus, we have the general result that the probability per unit interval for the occurrence of a zero spacing in the combined system of sequences will be nonvanishing.

If a large number of uncorrelated sequences is superposed, each of which contributes a vanishingly small fraction to the over-all density of levels, then neighboring levels evidently tend to become uncorrelated in position. Therefore, in this limit the distribution of the spacing (expressed in terms of the mean spacing, as always) will be a pure exponential.

The exact expression for the distribution of spacings $P(x)$ resulting from the superposition of any number, say n, of unrelated sequences, each contributing a certain fraction $q_i (i=1,\cdots n)$ to the total density of levels in the combined system, is derived in the Appendix. This is done on the assumption that each of the n sequences separately obeys a spacing distribution $p(x)$ having, like Wigner's distribution, the property $p(0)=0$. Although the expression for $P(x)$, given by Eq. (36), is somewhat complicated, the most important single feature of it has an exceedingly simple form, viz.,

$$P(0) = 1 - \sum_i q_i^2, \quad \sum_i q_i = 1 \, (i=1,\cdots n). \tag{4}$$

We digress briefly to discuss some implications of Eq. (4) which are of interest also when, as is often the case for neutron resonance levels, one does not know the
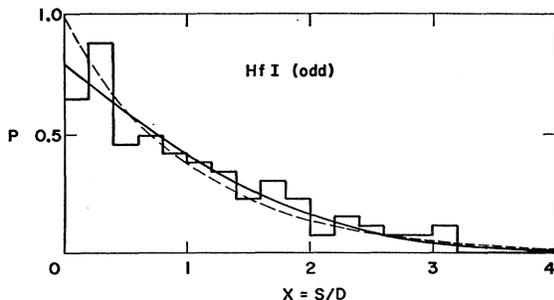

FIG. 4. Plot of the empirical distribution of nearest-neighbor spacings for the odd-parity levels of Hf I when the levels are not separated according to J value. The repulsion is sharply reduced compared with the distribution of Fig. 3. The solid curve represents the result of randomly superposing a number of appropriately weighted Wigner distributions. The limiting exponential distribution is also shown (dashed curve).

values of angular momentum (or parity) for a set of experimental levels.

(a) $P(0) \leqslant 1 - 1/n$. The equality holds if and only if $q_i = 1/n$. For example, if an examination of a set of energy levels indicates that $P(0) > \frac{1}{2}$, then one must conclude that the set is a superposition of at least *three* independent sequences.

(b) Consider $n=2$. Then $P(0) = 1 - q_1^2 - q_2^2, q_1 + q_2 = 1$. Therefore, if one knows that an experimentally observed set of energy levels consists of exactly two independent sequences, as is generally the case in the resonance scattering of slow neutrons on target nuclei with nonzero spin, then a determination of $P(0)$ yields the ratio of the level densities of the two spin systems.[19]

(c) $P(0) \to 1$ if $\sum_i q_i^2 \to 0$. However, since $\sum_i q_i = 1$, this can only occur if $q_i \to 0$, $n \to \infty$. Therefore, a certain residual amount of repulsion of levels remains when a finite number of sequences is superposed.

We now return to the particular case of the odd-parity levels of Hf I. We shall neglect the complications of the increasing level density with excitation energy and the incomplete overlap of the several J sequences, by ascribing a single over-all fractional density to each of the J sequences. Using the data of Table II one obtains $P(0) = 0.783$. The complete distribution, given by Eq. (36) of the Appendix, is represented by the solid curve of Fig. 4. The empirical distribution was obtained by our standard method and is represented by the histogram of Fig. 4. The histogram and the theoretical curve are seen to be in excellent qualitative agreement, the exponential distribution (the broken curve in Fig. 4) is approached, but is not attained.

5. The Distribution of Spacings between the Even-Parity Levels of Hf I

Generally speaking, the low-lying even-parity levels of the elements to be considered in this paper arise from the configurations d^n, $d^{n-1}s$, and $d^{n-2}s^2$. This results in a relatively simpler and smaller set of levels than the odd-parity set which is obtained by promoting one of the s or d electrons to a p orbit. Furthermore, the group of (known) even levels is generally concentrated near the ground state. For all these reasons our attention was drawn primarily to the odd-parity levels as representing a richer spectrum in which definite statistical rules are more apt to appear. However, as was pointed out by Meggers[20] some years ago, the even-parity levels of Hf I form a notable exception to the state of affairs described above. In this particular case, the number of even levels is roughly equal to the number of odd levels, as may be seen from Table II, and both sets are spread out over almost the entire energy range. It is therefore natural (1) to see whether the even levels repel each other when separated into J sequences and (2) to avail oneself of the rare opportunity of checking whether the

[19] This was already noted in reference 7.
[20] Cited in AEL (our reference 14), Vol. III, p. 143.

levels of the *same* J value but of *opposite* parity are uncorrelated in position.

The degree to which the even-parity levels repel each other may be judged from the histogram shown in Fig. 5, which is the exact counterpart of the histogram based on the odd-parity levels which was shown in Fig. 3. It appears that there is *some* repulsion as compared to the exponential distribution. However, the repulsion is definitely not as fully developed as for the odd-parity levels, as may be seen by a comparison with the Wigner distribution (solid curve). This behavior of the even levels of Hf I is fairly typical of the even levels for many of the elements to be considered in this paper. A discussion of this feature will be attempted in Secs. IV and V.

We shall now demonstrate that the repulsion of both the even-parity levels (shown in Fig. 5) and the odd-parity levels (shown in Fig. 3) is reduced when the odd and even levels having the *same* J value are combined. This constitutes a superposition of two sequences. While the result of Appendix 2 does not directly apply,[21] it is
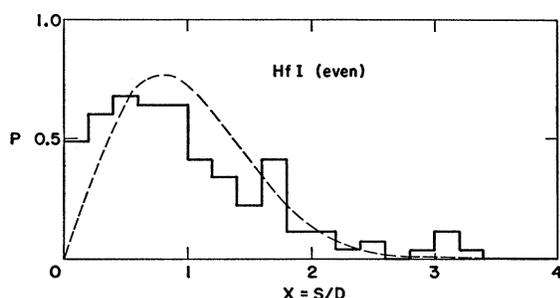
FIG. 5. Plot of the empirical distribution of nearest-neighbor spacings for the even-parity levels of Hf I when the levels are sorted according to J value (as in the histogram of Fig. 3). The repulsion of the levels is not as fully developed as for the odd-parity levels, as may be seen by comparison with the Wigner distribution (dashed curve).

qualitatively clear that, if the two systems of levels of the same density are uncorrelated in position, then the distribution based on the combined sequences must be closer to an exponential than are the distributions based on the separate sequences. This turns out to be so, as may be seen from the appropriate histogram shown in Fig. 6. (It should be kept in mind that, as before, the results for the various J sequences were lumped together in order to reduce statistical fluctuations.) Thus, we have obtained a qualitative verification that Wigner's rule (part 2) is fulfilled with regard to parity. It should be noted that the data necessary for checking the same point for nuclear levels does not seem to be available yet.[22]

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[21] The result (36) does not apply because it is based on the assumption that every sequence is governed by the *same* distribution. This restriction could be removed rather easily.

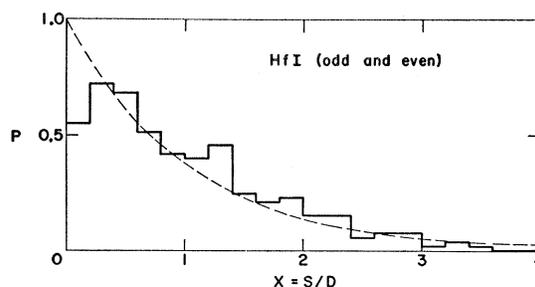[22] N. Rosenzweig and C. E. Porter, Bull. Am. Phys. Soc. **5**, 17 (1960).

FIG. 6. Plot of the empirical distribution of spacings for levels of Hf I, when the levels are sorted according to J value but not according to parity. (The results for the seven J sequences are combined, as usual, in order to reduce statistical fluctuations.) The superposition of the levels of opposite parity reduces the degree of repulsion observed for either the even- or the odd-parity levels (see Figs. 5 and 3, respectively).

III. DISTRIBUTIONS FOR THE ODD-PARITY LEVELS IN THE THREE LONG PERIODS

1. The Experimental Material

We now turn to the examination of the empirical distribution of the spacing for the odd-parity levels in the three long periods. The experimental data to be considered are the energy levels of the neutral atoms which are homologous with elements of the iron group.

TABLE III. Distribution of odd-parity energy levels with respect to J value for the elements in three regions of the periodic table. The integral and half-integral values of J are appropriate, respectively, for the elements of even and odd atomic number. The data, taken from AEL (except for Hf I), gives an indication of the number of spacings contributed by each spectrum to the distributions of Fig. 7.

J	Sc I	Ti I	V I	Cr I	Mn I	Fe I	Co I	Ni I
0, ½	9	12	40	15	22	12	23	4
1, 1½	18	37	72	45	43	37	45	15
2, 2½	18	49	90	65	58	58	52	25
3, 3½	12	47	89	72	60	63	49	23
4, 4½	6	36	58	69	48	54	25	12
5, 5½	2	19	33	51	31	38	9	4
6, 6½		8	9	30	14	17	1	1
7, 7½		1	1	11	2	3		
8, 8½				2				

J	Y I	Zr I	Nb I	Mo I	Tc I[a]	Ru I	Rh I	Pd I
0, ½	10	10	26	6		10	8	1
1, 1½	17	36	54	45		35	17	12
2, 2½	18	47	70	58		42	24	24
3, 3½	13	45	70	63		48	18	20
4, 4½	6	32	50	57		42	8	7
5, 5½	2	18	24	44		20	2	
6, 6½		7	7	20		7		
7, 7½		1	1	8		1		

J	Lu I[a]	Hf I	Ta I	W I	Re I	Os I	Ir I	Pt I[a]
0, ½		5	19	9	18	2	15	
1, 1½		25	47	36	42	29	34	
2, 2½		35	49	61	44	45	36	
3, 3½		37	54	61	49	49	40	
4, 4½		22	28	59	30	33	26	
5, 5½		7	14	45	19	14	11	
6, 6½		1	2	24	8	10	1	
7, 7½				4				

[a] Spectrum not sufficiently known or not sufficiently complex to be included in the computations.

With the exception of Hf I (already noted in Sec. II), we have used all the levels and only the levels which are listed in AEL. A summary of the elements included in this study, as well as the number of energy levels known for each of the elements, is contained in Table III, which also gives the distribution of these levels with respect to J value. The arrangement in Table III evidently corresponds to that of the periodic table in the sense that homologous elements are listed in the same column.

The spectra of the first long period[23] are characterized by relatively pure SL coupling. The SL coupling approximation provides a relatively poor description for the elements of the second period, and is largely inappropriate for the elements of the third period. These conditions are reflected in the fact that definite SL assignments have been made for 92% of the levels (listed in AEL) belonging to the elements of the first period, for 78% of the levels of the second period, and for only 18% of the levels of the third period.

2. Distribution of Spacings between Levels Having the Same J Value

As has been noted previously, parity and J value are known with practically complete reliability for every energy level listed in AEL. It is, therefore, an easy matter to construct the distribution of the spacing between neighboring odd-parity levels having the same J value for each of the elements in Table III. The method of computation is exactly the same as described in Sec. II, 3 for the odd levels of Hf I. Instead of plotting a separate histogram for each of the spectra, we have combined the data (after the computation of the spacings relative to the appropriate mean value for each J sequence), in order to obtain a single histogram for each *group of elements belonging to the same period*. In view of what has been said previously, this procedure evidently corresponds to a rough grouping according to the strength of the spin-dependent forces. For ease of comparison, the resulting three histograms are shown together in Fig. 7.

Histogram (c) of Fig. 7 is based on the 1156 spacings of the heavy atoms from Hf to Ir. The spectra of these elements, as in the case of Hf already discussed in Sec. II, are very similar to the neutron resonance levels in heavy nuclei, in that parity and total angular momentum are the only general constants of the motion that arise from the symmetry of the Hamiltonian, and one finds, as in the nuclear case, that the odd levels having the same J value repel each other approximately in accordance with Wigner's distribution.

On the other hand, the corresponding distribution based on the 1813 spacings of the light elements Sc to Ni (first long period) as shown in histogram (a) of Fig. 7, is much closer to the exponential distribution than to the Wigner distribution. The distribution based on 1162

spacings for the elements of the second period, namely Y to Pd, as represented by histogram (b) of Fig. 7, is intermediate between the extremes of the exponential and Wigner distributions.

In order to arrive at an understanding of these results in terms of the work up to this point, consider the extreme case in which the spin-dependent forces vanish completely.[24] Then not only parity π, but the total spin angular momentum S and the total orbital angular momentum L are separately constants of the motion. Furthermore, a state of a given S and L can be characterized by a value of the total angular momentum J, but the energy is independent of J. The set of degenerate states labeled by definite values of S, L, and π is called a term. Obviously, the zero spacings between the degenerate levels of a term do not fluctuate and must be excluded from our considerations. (A similar elimination of the magnetic sublevels in the absence of external fields was tacitly assumed in the Introduction.) This leads us to the following modified statement of Wigner's rules.

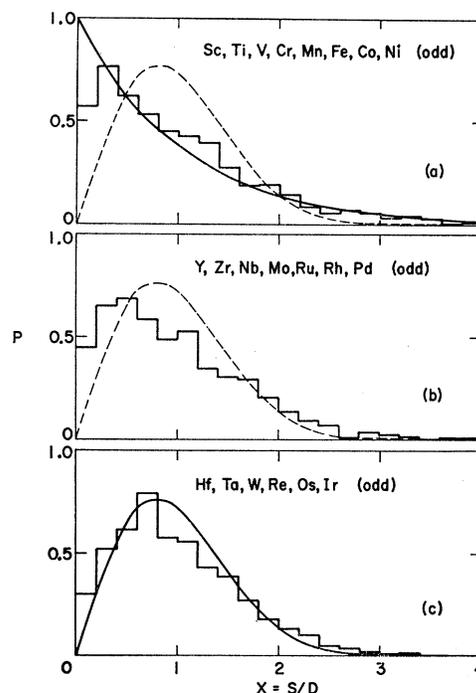1. Adjacent terms having the same values for S, L,

FIG. 7. Empirical distributions of nearest-neighbor spacings for the odd-parity levels of elements in the first, second, and third long periods (histograms a, b, and c, respectively). To obtain these figures, separate distributions were constructed for the J sequences of each element and then the results were combined. Comparison with the exponential and Wigner distributions (also shown) indicates that the degree of repulsion increases steadily as one goes from the first to the second and, finally, to the third period. This variation can be understood in terms of the corresponding increase in strength of the spin-dependent forces.

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[23] We have in mind only the elements listed in Table III.

[24] In connection with some of the remarks which follow see, for example, E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935).

and π repel each other approximately according to the Wigner distribution. 2. Terms which differ in any of the quantum numbers S, L, or π are not correlated in position.

The above statement, while it contains the essence of the matter, is not directly applicable to actual atomic systems because there are practically no spectra in which the spin-dependent forces vanish completely. In the case of Russel and Saunders in which these forces may be represented as a small perturbation in the form of a spin-orbit coupling, the positions of the *nearly* degenerate levels are given by the expression

$$E(S,L,J) = A(S,L)$$
$$+ B(S,L)[J(J+1) - L(L+1) - S(S+1)]. \quad (5)$$

In the above, E denotes the value of the energy characterized by S, L, and J and $A(S,L)$ represents the value that the degenerate S,L term would have in the absence of spin-dependent forces. It is easily verified that

$$A(S,L) = \sum_J (2J+1) E(S,L,J) / \sum_J (2J+1). \quad (6)$$

$A(S,L)$ is often called the "center of gravity" of the term in question.

If Eq. (5) holds rigorously, then the spacings of the nearly degenerate levels do not fluctuate statistically (they follow the Landé interval rule) and must be excluded from our considerations. This is easily done by formulating a statistical rule similar to the above except that the phrase "center of gravity of the term" replaces the word "term." The centers of gravity can be computed from the observed energy levels by means of Eq. (6).

The form of the modified rule which we shall *actually* verify (in the cases in which it may be expected to apply) is closely related to the above in that it takes into account the fact that a week spin-dependent perturbation will remove the degeneracy of the S,L terms, but it does not require a quantitative applicability of Eq. (5). Provided the spin-dependent perturbation is sufficiently small compared with the spacing between unperturbed S,L terms of the same kind, we may formulate the modified rule as follows.

1. Adjacent energy levels having the same values of S, L, J, and π repel each other approximately according to Wigner's distribution.

2. Levels having the same J value but differing in any of the quantum numbers S, L, or π are not correlated in position.

We now return to a discussion of the empirical distributions of Fig. 7. The elements of the first period are dynamical systems in which the condition for the modified rule (weak spin-dependent forces) are approximated rather well. It will be readily appreciated that histogram (a) is in accord with the second part of the rule. This is so because a sequence of odd levels all of which have the same value of J are derived from S,L terms of many different kinds (typically 8 to 12 different
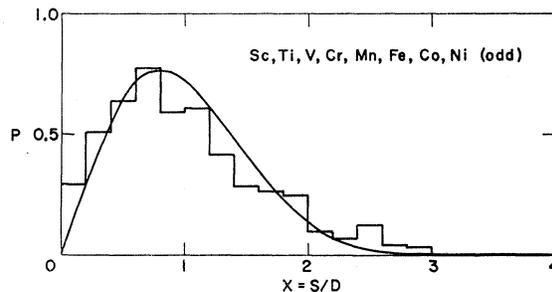

Fig. 8. Plot of the empirical distribution of spacings for the odd-parity levels of the first period, corresponding to a separation of the levels into sequences each of which is labeled by definite values of S, L, and J. Comparison with the Wigner distribution (solid curve) shows that a strong repulsion of levels is observed if the (approximate) symmetries resulting from (almost) complete absence of spin-dependent forces are taken into consideration.

types), so that each of the J sequences should be regarded as a random superposition of many unrelated sequences of levels in the sense of the Appendix. As in earlier sections, we find a sharp reduction in repulsion compared to the Wigner distribution. The exponential distribution is approached but is not attained. It should be noted, however, that the residual repulsion, which is seen in histogram (a) has its origin in two factors. One of these, which we have already encountered, is the fact that the number of different kinds of S,L terms, while large, is finite. This factor by itself cannot account for the appreciable deviation from the exponential in the first interval $(0, 0.2)$. The second aspect is that the spin-dependent forces, while small, have an influence which apparently goes beyond the removal of the degeneracy in that there is already a slight tendency for levels of the same J value to repel each other. [The second factor is even more important for the elements of the second period (histogram b) and becomes decisive for the elements of the third period.]

The (approximate) applicability of the modified rule to the elements of the first period can be tested further by constructing the empirical distribution of the spacing for the odd-parity levels having the same values for S, L, and J. (In doing this we simply ignore the 8% of the levels in AEL for which no S,L assignment is given.) The distribution, constructed in the usual way on the basis of 1332 spacings, is represented by the histogram of Fig. 8. The histogram is in excellent qualitative agreement with the Wigner distribution, and thereby the *first* part of the modified rule is also verified.

A practical matter connected with the reliability of the histogram of Fig. 8 must also be mentioned. When the levels of even the most complex spectrum are separated into sequences each one labeled by a fixed value of the triplet of numbers S, L, and J, then each one of the many sequences contains relatively few levels (typically 5 to 10 levels). On account of both the small number of levels and the dependence of the mean spacing on energy, this aggravates the problem of determining the mean spacing. In order to reduce the uncertainties
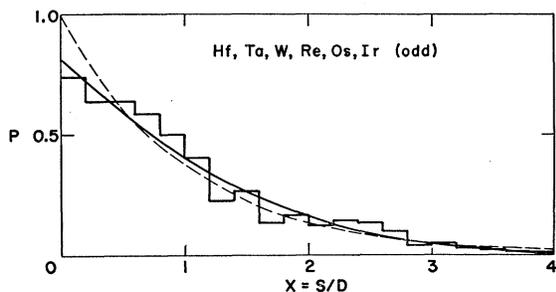
FIG. 9. Plots of the empirical distribution of spacings for the odd-parity levels of the elements of the third long period. The construction differs from the one leading to Fig. 7(c) in that the energy levels were not separated into J sequences. The solid curve represents the theoretical distribution obtained by superposing a number of appropriately weighted Wigner distributions. The limiting exponential distribution is also shown (dashed curve).

arising from these conditions we constructed the distribution in question also on the following basis. Only sequences containing at least seven levels were retained, and the "remainder of spacings" discussed in reference 18 was discarded. This procedure resulted in a total number of 630 spacings. The corresponding histogram (not shown) turns out to be very similar to the one in Fig. 8.

We have thus arrived at a good descriptive understanding of the histograms (c) and (a) of Fig. 7, the former being covered by the rule stated in the Introduction and the latter by its natural modification when spin-dependent forces are sufficiently weak. Histogram (b) evidently represents the intermediate case (in every sense of the word) which is not covered by either rule. In Sec. V we shall discuss a modified form of the random-matrix hypothesis which leads not only to the observed results in the two extremes but also yields qualitatively correct results for the intermediate case.

3. Superposition of J Sequences for the Elements of the Third Long Period

In the preceding section it was seen that the composite distribution [shown in Fig. 7(c)], based on the elements of the third long period, follows the first part of the Rule of Sec. I, viz., the levels of the same parity and J value repel each other approximately according to Wigner's distribution. We shall now verify the second part of that rule, that the repulsion is reduced in accordance with theoretical expectation when the odd-parity levels of a given element are *not* separated into sequences of a definite J value. An appropriate histogram (Fig. 9), again a composite for all the elements of the third row of Table III, clearly reflects a sharp reduction in repulsion.

As in the case of Hf I, considered in Sec. II, 4, a quantitative account of the observed distribution is obtained on the basis of the theory of the Appendix. As before, we neglect the complication of the increasing density with excitation energy by ascribing a single

over-all fractional density to each of the J sequences making up the spectrum of a particular element. The composite distribution for the group of elements is given by

$$P(x) = \sum_i w_i P_i(x). \qquad (7)$$

in which $P_i(x)$ is the distribution obtained for element i by superposing the appropriate number of Wigner distributions, in accordance with Eq. (36) of the Appendix, and w_i represents the fractional number of spacings contributed by element i to the histogram of Fig. 9. The numerical computations leading to $P(x)$ were carried out on the Argonne IBM-704 computer, and the result is represented by the solid line in Fig. 9. The agreement between the histogram, based on the experimental data, and the theoretical curve is excellent. While the degree of repulsion is greatly reduced by the superposition of the levels having all the different J values which occur, the residual effect is easily seen by comparison with the exponential distribution which is also shown in Fig. 9 (dashed curve).

IV. DISTRIBUTIONS FOR THE EVEN-PARITY LEVELS IN THE THREE LONG PERIODS

We now turn to the examination of the empirical distribution of the spacing for the even-parity levels in the three long periods, the work being completely analogous to that of Sec. III which dealt with the odd-parity levels. As has already been noted in connection with the spectrum of Hf I in Sec. II, the lowest lying even-parity levels constitute spectra of less complexity than the set of odd levels. It would therefore not be correct to infer from the results of Sec. III that the same statistical properties will necessarily show up in the even spectra. Actually, the statistical properties do appear, although the situation is not as clear-cut as in the case of the odd-parity levels.

1. The Experimental Material

The experimental data to be considered are the even levels of the same atoms considered in Sec. III. With the exception of Hf I (already noted in Sec. II), all the levels and only the levels listed in AEL are included in this study. The distribution of these levels with respect to element and J value is given in Table IV. The arrangement of Table IV evidently is such that homologous elements are listed in the same column.

The even spectra of the first long period (first row of Table IV) are characterized by relatively pure SL coupling. The SL coupling approximation provides only a fair description for the elements of the second period (second row of Table IV) but is not appropriate for the elements of the third long period (third row of Table IV). These conditions are reflected to some extent in the classification of the (even) levels in AEL, according to which definite S,L assignments have been made for 98% of the levels belonging to the first period, for 90% of the

levels of the second period, and for only 48% of the levels belonging to the third period.

2. Distribution of Spacings between Adjacent Levels Having the Same J Value

The distribution of the spacing between neighboring even-parity levels of the same J value was constructed for each of the elements of Table IV. As before, we used the method of Sec. II for estimating the value of the mean spacing. As in Sec. III, the data have been combined in order to obtain a single histogram for each *group of elements belonging to the same period*. This procedure evidently corresponds to a rough grouping according to increasing strength of the spin-dependent forces. For ease of comparison, the resulting three histograms are shown together in Fig. 10.

Histogram (a) of Fig. 10, based on 1089 even-parity levels of the elements Sc to Ni, and histogram (b), based on the 530 even-parity levels of the elements Y to Pd, follow the exponential distribution rather closely. The discussion of Sec. III immediately suggests that the observed distributions are in accord with the *second* part of the modified rule, which is applicable to systems in which the spin-dependent forces are relatively weak. The detailed explanation is the same as before, namely, each of the sets of levels of a fixed J value (for a given
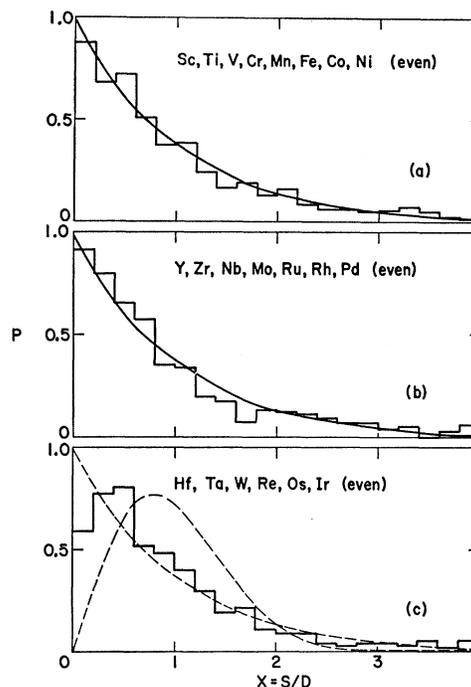

FIG. 10. Plots of the empirical distributions of nearest-neighbor spacings for the even-parity levels of elements belonging to the first, second, and third long periods (histograms *a*, *b*, and *c*, respectively). These figures are the exact counterpart of the histograms for the odd-parity levels shown in Fig. 7. No repulsion is evident for the elements of the first and second long periods. The repulsion is developed to some degree for the elements of the third long period.

TABLE IV. Distribution of even-parity levels with respect to J value for elements in three regions of the periodic table. The integral and half-integral values of J are, respectively, appropriate for the elements of even and odd atomic number. The data, taken from AEL (except for Hf I), gives an indication of the number of spacings contributed by each spectrum to the histograms of Fig. 10.

J	Sc I	Ti I	V I	Cr I	Mn I	Fe I	Co I	Ni I
0, ½	7	7	14	8	13	9	9	5
1, 1½	19	19	24	21	22	26	24	13
2, 2½	20	33	28	32	30	41	33	23
3, 3½	14	36	28	36	30	39	28	24
4, 4½	9	36	23	30	22	36	22	19
5, 5½	1	23	13	19	13	23	11	11
6, 6½		10	7	11	2	10	5	5
7, 7½		3	2	3		2	1	2

	Y I	Zr I	Nb I	Mo I	Tc I[a]	Ru I	Rh I	Pd I
0, ½	13	4	8	7		4	4	3
1, 1½	21	7	11	12		13	17	10
2, 2½	23	16	13	19		23	19	14
3, 3½	14	13	12	20		22	15	14
4, 4½	8	15	11	21		23	10	7
5, 5½	1	9	6	13		12	3	2
6, 6½		4	1	8		3		
7, 7½		1		1				

	Lu I[a]	Hf I	Ta I	W I	Re I	Os I	Ir I	Pt I[a]
0, ½		3	7	5	6	3	4	
1, 1½		22	14	8	11	7	13	
2, 2½		45	21	11	20	20	11	
3, 3½		37	10	10	15	24	15	
4, 4½		22	15	9	11	16	12	
5, 5½		9	6	8	6	6	4	
6, 6½		1	1	4	2	1		

[a] Spectrum not sufficiently known or not sufficiently complex to be included in our study.

element) arises from many different kinds of S,L terms. Thus, every such set is a superposition of many unrelated sequences which, according to the result obtained in the Appendix, yields a distribution of spacings which is very close to the exponential function in the cases under consideration.

Histogram (c) of Fig. 10, based on the 475 even-parity levels of the heavy elements Hf to Ir, reflects a distribution which is intermediate between the exponential and Wigner distributions. Neither the rule of Sec. I, nor the rule of Sec. III is applicable in this case in which the spin-dependent forces are of intermediate strength. The observed distribution can, however, be understood on the basis of a modified random matrix hypothesis which is suitable for the entire range of strength of spin-dependent forces. That will be taken up in Sec. V.

As in Sec. III, one is interested in testing further the applicability of the modified rule to the even-parity levels of the first and second periods by constructing the empirical distribution of the spacing for even levels having fixed values for S, L, and J. In such an attempt the difficulties resulting from the very small number of levels in a sequence of fixed S, L, and J is even more acute than for the odd-parity levels studied in Sec. III. For example, if only those sequences which contain at least seven levels are retained, then the total

number of spacings contributing to the histogram for the elements of the first period is reduced from 678 to 54 spacings. If all the sequences are kept, thereby giving a rather questionable determination of the mean spacing in many cases, one obtains a distribution which is closer to the exponential than to the Wigner distribution. This, contrary to expectation, indicates a violation of the first part of the modified rule.

Although the results of the preceding paragraph (only) seem inconclusive, let us suppose that the empirical distribution does in fact violate the first part of the modified rule, in that it reflects too little repulsion of the levels. Then it is interesting to note that all the results can still be understood on the assumption that a large number of the even-parity levels have been missed *at random* by the atomic spectroscopists. Suppose that a sequence of levels is governed by a distribution that, like Wigner's, has the property $P(0)=0$. Denote the distribution resulting from a random omission of a fraction f of the levels by $P_f(x)$, where x is the spacing divided by the apparent mean spacing which is larger than the true mean by the factor $1/(1-f)$. It seems obvious that the P_f will retain the property $P_f(0)=0$. On the other hand, it also seems clear that $P_f \to e^{-x}$ as $f \to 1$ because the surviving neighboring levels tend to become completely uncorrelated. Evidently, the limiting exponential distribution is reached via a set of functions in which the peak is monotonically shifted to smaller values of x as f goes from 0 to 1. A quantitative derivation of $P_f(x)$ has recently been given by Moldauer.[25] An application of his results to the problem at hand leads to the rough estimate $f \sim \frac{1}{2}$. It is unlikely that the atomic spectroscopists have failed to observe such a substantial fraction of the even-parity levels in the energy range under consideration.

There is still another explanation for a violation of the first part of the modified rule by the even parity levels, which we mention primarily because of its intriguing character. One can attempt to attribute the absence of repulsion to the existence of an additional (unknown) constant of the motion X which assumes a variety of values for the energy levels in question. To substantiate such a hypothesis by statistical methods one would have to sort the levels according to X and exhibit a high degree of repulsion for the resulting sequences.

V. THEORETICAL ASPECTS

As has already been mentioned, Wigner's rule, which governs the distribution of spacing in heavy nuclei as well as in the heavy atoms of the third long period, has been obtained on the basis of a statistical hypothesis for the Hamiltonian matrix. In this section we shall briefly review the previous work, and then propose a natural modification of Wigner's matrix hypothesis which leaves previous results unchanged, but in addition

leads to the rule of Sec. III (appropriate for systems in which spin-dependent forces are very weak) as well as to the results which are in at least qualitative agreement with the distributions observed in the intermediate case as exemplified by histogram (b) of Fig. 7.

1. Summary of Previous Work[26]

In order to obtain Wigner's rules, as given in Sec. I, we note that there exist, of course, representations in which the matrix of the Hamiltonian is real, symmetric, and diagonal with respect to total angular momentum J and parity π. We shall make a statistical hypothesis about the Hamiltonian matrix in one of these representations. The submatrix referring to a definite value of J and π will be denoted by

$$\mathbf{A}=\|a_{ij}\|, \quad a_{ij}=a_{ji}. \tag{8}$$

Although we shall consider finite-dimensional matrices (dimension N), we are very much interested in what happens as $N \to \infty$. The statistical hypothesis may be stated in two parts as follows.

1. In one (or more) of the above representations the matrix $\mathbf{A}$ has the form of a typical member of the ensemble of real and symmetric matrices specified by the joint distribution of the matrix elements

$$F(\mathbf{A})=f_{11}(a_{11})f_{12}(a_{12})\cdots f_{ij}(a_{ij})\cdots f_{NN}(a_{NN}), \; i \leqslant j \tag{9}$$

$$f_{ij}(a_{ij})=f_{ij}(-a_{ij}) \tag{10}$$

$$\langle a_{ij}^2\rangle_{\mathrm{av}}=\mu^2\sigma^2, \quad 1 \leqslant i < j \leqslant N \tag{11}$$

$$\langle a_{ii}^2\rangle_{\mathrm{av}}=\sigma^2, \quad 1 \leqslant i \leqslant N \tag{12}$$

$$\mu^2 \geqslant 1. \tag{13}$$

In words, the hypothesis states that aside from the condition of symmetry the matrix elements are distributed independently and symmetrically about zero. The second moments of the off-diagonal elements are all the same. The second moments of the diagonal elements are all the same and they are assumed to be no larger than the second moment for the off-diagonal elements.

2. There is no correlation between submatrices referring to different values of π or J. (Therefore, there is also no correlation between eigenvalues of different π or J.)

Let us now summarize what is known about the consequences and the validity of the first part of the hypothesis.

For small values of x, $P(x) \sim x$. In order to see this, consider the transformation of the variables

$$a_{11}a_{12}\cdots a_{NN} \to \lambda_1 \leqslant \lambda_2 \cdots \lambda_N, \alpha_1\alpha_2\cdots\alpha_{\frac{1}{2}N(N-1)}, \tag{14}$$

where the λ's are the eigenvalues ordered according to size and the α's are some parameters to complete the set. It can be shown that the Jacobian determinant which

[25] P. A. Moldauer (to be published).

[26] The work which is reviewed here is presented in much greater detail (and with a slightly different emphasis) in reference 6.

occurs in the transformation of the volume element has the form

$$G(\alpha_1\alpha_2\cdots\alpha_{\frac{1}{2}N(N-1)})\prod_{i<j}|\lambda_i-\lambda_j|. \qquad (15)$$

Aside from some singular behavior that might be introduced by the function $F(\mathbf{A})$, this shows that quite generally the probability density of the spacing $\lambda_2-\lambda_1 = x$ for small x goes as $P(x)\sim x$.

If one incorporates this important insight into the simple-minded approach and supposes that the spacing distribution is governed by a Poisson process in x^2 (rather than x), one obtains the Wigner surmise

$$p(x)=\tfrac{1}{2}\pi x\exp(-\tfrac{1}{4}\pi x^2). \qquad (16)$$

A somewhat fuller discussion is possible for one particular distribution of the matrix elements. We note that if $\mathbf{A}$ is real and symmetric then

$$a_{11}^2+a_{22}^2+\cdots+a_{NN}^2+2a_{12}^2+\cdots+2a_{N-1,N}^2$$
$$=trA^\dagger A=\sum_i\lambda_i^2. \qquad (17)$$

So let us take

$$\begin{aligned}f_{ij}(a_{ij})&=\exp(-2a_{ij}^2), \quad i<j\\f_{ii}(a_{ii})&=\exp(-a_{ii}^2).\end{aligned} \qquad (18)$$

Integrating over the domain of the variables α (only a verbal step is required!) one sees that the joint distribution of the eigenvalues is proportional to

$$\exp(-\sum_i\lambda_i^2)\prod_{i<j}|\lambda_i-\lambda_j|, \qquad (19)$$

a Wishart distribution.

Incidentally, Eq. (17) together with the invariance of the volume element $d\tau=da_{11}\cdots da_{\frac{1}{2}N(N-1)}$ under orthogonal transformations shows that the distribution (18) is invariant. Furthermore, it has been shown (in reference 6) that (18) is the *only* distribution of the type defined by Eqs. (9) and (10) which is invariant. The existence of this invariant distribution strengthened our belief that if the statistical model is valid (or approximately valid) in one representation it will remain so in many representations.

It was surmised by Wigner that provided the dimensionality N is sufficiently large, the distribution of spacings does not depend sensitively on the form of f_{ij} and that the "universal" distribution might be given to a good approximation[27] by Eq. (16). The evidence for the correctness of these conjectures comes mainly from numerically diagonalizing a set of randomly generated matrices by use of a fast digital computer. Several different forms for f_{ij}, with the restrictions on the second moments retained, were used. The parameter μ^2 was varied in the range from 1 to ∞, and the dependence of the results on dimensionality was studied up

to $N=20$. Within the limited scope of our calculations we found Wigner's conjectures to be entirely correct. (A further discussion of the dependence on N and on μ^2 in the range from 0 to 1 is given below.)

Since the conjectures seem to be correct it makes good sense to attempt to integrate the Wishart distribution in order to obtain an analytical form for the spacing distribution in the limit as $N\to\infty$. That has turned out to be a difficult mathematical problem which has not been solved to date.

An attempt has also been made to see whether the statistical model is already indicated in the shell-model calculations of the more complex nuclear spectra.[28] It is precisely in the shell-model representation that one would expect the statistical hypothesis to hold—if the system is sufficiently complex and the excitation energy is sufficiently high. The matrices which were readily available to us were those of Kurath[29] for the treatment of p-shell nuclei. Only the simplest statistics, such as the over-all distribution of off-diagonal matrix elements, have been checked so far. In turns out that for these matrices that distribution is nearly Gaussian.

Although this work deals almost exclusively with the statistical properties of *eigenvalues*, it should be noted that the random-matrix hypothesis of this section also implies definite statistical properties for the corresponding *eigenvectors*. This, of course, has important physical consequences. For example, the Porter-Thomas[30] distribution for the neutron width has been derived on this basis. In analogy with the work mentioned in the preceding paragraph we have also examined the statistical properties of the eigenvectors which are obtained in the shell-model calculations of both atomic and nuclear spectroscopy and this study has resulted in additional evidence for the correctness of the random-matrix hypothesis.[6]

2. Random-Matrix Hypothesis for the Hamiltonian in Representations in Which S, L, J, and π are Diagonal

If the spin-dependent forces vanish completely, then there exist representations in which the matrix of the Hamiltonian is real, symmetric, and diagonal with respect to S, L, J, and π. The modification in the random matrix hypothesis which is required in the light of the results of Secs. III and IV, consists in making the hypothesis in one of these bases. A schematic representation of a typical Hamiltonian matrix labeled by a definite value of π and J, which are denoted by π_1 and J_1, is shown in Fig. 11. In the absence of spin-dependent forces the matrix elements connecting different S,L blocks are zero, and energy levels having different S,L values are uncorrelated. The dimension of each submatrix is postulated to be proportional to the fractional

[27] While Eq. (16) is an excellent approximation, it is certainly not the exact asymptotic expression for the Wishart distribution. This follows from Professor Wigner's calculation of the second moment of the distribution (private communication) and also from the computation of another statistic by M. L. Mehta (to be published).

[28] C. E. Porter and N. Rosenzweig, Bull. Am. Phys. Soc. 4, 319 (1959); and reference 6.
[29] D. Kurath, Phys. Rev. 101, 216 (1956).
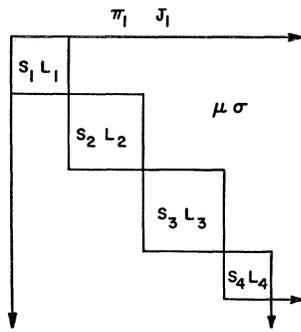[30] R. G. Thomas and C. E. Porter, Phys. Rev. 104, 483 (1956).

FIG. 11. A schematic representation of a typical matrix of the Hamiltonian in an S, L, J, π representation. The matrix is diagonal with respect to π and J but not, in general, with respect to S and L. The varying fractional density of levels contributed by each S, L type is represented by a corresponding size of each S, L block. The strength of the spin-dependent forces is determined by the parameter μ.

density of levels contributed (in reality) by the type of S,L term in question. As a result, the distribution of spacings based on the entire π,J matrix will be given by the superposition process of the Appendix, in agreement with experiment. If the π,J matrix consists of many different blocks, each of which contributes only a small fraction of the total number of levels, then the exponential distribution will be approached [as, for example, in Fig. 10(a)].

In order to obtain the Wigner distribution for the levels having the *same* values of π, J, S, and L, we postulate that the distribution of matrix elements within each S,L block is given by Eqs. (9) to (13) with $\mu = 1$ (for simplicity).

If the Hamiltonian contains a spin-dependent term, then the matrix elements connecting different S,L blocks do not vanish. In that case we postulate that these matrix elements are distributed independently and normally $(0,\mu\sigma)$. (The above case, in which the spin-dependent forces vanish, corresponds to $\mu=0$.) If $\mu \geqslant 1$, we have practically[31] returned to the conditions of our original hypothesis, and the distribution of spacings will be given by the Wigner distribution to a very good approximation. Thus, we have formulated a statistical hypothesis which gives satisfactory results in the extreme cases.

For the purpose of a quantitative study of the intermediate case, we shall simplify the above model somewhat without destroying its essential features by assuming that all S,L blocks are of the same size and that there is a large number of them. Furthermore, we make the simplifying assumption that all the off-diagonal matrix elements (i.e., also those within S,L blocks) are characterized by the same dispersion $\mu\sigma$. We have therefore returned to the matrix hypothesis embodied by Eqs. (9) to (13), except that we are now interested in the values of μ between 0 and 1.

The spacing distribution will evidently depend on two parameters of the model, viz., μ and N (not on σ). We already know that for a fixed value of N (sufficiently large) the Wigner distribution is approached for $\mu > 1$. Since there are N times as many off-diagonal as there

are diagonal matrix elements, it is to be expected that the Wigner distribution will be approached also for a fixed $\mu < 1$ and N sufficiently large. A plausibility argument based on second-order perturbation theory as well as Wigner's derivation of the "semicircle" law for the over-all distribution of a single eigenvalue[32] suggest that the combination of parameters which largely determines the spacing distribution is $N\mu^2$.

In order to obtain some quantitative information, we have extended our earlier numerical random-matrix computations to the range of μ from 0 to 1. Histograms of spacing distributions were obtained for $N=10$ and 20, and the results are shown in Fig. 12. The six histograms (a) through (f) are labeled by the value of the parameter $N\mu^2$. In two cases, viz., (d) and (e), results were obtained for both $N=10$ and 20 for the same value of $N\mu^2$, and they provide some evidence that it is largely the value of $N\mu^2$ which determines the distribution.[33] The range in $N\mu^2$ over which there is a rapid change in the nature of the spacing distribution occurs, roughly speaking, between the values 0.001 and 1. For values of $N\mu^2$ outside this interval the spacing distribution is already fairly close to the limiting exponential and Wigner distributions.
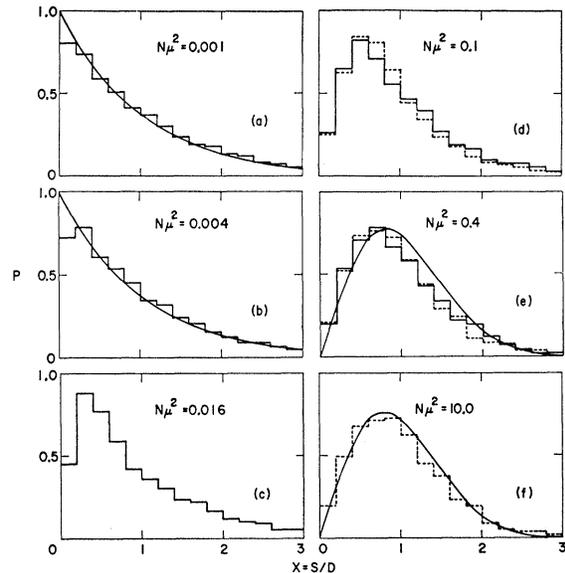

FIG. 12. Plots of the theoretical distribution of nearest-neighbor spacings, based on the random-matrix model defined in the text, as a function of $N\mu^2$. The results, shown as histograms, were obtained by diagonalizing a large set of randomly generated matrices by means of a fast digital computer. The results for $N=10$ (solid histograms) and $N=20$ (dashed histograms) are nearly the same for equal values of $N\mu^2$. The series of histograms (a) to (f) clearly shows the transition from the limiting exponential $(N\mu^2 \rightarrow 0)$ to the limiting Wigner distribution of repulsion $(N\mu^2 \gg 1)$. Qualitatively, this transition corresponds exactly to the trend depicted in the empirical distributions of Fig. 7.

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[31] This is not entirely the case because the dispersion of the off-diagonal matrix elements within S,L blocks was assumed to be σ and not $\mu\sigma$.

[32] E. P. Wigner, Ann. Math. 67, 325 (1958).

[33] The evidence is rather limited since N has only been varied by a factor of 2.

The dependence of the spacing distribution on the parameter $N\mu^2$ in the critical range may be further illustrated by focusing on a particularly sensitive, and from the empirical point of view very convenient, measure of repulsion, namely, the height of the first step in the histograms which, to within statistical fluctuations, is equal to the theoretical quantity $5\int_0^{0.2}P(x)dx$. This "measure of repulsion," as obtained from the above random-matrix computations is plotted against $\log(N\mu^2)$ in Fig. 13. The solid curve was interpolated between the calculated points. The dashed straight line segments in Fig. 13 represent estimates of asymptotic values based on the exponential and Wigner distributions. (The simplest analytical approximation to our "measure of repulsion" would be the first derivative of the spacing distribution evaluated for zero spacing.)

The above results are not only in agreement with the extreme cases of Secs. III and IV, in which the spin-dependent forces are either very small $(N\mu^2 \to 0)$ or rather large $(N\mu^2 > 1)$, but they also provide at least a qualitative understanding of the intermediate cases as exemplified by the empirical distributions of Figs. 7(b) and 10(c). If desired, a very rough value of $N\mu^2$ can be assigned to the empirical distributions.

The fact that $N\mu^2$ (or the corresponding more correct quantity which is unknown to us) is at times very small (as, for example, for the elements of the first and second long periods considered in Sec. III) implies that only a limited number of states interact significantly through the spin-dependent part of the Hamiltonian (in the $SLJ\pi$ scheme). On the other hand, it may happen that the effect of a small term in the Hamiltonain is amplified by connecting a large number of states with one another. General statements of this kind are, of course, well known. However, we wish to emphasize that the perturbation of the individual levels which are of significance in our work is quite small. What counts here is the displacement of levels relative to the mean

FIG. 13. A plot of the "measure of repulsion" as a function of $N\mu^2$. The open circles represent values obtained from numerical random matrix computations. The two dashed line segments correspond to asymptotic values as $N\mu^2 \to 0$ and ∞, and were estimated from the exponential and Wigner distributions, respectively.

spacing between neighboring levels. It seems quite possible that a root-mean-square shift per level of less than 15% of the mean spacing will suffice to convert the exponential to the Wigner distribution (or vice versa).

VI. CONCLUDING REMARKS

We have established that the phenomenon of the repulsion of energy levels occurs in the odd-parity spectra of the elements which are homologous with the iron group. (Similar results, which were not described in this paper, were obtained for the spectra of the singly and doubly ionized ions of the same elements. On the other hand, other regions of the periodic table were not explored.) We have found that the additional symmetries that arise when the spin-dependent forces are relatively weak must be taken into consideration. The random-matrix hypothesis of Sec. V, 2 provides a good, though somewhat oversimplified, picture of the phenomena. While our computations give an excellent indication of dependence of the degree of repulsion on the parameters μ and N of the model, it would be desirable to obtain an analytical insight into the situation.

At this stage we are primarily interested in the qualitative features of the phenomena, and refrain from stating, for example, whether or not the histogram of Fig. 7(c) is quantitatively consistent with the Wigner distribution. A statement of this kind must, we think, await a more precise theoretical formulation of the role played by the energy dependence of the mean spacing. In passing, we merely note that there may be a useful connection here between the density of eigenvalues of a random matrix (given asymptotically by Wigner's semicircle law) and the variation in density which occurs in the atomic spectra.

While the repulsion of levels evidently occurs in atomic spectra, the complexity of the atomic systems is not so great that the statistical properties are fully developed in every respect. The Landé interval rule and the tendency of configurations of opposite parity to be located in different regions of excitation energy are well-known examples of nonstatistical behavior which we had to take into consideration. More subtle structural effects of a nonstatistical nature may be present within the set of even-parity levels.

The results of this work, together with those previously obtained in nuclear physics, certainly strengthen the idea that the following general principle holds for all sufficiently complex quantum systems. Energy levels of the same symmetry type repel each other (approximately according to Wigner's distribution), whereas levels of different symmetry are not correlated in position. This would mean that a study of the distribution of spacings is potentially capable of giving information about the symmetry properties of the physical system in question. This point of view may be illustrated by means of the histogram of Fig. 7(a),
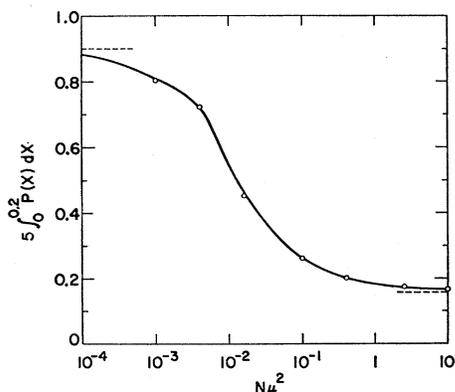
which suggests immediately that there are other good quantum numbers besides π and J (viz., S and L).

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APPENDIX

1. Dependence of Results on the Estimate of the Mean Spacing $D(E)$

As noted in Sec. II, the entire work is subject to the inherent complication that the mean spacing $D(E)$ decreases fairly rapidly with increasing excitation energy E. We shall obtain an indication of the dependence of some of our empirical results on the estimate of $D(E)$, by studying the "measure of repulsion" of Sec. V, given by

$$M = 5 \int_0^{0.2} P(x) dx,$$

as a function of k [the number of levels in Eq. (3)]. As examples, we consider what are probably the most significant empirical results of our investigation, namely, the distributions for the odd-parity levels in the three long periods dealt with in Sec. III. We focus out attention on the distributions shown in Fig. 7. These distributions were constructed again with values of k ranging from 3 to 21 and with the restriction (not made in Sec. III) that the "remainders" consisting of less than k levels are discarded (see reference 18). The results are summarized in Table V, in which the number of spacings T contributing to the entire distribution (not only to M) is also recorded.

It is plain that, although M varies with k, the qualitative differences for the three groups of elements are independent of k. The values of M which are representative for the first, second, and third periods are 0.65, 0.45, and 0.30, respectively. (The limiting Wigner and

exponential distributions correspond to values of 0.16 and 0.90, respectively.)

Next, we focus our attention on the variation of M with k within each group of elements. The method of Sec. II for estimating $D(E)$ would give $M=0$ for $k=2$. In this (absurd) extreme each spacing would also serve as the mean spacing appropriate for it. This artificially large repulsion ($M=0$) persists to a lesser extent up to $k=6$ or 7. Beginning with $k=7$, M increases slowly with increasing values of k, and the effect is most marked for the elements of the first period. These trends can be understood to some extent by considering the distribution of the mean[34] [the mean is defined by formula (3)] as a function of k. If the mean *were* constant as a function of energy then the most probable value of the estimated mean D_k would be smaller than the true mean D_∞; the approximate value of the ratio would be given by

$$D_k/D_\infty \approx 1 - 1/k$$

for the exponential distribution of spacings and by

$$D_k/D_\infty \approx 1 - 1/2k$$

for a distribution of the Wigner type. Clearly, the use of D_k which is too small leads to an apparent repulsion which is too large (M too small). From the above expressions it also follows that for a given value of k, the effect is larger for the exponential distribution (which is applicable to the elements of the first period) than for a distribution of the Wigner type (which is more appropriate for the elements of the second and third periods). If it were not for the strong energy dependence of $D(E)$, we would obtain the best possible estimate of D by using all the levels (k as large as possible). Actually, we adopted the value $k=7$, which is about the

TABLE V. The dependence of M, the degree of repulsion, on k, the number of levels used in the computation of the mean spacing. M is based on the same empirical distribution shown in Fig. 7 of Sec. III. Although M varies with k somewhat, the qualitative differences for the three groups of elements is independent of k. The number of spacings T, which remain after groups of less than k levels are discarded, is also listed.

	First long period		Second long period		Third long period	
k	M	T	M	T	M	T
3	0.32	1784	0.24	1130	0.21	1136
5	0.51	1732	0.39	1088	0.29	1104
6	0.53	1690	0.39	1065	0.30	1060
7	0.56	1656	0.46	1038	0.29	1062
8	0.59	1673	0.39	1015	0.31	1029
9	0.62	1640	0.43	1000	0.29	1032
11	0.61	1560	0.47	920	0.30	960
13	0.64	1488	0.47	864	0.33	948
21	0.71	1280	0.47	760	0.38	800

[34] N. Rosenzweig, L. M. Bollinger, L. L. Lee, Jr., and J. P Schiffer, *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958* (United Nations, Geneva, 1958), Vol. 14, p. 58. There is a misprint in formula (24) of this paper. NS^* should be replaced by $2NS^*$.

smallest possible value which gives meaningful results. In a more quantitative study in the future, the corrections implied by this discussion should certainly be included (see also Sec. VI).

2. Random Superposition of a Number of Sequences of Energy Levels

We shall now derive the distribution of spacing resulting from the random superposition of n unrelated sequences, a result which has been referred to repeatedly in this work.[35] Let ρ_i be the density of levels of the ith sequence and let $p(\rho_i s)\rho_i ds$ be the probability that a nearest-neighbor spacing in sequence i has a value between s and $s+ds$ [this interval will be denoted by $(s, s+ds)$]. The function $p(x)$ is assumed to be the same for all sequences. $p(x)$ is normalized to unity and, since the mean value of the spacing is the inverse of the density, the first moment of $p(x)$ must also be unity, i.e.,

$$\int_0^\infty p(x)dx = \int_0^\infty xp(x)dx = 1. \tag{20}$$

We are primarily interested in functions $p(x)$ which, like Wigner's distribution, have the property

$$p(0) = 0. \tag{21}$$

Now consider the system of levels resulting from the superposition of all n sequences. The total density of levels is given by

$$\rho = \sum_i \rho_i. \tag{22}$$

Let $P^*(s)ds$ be the probability[36] that a spacing lies in $(s, s+ds)$. Our aim is to express $P^*(s)$ in terms of the fundamental probability $p(x)$. First we write P^* as a sum which exhausts all mutually exclusive possibilities, i.e.,

$$P^*(s) = \sum_{i,j} \frac{\rho_i}{\rho} p_{i,j}(s), \tag{23}$$

where $p_{i,j}(s)ds$ is the probability that, given a level of sequence i at $s=0$, the nearest neighbor (in the positive sense) will lie in $(s, s+ds)$ and belong to sequence j.

Next, we write down some probabilities which are needed for the evaluation of $p_{i,j}(s)$. Given that a level of sequence i occurs at $s=0$, the probability that the *next* level of sequence i occurs in $(s, s+ds)$ is given by

$$\rho_i p(\rho_i s)ds. \tag{24}$$

Given that a level of sequence i occurs at $s=0$, the probability that a level of sequence $j(i\neq j)$ occurs in

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[35] The case $n=2$ is considered in references 7 and 12. Our treatment is a generalization of a recent unpublished derivation by P. A. Moldauer (also for $n=2$) to whom we are indebted for showing us his manuscript.

[36] s is expressed in energy units, for example, electron volts or wave numbers. We reserve P (without *) for the probability density in which the spacing is expressed in terms of the mean spacing for the combined system of levels.
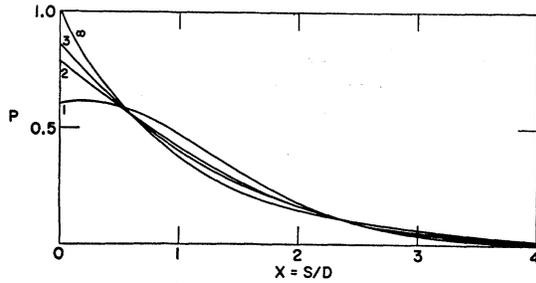
$(s, s+ds)$ is given by

$$\rho_j ds \int_0^\infty p(x+\rho_j s)dx. \tag{25}$$

If we put

$$R(y) = \int_0^\infty p(x+y)dx, \tag{26}$$

then the probability (25) becomes $\rho_j ds R(\rho_j s)$. Given that a level of sequence i occurs at $s=0$, the probability that a level of sequence i does *not* occur in $(0,s)$ is given by

$$\int_s^\infty \rho_i p(\rho_i x)dx = R(\rho_i s). \tag{27}$$

Given that a level of sequence i occurs at $s=0$, the probability that a level of sequence $j(i\neq j)$ does not occur in $(0,s)$ is, in view of Eq. (25), given by

$$\rho_j \int_s^\infty \int_0^\infty p(x+\rho_j y)dxdy = \int_0^\infty \int_0^\infty p(x+y+\rho_j s)dxdy$$
$$= \int_0^\infty xp(x+\rho_j s). \tag{28}$$

Let us put

$$D(y) = \int_0^\infty xp(x+y)dx. \tag{29}$$

Then the probability (28) is given by $D(\rho_j s)$. Using the above results, one can express $p_{i,j}$ as

$$p_{i,i}(s) = \frac{\rho_i p(\rho_i s)}{D(\rho_i s)} \prod_{k=1}^n D(\rho_k s), \tag{30}$$

and, if $i\neq j$,

$$p_{i,j}(s) = \rho_j \frac{R(\rho_j s)R(\rho_i s)}{D(\rho_j s)D(\rho_i s)} \prod_{k=1}^n D(\rho_k s). \tag{31}$$

An expression for $P^*(s)$ may be obtained by substituting Eqs. (30) and (31) into (23). Before doing that, we introduce the variable x which denotes the spacing divided by the mean spacing for the combined system of levels, i.e.,

$$\rho s = x, \tag{32}$$

the distributions for s and x being related through

$$P^*(s)ds = P(x)dx. \tag{33}$$

It is convenient to replace the densities ρ_i by the *fractional* densities q_i defined by

$$q_i = \rho_i/\rho, \quad \sum_i q_i = 1. \tag{34}$$

By use of the abbreviation

$$\Pi(x) = \prod_{k=1}^n D(q_k x), \tag{35}$$

the distribution $P(x)$ which we set out to calculate may

FIG. 14. Plots of the distribution of spacings implied by Eq. (36) for the random superposition of J sequences; the fractional density of levels q_J contributed by each sequence is given by Eq. (42). The various curves correspond to several values of σ as noted in the figure.

be expressed as

$$P(x) = \prod(x) \left\{ \sum_i q_i^2 \frac{p(q_i x)}{D(q_i x)} + \left[\sum_i q_i \frac{R(q_i x)}{D(q_i x)} \right]^2 \right.$$

$$\left. - \sum_i \left[q_i \frac{R(q_i x)}{D(q_i x)} \right]^2 \right\}. \quad (36)$$

We shall now derive the most important properties of $P(x)$. First, note that

$$R(0) = D(0) = 1, \quad (37)$$

these relations being entirely equivalent to Eq. (20). Applying (21), (34), and (37) to (36) one obtains the most important single feature of superposing a number of unrelated sequences, viz.,

$$P(0) = 1 - \sum_i q_i^2,$$

which depends on only one detail of the fundamental distribution, namely, $p(0) = 0$. The value of the first derivative at the origin also has a fairly simple form, viz.,

$$P'(0) = -1 + 3 \sum_i q_i^2 + [p'(0) - 2] \sum_i q_i^3. \quad (38)$$

The result (38) evidently depends on two details of the fundamental distribution. (For the Wigner distribution $p'(0) - 2 = -0.429$, and in this case the third term of expression (38) is frequently small compared to the sum of the first two terms.)

Next, consider the superposition of n sequences with all the fractional densities equal to $1/n$. Denoting the spacing distribution by $P_n(x)$ in this case, we will show that $P_n(x) \to e^{-x}$ as $n \to \infty$. Letting $y = x/n$, one obtains

$$P_n(ny) = D^n(y) \left[\frac{1}{n} \frac{p(y)}{D(y)} + \frac{R^2(y)}{D^2(y)} \left(1 + \frac{1}{n} \right) \right]. \quad (39)$$

In view of Eqs. (21) and (37), the expression in the square brackets becomes unity in the limit as $n \to \infty$ ($y \to 0$). Next consider $D(y)$, which we assume to be expandable in a power series about zero. Since $D'(0) = -1$, we have to first order in y that

$$D(y) \sim 1 - y = 1 - (x/n), \quad (40)$$

from which it follows that

$$P_\infty(x) = \lim_{n \to \infty} \left(1 - \frac{x}{n} \right)^n = e^{-x}. \quad (41)$$

The exponential function will, of course, be the limiting case for other sequences. However, Eq. (37) shows that a necessary condition is $\sum_i q_i^2 \to 0$. Accordingly, the exponential distribution cannot be attained if $q_i \neq 0$ for any one sequence, even if an infinite number of sequences are superposed. This may be illustrated by means of the well-known formula for the fractional density of nuclear levels having spin J and the same parity,[37] namely,

$$q_J = \exp(-J^2/2\sigma^2) - \exp[-(J+1)^2/2\sigma^2],$$
$$J = 0, 1, \cdots, \infty. \quad (42)$$

Adopting the Wigner distribution, one obtains

$$R(x) = \exp(-\tfrac{1}{4}\pi x^2),$$

$$D(x) = 1 - \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \int_0^{x(\frac{1}{2}\pi)^{\frac{1}{2}}} \exp(-\tfrac{1}{2}y^2) dy. \quad (43)$$

The function $P(x)$, representing the distribution of spacings that results from the superposition of all the sequences implied by Eq. (42), was computed numerically for some values of σ in the range from 1 to ∞ and the results are shown in Fig. 14.

[37] H. A. Bethe, Revs. Modern Phys. **9**, 53 (1937); and C. Bloch, Phys. Rev. **93**, 1094 (1954).