an analytical expression (Roothaan procedure). None of the eigenvalues differ by more than 0.01 ry except for a difference of 0.02 ry for $\epsilon_{3s,3s}$ and 0.06 ry for $\epsilon_{1s,1s}$. The sum of one-electron energies of the configuration for the present results is 1993.418 rydbergs compared to Watson's 1993.144. In view of the deviations of our numerical results for hydrogenlike configurations, no better agreement could be expected.

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"Repulsion of Energy Levels" in Complex Atomic Spectra

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Rosenzweig and Porter have shown a "repulsion of energy levels" in spacing distributions determined from energy levels in complex atomic spectra. The present paper extends their work by showing that these spacing distributions can be determined from calculated positions of the levels in these spectra. Since calculated data are available for spectra where the observed data are scarce or incomplete, this partially overcomes limitations imposed by statistical inaccuracy when direct use is made of the observed data. The equivalence of the two approaches is demonstrated by showing that calculated data for Ta II yield the same spacing distribution as obtained from observed data for Ta II and Re I combined. These are complex spectra in which a fully developed repulsion effect is present. A similar demonstration of equivalence is carried out for spectra of Ru I and Mo I, where the repulsion effect is in an intermediate state of development. The results also indicate that numbers easily evaluated from the radial parameters of the theory will indicate roughly the degree of repulsion, replacing to some extent the need for an explicit calculation of the spacing distribution.

1. INTRODUCTION

STATISTICAL models are often used to interpret nuclear data. Usually, mean values of the observables are calculated, but recent increases in the quantity and quality of observed data have dictated a need for calculating distributions about the mean. Wigner has suggested a formula for the distribution of nearest-neighbor level spacings (between levels of the same total angular momentum and parity), S, when the average spacing of such pairs is D.[1] Expressed in terms of the ratio $x=S/D$, this formula is

$$P(x)=\tfrac{1}{2}\pi x \exp(-\tfrac{1}{4}x^2). \quad (1)$$

The distinguishing feature of formula (1) is the "repulsion effect." If levels occurred randomly, with the probability the same per unit energy interval over a given range of energy, then the distribution of nearest-neighbor level spacings would follow instead the Poisson formula,

$$P(x)=e^{-x}. \quad (2)$$

Formula (1) predicts zero probability for zero spacing, whereas formula (2) makes the zero spacing most probable. If spacings in the first one-third-interval are counted (i.e., the number of spacings between zero and a third of D), then formula (1) predicts that about 9% of all the spacings will be in this interval, while formula (2) predicts 28%. In the first two-thirds-interval the predictions still differ considerably, being 30% and 50% of all spacings for formulas (1) and (2), respectively. For large values of x there is also a difference between the formulas; 5% and 15% of the spacings are greater than $2D$ according to formulas (1) and (2), respectively. In this paper, it is considered that a spacing distribution shows a "full" repulsion effect only when there is close agreement with the predictions of formula (1) for the first one-third-interval, the first two-thirds-interval, and the number of spacings greater than $2D$. For convenience, all the spacing distributions are normalized to a total of 74 spacings. The corresponding spacing distributions from formulas (1) and (2) are given in Table I.

The deficiency of small spacings can be understood intuitively as a "repulsion effect" by considering the well-known interpretation of a second-order perturbation as a mutual repulsion between two levels. The deficiency of large spacings can be interpreted as a secondary result of this, if it is assumed that the expansion of short intervals is preferentially (when possible) at the expense of an adjacent large interval,

[1] E. P. Wigner, Proceedings of the Conference on Neutron Physics by Time of Flight, Gatlinburg, Tennessee, 1956 [Oak Ridge National Laboratory Report ORNL-2309 (unpublished), p. 59].

TABLE I. Nearest-neighbor spacing distributions. The interval is measured in units of the mean spacing D, and the normalization is for a total of 74 spacings.

Interval	0–1/3	1/3–2/3	2/3–1	1–4/3	4/3–5/3	5/3–2	2–3	3–4	>4
Formula (1)	6.2	15.6	18.4	15.4	10.0	5.2	3.1	0.1	0
Formula (2)	21.0	15.0	10.8	7.7	5.5	4.0	6.3	2.3	1.4

resulting in an apparent contraction of the latter. Though mutually connected in this simplified picture, the deficiencies of large and small spacings are not related unless the perturbations are large enough to produce a full repulsion effect. It is known that for weak perturbations a considerable deficiency of small spacings can be demonstrated in the absence of any appreciable reduction in the number of large spacings. Reference to the "repulsion effect" has usually been used only in connection with the deficiency of small spacings. Our calculations show that a decrease in large spacings is easily demonstrated; since this is the distinctive feature of a "full" repulsion effect, we have also emphasized this deficiency.

Empirical confirmation of formula (1) has been obtained by analysis of the spacings between slow-neutron scattering resonances.[2] Very close neutron resonances could not be resolved, and significant corrections had to be made to allow for this. A deficiency of small spacings was demonstrated in agreement with the prediction of formula (1), but statistical uncertainty prevented the demonstration of a deficiency in the number of large spacings.

Rosenzweig and Porter have considered levels of atomic spectra[3,4] in odd configurations of the third long period; they were able to demonstrate deficiencies of both large and small spacings that were very close to the predictions of formula (1). An exceptionally large amount of atomic data was available for their analysis[5] (admitting a total of 1156 spacings). They found small departures from formula (1) that could not be attributed to statistical inaccuracy. They could be attributed to the fact that the experimental data were incomplete. No simple procedure was available to correct for this. However, it can be assumed that the levels are missed at random. The corrections[6] are then smaller than for the nuclear spectra where the omissions were systematically correlated to the smaller spacings.

In odd configurations of the second long period the deficiencies of both large and small spacings were not as great as predicted by formula (1).[3] For odd configurations of the first long period, the distribution of formula (2) applied, except for a small deficiency of spacings in the first one-fifth interval. These are spectra where the perturbations are too weak to produce a full repulsion effect. This conclusion applies as an average result for the whole long period.

In I, spacing distributions were also determined for the levels of the even configurations of the three long periods. These spectra are considered in detail in the present paper and the results will be considered later.

The work of the present paper utilizes both calculations and experimental observations for atomic spectra. This eliminates uncertainty associated with lack of completeness in the experimental data. At the same time, the statistical fluctuations are reduced, since the calculations effectively increase the amount of data that is analyzed.

A direct approach to the derivation of formula (1) is illustrated for low-order matrices in II.[7] It has also been shown empirically that it closely reproduces spacing distributions of eigenvalues of matrices whose elements are generated from random members.[3,4,8,9] It is expected that the eigenvalues of matrices derived from sufficiently complex physical systems will show the same spacing distribution as the eigenvalues of random matrices. If that assumption is made in connection with the work of the present paper, then instead of a "verification" of formula (1), the emphasis is on determining whether or not the system is complex enough for the formula to apply.

Descriptions of matrices are presented in the present paper to establish a correspondence with the random matrices, and give some measure of the "complexity" of the spectrum.[10] From a simple viewpoint, complexity is increased (a) the larger the orders of the matrices, (b) the larger the off-diagonal elements of the matrices (or, equivalently, the larger the radial parameters that define these elements), and (c) the larger the number of different interactions. A full discussion is outside the scope of the semiquantitative treatment of the present paper. It is expected that a later paper will extend the present work to consider the correspondence to random matrices that is illustrated in II.

[2] J. A. Harvey and D. J. Hughes, Phys. Rev. **109**, 471 (1958).
[3] N. Rosenzweig and C. E. Porter, Phys. Rev. **120**, 1698 (1960). This is referred to as I.
[4] C. E. Porter and N. Rosenzweig, Suomalaisen Tiedeakat. Toimituksia (1960). This is referred to as II.
[5] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1958), Vol. III.
[6] P. A. Moldauer (to be published).
[7] However, see also L. Dresner, Phys. Rev. **113**, 633 (1959), and M. L. Mehta, Nuclear Phys. **18**, 395 (1960).
[8] S. Blumberg and C. E. Porter, Phys. Rev. **110**, 786 (1958).
[9] N. Rosenzweig, Phys. Rev. Letters **1**, 101 (1958).
[10] In describing the matrices, the notation of atomic theory is used for convenience, but an exposition of the terminology of atomic theory is not attempted.

2. OUTLINE OF METHOD

The calculations of the present paper utilize a set of seven matrices that are applicable to atomic spectra with three configurations commonly specified as $(d+s)^4$ or $(d+s)^8$, corresponding to the use of a positive or negative value, respectively, for the spin-orbit parameter (see Fig. 1). Values of the individual matrix elements have been published in papers referenced elsewhere.[11,12] The nonvanishing elements are linear combinations of fifteen adjustable parameters. The distribution of these parameters in the matrices is shown in Fig. 1. The parameters H_2 and G_2 determine the configuration interaction. The parameters ζ, ζ', and ζ'' define the spin-orbit interaction. These two interactions are the most important ones that give nondiagonal matrix elements. The other parameters originate in the electrostatic interaction, and contribute mainly to the diagonal elements of the matrices. (There are a few instances where B and B' contribute to nondiagonal elements, but these exceptions have been ignored for simplicity.) By simple permutations of the rows and columns, the matrices may be presented in a form which is diagonal in the SL-value, as shown in Fig. 2. This presentation is more appropriate for consideration of "constants of the motion," and is the same as Fig. 11 of I.

When the spin-orbit parameters are set equal to zero (but other parameters retain appropriate values), the eigenvalues and eigenvectors obtained from the matrices are referred to as "third-order" eigenvalues

A, B, C, ζ, α (d^4 or d^6s^2)	H_2	G_2
H_2	A', B', C', ζ', G_2, α (d^3s or d^7s)	H_2
G_2	H_2	A'', B'', C'', ζ'', α (d^2s^2 or d^8)

FIG. 1. Matrices of $(d+s)^4$ and $(d+s)^8$ configurations. The partitioning emphasizes configuration interaction and shows the distribution of parameters. The orders of the matrices and diagonal submatrices as a function of the J value are as follows:

J value	0	1	2	3	4	5	6
d^4	5	4	8	6	7	2	2
d^3s	2	7	10	8	6	4	1
d^2s^2	2	1	3	1	2	0	0
Over-all	9	12	21	15	15	6	3

[11] R. E. Trees, W. F. Cahill, and P. Rabinowitz, J. Research Natl. Bur. Standards **55**, 335 (1955).
[12] R. E. Trees, J. Opt. Soc. Am. **49**, 838 (1959).

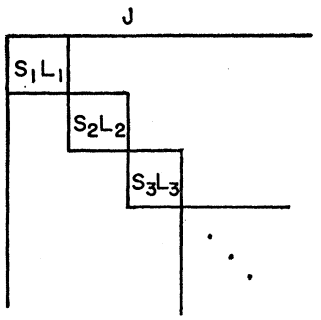

FIG. 2. Matrices of $(d+s)^4$ and $(d+s)^8$ configurations. The partitioning emphasizes spin-orbit interaction. The matrices are the same as shown in Fig. 1, except for simple permutations of the rows and columns. The order of the diagonal submatrices as a function of the J value are as follows (numbers in parentheses indicate a multiplicity of that particular order of submatrix):

J value	0	1	2	3	4	5	6
S_1L_1	5	5	5(3)	5	5	2(2)	2
S_2L_2	3	3	3	3	4	1(2)	1
S_3L_3	1	1(4)	1(3)	2(2)	2(2)		
S_4L_4				1(3)	1(2)		
Over-all	9	12	21	15	15	6	3

and eigenvectors.[13] When spin-orbit interaction is weak in a given spectrum, the eigenvectors can be well characterized by specification of a single dominant third-order eigenfunction. The SL value can then be regarded as a constant of the motion. The refinement introduced in I to take account of these constants has been omitted in the present paper, again for simplicity. Third-order eigenvectors have been published for Ru I,[14] and it has been shown that a single dominant component accounts for more than 50% of the eigenvector in all but three of 59 observed levels. In Ta II, the spin-orbit parameter is twice as large, but unpublished calculations show that the eigenvectors can still be well described by a single third-order eigenfunction. When spin-orbit interaction is very strong, the eigenvalues approach the values of jj coupling[15]; the latter eigenvalues are listed in Table II. It is simple to show that the spacing distribution has an excess of small spacings beyond the predictions of the Poisson formula (2). In this case, the constants of the motion are the j values of the individual electrons.

The set of parameters designated as A in Table III applies to the spectrum of Ta II. The calculations leading to these parameters have been described,[11] but the eigenvalues of the matrices were not given. Calculated eigenvalues and g values are therefore given in Table IV. For Ta II, another procedure was used to obtain parameters designated as B (Table III).[16]

[13] C. W. Ufford, Phys. Rev. **44**, 732 (1933).
[14] R. E. Trees, J. Research Natl. Bur. Standards. **63A**, 255 (1959).
[15] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1951), Chap. X.
[16] In determining parameters B, the parameter α was fixed to have the value 60 cm^{-1}, while other parameters were determined by least squares.

TABLE II. Eigenvalues of matrices of $(d+s)^4$ in jj coupling. Numbers in parentheses specify multiplicities of the eigenvalues.

$J=0$	1	2	3	4	5	6
-6ζ	$-9/2\zeta'$	$-9/2\zeta'$	$-7/2\zeta$	$-7/2\zeta$	$-2\zeta'$	$-\zeta$
$-3\zeta''$	$-7/2\zeta$	$-7/2\zeta$	$-2\zeta'(3)$	$-2\zeta'(2)$	$-\zeta$	$1/2\zeta'$
$-2\zeta'$	$-2\zeta'(2)$	$-3\zeta''$	$-\zeta(2)$	$-\zeta(3)$	$1/2\zeta'(2)$	$3/2\zeta$
$-\zeta(2)$	$-\zeta$	$-2\zeta'(3)$	$-1/2\zeta''$	$-1/2\zeta''$	$3/2\zeta$	
$1/2\zeta'$	$-1/2\zeta''$	$-\zeta(4)$	$1/2\zeta'(4)$	$1/2\zeta'(3)$	$3\zeta'$	
$3/2\zeta$	$1/2\zeta'(3)$	$-1/2\zeta''$	$3/2\zeta(3)$	$3/2\zeta(2)$		
$2\zeta''$	$3/2\zeta(2)$	$1/2\zeta'(4)$	$3\zeta''$	$2\zeta''$		
4ζ	$3\zeta'$	$3/2\zeta(2)$		$3\zeta'$		
		$2\zeta''$		4ζ		
		$3\zeta'(2)$				
		4ζ				

The parameter sets A and B differ enough so that comparison of the results will give some indication of statistical uncertainty. Excepting this instance, no effort has been made to determine the statistical fluctuations that would be produced if the parameters were systematically varied by small amounts. In other cases, unrealistically large variations of the parameters have been used instead. This is to illustrate large changes that are expected to result. Since these large changes can be consistently demonstrated, the statistical uncertainty does not seem to be an important factor.

The parameters C of Table III are applicable to Ru I; the eigenvalues obtained with these parameters have been published.[12]

The calculations of spacing distributions were carried out on the 704 computer with a code similar to one described previously for the SEAC.[11] On a typical run that required 17 min of machine time, the seven matrices were generated, each with eight sets of parameters, for a total of 56 matrices. For each matrix, the diagonal elements were selected, sequenced in order of increasing magnitude, and printed on tape. The differences between nearest-neighbor diagonal elements were then obtained, sequenced, and printed on the tape. Eigenvalues were next computed. The procedure described for the diagonal elements was repeated for the eigenvalues. From these results, the spacing distributions were then determined by use of a desk calculator. The difference between the largest and smallest value was divided by the order of the matrix less one to obtain the mean spacing. The number of nearest-neighbor differences was then counted in intervals of length $\frac{1}{3}D$ in the range of spacings from 0 to $2D$, and in intervals of length D beyond that. The counts for corresponding intervals were then added for the seven matrices associated with any one set of parameters.

TABLE III. Values of parameters (cm^{-1}). Unprimed parameters refer to $d^4(d^6s^2)$, single primed to $d^3s(d^7s)$, and double primed to $d^2s^2(d^8)$ with ζ positive (negative). A, B—Ta II. C—Ru I.

Individual parameter symbols	Parameter set A	B	C
A	26 944	26 512	20 874
A'	20 439	21 055	14 518
A''	13 911	14 655	14 752
B	483	492.6	596.7
B'	483	516.4	542.6
B''	483	540.2	485.7
C	1841	1507.6	2740.4
C'	1841	1548.0	2578.6
C''	1841	1588.4	2412.6
ζ	1776	1719.7	−970.6
ζ'	1776	1738.0	−915.9
ζ''	1776	1756.3	−837.8
G_2	2872	3001.1	1736.0
H_2	538	544.4	329.9
α	0	60	29.41

3. RESULTS

The variances of the diagonal and off-diagonal elements of the matrices will be estimated first. From the ratio of these variances, μ^2, the quantity $N\mu^2$ is estimated, where N is the order of the matrix (the notation used here is the same as in I). The quantity $N\mu^2$ measures the degree of repulsion in matrices whose elements are generated from Gaussian distributions. In the latter matrices, as shown in I, the repulsion effect was fully developed for values of $N\mu^2>0.2$, while negligible repulsion effects were present for values of $N\mu^2<0.002$.

The diagonal elements of the matrices are considered to have the spacing distribution described by formula (2). This corresponds, approximately, to assuming that the probability distribution of the elements is uniform over the interval $N\bar{D}$, where N is the order of the matrix and $\bar{D}$ is the mean value of the nearest-neighbor spacings of diagonal elements of the matrix. The variance (about the mean) is then,

$$\frac{1}{N\bar{D}}\int_{-N\bar{D}/2}^{N\bar{D}/2} x^2dx=\frac{N^2\bar{D}^2}{12}\equiv\sigma^2. \tag{3}$$

Values of $\bar{D}$ are given in Table V. This quantity should be distinguished from the mean spacing between eigenvalues, D, which is used in the determination of the spacing distribution of eigenvalues.

For nondiagonal elements, the variance is defined as a sum of three contributions, one derived from the spin-orbit interaction and the other two from the configuration interaction.

$$\mu^2\sigma^2\equiv(f\zeta^2+gG_2{}^2+hH_2{}^2)/N^2. \tag{4}$$

The coefficients f, g, and h are listed in Table VI. Coefficient f was obtained by summing the squares of the coefficients for the eigenvalues in jj coupling

TABLE IV. Calculated and observed energies (in cm^{-1}) and g values for parameters A (Ta II).

Ta II (obs) Energy	Ta II (obs) g value	Ta II (Calc A) Calc energy	Calc-Obs	Calc g value	Calc-Obs
					$J=0$
4125		4131	6		
12 601		12 579	−22		
		16 306			
23 381		23 074	−307		
		26 928			
		31 819			
		38 429			
		47 254			
		68 561			
					$J=1$
0	0.004	70	70	0.039	0.035
5331	1.550	5327	−4	1.562	0.012
10 713	2.353	10 633	−80	2.358	0.005
13 475	1.498	13 579	104	1.521	0.023
14 628	0.861	14 504	−124	0.853	−0.008
17 375	1.168	17 441	66	1.160	−0.008
23 406	1.2	23 155	−251	1.228	0.0
26 234	1.332	26 043	−191	1.279	−0.053
29 963	1.004	30 495	532	0.995	−0.009
		32 820		0.998	
		37 229		0.515	
		46 069		1.492	
					$J=2$
1031	1.021	1134	103	1.009	−0.012
3180	0.740	3626	446	0.766	0.026
5658	1.348	5649	−9	1.320	−0.028
9690	1.047	9564	−126	1.067	0.020
11 875	1.426	11 832	−43	1.396	−0.030
13 560	1.119	13 430	−130	1.130	0.011
14 495	1.476	14 730	235	1.467	−0.009
17 168	1.201	17 039	−129	1.235	0.034
18 501	1.441	18 440	−61	1.430	−0.011
22 929	0.697	22 976	47	1.071	0.374
23 295	1.106	23 049	−246	0.757	−0.343
28 044	1.358	27 394	−650	1.356	−0.002
29 844	0.833	30 134	290	0.752	−0.081
30 406	1.051	31 004	598	1.161	0.110
		33 678		1.026	
		35 894		1.395	
		37 092		1.140	
		42 828		0.933	
		43 116		1.248	
		47 407		1.007	
		57 395		1.002	

Ta II (obs) Energy	Ta II (obs) g value	Ta II (Calc A) Calc energy	Calc-Obs	Calc g value	Calc-Obs
					$J=3$
2642	1.243	2775	133	1.246	0.003
6831	1.089	6875	44	1.082	−0.007
11 767	0.908	11 571	−196	0.912	0.004
12 436	1.585	12 265	−171	1.609	0.024
14 581	0.988	14 413	−168	1.000	0.012
15 726	1.455	16 049	323	1.460	0.005
18 554	1.347	18 580	26	1.336	−0.011
23 620	1.065	23 638	18	1.086	0.021
24 870	0.988	24 813	− 57	0.994	0.006
26 829	0.854	27 246	417	0.841	−0.013
30 624	1.257	31 252	628	1.234	−0.023
		32 316		1.130	
		36 246		1.301	
		41 859		1.059	
		45 089		1.039	
					$J=4$
4416	1.346	4553	137	1.337	−0.009
9746	1.219	9444	−302	1.223	0.004
12 705	1.019	12 222	−483	1.019	0.000
14 205	0.994	12 760	−1445	1.041	0.047
15 851	0.919	15 601	−250	1.081	0.062
17 231	1.191	17 171	− 60	1.135	−0.056
18 494	1.227	18 510	16	1.334	0.107
23 083	1.033	23 023	− 60	1.074	0.041
24 433	0.985	24 532	99	0.934	−0.051
25 385	1.085	25 001	−384	1.119	0.034
28 165	1.094	28 814	649	1.053	−0.041
31 532	1.129	31 570	38	1.121	−0.008
		36 200		1.085	
		42 688		1.220	
		47 397		1.023	
					$J=5$
6187	1.410	6305	118	1.377	−0.033
12 831	1.280	13 948	1117	1.147	−0.133
18 186	1.100	17 897	−289	1.099	−0.001
24 226	1.003	23 521	−705	1.010	0.007
25 414	1.060	25 916	502	1.057	−0.003
31 267		31 329	62	1.177	
					$J=6$
17 982	1.146	17 569	−413	1.167	0.021
26 011	1.112	26 551	540	1.134	
		31 818			

(Table II). Coefficients g and h were obtained by direct evaluation from the matrices.

For the parameter sets of Table III, G_2 is roughly six times H_2. In Table VI are given the ratios $[(h+36g)/f]^{\frac{1}{2}}$; this is the approximate ratio of the value of ζ to H_2 that is required to yield equal contributions to $N\mu^2$ for the configuration and spin-orbit interactions. The required ratio is about 5, while the ratio actually present for parameters of Table III is about 3. The spin-orbit interaction therefore contributes to the repulsion $9/25(\sim 1/3)$ the amount contributed by configuration interaction.

TABLE V. Mean spacing, $\bar{D}$, for diagonal elements of the matrices (cm^{-1}).

Set of parameters \ J value	0	1	2	3	4	5	6
A	5668	3193	2442	2523	2543	4467	6268
B	5071	2900	2271	2342	2348	4246	5711
C	7202	2977	2588	2655	2946	4906	6825

TABLE VI. Coefficients in the variances of nondiagonal matrix elements.

Coeff. \ J value	0	1	2	3	4	5	6
f	73.5	56	101.25	43.25	57.75	16.75	3.5
g	22	6	18	6	12	0	0
h	1160	1320	3090	1110	990	130	40
$[(h+36g)/f]^{\frac{1}{2}}$	5.15	5.22	6.06	5.55	4.95	2.88	3.38

TABLE VII. Values of $N\mu^2$ as a function of J value and parameter set.

Set of parameters \ J value	0	1	2	3	4	5	6
A	0.384	0.414	0.296	0.283	0.312	0.252	0.256
B	0.489	0.507	0.348	0.333	0.371	0.275	0.306
C	0.081	0.163	0.092	0.088	0.079	0.065	0.069

The quantities $N\mu^2$ which define the degree of repulsion are then evaluated from the formula

$$N\mu^2=\frac{12}{N^3\bar{D}^2}(f\xi^2+gG_2^2+hH_2^2), \tag{5}$$

by combining the data of Tables III, V, and VI; the results are given in Table VII. The quantities $N\mu^2$ are closely similar for different J values of any one set, which justifies combining the data from different matrices.

The spacing distributions of the diagonal elements of the matrices are given in Table VIII. These distributions have about the same number of spacings in the first two-thirds interval as called for by formula (2)—31 to 33 observed, as compared to 36 called for by the formula. There are 9 to 10 spacings greater than $2\bar{D}$, in agreement with the 10 called for by the formula.

Table IX gives the spacing distributions for the eigenvalues of the matrices. From parameters of sets A and B, modified sets have been derived by setting configuration interaction integrals H_2 and G_2 equal to zero, and these sets are specified with a prime in Table IX. For sets A, B, and C, other sets are also derived by multiplying the three spin-orbit parameters by simple factors of 0, $\frac{1}{2}$, $\frac{3}{2}$, and/or 2; where such a factor is used, it is indicated in parentheses following the letter of the original set.

The levels of the low even configurations of Ta II show a fully developed repulsion, as indicated by the results for the two sets of parameters A and B. However, the repulsion may have just reached the stage of full development. The spacings in the first third-interval slightly exceed the number predicted by formula (1). This excess seems to be greater than expected from statistical variation. When the spin-orbit parameter is increased [parameters $A(\frac{3}{2})$ and $A(2)$] there is a decrease in the number of small spacings, while when it is decreased [parameters $A(\frac{1}{2})$], there is an increase of small spacings in the first two-thirds interval and also of spacings greater than $2D$. If the spin-orbit interaction is set equal to zero, then no repulsion is present, as shown for the parameter sets $A(0)$ and $B(0)$. Though $N\mu^2$ is reduced by only 25%, the repulsion disappears because the matrices are then resolved into separate matrices (Fig. 2), and the spacing distribution really corresponds to a superposition of several sets of independent eigenvalues. The over-all spacing distribution for such a superposition has been calculated,[3,17] and it has been shown that formula (2) is approached as the number of superposed sequences is increased.[3] When configuration interaction is set equal to zero, repulsion is again absent, as shown for parameter sets A' and B'. In this case, the eigenvalues for two larger submatrices, originating in the $5d^4$ and $5d^36s$ configurations, have primary importance in determining the spacing distribution. If $N\mu^2$ is large enough, a repulsion effect about half as great as called for by formula (1) is expected.[3] This is demonstrated by the spacing distribution for parameter set $A'(2)$, obtained from set A by doubling the spin-orbit parameters but still keeping configuration interaction integrals equal to zero.

TABLE VIII. Spacing distributions for diagonal elements of the matrices.

Interval \ Set of parameters	A	B	C
0−1/3	16	20	19
1/3−2/3	16	13	12
2/3−1	14	11	15
1−4/3	8	12	13
4/3−5/3	6	6	2
5/3−2	5	2	3
2−3	6	6	8
3−4	2	3	1
>4	1	1	1

The results for Ta II indicate that a full repulsion effect should be demonstrable in the low even configurations of the third long period. Though the Ta II results indicate only a bare attainment of full repulsion, the five-, six-, and seven-electron spectra of this period have a more complicated system of levels, and the interaction parameters are larger, in general, than those in Ta II.[11,18] These factors insure that the observed data will show a full repulsion if eigenvalues of the matrices for Ta II represent the true repulsion in Ta II.

Using the calculations simply as a guide to the completeness of the data, we determined the spacing distribution from Kiess's latest data for Ta II, as reproduced in Table IV; levels for J values of 0, 5, and 6 were excluded because their sequences were too short. In addition, the observed data for Re I which are reproduced in Table I of reference 18 were used; here, levels with J values of 1/2, 11/2, and 13/2 were omitted, along with the lowest and two highest levels for the J value of 5/2. This set of 74 spacings, by chance the same number as obtained from the matrices, has the distribution given in Table X, in close agreement with the distribution obtained from the matrices by use of the sets of parameters A and B.

The results of I for levels of the even configurations

[17] I. I. Gurevich and M. I. Pevsner, Nuclear Phys. 2, 575 (1957).
[18] R. E. Trees, Phys. Rev. **112**, 165 (1958).

TABLE IX. Spacing distributions for eigenvalues. A number in parentheses indicates a factor used to multiply ζ; a prime indicates that the configuration interactions are set equal to zero.

Interval \ Parameter set	A	A'	$A(0)$	$A(\frac{1}{2})$	$A(\frac{3}{2})$	$A(2)$	$A'(2)$	B	B'	$B(0)$	C	$C(0)$	$C(2)$
0−1/3	7	16	17	8	8	5	10	11	16	15	12	19	12
1/3−2/3	15	12	15	22	13	13	22	12	16	19	22	13	16
2/3−1	20	12	15	11	17	28	12	19	10	9	17	16	24
1−4/3	13	13	7	14	19	10	10	11	13	9	4	9	6
4/3−5/3	12	10	6	7	10	11	7	10	5	9	8	2	5
5/3−2	2	3	4	5	5	3	5	9	7	4	4	8	5
2−3	4	6	7	6	1	4	7	1	5	6	4	4	4
3−4	1	1	2	1	1	0	1	1	1	3	1	2	0
>4	0	1	1	0	0	0	0	0	1	0	2	1	2

of the third long period indicates that about fifteen spacings should fall in the first one-third interval, and that the number of large spacings should agree with formula (2). This may be partly because incomplete experimental data were utilized in the analysis of I. However, the strong influence of the Hf I data on the combined data for all levels of even configurations in the third long period should be noted (see Table IV of I). The spacing distribution for the even configurations of Hf I alone is given in I, and there is a similar absence of full repulsion. However, Hf I is not typical of the spectra of the third long period, because even configurations are present that are entirely unknown in spectra of the rest of the period. The matrices applicable to these configurations have not been published, so it would be impractical to include calculations for Hf I in the present paper.

In the second long period, the interaction parameters are much smaller, as seen from the parameter set C which is applicable to the $(4d+5s)^8$ configurations of Ru I (Table III). For these parameters, $N\mu^2$ is about 0.09 (Table VII), half the minimum value of 0.2 that is required for the development of full repulsion in random matrices, but well in excess of 0.002, where repulsion disappears. The results in Table IX indicate that for set C there is a decreased number of spacings in the first third interval, though this decrease is not as large as called for by formula (1). The numbers of spacings in the first two-thirds interval and in intervals greater than $2D$ are not decreased, but agree with the predictions of formula (2). Set $C(2)$, obtained by doubling the spin-orbit parameters, shows a decrease of spacings in the first two-thirds interval also, but the number of spacings greater than $2D$ is still unchanged. As expected from the discussion above, the set $C(0)$ with vanishing spin-orbit interaction, has a distribution showing no repulsion effect. Though statistical fluctuations would be too great to allow us to reduce the size of the first interval for this small sample of data, it is possible that in a smaller interval the predictions of formula (1) would be approached more closely. In general, it is expected that repulsion effects can be demonstrated in the smaller spacings when the interactions are weak, if the size of the first interval is decreased accordingly.[19]

The same degree of repulsion shown by the eigenvalues of the matrices for Ru I can be demonstrated in the observed data for even configurations of the second long period. It is important to stay as close as the available data will allow to the right-hand side of the periodic chart, however, because the spin-orbit parameter is very much smaller on the left-hand side of the chart. In this case, the observed data for Ru I that is reproduced in reference 12 was utilized; levels with J values of 0, 5, and 6 were omitted, along with the three highest levels for J value of 3 and the highest level for the J values 2 and 4. In addition, the observed data for Mo I which are reproduced in reference 20 were used; here, levels with J values of 0 and 6 were omitted, along with the lowest and highest level with J value of 3 and the three highest levels with J value of 4. This yielded a set of 92 spacings with a distribution substantially the same as determined from the matrices for Ru I, as shown by the results given in Table X. The over-all total has been renormalized to 74 spacings to simplify the comparison. In I, the spacing distribution obtained for even configurations of the second

TABLE X. Spacing distributions of observed energy levels, for low even configurations. Observed data for the second long period are taken from Mo I and Ru I, for the third long period from Ta II and Re I.

Interval \ Period	Second	Third
0−1/3	12.1	7
1/3−2/3	19.3	15
2/3−1	13.7	22
1−4/3	8.8	8
4/3−5/3	7.3	11
5/3−2	4.0	9
2−3	6.4	2
3−4	2.4	0
>4	0	0

[19] This was pointed out by Racah during a colloquium at the Bureau of Standards.

[20] R. E. Trees and M. M. Harvey, J. Research Natl. Bur. Standards **49**, 397 (1952).

long period shows no evidence of repulsion, even though the first interval is only a fifth of the mean spacing. This is probably because data from both sides of the periodic table were utilized for the work in I.

4. DISCUSSION

The use of eigenvalues to determine spacing distributions makes more data available for the determination. The results of the last section indicate that the calculations will faithfully represent the observations. It is not *a priori* evident that this would be the case, even though the mean error of the calculation is small. A reasonable estimate[3] shows "it is 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)". It is, of course, considered that the shifts for each level are carefully chosen. A mean error of this magnitude in a calculation would probably not, however, lead to a spacing distribution that differs appreciably from that of the observed data, because the errors of theory correspond better to random shifts of the levels. The mean error for the Ru I calculation is ± 63 cm^{-1}, less than 5% of the mean spacing.[12] The mean error for parameter set A is ± 409 cm^{-1}, but if two levels with exceptionally large errors are ignored (i.e., 14 205 and 12 831), the mean error is reduced to ± 200 cm^{-1}, which is about 10% of the mean spacing between eigenvalues.

The simple indications of complexity given in the introduction can be misleading. For instance, the observed data for Hf I include almost all the levels in the even configurations of $(d+p+s)^4$. In the even configurations of other spectra of the third long period (including the isoelectronic spectrum of Ta II), levels containing a p electron are unknown. It is expected that the inclusion of a p electron in the configurations will increase the repulsion as confirmed by the results of I for the odd configurations. This is so because the strong spin-orbit interaction of the p electron is added to the perturbations already present. Along with this, the system of allowed levels is more complex, so that any given level is perturbed by a larger number of other levels. However, as shown in Fig. 5 of I, a full repulsion is not present for the even configurations in Hf I. Consideration of constants of the motion, such as configuration assignments and the SL values, would be necessary before the contradictions that arise from the simple viewpoint could be explained. Approximate procedures for doing this have been utilized in I, namely, the consideration of SLJ sequences instead of simply J sequences. These procedures would not be applicable in the work of the present paper because too few spacings are available.

For the same reason, too much reliance should not be placed on the values of $N\mu^2$ as measures of the degree of repulsion, even though the results agree with what is expected from the random matrices. The uncertainty associated with the significance of $N\mu^2$ is related to the fact that the magnitudes of the nondiagonal elements depend strongly on the particular representation used for the matrices. This in turn can be attributed to the presence of constants of the motion. The largest contribution to $N\mu^2$ arises in the configuration interaction. But it is possible to change the form of the matrices by using the third-order eigenfunctions as a new system of base vectors, and then these contributions to $N\mu^2$ are removed from the nondiagonal elements. As a result, $N\mu^2$ is reduced by about 75%, though the eigenvalues of the matrices are, of course, unchanged. The diagonal elements still show the spacing distribution described by formula (2) (see parameter sets A' and B'), so that there is no simple way of distinguishing the two equivalent forms of the matrices.

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