

K shells at the iodine nucleus is 0.116.¹² To obtain the ratio of L_I to K captures, this value must be multiplied by the square of the ratio of neutrino energies for L_I and K capture, $(E_{L_I}/E_K)^2$. The binding energies of K and L_I electrons in iodine are 33.20 and 5.20 keV respectively; therefore, if the measured ratio of L_I to K captures is taken as 0.30 ± 0.15 , and if E is the decay energy, then $0.30 \pm 0.15 = 0.116[(E - 5.20)/(E - 33.2)]^2$. From this, one obtains $E = 80 \pm_{18}^{60}$ keV. The $\log(ft)$ values corresponding to decay energies of 62, 80, and 240 keV (and to the corresponding L_I/K capture ratios) are 4.9, 5.1, and 6.0. According to the analysis of Fœnberg and Trigg,¹³ the first two of these values definitely fall in the range of allowed transitions, but

¹² M. E. Rose and J. L. Jackson, Phys. Rev. **76**, 1540 (1949).

¹³ E. Fœnberg and G. Trigg, Revs. Modern Phys. **22**, 399 (1950).

$\log(ft)$ should probably be no larger than 5.8, which would correspond to an upper limit of about 180 keV for the decay energy. The proposed decay scheme is shown in Fig. 3.

In a paper¹⁴ published after the completion of the present investigation I. Bergström reported finding L and M conversion lines of a 35.5-keV gamma-ray in an aged sample of 18-hour Xe^{125} , and concluded that they arose from the decay of I^{125} through the 35-keV level of Te^{125} . He also reported the absence of conversion lines of the 109-keV gamma-ray in the Xe^{125} sample. Thus, Bergström's results are in accord with the conclusions drawn in the present paper.

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¹⁴ I. Bergström, Phys. Rev. **82**, 111 (1951).

Configuration Interaction in the Pb III Spectrum

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The Slater and the configuration perturbation parameters were evaluated for configurations of Pb III by fitting the calculated to the observed term values. The wave functions of 52 levels were determined in terms of the (LS) functions, and for many of the levels were found to be linear combinations of the (LS) functions of two or more configurations. The g -values, hyperfine structure interval factors, and isotope shifts evaluated from the precise wave functions are in excellent agreement with the observed values. Thus the theory gives an internally consistent explanation of the spectroscopic properties. Since the isotope shifts were calculated as a field effect the agreement shows that the specific mass effect is relatively unimportant for heavy elements. The values of the shift and hyperfine structure interaction constant for the $6s$ electron obtained from this analysis are 0.50 cm^{-1} and 2.60 cm^{-1} , respectively.

I. INTRODUCTION

MANY calculations have been performed to test Slater's¹ theory of complex spectra for unperturbed configurations. The Slater method gives expressions for the energies of the levels arising from a given electronic configuration in terms of parameters which are integrals of the radial parts of the wave functions. The standard procedure is to evaluate these parameters from the observed energies of some of the levels and check them by calculating the energies of the other levels of the configuration. In a number of cases a more complete check has been effected by using these parameters to calculate the wave functions and from these wave functions evaluating other spectroscopic observables.²⁻⁵ In those cases where the calculated values did

not agree with the observed values the discrepancies were attributed in general to configuration interaction.

The theory of configuration interaction was formulated by Condon,⁶ and Ufford and Shortley.⁷ For the electrostatic interaction they have shown that, in an (LS) representation, there are off-diagonal matrix elements only between those levels of configurations of the same parity that have the same term-type L , the same multiplicity S , and the same J . In the case of perturbed configurations there are an increased number of parameters and it becomes much more important to check the theory by calculating other spectroscopic observables. Little has been done in the way of definite and detailed calculations of these effects.

Bacher⁸ used numerical wave functions to calculate the off-diagonal matrix elements between the p^2 and sd configurations of Mg I and showed that the configura-

¹ J. C. Slater, Phys. Rev. **34**, 1293 (1929).

² D. R. Inglis and N. Ginsberg, Phys. Rev. **43**, 194 (1933).

³ M. F. Crawford, Phys. Rev. **47**, 768 (1935).

⁴ A. T. Goble, Phys. Rev. **48**, 346 (1935).

⁵ J. B. Green and B. Fried, Phys. Rev. **54**, 876 (1938); and others.

⁶ E. U. Condon, Phys. Rev. **36**, 1121 (1930).

⁷ C. W. Ufford and G. H. Shortley, Phys. Rev. **42**, 167 (1932).

⁸ R. F. Bacher, Phys. Rev. **43**, 264 (1933).

tion interaction was adequate to account for the anomalous distribution of the sd levels. Ufford,⁹ Marvin,¹⁰ Many,¹¹ and Rohrlich¹² have performed calculations and each noted that consideration of the configuration interactions improved the general agreement between their calculated and observed energies. Marvin¹⁰ calculated wave functions for Co I and from these determined the effect of the perturbations on the Zeeman g -values. However, in Co I the coupling is near (LS) and since perturbations only occur between similar (LS) terms the g -values are not sensitive to configuration interaction.

A more critical test of the theory would be a detailed calculation for a spectrum in which there are strong configuration interactions, in which the coupling is such that the spectroscopic observables are sensitive to the interactions and finally for which the experimental values are known for comparison with the calculated values. Pb III is such a spectrum. Both its even and odd levels are highly perturbed. A fairly complete term analysis has been made for the spectrum,¹³ and other spectroscopic observables are known for most of the levels. The hyperfine structure interval factors and isotope shifts have been measured by Crawford, McLay, and Crooker¹³ and the g -values by Green and Loring.¹⁴

II. DETERMINATION OF THE PARAMETERS

A. Unperturbed Configurations

To evaluate the parameters appearing in the energy matrix from the observed energies of the levels of an unperturbed configuration the procedure is: (1) To set up the energy matrices for the configuration in terms of the parameters (one matrix for each J value). (2) To equate the sum of the diagonal elements of each of these matrices to the sum of the observed energies of the levels with the corresponding value of J and obtain a set of linear equations for the parameters.

If there are more equations than parameters, a least-square method can be used to find the best values of the parameters. If the number of equations equals the number of parameters, the solution is direct. If there is one less equation than parameters, all parameters can be expressed in terms of one independent parameter. This independent parameter is then varied until the best fit between predicted and observed energies of the levels is obtained when the complete secular equations are solved. For unperturbed configurations the evaluation of the parameters is direct even for complicated configurations.

⁹ C. W. Ufford, Phys. Rev. **44**, 732 (1933).

¹⁰ H. H. Marvin, Phys. Rev. **47**, 521 (1935).

¹¹ A. Many, Phys. Rev. **70**, 511 (1946).

¹² F. Rohrlich, Phys. Rev. **74**, 1372 (1948).

¹³ Crawford, McLay, and Crooker, unpublished data; Phys. Rev. **54**, 313(A) (1938). A. M. Crooker, Can. J. Research **A14**, 115 (1936).

¹⁴ J. B. Green and R. A. Loring, Phys. Rev. **43**, 459 (1933).

B. Perturbed Configurations

If the observed energies of the levels do not fit the energy matrices for each configuration separately a perturbation between configurations is indicated. The procedure for evaluating the parameters is the same as for unperturbed configurations except that the matrices for all configurations involved in the perturbation must be considered together, with the proper off-diagonal elements between them. The number of parameters will be the same as for the individual configurations without perturbations plus the off-diagonal parameters between levels of the same term-type and multiplicity. However, the number of diagonal sums is sharply reduced, by a factor of two or more, since all levels with the same J from all perturbing configurations must be included in one sum where before there were as many sums as configurations. In this case the number of linear equations is considerably less than the number of parameters. Thus there are an increased number of independent parameters. These independent parameters must be varied by successive approximations until the best fit of calculated and observed energies is obtained. This process of successive approximations is extremely complicated. In the Pb III spectrum there are two independent parameters for the even terms and six for the odd terms.

When it is necessary to use the method of successive approximations, often a good first approximation can be obtained by using the unperturbed values of the parameters. When this first approximation is not good, as is the case when the perturbation is appreciable, better estimates of certain of the parameters can be obtained from unperturbed levels of other configurations of the same spectrum or from data for configurations of other stages of ionization of the same element. However, these roughly estimated values of the parameters must be improved before any measure of the perturbation can be obtained.

For two perturbing configurations it was found convenient to split the diagonal sum equation for a given J value into two equations, each corresponding to the diagonal sum of an unperturbed configuration, and to correct these two parts by adding a parameter P to one equation and subtracting it from the other. In this way the diagonal sum for both configurations together is unchanged, while the sum for the individual configurations is altered due to perturbation. This "perturbation parameter" P is a measure of the off-diagonal element between configurations and replaces it as one of the independent parameters in the calculation. This can be extended to the case where more than two configurations are involved. For the odd terms there was a large amount of work in each approximation since it was necessary to expand a fifth- and a sixth-order determinant and solve the resultant secular equations for the energies of the levels. Thus it was important to gain from each calculation as much information

TABLE I. *6snd* configurations.

<i>n</i>	<i>F_d</i>	<i>G_d</i>	<i>a_d</i>	Energy levels <i>J</i> = 2		diff.
				calc.	obs.	
6	155055	-3297	604	151758	151884	125
				158050	157925	
7	202512	726	259	201597	201597	0
				203302	203302	
8	221662	220	158	221301	221307	6
				221944	221938	
9	232295	123	102	232075	232097	22
				232464	232442	

as possible to permit the choice of an improved set of parameters for the next approximation. This was accomplished by leaving the off-diagonal elements between configurations as parameters in the numerical matrices even though, inherently, they were fixed by the choice of "perturbation parameters" *P*. The matrix then was converted to a secular determinant by introducing *W* into the diagonal terms and was expanded

TABLE II. *6snp* configurations.

<i>n</i>	<i>F_p</i>	<i>G_p</i>	<i>a_p</i>	Energy levels <i>J</i> = 1		diff.
				calc.	obs.	
6	82960	10183	12380	63965	64391	425
				75765	75340	
7	174981	664	3400	171290	171081	210
				176970	177181	
8	208400	283	1409	206968	206979	11
				209329	209318	

into several parts, namely, the unperturbed part (i.e., the determinant without contributions due to the presence of the off-diagonal elements between configurations) and parts in which the off-diagonal elements appeared as coefficients. These parts were plotted qualitatively against *W* to show the signs of the contributions of the various parts to the value of the determinant. The resultant of these graphs should be zero at

TABLE III. *6snf* configurations.

<i>n</i>	<i>F_f</i>	<i>G_f</i>	<i>a_f</i>	Energy levels <i>J</i> = 3		diff.
				calc.	obs.	
5	1353	-16	40	190279	189785	495
				190407	190901	
6	665	201	15	214455	214477	22
				214868	214846	

TABLE IV. Energies for *6p²*.

<i>J</i>	calc.	obs.	diff.
2	183024	178432	4600
	160224	164818	
0	194783	188615	6170
	136382	142551	

the values of *W* that are observed energies of the levels. These "perturbation diagrams" are useful in determining the direction in which a parameter must be changed to improve the agreement between the calculated and observed values of the energies, and can be plotted from very approximate values of the parameters.

III. ENERGIES ON LEVELS NEGLECTING CONFIGURATION INTERACTION

The energy matrices for the configurations of Pb III are given in Condon and Shortley's *Theory of Atomic Spectra*.¹⁵ For *sl* configurations the formulas are

$$\begin{aligned}
 {}^3L_{l+1} &= F_l - G_l + \frac{1}{2}la_l \\
 \left. \begin{aligned}
 {}^1L_l \\
 {}^3L_l
 \end{aligned} \right\} &= F_l - \frac{1}{4}a_l \pm [(G_l + \frac{1}{4}a_l)^2 + \frac{1}{4}l(l+1)a_l^2]^{\frac{1}{2}} \quad (1) \\
 {}^3L_{l-1} &= F_l - G_l - \frac{1}{2}(l+1)a_l
 \end{aligned}$$

The matrices for the other configurations can be obtained from the matrices in Table VII by neglecting the off-diagonal elements between configurations.

In evaluating the parameters some levels are fitted exactly while the entire error is forced into the remaining levels. For example in the *sl* configurations the levels with the highest and lowest *J*-values are fitted exactly. The energies of the levels are relative to ¹S₀ of the 5*d*¹⁰6*s*² configuration as zero and are those given by Crawford, McLay, and Crooker.¹³ Tables I to V give the parameters and the calculated and observed energies of the levels which are not fitted exactly. The units are wave numbers (cm⁻¹).

The results in Table I show good agreement between calculated and observed energies for 6*s*7*d*, 6*s*8*d*, and

TABLE V. Energies for 5*d*⁹6*s*²6*p*.

<i>J</i>	calc.	obs.	diff.
1	197100	197319	-200
	183750	184268	-500
	175200	174600	+600
2	198800	199344	-500
	177650	177906	-250
	174600	173986	+600
	154550	154494	+50

¹⁵ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935).

TABLE VI. Energy matrices for Pb III.

Even levels ^a						
J=3		J=1				
Level	³ D ₃ (sd)	Level	³ D ₁ (sd)	³ P ₁ (p ²)		
³ D ₃	F _d -G _d +a _d	³ D ₁	F _d -G _d -(3/2)a _d	R _d -½R _e -½a _p		
J=0						
Level	³ P ₀ (p ²)	¹ S ₀ (p ²)	¹ S ₀ (6s7s)			
³ P ₀	R _d -½R _e -a _p	-√2a _p	D			
¹ S ₀		R _d +(10/25)R _e	F _s +G _s			
¹ S ₀						
J=2						
Level	³ P ₂ (p ²)	¹ D ₂ (p ²)	¹ D ₂ (sd)	³ D ₂ (sd)		
³ P ₂	R _d -½R _e +½a _p	(1/√2)a _p	A	(3/2)½a _d		
¹ D ₂		R _d +(1/25)R _e	F _d +G _d	F _d -G _d -½a _d		
¹ D ₂						
³ D ₂						
Odd levels ^b						
J=0		J=4				
Level	³ P ₀ (d ³ p)	³ P ₀ (sp)	Level	³ F ₄ (d ³ p)	³ F ₄ (sf)	
³ P ₀	-F ₀ -7F ₂	B	³ F ₄	-F ₀ -2F ₂	C	
³ P ₀	+(3/2)a _d +½a _p	F _p -G _p -a _{τp}	³ F ₄	-a _d +½a _p	F _f -G _f +(3/2)a _f	
J=1						
Level	³ P ₁ (sp)	¹ P ₁ (sp)	³ P ₁ (d ³ p)	¹ P ₁ (d ³ p)	³ D ₁ (d ³ p)	
³ P ₁	F _p -G _p -½a _{τp}	½a _{τp}	B	B'		
¹ P ₁		F _p +G _p	-F ₀ -7F ₂	¾√2a _d -¼√2a _p	-¼√3a _d -¼√3a _p	
³ P ₁			+¾a _d +¼a _p			
¹ P ₁				-F ₀ -7F ₂ +20G ₁	(¼√6)a _d -(¼√6)a _p	
³ D ₁					-F ₀ +7F ₂	
					+(5/4)a _d -¼a _p	
J=3						
Level	³ F ₃ (sf)	¹ F ₃ (sf)	³ F ₃ (d ³ p)	¹ F ₃ (d ³ p)	³ D ₃ (d ³ p)	
³ F ₃	F _f -G _f -½a _f	√3a _f	C	C'		
¹ F ₃		F _f +G _f	-F ₀ -2F ₂	(2/√3)a _d +(1/√3)a _p	-(√2/3)a _d -(√2/3)a _p	
³ F ₃			+¾a _d -½a _p			
¹ F ₃				-F ₀ -2F ₂	-(1/√6)a _d +(1/√6)a _p	
³ D ₃				+90G ₃		
					-F ₀ +7F ₂	
					-(5/6)a _d +½a _p	
J=2						
Level	³ P ₂ (sp)	³ P ₂ (d ³ p)	³ D ₂ (d ³ p)	¹ D ₂ (d ³ p)	³ F ₂ (d ³ p)	³ F ₂ (sf)
³ P ₂	F _p -G _p +½a _{τp}	B	9√3(-d'-p')*	9√2(-d'+p')	0	
³ P ₂		-F ₀ -7F ₂				
³ D ₂		+(3√5)(-3d'-p')		(√30)(5d'+p')	(4√7)(-d'-p')	
¹ D ₂			-F ₀ +7F ₂			
³ F ₂			+(√5)(5d'-p')	-F ₀ +7F ₂	-(2√42)(-d'+p')	
³ F ₂					-F ₀ -2F ₂	C
					-(8√5)(-2d'+p')	
						F _f -G _f -2a _f

^a In the matrices for the even terms, p² refers to configuration 5d¹⁰6p², sd to configuration 6s6d, a_d=a_{6d} and a_p=a_{6p}.
^b In the matrices for the odd terms sp refers to the 6s7p configuration, sf to the 6s5f configuration, and d³p to the 5d⁹6s²6p configuration, a_p=a_{6p}, a_d=a_{6d}, and a_f=a_{6f}.
 * Note d'=(1/12√5)a_{6d}, p'=(1/12√5)a_{6p}.

6s9d. We conclude that these levels are not perturbed. The agreement for the levels of 6s6d appears fairly good, but Bacher³ has shown that a negative value of G_d is not probable. A strong perturbation is thus indicated.

Table II shows that the 6s6p and 6s7p configurations

are perturbed. The 6s8p levels are not appreciably perturbed.

Table III shows that the 6s5f levels are strongly perturbed since a negative value of G_{5f} is not acceptable. The agreement for the 6s6f levels is fair, but from the detailed analyses of the other configurations there is

TABLE VII. $6sns$ configurations. T =term value relative to ionization. n^* =effective quantum number.

n	3S_1 sequence		T obs.	1S_0 sequence		diff. ($T_e - T_0$)
	T obs.	$(n - n^*)$		$(n - n^*)$	T calc.	
7	107438	3.967	103739	3.913	102640	-1100
8	59629	3.930	58121	3.877	58270	+150
9	38178	3.914	37612	3.875	37612	0
10	26568	3.903	26278	3.871	26278	0

evidence that the $J=3$ levels are displaced to higher term values by about 22 cm^{-1} . Assuming this displacement the parameters are $a_{6f}=15$ and $G_{6f}=180$. This perturbation of the $J=3$ levels has no appreciable effect on their wave functions.

The parameters calculated for the $6p^2$ configuration are $R_d=170,287$, $\frac{1}{5}R_e=6767$, $a_p=16,176$; and for the $5d^96s^26p$ configuration are $-F_0=176,786$, $F_2=510$, $G_1=586$, $a_{6p}=12,800$, $a_{5d}=8840$.

Tables IV and V show that both the $6p^2$ and $5d^96s^26p$ configurations are highly perturbed. The $J=3$ levels for $5d^96s^26p$ have not been calculated since there are insufficient experimental observations.

IV. ENERGIES CONSIDERING PERTURBATIONS

The energy levels of configurations that are shown by the calculations in the previous section to be perturbed are recalculated taking configuration interaction into account. The off-diagonal elements were calculated explicitly in terms of the integrals of the radial parts of the wave functions. However, it is not necessary to know the exact form of these elements unless they are to be evaluated absolutely, as Bacher⁸ did, from central-field wave functions. Hence in the matrices of Table VI the off-diagonal elements between configurations are merely written as parameters A , B , C , etc.

A. Even Levels

The levels of $6s6d$, $6p^2$, and $6s7s$ perturb each other. If the "perturbation parameters" P are added to the diagonal sum equations for these configurations we obtain 7 linear equations in 9 unknowns. Thus we have two independent parameters which must be varied until the best fit of all calculated and observed energies is obtained. Fortunately a good estimate of one parameter can be made by examining the perturbation of the 1S_0 and 3S_1 levels of the $6sns$ series. The Rydberg-Ritz relationship $n - n^* = a + bT$ predicts that a plot of T , the term value relative to ionization, against $(n - n^*)$, the quantum defect, should be a straight line for an unperturbed sequence. A plot of the data in Table VII shows that the 3S_1 sequence is unperturbed, but that the 1S_0 sequence is perturbed by a level between the $n=7$ and $n=8$ members. Considering the $n=9$ and $n=10$ members of the 1S_0 sequence as unperturbed and drawing a straight line through them the unperturbed positions of the $n=7$ and $n=8$ members can be estimated. Since the displacement of the $n=8$ member from its unperturbed position is very much less than the displacement of the $n=7$ member, as seen from Table VII, the perturbation calculation was simplified by including only the $n=7$ member.

The one remaining independent parameter was then varied and the best fit was obtained with the following values of the parameters: $R_d=167,047$, $\frac{1}{5}R_e=6367$, $a_p=10,500$, $F_{6d}=159,555$, $G_{6d}=1201$, $a_{6d}=605$, and $F_{7s}+G_{7s}=154,983$. The off-diagonal elements are $A=10,300$ and $D=10,210$. The energies and wave functions calculated using these values of the parameters are shown in Table VIII. All levels which were perturbed have been brought into agreement with the observed values to within an average error of 100 cm^{-1} . For the unperturbed calculations the average error was 3600 cm^{-1} . This improvement in the agreement is a good confirmation of the theory of configuration interaction, but a more complete check will be effected by using these wave functions to compute the g -values, hfs interval factors and isotope shifts in Sec. V.

B. Odd Levels

The unperturbed calculations for the odd configurations $6s6p$, $6s7p$, $5d^96s^26p$, and $6s5f$ indicate a mutual perturbation of their levels. It would be extremely difficult to handle a calculation if all four configurations were considered at one time. Only the mutual perturbation of $5d^96s^26p$, $6s7p$, and $6s5f$ was considered. It was possible, however, to make approximate allowances in this calculation for the effect of $6s6p$ on the other three configurations. This was accomplished by examining the perturbation of the $6snp$ series using the Rydberg-Ritz relationship. From this relationship the approximate unperturbed positions of the $6snp$ levels were determined and a set of parameters fitted to these values. The Rydberg-Ritz relationship showed that for $6s6p$ the $J=0$ level is perturbed relatively more than the other levels. Accordingly only the $J=0$ level of $6s6p$ was included in the diagonal sum equations of $6s7p$, $5d^96s^26p$, and $6s5f$. The calculated energies and wave functions of the $6s6p$ levels listed in Table VIII are obtained from the parameters $F_{6p}=83,100$, $G_{6p}=9900$ and $a_{6p}=12,000$; in addition for the $J=0$ level a displacement of -700 cm^{-1} arising from the perturbation by $6s7p$ and $5d^96s^26p$ is included.

When the perturbation parameters P were included in the unperturbed diagonal sums there were 7 equations for 13 parameters (i.e., 6 independent parameters). The value of the magnetic parameter a_{7p} was estimated from a_{6p} and a_{8p} to be approximately 3100. The value of a_{6p} to be used for the $5d^96s^26p$ configuration was known from other configurations to be between 12,000 and 13,000. Liberal use was made of the perturbation diagrams described in Sec. II in arriving, after many trials, at the final set of parameters. The parameters are $-F_0=176,926$, $F_2=572$, $G_1=578$, $a_{6p}=12,900$, $a_{5d}=8780$, $G_{7p}=1100$, $F_{7p}=175,050$, $a_{7p}=3100$, and the

off-diagonal parameters $B=1700$, $B'=-3000$, $C=1400$, also $F_{5f}-G_{5f}-2a_{5f}=190,150$.

An approximate calculation was carried out for the $J=3$ levels, but since the $6s^{\circ}$ level has not been located the calculated values of the energies are much more uncertain. On this account, the wave functions were not calculated for the $J=3$ levels. The $6s^{\circ}$ level would have largely $5d^96s^26p$ character and thus the only strong transitions would be with $5d^96s^26d$ levels. These transitions would be in the ultraviolet and thus difficult to observe. The other $J=3$ levels from the d^9p configuration have more of the $6s5f$ character. It is because of this that their combinations with levels of sd character were sufficiently strong to be observed.

Although these calculations for the odd levels were extremely complicated the agreement as shown by the energy differences in Table VIII is excellent. The error for the perturbed levels has been reduced from an average of approximately 400 cm^{-1} in the unperturbed calculation (Table V) to an average error of less than 100 cm^{-1} in the perturbed calculation. This final error is well within the limit of accuracy of the numerical solution of the determinants. This does not appear to be a large correction, but since the odd configurations overlap each other this perturbation of the energies represents a large perturbation of the wave functions. Thus we have an appreciable intermingling of the character of the interacting levels. The wave functions of the levels can now be calculated from the numerical energy matrices as linear combinations of the (LS) wave functions of the mutually perturbing configurations. The coupling coefficients in the linear combinations are the elements of the transformation matrices which will convert the energy matrix in the (LS) representation to the intermediate system, that is, will diagonalize the energy matrix.⁴

V. CALCULATION OF THE OTHER SPECTROSCOPIC OBSERVABLES

The wave function of a given level is expressed as a linear combination of the (LS) wave functions by means of the (LS) coupling coefficients K or as a linear combination of the (jj) wave functions by means of the (jj) coupling coefficients C . From these coupling coefficients the other spectroscopic observables can be calculated. The values of the wave functions in (LS) representation, and the calculated spectroscopic observables (g -values, hfs interval factors and isotope shifts) appear in Table VIII. The observed values are listed in the table for comparison.

A. g -Values

The Zeeman g -values can be calculated simply from the (LS) g -values and the (LS) coupling coefficients of the levels.¹⁶ The calculation of the g -values using the wave functions determined from the energy levels does

¹⁶ J. B. Green, Phys. Rev. **64**, 151 (1943).

not involve the introduction of any additional experimentally determined quantity. This is a good independent check of the wave functions because in Pb III where the coupling is not near (LS) the g -values are sensitive to the perturbation.

For the most part the calculated g -values are in excellent agreement with the observed g -values. There seems to be a slight discrepancy in the values for the 10_2° and 14_2° levels. The g -value for the former is too high and the latter too low by approximately the same amount. The calculation for these levels is extremely sensitive to the perturbation and it is possible that the evaluation of the intermingling of their characters is slightly in error.

B. Hyperfine Structure Interval Factors

The hyperfine structure (hfs) interval factors of the various levels of the configurations can be calculated by the method of Breit and Wills¹⁷ as functions of the hfs interaction constants of the valence electrons and the coefficients, C 's, of the (jj) wave functions. The hfs interval factor $a(J)$ of a level of a many-electron configuration is a function of the one-electron interaction constants $a(j)$. The formula for a non- s electron as given by Goudsmit¹⁸ is

$$a(j) = \frac{\Delta\nu l(l+1)K(j, Z_i)g(I)}{Z_i j(j+1)(l+\frac{1}{2})\lambda(l, Z_i)1838} = a' \text{ for } j=l+\frac{1}{2} \\ = a'' \text{ for } j=l-\frac{1}{2}. \quad (2)$$

For an s electron the interaction constant is

$$a(s) = \frac{8R\alpha^2 Z_i Z_0^2 K(\frac{1}{2}, Z_i)g(I)}{3n^*31838}. \quad (3)$$

The symbols are defined by Goudsmit. If two configurations interact the wave function for each level is expressed as a linear combination of the (jj) wave functions of all levels with the same J . Thus the hfs interval factor of a given level can be written in terms of the one-electron interaction constants and the (jj) coupling coefficients for that level. The C 's are calculated from the (LS) coupling coefficients K by means of the (jj) \leftrightarrow (LS) transformation matrices.¹⁵ The $a(j)$'s can be calculated from Goudsmit's formulas (2) and (3) if $g(I)$ is obtainable from an unperturbed J level.

The hfs formulas for the p^2 , sf , sd , sp , and $nsn's$ configurations are given by Breit and Wills.¹⁷ The formulas for a d^9p configuration are the same as for a dp configuration and have been calculated for this work. They are

$$A(J=4) = \frac{5}{8}a_d' + \frac{3}{8}a_p', \\ A(J=3) = (1/24)C_1^2(17a_d' + 7a_p') + \frac{1}{2}C_2^2(a_d'' + a_p'') \\ + \frac{1}{8}C_3^2(5a_d' + a_p'') + (1/3)^3 C_1 C_2 a_d''' \\ - (5/9)^3 C_1 C_3 a_p''';$$

¹⁷ G. Breit and L. A. Wills, Phys. Rev. **44**, 470 (1933).

¹⁸ S. Goudsmit, Phys. Rev. **37**, 663 (1931) and **43**, 636 (1933).

where the C 's are defined by the relation,

$$(3)_3 = C_1(5/2, 3/2) + C_2(3/2, 3/2) + C_3(5/2, 1/2),$$

in which $(3)_3$ symbolizes the wave function of a state with $J=3$, $m=3$ in intermediate coupling and $(5/2, 3/2)$ symbolizes the (jj) wave function of the state $J=3$, $m=3$ arising from the $(5/2, 3/2)$ jj -sub group, and so on.

$$\begin{aligned} A(J=2) = & (1/12)C_1^2(11a_d' + a_p') + \frac{1}{2}C_2^2(a_p' + a_d'') \\ & + \frac{1}{6}C_3^2(7a_d' - a_p'') + \frac{1}{4}C_4^2(3a_d'' + a_p'') \\ & + (7/3)^{\frac{1}{2}}C_1C_2a_d''' - (14/9)^{\frac{1}{2}}C_1C_3a_p''' \\ & - \sqrt{2}C_2C_4a_p''' + (2/3)^{\frac{1}{2}}C_3C_4a_d''', \end{aligned}$$

where

$$\begin{aligned} (2)_2 = & C_1(5/2, 3/2) + C_2(3/2, 3/2) \\ & + C_3(5/2, 1/2) + C_4(3/2, 1/2). \end{aligned}$$

$$\begin{aligned} A(J=1) = & \frac{1}{4}C_1^2(7a_d' - 3a_p') + \frac{1}{2}C_2^2(a_d'' + a_p'') \\ & + \frac{1}{4}C_3^2(5a_d'' - a_p'') - (3/5)^{\frac{1}{2}}C_1C_2a_d''' - \sqrt{3}C_2C_3a_p''', \end{aligned}$$

where $(1)_1 = C_1(5/2, 3/2) + C_2(3/2, 3/2) + C_3(3/2, 1/2)$.

A value of $a_{6s} = 2.60 \text{ cm}^{-1}$ is obtained from the hyperfine structure of the 3D_1 and 3D_3 levels of $6s6d$ and $6s7d$. These levels are unperturbed and independent of coupling and give the value of a_{6s} to within 4 percent. Using this value of a_{6s} and Goudsmit's formulas we can calculate the values of the interaction constants for the other electrons. From the term value of $5d^{10}6s$ of Pb IV $n^* = 2.265$ for the $6s$ electron, $Z_i = 78$, $Z_0 = 4$. Thus we obtain from Eq. (3) a value of $g(I) = 0.99(4)$. Substituting this value in Eq. (2) and using for the p electron $Z_i = 78$ and $\Delta\nu_{6p} = 18,000$ we find $a_{6p}'' = 0.52$ and $a_{6p}' = 0.05$. Using also $\Delta\nu_{7p} = 4000$ we obtain $a_{7p}'' = 0.13$ and $a_{7p}' = 0.01$. For the d electron an approximate value of $Z_i = 70$ was used.¹⁹ Thus $\Delta\nu_{5d} = 22,000$ gives $a_{5d}'' = 0.21$ and $a_{5d}' = 0.09$. The other interaction constants a_{6p}''' , a_{7p}''' , a_{6d}''' , a_{6d}' , a_{6d}'' , and a_{6d}''' are all negligible. These values show that the contributions of the $6p$ and $5d$ electrons to the hfs interval factor of a level cannot be neglected relative to the contribution of the $6s$ electron. However, since in general they are appreciably smaller than a_{6s} , they need not be known to the same precision. Hence, the approximate values calculated here are adequate.

Even Levels

The calculated hfs of all the levels are in very good agreement with the observations. For those levels for which the hfs has been resolved the quantitative agreement is quite satisfactory. For those levels whose hyperfine structures have not been resolved the agreement is also satisfactory in that the theory predicts small interval factors.

Odd Levels

The calculated values of hfs interval factors are in good agreement with those measured by Crooker except

¹⁹ E. Fermi and E. Segrè, *Z. Physik* **82**, 729 (1933).

in two respects: Firstly, the values for the 10_2° and 14_2° levels indicate that there is a slight error in the wave functions for these levels as evidenced also from the calculation of their g -values. Secondly, the interval factor given by Crooker for 16_1° , designated $c8_1^\circ$ in his paper, is $\sim -0.2 \text{ cm}^{-1}$ compared to the predicted value $+0.1$. Crooker inferred a negative interval for this level because no Pb^{207} component was directly observable in the patterns of 32384 cm^{-1} ($4_2 - 16_1^\circ$) and 30485 cm^{-1} ($5_0 - 16_1^\circ$), indicating that the stronger Pb^{207} components were merged with the Pb^{206} and Pb^{208} components. This single discrepancy suggested that possibly Crooker's conclusion was in error. Accordingly the structures of these two lines were re-examined with a Leeds and Northrup microphotometer and their density contours reduced to intensity contours. The contour of 32384 cm^{-1} showed that the two clearly resolved components had an intensity ratio equal to the relative abundance of Pb^{206} and Pb^{208} , and that between these two components there was the intensity contribution expected for the Pb^{207} components. The intensity between these two components cannot be ascribed to lack of resolution since on the same plate another two-component pattern with smaller separation showed a much deeper minimum. The hfs separation of 16_1° then must be normal, and smaller than the separation of the level 4_2 since a well-defined Pb^{207} component was not observed between the even isotopic components. An analysis of the intensity contour of 30485 cm^{-1} confirmed this conclusion. Thus the interval factor of 16_1° is $+0.10 \text{ cm}^{-1}$, in agreement with the calculated value.

This comparison forms an independent check on the validity of the wave functions determined from the multiplet structure since effectively only one observable, namely $a_{6s} = 2.60$,²⁰ has been used in addition to the wave functions determined from the energies. The values of the hfs interaction constants of the other valence electrons were calculated by the approximate formulas of Goudsmit.¹⁸ Undoubtedly, by making a slight adjustment in these interaction constants a closer agreement between predicted and observed values could have been obtained. However, the consistency of the theory is more clearly illustrated by using the minimum number of experimentally determined quantities.

C. Isotope Shifts

The theory of isotope shifts in heavy elements was developed by Bartlett,²¹ Rosenthal and Breit,^{22,23} and Racah.²⁴ According to their theory the levels of the lighter isotope will be slightly more stable than the

²⁰ This value leads to a nuclear magnetic moment in good agreement with that obtained by the induction method. Schawlow, Hume, and Crawford, *Phys. Rev.* **76**, 1876 (1949).

²¹ J. H. Bartlett, *Nature* **128**, 408 (1931).

²² J. E. Rosenthal and G. Breit, *Phys. Rev.* **41**, 459 (1932).

²³ G. Breit, *Phys. Rev.* **42**, 348 (1932) and **44**, 418 (1933).

²⁴ G. Racah, *Nature* **129**, 723 (1932).

corresponding levels of the heavier and the shifts between corresponding levels will depend on the type of valence electron, decreasing in order of ns , $np_{1/2}$, $np_{3/2}$, $nd_{3/2}$, etc., with the shift due to the s electron being by far the largest, and decreasing with increasing n for all types of electrons. The shifts for all levels of an unperturbed configuration will be approximately the same since they are due principally to the $6s$ electrons.

When two or more configurations A , B , C , etc., perturb each other the isotope shift of a perturbed level can be calculated as follows.²³ Neglecting the contribution to the isotope shift (I.S.) of all except the $6s$ electrons, the I.S. of all levels of A without perturbation would be $(\text{I.S.})_A$, where $(\text{I.S.})_A$ depends on the number of $6s$ electrons in the configuration; likewise for configurations B , C , etc. Then the isotope shift of the perturbed level is given by

$$(\text{I.S.}) = \sum K_A^2 (\text{I.S.})_A + \sum K_B^2 (\text{I.S.})_B + \dots,$$

where K_A is the (LS) coupling coefficient of a level of configuration A in the wave function of the perturbed level, and so forth. Since the K_A 's and K_B 's, etc., have been determined from the energies of the levels, the isotope shifts can be calculated if the shift per $6s$ electron is known.

The datum for isotope shifts of Pb III in Table VIII is zero shift for the $5d^{10}6s$ configuration of Pb IV. Relative to this datum the configuration $5d^96s^26p$ has one extra $6s$ electron, and $5d^{10}6p^2$ is short one $6s$ electron. The configurations $6snp$, $6snd$, $6snf$, and $6sns$ have the same number of $6s$ electrons as $5d^{10}6s$. Taking the isotope shift per $6s$ electron to be 0.50 cm^{-1} the unperturbed isotope shift is $+0.50 \text{ cm}^{-1}$ for each level of the configuration $5d^96s^26p$, -0.50 cm^{-1} for each level of the configurations $5d^{10}6p^2$, and 0 cm^{-1} for the $6snl$ configurations. For the $6sns$ configurations there will be a small positive shift due to the ns electron.

The excellent agreement between the observed and calculated values of the isotope shifts is perhaps the most direct confirmation of configuration interaction, since without interaction all shifts would be either $+0.50$, -0.50 , or 0 cm^{-1} . Errors of the order of 5 percent are introduced by neglecting the shift due to the $6p_{1/2}$ electron,²⁵ but in general this is smaller than the experimental errors in the measured shifts. The observed isotope shift of a level gives very directly a measure of the perturbation of the level by levels of

other configurations. This calculation also shows that the isotope shifts in Pb III can be quantitatively accounted for on the basis of the field theory alone, and is the best evidence to date that the specific mass effect is relatively unimportant for the heavy elements.²⁵

VI. $6sng$ CONFIGURATIONS

The levels of the even isotopes for the $6sng$ configurations have anomalous distributions. Wolfe's equations,²⁶ which involve an additional parameter can, of course, be fitted to the levels. Using one of the two sets of parameters obtainable by fitting Wolfe's equations the hyperfine structures due to the odd isotope were consistently explained. In this calculation it was necessary to work directly with the F matrices, because the multiplet and hyperfine structures are comparable. However, the values of the parameters required to account for the observed hyperfine structures appear to be anomalous on the basis of the simple theory, since the spin-orbit parameter is positive and appreciably larger than the spin-orbital parameter which is negative. The negative value of the latter suggested that perturbations by levels of configurations in which a core electron is excited should be considered.²⁷ An approximate calculation of the perturbations by levels of $5d^96s^26d$ indicated that they are not the cause of the anomalous distribution. It may be that the anomalous parameters obtained with Wolfe's equations are the result of neglecting the spin-spin magnetic interaction.²⁸ If the latter is included in the formulas a direct comparison cannot be made since there are more parameters than observables. A test would require the evaluation of some of the parameters from numerical wave functions.

VII. CONCLUSIONS

This calculation shows that the theory is capable of giving an internally consistent explanation of multiplet structure, hyperfine structure, isotope shifts, and g -factors; and that remarkably good agreement can be obtained if one is willing to spend sufficient time on the evaluation of the parameters. In principle the theory could be further checked by calculating relative intensities, but this was not done since relative intensities in Pb III have not been measured.

²⁵ M. F. Crawford and A. L. Schawlow, Phys. Rev. **76**, 1310 (1949).

²⁶ H. C. Wolfe, Phys. Rev. **41**, 443 (1932).

²⁷ M. Phillips, Phys. Rev. **44**, 644 (1933).

²⁸ H. H. Marvin, Phys. Rev. **71**, 102 (1947).