

Application of Slater–Condon Theory with Configuration Interaction to the $5d^{10}6s6p$, $5d^96s^26p$, $5d^{10}6s7p$, and $5d^{10}6s5f$ Configurations in Hg I, Tl II, Pb III, and Bi IV

W. C. Martin, Jack Sugar, and Jack L. Tech
National Bureau of Standards, Washington, D. C. 20234
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The calculations were based on fitting radial parameters to the observed energy levels, but with a requirement of regularity in the behavior of each parameter value along the isoelectronic sequence. Some parameters or ratios of parameters were fixed at values based on isoelectronic comparisons or adjusted Hartree–Fock values. The calculated levels, g values, and LS percentage compositions are given for each atom, and comparisons with experimental data are made. The results support new $5d^96s^26p$ levels recently found in Hg I, Tl II, and Bi IV, and one experimental $5d^96s^26p$ level in Pb III is rejected as unreal. The calculated ratio of the lifetimes of the Hg I $5d^{10}6s6p^3P_1^0$ and $^1P_1^0$ levels is compared with the experimental value. Some comparisons of calculated and observed isotope shifts are made for Hg I, Tl II, and Pb III. The leading percentages in the jj coupling scheme are listed for levels having assigned jj names ($5d^96s^26p$ levels in all four atoms and $5d^{10}6s7p$ levels in three atoms).

INTRODUCTION

A large number of experiments involving excited energy levels of Hg I have been carried out over the years, and the spectra of the Hg I isoelectronic sequence have been analyzed¹ through Bi IV. Although probable effects of configuration interaction (CI) have frequently been noted in discussions of various experimental data, no systematic application of intermediate coupling theory with CI appears to have been made to the important configurations throughout the sequence. The lower odd-parity levels belong to the $5d^{10}6snp$ ($n \geq 6$), $5d^96s^26p$, and $5d^{10}6snf$ ($n \geq 5$) family, and the largest perturbations are due to interactions of these configurations.² We first discuss the choice of included configurations and the procedures of our calculations for the odd levels, and then give the detailed results and comparisons with observations for each spectrum.

GENERAL METHOD

The configurations and interactions included in the calculations are shown in Table I. The basic energy matrices for these configurations were recalculated and several interactions added by use of computer programs originally obtained from the Laboratoire Aimé Cotton (Orsay, France). The electrostatic interaction parameters with subscripts are as defined in Condon and Shortley,³ except that we use Racah's reduction $G_3(pd) = \frac{3}{245} G^3(pd)$. The additive parameter common to all levels of a configuration is designated A , A' , etc., according to the configuration. The electrostatic-interaction elements connecting the d^9s^2p configuration with two $d^{10}sp$ configurations and with $d^{10}sf$ were included in the matrices, the numerical coefficients of the radial integrals having been evaluated from formulas derived by Briggs.⁴

The matrix diagonalizations and level-fitting calculations were carried out on the NBS Univac 1108 computer.⁵ The method for adjustment of the free parameters to give a least-squares fit of the levels, as well as the method used to obtain transformations between different coupling schemes, is based on procedures described by Racah.⁶ The standard error given with a parameter value is a measure of the rigidity of the value as defined by the equations and the observed levels; this computed error is not necessarily a good measure of the physical correctness of the value, especially if it corresponds to a very small percentage error. The least-squares adjustments of the parameter values were "converged" in each case only to a point where any indicated further change in each parameter value was small compared to the standard error for the parameter. The parameter values are reported exactly as used in the final diagonalizations, regardless of the standard errors.

For a number of reasons it is not possible to obtain meaningful results for these configurations by merely fitting the observed levels with all parameters free. We found that requiring fairly regular behavior of all parameters along the isoelectronic sequence was the most useful guide. Additional limits on the acceptable values of some parameters were obtained by comparisons with Hartree–Fock⁷ (HF) calculations and with experimental values from atoms in other related sequences. HF values for some of the parameters in Hg I and Pb III are included in Table I.

INTERACTIONS OF $5d^96s^26p$ WITH OTHER ODD CONFIGURATIONS

We did not attempt to include all the significantly interacting odd configurations in the calculations of these spectra. In Hg I, for example, all the $6snp$ configurations with $n \geq 7$ are overlapped and

TABLE I. Parameter values for four odd configurations in the Hg I isoelectronic sequence (units in cm^{-1}).

Config.	Parameter	Hg I		Tl II	Pb III		Birv
		HF	Fitted	Fitted	HF	Fitted	Fitted
$5d^{10}6s6p$	A		$48\,535 \pm 61$	$66\,681 \pm 72$		$83\,581 \pm 76$	$100\,172 \pm 127$
	$G_1(sp)$	9935	$6\,381 \pm 81$	$8\,777 \pm 96$	16275	$10\,422 \pm 102$	$11\,783 \pm 170$
	ξ_p	2101	$4\,288 \pm 75$	$8\,124 \pm 90$	7592	$12\,248 \pm 95$	$16\,758 \pm 160$
	$\lambda\xi_p$		$3\,528 \pm 410$	$7\,420 \pm 344$		$11\,588 \pm 300$	$16\,074 \pm 440$
$5d^96s^26p$	A'		$81\,413 \pm 51$	$127\,454 \pm 55$		$176\,857 \pm 55$	$230\,406 \pm 126$
	$F_2(dp)$	436	415 ± 15	588 ± 14	745	675 ± 16	825 ± 17
	$G_1(dp)$	328	322 ± 12	499.9 ± 9	542	587 ± 24	767 ± 49
	$G_3(dp)$	51	56.4	91.2 ± 10	91	104.4 ± 11	135
	ξ_d	6121	$6\,094 \pm 41$	$6\,857 \pm 39$	8437	$8\,414 \pm 42$	$9\,670 \pm 121$
	ξ_p	3244	$4\,894 \pm 76$	$9\,276 \pm 96$	8945	$13\,168 \pm 93$	$16\,068 \pm 198$
$5d^{10}6s7p$	A''		$70\,904 \pm 56$	$121\,924 \pm 69$		$175\,233 \pm 154$	$230\,460 \pm 150$
	$G_1(sp)$	1067	770 fix	900 fix	1738	$1\,231 \pm 192$	1400 fix
	ξ_p	365	677 ± 73	$1\,856 \pm 75$	2077	$3\,489 \pm 104$	$4\,844 \pm 156$
$5d^{10}6s5f$	A'''		$77\,243 \pm 41$	$136\,236 \pm 53$		$190\,492 \pm 59$	$235\,191 \pm 168$
	$G_3(sf)$		1 fix	100 fix	1154	409 ± 59	$1\,317 \pm 169$
	ξ_f		0 fix	0 fix	12	11 fix	100 fix
CI	$R^2(5d6p, 6s6p)$	-10863	-9000 fix	-11000 fix	-17029	-14000 fix	-17000 fix
	$R^1(5d6p, 6p6s)$	-10565	-9000 fix	-11000 fix	-16181	-13300 fix	-16000 fix
	$R^2(5d7p, 6s6p)$	-3567	-4084 ± 205	-4334 ± 275	-5194	-4923 ± 670	-7651 ± 670
	$R^1(5d7p, 6p6s)$	-3547	-4084	-4334	-4875	-4621	-7181
	$R^2(5d5f, 6s6p)$		550 fix	3549 ± 2030	8219	$10\,428 \pm 950$	$15\,802 \pm 1470$
	$R^3(5d5f, 6p6s)$		382 fix	2468	5448	7242	10973
	$\xi_{6p,7p}$		1700 fix	3880 fix		6540 fix	9010 fix

perturbed by the $5d^96s^26p$ configuration.⁸ However, the strongest interactions of $5d^96s^26p$ are with $5d^{10}6s6p$ and $5d^{10}6s7p$, and we included only these configurations from the $6snp$ family. Our procedure was varied in each case to minimize effects due to the omission of additional perturbing configurations from the calculation.

The parameters for the interaction of $5d^96s^26p$ with $5d^{10}6s6p$, $R^1(5d6p, 6p6s)$ and $R^2(5d6p, 6s6p)$, were fixed at the values in Table I after the calculations for the whole sequence were fairly advanced. All other parameters (internal and interconfiguration) having a large effect on the energy levels were free to vary in the level-fitting adjustments, or were determined by appropriate fixed ratios to freely varying parameters. Inclusion of the $5d^{10}6s6p-5d^96s^26p$ interaction with $R^1(5d6p, 6p6s)$ and $R^2(5d6p, 6s6p)$ fixed at their HF values resulted in unacceptably irregular behavior (along the isoelectronic sequence) of the values obtained for some of the other parameters. A 15–20% reduction of the HF values for R^1 and R^2 in Hg I and Tl II gave reasonably consistent results for the other parameters, both within each spectrum and throughout the sequence. This reduction of these two parameters was then applied to the sequence; for each of the three ions in Table I, the reduction is

about equivalent to using the HF value calculated for the preceding sequence member. Thus, although the two parameters are fixed in each calculation, their values were indirectly influenced by the observed level structures along the sequence. A more direct evaluation of $R^1(5d6p, 6p6s)$ and $R^2(5d6p, 6s6p)$, by allowing them to vary at a fixed ratio in the least-squares calculations, gave very large standard errors (poorly defined parameter values) in each case. The best defined values, obtained in Pb III, were very close to the corresponding fixed values in Table I, but had standard errors about one-half as large as the values themselves.

The relative effect of the $5d^{10}6s6p-5d^96s^26p$ interaction is strongest in Hg I (see below). We believe our procedure has given a more reliable evaluation of this interaction and, consequently, more accurate eigenvectors for the $6s6p$ configuration than were previously obtained.

We have allowed the parameters of the $5d^{10}6s7p-5d^96s^26p$ interaction, $R^2(5d7p, 6s6p)$ and $R^1(5d7p, 6p6s)$, to absorb a considerable part of the otherwise uncompensated perturbations due to the omitted $6snp$ ($n \geq 8$) configurations. As a result, the values accepted for these two parameters are somewhat less regular in the isoelectronic sequence than the values of the other parameters in Table I. In order

to minimize the distortion of these parameters, only R^2 was allowed to vary in the level fitting. In the Hg I and Tl II calculations, we fixed the ratio R^2/R^1 at approximately the HF ratio for Hg I; for Pb III and Bi IV this ratio was fixed at the HF value for Pb III.

The interaction of $5d^96s^26p$ with $5d^{10}6s5f$ is large in Pb III and Bi IV, the values of the two relevant parameters being well defined when their ratio was fixed at approximately the HF value for Pb III (Table I). The corresponding values for Tl II have a large error but fit well into the sequence.⁹ Both parameter values were fixed in Hg I, but the value of $R^2(5d5f, 6s6p)$ was actually obtained from a separate calculation by fitting an observed mutual perturbation of two levels (below). The HF calculations for Hg I $5d^{10}6s5f$ did not easily converge and were abandoned as not needed.

$\zeta_{6p,7p}$ AND THE λ PARAMETER FOR $5d^{10}6s6p$

The existence of accurate experimental data of several types for the levels of Hg I $5d^{10}6s6p$ made it worthwhile to include in the calculations some additional effects for this configuration besides its interaction with $5d^96s^26p$. The spin-orbit energy has matrix elements connecting $5d^{10}6s6p$ with the higher $5d^{10}6snp$ configurations, and we have included the strongest such interaction, that with $6s7p$. The value of the corresponding radial integral $\zeta_{6p,7p}$ is approximately equal to $(\zeta_{6p}\zeta_{7p})^{1/2}$, since it is determined almost entirely in a region near the nucleus where the $6p$ and $7p$ wave functions are practically identical except for a scale factor.¹⁰ The values of $\zeta_{6p,7p}$ in Table I were obtained by a method equivalent to imposing the condition $\zeta_{6p,7p} = (\zeta_{6p}\zeta_{7p})^{1/2}$ in the least-squares adjustments.

Instead of introducing explicit electrostatic interaction between $6s6p$ and the higher $6snp$ configurations, we have used the λ of King and Van Vleck¹¹ as a fourth free parameter to fit the $6s6p$ levels. This parameter is best regarded here as equivalent to an effective operator of mixed electrostatic spin-orbit type.¹² The effect of λ is measured by its deviation from unity, and the values we obtain for the sequence Hg I $6s6p$ through Bi IV $6s6p$ are 0.823, 0.913, 0.946, and 0.959, respectively. These values are, as expected, closer to unity than are the corresponding values obtained by fitting the $6s6p$ levels with no CI effects explicitly included. For example, King and Van Vleck's value of λ for Hg I $6s6p$ was 0.758.

The λ refinement was not used for the $6s7p$ configuration, since the approximations already explained probably have a larger effect on the $6s7p$ eigenvectors than would λ_{7p} . A similar refinement for $5d^96s^26p$ would probably best be accomplished by the use of explicitly term-dependent Slater integrals.

RESULTS FOR Hg I

$5d^{10}6s6p$

The calculated positions, g factors, and compositions¹³ are given in Table II. The indirect effect of the four internal $6s6p$ parameters (Table I) on the levels of the higher configurations was so small compared to their direct effect on the four $6s6p$ levels that the latter were fitted almost exactly by the over-all least-squares procedure. All three of the CI parameters involving $6s6p$ were fixed, as explained above. The inclusion of CI increases the value of $G_1(6s6p)$ by almost 500 cm^{-1} over the value obtained by King and Van Vleck,¹¹ but the fitted value is still much smaller than the HF value. The HF value of ζ_{6p} for $6s6p$ is, however, only one-half the fitted value.

The largest perturbation of the $6s6p$ configuration is a repulsion between the 1P_1 level and each of the two $5d^96s^26p$ levels having large 1P_1 components [$5d^9(^2D_{5/2})6s^26p_{3/2}$ and $5d^9(^2D_{3/2})6s^26p_{1/2}$ in Table II]. The calculated depression of $6s6p^1P_1$ due to interaction with both $5d^96s^26p$ and $5d^{10}6s7p$ is almost 1200 cm^{-1} . The contribution from $5d^96s^26p$ to the composition of the $6s6p^1P_1$ level is calculated to be 4.0%.

This contribution from d^9s^2p probably accounts for a significant part of the 0.015 cm^{-1} by which the (200–202) isotope shift of the $6s6p^1P_1$ level exceeds the corresponding shift of the $6s6p^3P$ levels.¹⁴ If the shift associated with each pure configuration contributes to the net shift of the $6s6p^1P_1$ level in proportion to the configuration percentage,¹⁵ a 4% total from d^9s^2p accounts for 0.010 cm^{-1} of the observed difference in the shifts.

The effect of CI on the calculated g value of the $6s6p^3P_2$ level is of interest because of its bearing on an estimate of the combined diamagnetic and relativistic corrections to the g values of the $6s6p$ levels. Our calculated g values for these levels include the effect of the anomalous magnetic moment of the electron, but no other corrections to the Landé values. The corresponding theoretical g value for the 3P_2 level without CI is 1.50116. Since any unlisted contribution to the composition of this level in Table II is less than 0.0005%, the reduction of the discrepancy between the calculated and observed^{16(a)} g values from 0.00017 to 0.00009 is entirely owing to a 0.019% ($d^9s^2p^3D_2$) component in the eigenvector with CI. The calculated g value is most sensitive to the value of the CI parameter $R^2(5d6p, 6s6p)$; the 1D_2 component rises to 0.03% for a value of $R^2 = R^1 = -11000 \text{ cm}^{-1}$ and passes through zero (with a sign change) at a value of $R^2 = R^1$ between -7000 and -8000 cm^{-1} . It thus appears very probable that the true eigenvector for this level has a 1D_2 component large enough to reduce significantly (from 0.00017) the inferred g -value correction. Our best guess is that the addi-

TABLE II. Calculated levels, g values, and percentage compositions for four odd configurations in HgI. Percentages preceded by asterisks (*) were obtained from eigenvector expansion coefficients having opposite signs to the other components for the level. The best LS names for the $5d^8 6s^2 6p$ levels are indicated by underlined percentages in the appropriate columns.

Name	J	Obs. level (cm ⁻¹)	Calc. level (cm ⁻¹)	$o-c$ (cm ⁻¹)	Obs. g_J	Calc. ^a g_J	% jj	$5d^8 6s^2 6p$ $3P^0$ $1P^0$	$5d^8 6s^2 6p$ $1D^0$ $1F^0$	$5d^8 6s^2 6p$ $3P^0$ $1P^0$	$5d^8 6s^2 6p$ $3F^0$ $1F^0$	$5d^8 6s^2 6p$ $3P^0$ $1P^0$	$5d^8 6s^2 6p$ $3F^0$ $1F^0$
$5d^8 6s^2 6p^3 P^0$	0	37645	37645	0				99.45	0.25	0.25	0.30	0.13	0.30
	1	39412	39411	1	1.48612 ^b	1.4870		96.73	0.31	0.03	0.13	0.08	0.13
	2	44043	44043	0	1.50099 ^c	1.50108		99.08	0.82	0.02	0.08	0.08	0.08
$5d^8 6s^2 6p^3 P^0$	1	54069	54068	1	1.016 ^d	1.0169		2.78	0.19	*3.8	*0.39	0.10	*0.39
	2	68887	69000	-113	1.444	1.444	58	*0.28	50.6	*1.9	0.90	34.7	0.02
$5d^8 6s^2 6p^3 P^0$	3	70932	70834	98	1.0867 ^c	1.0876	99				50.7	*35.8	
	0	69517	69499	18				*0.33	0.24			99.43	
	1	69662	69701	-39	1.474	1.474		*0.09	0.69	*0.02		94.1	*4.6
$5d^8 6s^2 6p^3 P^0$	2	71208	71231	-23	1.452	1.452		0.50	*22.7		*0.94	64.8	
	1	71295	71220	75	1.025	1.025		*0.03	0.93	*3.8		4.1	90.6
	4	76945	76892	53	1.250	1.250	89				88.8		11.2
$5d^8 6s^2 6p^3 P^0$	2	78677	78734	-57	1.117 ^e	1.097	90	*0.12	20.2	*21.0	45.6	*12.5	*0.44
	1	78813	79457	(-644)	1.210 ^e	1.236	81	*0.30	58.1	*23.2		*1.2	*3.0
	3	80128	80137	-9	1.258	1.258	99				*0.34	22.3	
$5d^8 6s^2 6p^3 F^0$	2	77237	77239	-2	0.667	0.667		*0.02	*0.02		0.05		99.9
	3	77239	77243	-4	1.083	1.083						0.01	100.0
	4	77287	77286	1	1.250	1.250					*11.2		88.8
	3	77242	77244	-2	1.000	1.000							*0.02
$5d^8 6s^2 6p^3 F^0$	2	85675	85675		0.749	0.749	96	*0.10	*0.10	0.04	24.2	75.7	*0.01
	1	88760	88784	-24	0.931	0.931	87	*0.01	1.9	62.3			1.5
$5d^8 6s^2 6p^3 F^0$	0	90275	90275				100	*0.22	92.5				*0.27
	3	93156	93156		1.071	1.071	100			*9.1	49.0	42.0 ^f	
	1	93737	93717	20	0.831	0.831	94	0.06	*29.5	*6.8		0.05	*0.10
$5d^8 6s^2 6p^3 F^0$	2	95016	95016		1.092	1.092	98	0.01	*5.5	53.2	26.1	*9.9	0.01
	2	95016	95016		1.092	1.092	98	0.01	*5.5	53.2	26.1	*9.9	0.01

^aThe anomaly in the spin magnetic moment of the electron was taken into account only for g_J factors calculated to more than three decimal places.
^bT. A. M. Van Kleeef and M. Fred, *Physica* 29, 389 (1963).
^cW. W. Smith, *Phys. Rev.* 137, A330 (1965).
^dReference 16(a).
^eAverage of the values reported in e and Ref. 16(c). The uncertainty is about ± 0.005 .
^fThe LS designation for this level does not correspond to its leading component.

tion of any significant CI with $5d^{10}6s6p$ not already included here would further lower the calculated g value.

The g value of the 3P_1 level has also been measured very accurately (Table II). If the four-parameter theory without CI^{11} is fitted to the four $6s6p$ levels, the resulting g value for 3P_1 (1.4887) is 0.0026 greater than the observed value, as compared with the discrepancy of 0.0009 that we obtain. However, the latter disagreement is 10 times larger than our best estimate of the upper limit of the combined diamagnetic and relativistic correction for the g value of the 3P_2 level. Since the equivalent correction for the 3P_1 and 1P_1 levels is supposed to be only slightly larger^{16(b)} than the correction for 3P_2 , most of the 0.0009 discrepancy for the 3P_1 level presumably results from error in its calculated composition. An alternative method of applying the single-configuration method is simply to fit the observed g value for the 3P_1 level.^{16(c)} (The g values for the 1P_1 level calculated by the various four-parameter methods are all within the range allowed by the available measurements.) However, the resulting 3.00% mixture in the LS composition of the two $J=1$ levels is obtained at the expense of the level fit.

Another test of the $6s6p$ wave functions is afforded by the experimental values of the lifetimes $\tau({}^3P_1)$ and $\tau({}^1P_1)$. Only the 1P_1 components in each eigenvector need be considered in the calculations, since both lifetimes are against electric-dipole radiative decay to the $6s^2S_0$ ground level. The King-Van Vleck¹¹ pure-configuration fit predicts a value of 101 for the $\tau({}^3P_1)/\tau({}^1P_1)$ lifetime ratio, as compared with the observed value¹⁷ of $(1.17 \times 10^{-7} \text{ sec})/(1.34 \times 10^{-9} \text{ sec}) = 87 \pm 3$. The 3.00% mixture of the pure-configuration 3P_1 , 1P_1 components, mentioned above, gives $\tau({}^3P_1)/\tau({}^1P_1) = \frac{97}{3} \left(\frac{54069}{39412} \right)^3 = 83.5$, the cubed ratio being that of the wave numbers. In order to obtain this ratio from the compositions in Table II, it is necessary to know the ratios of the dipole transition integrals¹⁸ $I(6s, 6p)$, $I(5d, 6p)$, and $I(6s, 7p)$. With the HF values for these ratios, we calculate¹⁹ $\tau({}^3P_1)/\tau({}^1P_1) = 80.1$, which agrees with observation better than the pure-configuration level-fit ratio. However, our wave functions would require a value of about -12 for the ratio¹⁹ $I(6s, 6p)/I(5d, 6p)$ in order to yield $\tau({}^3P_1)/\tau({}^1P_1) = 84$. The HF value of -4.3 for this transition-integral ratio is unlikely to be in error by a factor of 3; we conclude that a small but real discrepancy exists between our calculation and a value of 87 ± 3 for the lifetime ratio. This discrepancy could well be due to approximations in our calculation.²⁰

$$5d^9 6s^2 6p \text{ and } 5d^{10} 6s 7p$$

The interaction between these two configurations was included early in our calculations, because of

the obvious distortion of $6s7p$. The fitted values of $F_2(dp)$, $G_1(dp)$, and ζ_d are well defined and close to the HF values. The value of $G_3(dp)$ is accurately fixed at a value relative to $G_1(dp)$ based on the Tl II and Pb III results and on scaling the HF value. $G_3(dp)$ occurs only in the matrix for $J=3$, and our calculations at one stage were helpful to Learner and Morris²¹ in their discovery of the two lower levels of Hg I $5d^9 6s^2 6p$ having this J value.

The value of $G_1(6s7p)$ was fixed relative to the fitted value of $G_1(6s6p)$ according to the corresponding ratio in Pb III. The ratio of the adopted value of $G_1(6s7p)$ to the HF value is also about equal in these spectra. The fitted value of ζ_{7p} , $667 \pm 73 \text{ cm}^{-1}$, is consistent with the value $560 \pm 85 \text{ cm}^{-1}$ obtained from the systematic Z dependence of this interaction.²²

The jj structure²¹ of $5d^9 6s^2 6p$ could be surmised from the separation of the four resulting terms (Table II), and is confirmed by the leading percentages in this scheme (given under “% jj ”). The names in Table II are shortened to $(j_1 j_2)_J$ designations in the following discussion. The most appropriate LS names for the $5d^9 6s^2 6p$ levels are also indicated in the table.

The fit of the $d^9 s^2 p$ levels is fairly good except for the $(\frac{5}{2}, \frac{3}{2})_1$ level at 78813 cm^{-1} . Although the calculated leading LS percentage for this level is 58% 3P , its second component of 23% 1P is sufficient to make its interactions with $6s6p {}^1P_1$ and $6s7p {}^1P_1$ stronger than its respective interactions with the two corresponding $6snp {}^3P_1$ levels [note the relative percentages from $6snp {}^1P_1$ and 3P_1 in the composition of the $(\frac{5}{2}, \frac{3}{2})_1$ level]. Part of the explanation is that this $d^9 s^2 p$ level is closer to each of the two $d^{10} snp {}^1P$ levels included in the calculation than to the corresponding 3P levels. An additional factor is that in the LS -representation energy matrix the elements connecting $d^9 s^2 p {}^1P$ with the $d^{10} snp$ terms are -2.3 times the elements connecting the corresponding 3P terms [assuming $R^2(dp, sp) = R^1(dp, ps)$, as for Hg I in Table I]. The strong interaction between the level at 78813 cm^{-1} and the $6snp {}^1P$ series probably explains the previous misnaming of the level as 1P_1 . Since our calculation includes the upward perturbation of the 78813-cm^{-1} level by four lower $6snp$ levels, but omits the corresponding depression due to its interaction⁹ with the $6snp {}^1P_1$ and 3P_1 series members having $n \geq 9$, it is reasonable that the calculated position is too high by a relatively large amount. The experimental position of this level was omitted from the least-squares adjustment to avoid a distortion of the parameters by the uncompensated perturbation, as indicated by parentheses for its deviation from the calculated position.

The (200–202) isotope shift of 0.150 cm^{-1} observed for the $(\frac{5}{2}, \frac{3}{2})_1$ level (relative to the $6s6p {}^3P$ term)

is 37% less than the best available value of the shift for the pure d^9s^2p configuration.¹⁴ Since the total contribution from $6s6p$ and $6s7p$ to the composition in Table II is only 6%, we deduce that the neglected $6snp$ ($n \geq 8$) components would contribute about 30%.

The level at 88760 cm^{-1} , formerly designated $d^9s^2p \ ^3P_1$ is calculated to have 62% 1P_1 purity, but the jj name $(\frac{5}{2}, \frac{1}{2})$ is seen to be best.

The $d^9s^2p \ ^3P_2$ designation was previously assigned to the most appropriate level, 68887 cm^{-1} [referred to here as $(\frac{5}{2}, \frac{1}{2})_2$]. However, this level and the $6s7p \ ^3P_2$ level have a calculated mixture of about 34%. This large mixture is supported by the observed (200–202) isotope shifts of these two levels, 0.174 cm^{-1} for $(\frac{5}{2}, \frac{1}{2})_2$ and $\sim 0.080 \text{ cm}^{-1}$ for the $6s7p \ ^3P_2$ level, both relative to the $6s6p \ ^3P$ levels. The data¹⁴ show that the corresponding shift for the pure $6s7p$ configuration would be only about 0.012 cm^{-1} . Again assuming that the isotope shifts mix according to the configuration percentages, we obtain a predicted shift of 0.160 cm^{-1} for the $(\frac{5}{2}, \frac{1}{2})_2$ level and 0.091 cm^{-1} for the $6s7p \ ^3P_2$ level.

McDermott and Lichten^{16(a)} have measured the g value of a metastable level in HgI having an appearance potential of about 9.0 V. The g value they obtained, 1.0867(5), is in good agreement with our calculated g value for the d^9s^2p level $(\frac{5}{2}, \frac{1}{2})_3$, as shown in Table II. Learner and Morris²¹ have shown that a level at 73119 cm^{-1} , to which the above observed g value was formerly assigned, is almost certainly not real. Their new level at 70932 cm^{-1} is seen to be in satisfactory agreement with the calculated position for the $(\frac{5}{2}, \frac{1}{2})_3$ level. This position explains the metastability of the level quite simply, since the only three even-parity levels that lie lower have J values of 0 or 1. The lowest level having $J=3$ has usually been referred to as $d^9s^2p \ ^3D_3$, even though the major components in the eigenvector obtained by Murakawa²³ for the level agree rather well with our values of 50.7% 3F_3 , 35.7% 1F_3 , and 13.6% 3D_3 . The level best suited for the $d^9s^2p \ ^3D_3$ name (77% pure) has recently been found²¹ at 80128 cm^{-1} . The earlier designation for this missing level had been 3F_3 ; the jj purity is 99% $(\frac{5}{2}, \frac{3}{2})$.

$5d^{10}6s5f$

The quantum-defect plots for the $6snf$ series show perturbation of only a few cm^{-1} or less, except for the $6s5f \ ^3F_4$ level. It thus seems justified to conclude from the generally small internal spreads of the $6snf$ configurations that the unperturbed values of $G_3(6s5f)$ and ζ_{5f} are at most a few cm^{-1} . Since ζ_{5f} is expected to be less than 1 cm^{-1} on theoretical grounds, we fixed these two parameters at the values in Table I.

The $6s5f \ ^3F_4$ level is almost 50 cm^{-1} above the other $6s5f$ levels, and the only possible perturbing level is $5d^96s^26p \ (\frac{5}{2}, \frac{3}{2})_4$ at 76 945 cm^{-1} . The matrix element connecting these interacting levels is $-0.22678 R^2(df, sp)$, and one obtains a value $|R^2| = 529 \text{ cm}^{-1}$ by assuming that the two observed positions arise from mutual displacements of 49 cm^{-1} . The value of R^2 was fixed at a slightly larger value in the over-all calculation (Table I), in order to fit the $6s5f$ levels more exactly. $R^3(df, ps)$ is fixed at a value $R^2/1.44$, corresponding to the ratio adopted for these parameters in Pb III (see below).

The mixing of the two $J=4$ levels (11%) is less than the 14.4% mixture obtained from the original 2×2 matrix, because the over-all least-squares fitting gives the position of the d^9s^2p level at 53 cm^{-1} below the observed position; the discrepancy is within the accuracy of either method. The calculation shows that the other two $6s5f \ ^3F$ levels and the 1F level have high purity.

TI II

The value of $G_1(6s7p)$ was fixed because the fitted value was too small on the basis of comparisons like those already described. The ratio of the adopted value of $G_1(6s7p)$ to the fitted value of $G_1(6s6p)$ agrees with the HF ratio of these quantities (13% less than the corresponding ratio of the fitted values in Pb III).

Both the $6s5f$ and $6s6f$ configurations are distorted by interaction with d^9s^2p , but we again included only $6s5f$ in the calculation. The ζ_{5f} parameter is negligible to our accuracy, and the results are also not very sensitive to the value of $G_3(6s5f)$. We fixed $G_3(6s5f)$ at 100 cm^{-1} as a compromise between the smaller (poorly defined) fitted value and the HF value of 191 cm^{-1} ; note that the fitted value in Pb III is less than one-half the HF value. With the ratio $R^2(df, sp)/R^3(df, ps)$ fixed as before, we obtained rather poorly defined but acceptable values of these parameters from the level fit [note the successive values of $R^2(df, sp)$ in Table I].

The complete LS compositions of the levels are given in Table III, with underlined percentages and asterisks being used as in Table II. The levels of the $5d^96s^26p$ and $5d^{10}6s7p$ configurations in TI II are assigned jj -coupling names, the preference over the LS names being based on the leading jj percentages as listed.

Two observed levels of d^9s^2p , $(\frac{5}{2}, \frac{1}{2})_3$ and $(\frac{5}{2}, \frac{3}{2})_2$, were not entered into the least-squares adjustments. The former level has recently been located²⁴ [at $(112\,116 \pm 5) \text{ cm}^{-1}$] as a limit for absorption series in TI I and was not available when our calculations were completed. The second largest LS component for the $(\frac{5}{2}, \frac{3}{2})_2$ level is 22% 3P_2 , and its strongest calculated interaction results in an upward displacement by $6s7p \ ^3P_2$. The omission

TABLE III. Calculated levels, g values, and percentage compositions for four odd configurations in Tl II.

Name	J	Obs. level (cm ⁻¹)	Calc. level (cm ⁻¹)	$o-c$ (cm ⁻¹)	Calc. g_J	% f_j	5d ⁴ 6s6p		5d ⁴ 6s ² 6p		5d ⁴ 6s7p		5d ⁴ 6s5f			
							3P ⁰	1P ⁰	3D ⁰	1D ⁰	3F ⁰	1F ⁰	3P ⁰	1P ⁰	3F ⁰	1F ⁰
5d ⁴ 6s6p 3P ⁰	0	49451	49450	1			99.56						0.32			
	1	52393	52393	0	1.473		94.32	*5.35					0.14			
	2	61725	61725	0	1.500		99.56		0.01				*0.10			
5d ⁴ 6s6p 1P ⁰	1	75660	75660	0	1.029		5.43	92.76					*0.24	0.01		
5d ⁴ (³ D _{3/2})6s ² 6p _{1/2}	2	110387	110390	-3	1.384	93	*0.25		21.6	*5.4	2.0		0.94			
	3	112116	112033	(83)	1.093	99			15.2		51.0	*33.7				0.06
5d ⁴ 6s _{1/2} 7p _{1/2}	0	119361	119326	35		99	*0.34						99.4			
	1	119576	119610	-34	1.419	94	*0.08	0.33					82.7	*15.4		
5d ⁴ 6s _{1/2} 7p _{3/2}	2	122029	122005	24	1.481	96	0.10						96.1			
	1	122379	122398	-19	1.086	80	*0.05	*0.07	*1.7	1.2	*0.95		11.8	73.1		
5d ⁴ (³ D _{5/2})6s ² 6p _{3/2}	4	124006	124006		1.250	100										
	2	125437	125753	(-316)	1.021	68	*0.08		*17.3	17.3	99.6		*2.8		0.44	
	1	126204	126252	-48	1.239	54	*0.10	*0.20	22.4		*39.9		*5.0	*6.6	*0.24	
	3	128663	128642	21	1.252	99			53.3	*4.2					*0.01	
5d ⁴ (³ D _{3/2})6s ² 6p _{1/2}	2	129158	129119	39	0.864	72	*0.01						*0.08		0.59	
	1	134362	134382	-20	0.897	70		1.15	*1.6	50.3	44.9		0.13	4.6		
5d ⁴ 6s5f ³ F ⁰	3	136115	136103	12	1.083											
	2	136216	136196	20	0.669				*0.08		0.17	0.53			99.23	
	4	136230	136189	41	1.250				*0.13	*0.23	*0.54				99.07	
5d ⁴ 6s5f ¹ F ⁰	3	136263	136336	-73	1.000						*0.44				99.56	
5d ⁴ (³ D _{3/2})6s ² 6p _{3/2}	0	138433	138433			100	*0.11				99.6		*0.32			100.0
	3	142781	142792	-11	1.071	99			*9.1		48.2	41.9 ^a			*0.71	
	1	143612	143483	129	0.857	93	*0.13	0.03	57.5				0.04	*0.24		
	2	145092	145203	-111	1.083	98	0.01		57.6	25.6	*11.6		0.02		0.09	

^aThe LS designation for this level does not correspond to its leading component.

of downward perturbations by $6snp$ ($n \geq 8$) 3P_2 levels probably accounts for a large part of the deviation observed minus calculated (o - c) of this level in Table III. The calculation also omits the depression of $(\frac{5}{2}, \frac{3}{2})_2$ due to interaction with the $6snf$ 3F_2 series, except for $n = 5$. The observed $6s5f$ and $6s6f$ levels indicate that the upward displacements of the $6snf$ 3F_2 levels due to this interaction are the largest perturbations of the $6snf$ series.

The interaction of the $5d^{10}6snp$ 1P_1 series with the $5d^96s^26p$ 1P_1 level at $134\,362\text{ cm}^{-1}$ [named $(\frac{3}{2}, \frac{1}{2})_1$ in Table III] is nicely shown in Ellis and Sawyer's²⁵ quantum-defect plot. (However, the interaction of the $6s7p$ 1P_1 member of this series is strongest with the $5d^96s^26p$ level at $126\,204\text{ cm}^{-1}$, which is mainly 3P_1). The low position of the d^9s^2p $(\frac{3}{2}, \frac{1}{2})_1$ level, compared with the relative position of the corresponding level in Au II d^9p , is not due to interaction with $6s8p$ in Tl II, as suggested by Ellis and Sawyer.²⁵ Since the two $6snp$ configurations included in our calculation both lie below the d^9s^2p $(\frac{3}{2}, \frac{1}{2})_1$ level, the agreement between the observed and calculated positions for $(\frac{3}{2}, \frac{1}{2})_1$ shows that the net effect of interaction with the $6snp$ series is to raise, not lower, the level. The perturbation of this level by the $6snp$ ($n \geq 8$) levels must be relatively small. The main cause of the difference in the level structures of Tl II d^9s^2p and Au II d^9p , which is evident for a number of levels in Ellis and Sawyer's Fig. 3, is the differences in the relative values of the important parameters in the two ions.

The Tl II levels for which isotope shifts have been measured²⁶ include the three $5d^96s^26p$ levels having the largest percentages from $5d^{10}6s7p$ and the corresponding three $5d^{10}6s7p$ levels (Table IV). A comparison of the observed shifts with values calculated by using the percentages in Table III thus affords a test of the predicted configuration mixing. The three pure-configuration shifts given in Table IV were obtained by fitting three observed shifts, one level from each configuration. The relative order of the configuration mixing in the remaining five levels, as indicated by the observed shifts, is reproduced by the calculated shifts. The quantitative agreement is also fairly good. The disagreement for the d^9s^2p $(\frac{5}{2}, \frac{3}{2})_1$ level could well be due to neglected configurations; an additional contribution of about 4% from the $6snp$ configurations to the composition of this level would give agreement with the observed shift.

Pb III

Our results for this ion are given in Table V. The calculation again fits the $6s6p$ levels exactly, essentially by adjustment of the four internal $6s6p$ parameters to the values in Table I. Excluding these four levels and four parameters, we have

18 known levels (of the 20 predicted for the remaining three configurations) determining 13 free-parameter values. The internal consistency of the results is the best of the four spectra. All the observed levels believed to be real were included in the least-squares adjustments, and both of the troublesome parameters $G_1(6s7p)$ and $G_3(5d6p)$ took satisfactory values when allowed to vary.

A fairly well-defined value for $G_3(6s5f)$ was obtained from the fit, as shown. It is likely that neglected interactions have distorted the fitted value to some extent, but we believe the HF value (2.8 times the fitted value) is too large. The HF value of $G_3(6s5f)$ in Bi IV (3070 cm^{-1}) is 2.3 times the fitted value. The $5d^96s^26p$ - $5d^{10}6s5f$ interaction has become large enough in Pb III to give a well-defined value of $R^2(df, sp)$, with its ratio to $R^3(df, ps)$ fixed.²⁷ The resulting values of R^2 and R^3 are seen to agree fairly well with the HF values.

Hume and Crawford² included CI between $5d^96s^26p$, $5d^{10}6s7p$, and $5d^{10}6s5f$ in their calculation for Pb III. Their results were less complete than ours, mainly because their diagonal-sum technique could not be applied in an exact way to the matrix for $J = 3$ [the d^9s^2p $(\frac{5}{2}, \frac{1}{2})_3$ level is not known]. Thus they obtained no values for the $6s5f$ parameters or for $G_3(5d6p)$, and no calculated levels or eigenvectors were reported for $J = 3$. Their values for the other $5d^96s^26p$ parameters, and for the $5d^{10}6s7p$ parameters, are similar to ours. Their values for the CI parameters are equivalent²⁸ to $R^2(5d7p, 6s6p) = -6010\text{ cm}^{-1}$, $R^1(5d7p, 6p6s) = -4985\text{ cm}^{-1}$, and $R^2(5d5f, 6s6p) = 6173\text{ cm}^{-1}$. They reported no value for C' [necessary to obtain

TABLE IV. Observed and calculated isotope shifts for some odd levels of Tl II. Shifts are between the 203 and 205 isotopes, with $6s9s^1S$ as the datum level.

Name	J	Config. shift ^a (cm ⁻¹)	Calc. shift ^b (cm ⁻¹)	Obs. shift ^c (cm ⁻¹)
$5d^{10}6s6p$ $^1P^0$	1	(0.060)	(0.065)	> 0.060
$5d^{10}6s_{1/2}7p_{1/2}$	0	(0.022)	(0.023)	0.023
	1		0.027	0.027
$5d^{10}6s_{1/2}7p_{3/2}$	2		0.035	0.040
	1		0.072	0.058
$5d^9(^2D_{5/2})6s^26p_{3/2}$	2	(0.358)	(0.348)	0.348
	1		0.318	0.302
$5d^9(^2D_{3/2})6s^26p_{1/2}$	1		0.339	0.338

^aValues assumed for theoretically pure configurations.

^bCalculated by assuming that the shifts mix according to the percentages in Table III. Values in parentheses were used to determine the pure-configuration shifts. The value of the assumed shift for the $6s6p$ 1P level is relatively unimportant for the other levels.

^cReference 26.

TABLE V. Calculated levels, g values, and percentage compositions for four odd configurations in Pb III.

Name	J	Obs. Level (cm ⁻¹)	Calc. Level (cm ⁻¹)	o-c (cm ⁻¹)	Obs. g_J	Calc. g_J	% ij	$5d^{10}6s6p$		$3P^0$	$1P^0$	$5d^86s^26p$		$3F^0$	$1F^0$	$3P^0$	$5d^{10}6s7p$	$3F^0$	$5d^{10}6s5f$	
								$3P^0$	$1P^0$			$3D^0$	$1P^0$							
$5d^{10}6s6p^3P^0$	0	60 397	60 398	-1				99.55		0.10										
	1	64 391	64 391	0	1.461			92.00	*7.69	0.10	0.04						0.36			
	2	78 985	78 986	-1	1.500			99.66		0.23							*0.11			
$5d^{10}6s6p^1P^0$	1	95 340	95 340	0	1.040			7.80	91.09	0.03	*0.87						*0.21			
	2	154 494	154 416	78	1.368		96	*0.16		66.7		23.8	*6.6	2.3			0.35			
	3	156 053	156 053		1.096		99					16.2		50.2	*33.4					0.24
$5d^8(^2D_{3/2})6s^26p_{1/2}$	0	170 917	170 837	80			99	*0.38		0.31							99.3			
	1	171 081	171 166	-85	1.38	1.398	92	*0.09	0.27	3.4	0.06	1.0					77.2	*17.9		
	4	173 329	173 343	-14			98													1.95
$5d^8(^2D_{3/2})6s^26p_{3/2}$	1	174 601	174 624	-23	1.14	1.175	59	*0.09	*0.12	51.3	*10.2	16.5					0.14			
	2	177 906	178 017	-111	1.08	1.041	56	*0.05		11.1		*5.6	62.2	15.0			*5.5			0.58
	3	178 957	178 915	42		1.250	99					75.0		*0.80	24.2					*0.04
$5d^8(^2D_{3/2})6s^26p_{1/2}$	2	173 986	174 052	-66	0.97	0.968	45			*15.6		13.1	*3.9	55.0			*11.1			1.2
	1	184 268	184 284	-16	0.96	0.935	52		0.74	*0.56	70.2	14.8					1.3			12.5
	2	176 023	176 036	-13	1.34	1.375	83			*1.1		0.08	1.9	13.5			82.9			0.38
$5d^{10}6s5f^3F^0$	1	177 181	177 136	45	1.15	1.111	69			*13.8	*5.0	*12.5					20.9	47.7		
	3	189 785	189 756	29	1.09	1.081				0.14		*0.56		1.7	3.7					94.0
	2	190 288	190 308	-20	0.67	0.676						*0.99	*0.84	*1.1						97.0
$5d^{10}6s5f^1F^0$	4	190 429	190 433	-4	1.25	1.250								*2.0						98.05
	3	190 901	190 901	0	1.00	1.000														0.01
	0	191 526	191 526				100	*0.08		99.6							*0.33			
$5d^8(^2D_{3/2})6s^26p_{3/2}$	3	196 847	196 874	-27	1.03	1.072	94					*8.3	47.3	38.7*						*5.7
	1	197 319	197 233	86	0.878	0.878	94	0.02	*0.08	*30.8	*13.6	55.2					0.04			*0.25
	2	199 344	199 325	19	1.073	1.073	98	0.01		*5.1		56.3	24.5	*13.1			0.02			0.86

*The LS designation for this level does not correspond to its leading component.

$R^3(5d5f, 6p6s)$], since this parameter occurs only in the matrix for $J=3$.

Another calculation with which a comparison may be made is that²⁹ for Tl III ($5d^96s6p + 5d^{10}7p$). The omission of $5d^{10}6p$ and $5d^{10}5f$ from this Tl III calculation probably accounts for a good part of its rms error³⁰ of 291 cm^{-1} , as compared with the rms error of 101 cm^{-1} obtained here for Pb III. The interactions common to both calculations would in general be expected to take values in Tl III, intermediate between their values in Tl II and Pb III. This is the case for the Tl III values²⁹ of $G_1(6s6p)$, $G_3(5d6p)$, ζ_{6p} , ζ_{5d} , and ζ_{7p} . The values of $F_2(5d6p)$ and $G_1(5d6p)$ in Tl III are consistent with this expectation only if the standard errors of the parameters in the three calculations are allowed for. The values obtained for $|R^2(5d7p, 6s6p)|$ and $|R^1(5d7p, 6p6s)|$ in Tl III were 7100 ± 2660 and $5580 \pm 612 \text{ cm}^{-1}$, respectively. These values are also consistent with the corresponding values in Pb III, in view of the rather large errors.

The effect of the $5d^96s^26p-5d^{10}6s5f$ interaction in Pb III is strongest between $(\frac{5}{2}, \frac{3}{2})_3$ and $6s5f \ ^3F_3$. This is shown by the depression of the 3F_3 level to a position 503 cm^{-1} below 3F_2 , and by the 6% mixture of these two $J=3$ levels. Part of the $6s5f \ ^3F_3-^3F_2$ inversion is also due to a net upward displacement of 3F_2 , mainly by interaction with the $d^9s^2p (\frac{3}{2}, \frac{1}{2})_2$ level.

The calculated position for the $d^9s^2p (\frac{3}{2}, \frac{3}{2})_0$ level is 1354 cm^{-1} below the value 192880 cm^{-1} given² for the observed level. Since the only odd levels having $J=0$ that are not included in the calculation are well above the $(\frac{3}{2}, \frac{3}{2})_0$ level, the calculated position cannot be too low by such a large amount. The 192880-cm^{-1} level is thus almost surely false; all the other unknown odd levels would lie much higher. We find that the interaction of the $6s6p \ ^3P_0$ and $d^9s^2p (\frac{3}{2}, \frac{3}{2})_0$ levels, discussed by Hume and Crawford, gives a mutual repulsion of only $\sim 100 \text{ cm}^{-1}$.

The jj designation for the $d^9s^2p (\frac{3}{2}, \frac{1}{2})_{2,1}$ pair of levels is seen to be less appropriate than the LS names. Each of these levels has a large $(\frac{5}{2}, \frac{3}{2})$ component, and the two nominal $(\frac{5}{2}, \frac{3}{2})_{1,2}$ levels have large $(\frac{3}{2}, \frac{1}{2})$ components. The compositions of the four levels are further complicated by an average contribution of 11% from $5d^{10}6s_{1/2}7p_{3/2}$. Our compositions for these four levels are significantly different from those of Hume and Crawford,² especially for the two levels having $J=2$. Our results are supported by reasonable agreement between the calculated and experimental g values (largest disagreements ± 0.04), whereas the differences between the observed and previously calculated g values² for $(\frac{5}{2}, \frac{3}{2})_2$ and $(\frac{3}{2}, \frac{1}{2})_2$ were 0.18 and -0.17 , respectively.

Hume and Crawford listed observed hfs interval

factors and isotope shifts for Pb III and compared these with calculated values. We recalculated the isotope shifts for the levels in Table V, making the same approximations they used, and obtained agreement with all the observed shifts to $\pm 0.04 \text{ cm}^{-1}$ or better.³¹ In particular, we obtained a shift of 0.44 cm^{-1} for the $d^9s^2p (\frac{3}{2}, \frac{1}{2})_2$ level discussed above, as compared with the observed value of 0.46 cm^{-1} , and with the previously calculated value² of 0.37 cm^{-1} . We have not recalculated the hfs factors.

The average purity of the $5d^96s^26p$ levels in the jj scheme is 91% in Hg I, but only 83% in Pb III. This drop in the jj purity is mainly due to the relatively different effects of the increased nuclear charge on the $5d$ and $6p$ radial wave functions. The HF results give an 11% decrease in the average radial distance for $5d$, compared to a corresponding 30% decrease for $6p$, between Hg I and Pb III. The value of ζ_d increases by a factor of only 1.4, whereas the collapsed $6p$ wave function causes $F_2(5d6p)$ and $G_1(5d6p)$ to increase by an average factor of 1.7 (and ζ_{6p} by a factor of 2.7). The larger electrostatic interactions in Pb III, relative to the ζ_{5d} interaction, decrease the "goodness" of the j values for the $5d^9$ core. This coupling change along the sequence, opposite to that usually expected, is similar to the more rapid changes found for p^5nd (or nf) configurations in the rare-gas sequences.³²

In the LS coupling, the average purity of Pb III $5d^96s^26p$ is 66%. The best LS names are indicated in Table V, the names of the three levels having $J=3$ being different from the previous tentative designations.¹

Bi IV

The observed levels of Bi IV now include the lowest and highest levels of the $5d^96s^26p$ configuration (Table VI).³³ The position of the $5d^{10}6s5f$ configuration relative to the total spread of $5d^96s^26p$ is considerably lower in Bi IV than an extrapolation of this relative position in the first three isoelectronic sequence members would have indicated (Fig. 1). However, Fig. 1 shows that the energies of both configurations behave monotonically with Z , relative to a hydrogenic level for the same ionization stage. The $6s5f$ energy in Hg I is very close to the hydrogenic $4f$ level,³⁴ whereas the Bi IV $6s5f$ energy is more than 20000 cm^{-1} below the hydrogenic $4f$ position for a core-charge of 4 units. The consistencies of the quantum defects of the $5f$ and $6f$ electrons in the Hg I sequence with observed nf defects in other nearby ions is shown in Fig. 2. The trends apparent in Fig. 2 can be understood from consideration of the effective potential for the f electrons³⁴ and the changes in this potential with increasing ionization.^{35,36}

The fixed value of ζ_{5f} in the Bi IV calculations

TABLE VI. Calculated levels, g values, and percentage compositions for four odd configurations in Bi iv.

Name	J	Obs. level (cm ⁻¹)	Calc. level (cm ⁻¹)	$o-c$ (cm ⁻¹)	Calc. g_J	% jj	$5d^1 6s 6p$	$5d^1 6s 6p$	$5d^1 6s 6p$	$5d^1 6s^2 6p$	$5d^1 6s 7p$	$5d^1 6s 5f$		
							$3P^0$	$1P^0$	$3P^0$	$1D^0$	$3F^0$	$1F^0$	$3F^0$	$1F^0$
$5d^1 6s 6p \ ^3P^0$	0	70 963	70 963	0			99.57							
	1	75 926	75 926	0	1.451		89.97	0.08					0.35	
	2	96 423	96 423	0	1.500		99.72	0.04					0.18	
								0.17					*0.11	
$5d^1 6s 6p \ ^1P^0$	1	114 602	114 603	-1	1.050		9.85	*0.61					*0.17	
$5d^1 (^2D_{3/2}) 6s^2 6p_{1/2}$	2	205 551	205 540	-10	1.096	95	*0.12		23.6	*6.6	2.4		0.47	0.03
	3	224 292	225 846	(-1554)	0.809	98	0.01		16.0		50.5	*32.7		0.81
$5d^1 (^2D_{5/2}) 6s^2 6p_{1/2}$	2	237 701	240 863	(-3162)	0.963	40	0.50		8.0	*0.05	65.9		*1.7	13.8
	1	224 600	224 591	9		99	*0.37	60.2	12.8				2.7	21.1
	1	224 600	224 626	-26	1.373	85	*0.10	0.26	3.4				98.9	
								9.4					68.6	*18.0
$5d^1 (^2D_{3/2}) 6s^2 6p_{3/2}$	4	225 617	225 596	21	1.250	85					84.7			15.3
	1	228 127	228 029	98	1.177	56	*0.05	*0.11	18.6				*1.4	19.5
	2	230 637	230 693	-56	1.209	38	0.01		*7.1	37.1 ^a	4.0		39.5	5.8
	3	233 238	233 321	-83	1.205	61			52.1		*0.71	9.2		*37.8
														0.13
$5d^1 6s_{1/2} 7p_{3/2}$	1	231 913	231 880	33	1.106	67	*0.01	*14.6	*11.8		26.8	40.7		1.6
	2	232 627	232 638	-11	1.347	58	*0.14	10.9	*4.1	25.0	0.13		*58.2	
$5d^1 6s 5f \ ^3F^0$	3	233 955	233 988	-33	1.127				23.2		*0.14	17.0		59.5
	2	235 172	235 215	-43	0.692			0.03	*0.56	*6.4	*14.5		*0.01	78.5
	4	235 657	235 548	109	1.250						*15.3			84.7
$5d^1 6s 5f \ ^1F^0$	3	236 518	236 518	0	1.000							0.01		0.35
														99.64
$5d^1 (^2D_{3/2}) 6s^2 6p_{3/2}$	0	247 493	247 463	30		99	*0.05						*0.70	
	3	253 544	253 852	-308	1.071	98			*8.7		48.7	41.1 ^b		*1.6
	1	254 812	254 658	154	0.879	93	0.02	*0.07	*29.2	*16.6			0.06	*0.62
	2	257 039	256 920	119	1.076	99	0.04		56.7	24.8	*13.0		0.04	0.31

^aAlthough the largest single LS component in the calculated eigenvector for this level is from $5d^1 6s 5f \ ^3F^0$, the level belongs mainly to $5d^1 6s^2 6p$, in accordance with the assigned LS and jj names.
^bThe LS name for this level does not correspond to the largest percentage.

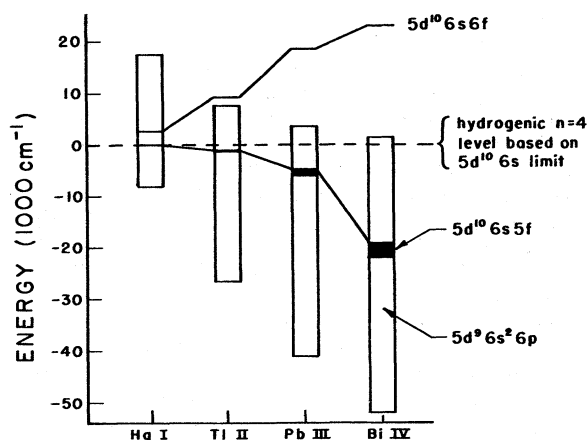


FIG. 1. Relative positions of three configurations in the Hg I isoelectronic sequence. Zero energy for each ionization stage is taken at a position below the $5d^{10}6s$ limit equal to the $4f$ -electron energy in the hydrogenic ion of the same ionization.

(Table I) was based on a HF value of 93 cm^{-1} . The parameters $G_3(5d6p)$ and $G_1(6s7p)$ were handled exactly as in the Hg I calculation, and the values of the various CI parameters have already been discussed.

The two levels assigned to the d^9s^2p ($\frac{3}{2}, \frac{1}{2}$) term in Table VI were excluded from the level-fitting adjustments. The calculated position of the $(\frac{3}{2}, \frac{1}{2})_1$ level includes an upward perturbation of 3047 cm^{-1} , due to interactions with $d^{10}6s7p$ and $d^{10}6s6p$ [mostly due to interaction with the $6s7p$ ($\frac{1}{2}, \frac{3}{2})_1$ level]. This included perturbation is thus about equal to the $o-c$ of -3162 cm^{-1} obtained for this level. The observed level appears to be well supported by the data,³⁷ and we conclude that the depression due to interactions with the $6snp$ ($n \geq 8$) levels (omitted from the calculation) is responsible for much of its large deviation from the calculated position. The strongest interaction of the $(\frac{3}{2}, \frac{1}{2})_2$ level is with the $6s5f^3F_2$ level, the resulting depression of $(\frac{3}{2}, \frac{1}{2})_2$ being 1202 cm^{-1} . Inclusion of the higher $6snf^3F_2$ levels would probably not lower the calculated $(\frac{3}{2}, \frac{1}{2})_2$ position by a further 1550 cm^{-1} , so as to entirely cancel the deviation in Table VI, but it might reduce this deviation substantially.

The configuration mixing of the d^9s^2p ($\frac{3}{2}, \frac{1}{2}$) and $(\frac{5}{2}, \frac{3}{2})$ terms with both the $6s5f^3F$ and $6s7p$ ($\frac{1}{2}, \frac{3}{2}$) terms is so strong that none of the 11 levels of these four terms has greater than 85% configurational purity. The $6s5f^3F_2$ and 3F_4 levels are each calculated to be raised by more than 1500 cm^{-1} , due to interaction with d^9s^2p . A large distortion of the $6s5f^3F$ term results, with 3F_3 being much the lowest level because its calculated upward perturbation is only 175 cm^{-1} .

The interval of each of the $6s7p$ jj doublets is greatly altered by interaction with d^9s^2p . This

interaction depresses the $6s_{1/2}7p_{1/2}$ ($J=1$) level by a calculated 666 cm^{-1} , and the $6s_{1/2}7p_{1/2}$ ($J=0$) level by only 152 cm^{-1} . A calculated interval of 550 cm^{-1} between these levels without the interaction is thus reduced to 35 cm^{-1} (calculated) with the interaction. The observations³⁷ do not give these two levels directly, but instead four hyperfine levels are observed from 224585 cm^{-1} (lower level with $F=\frac{9}{2}$) to 224612 cm^{-1} ($F=\frac{11}{2}$). An observed position of 224600 cm^{-1} was used for both fine-structure levels in our least-squares calculation (Table VI).³⁸ Because of the small fine-structure interval, the intermediate hyperfine level ($F=\frac{9}{2}$) of the three hfs levels based on the theoretical $J=1$ level interacts with the $F=\frac{9}{2}$ level based on the $J=0$ level³⁷; their "unperturbed" separation of 19.4 cm^{-1} is increased to the observed 22.4 cm^{-1} , and their J values are not exact quantum numbers. This hfs perturbation is not due to configuration mixing in the level compositions, but to the fortuitous great reduction of the fine-structure separation induced by CI.

The normal interval for a $s_{1/2}p_{3/2}$ term has the $J=1$ level above the $J=2$ level. If the Bi IV $6s_{1/2}7p_{3/2}$ levels were unperturbed, this interval would be almost 2000 cm^{-1} . The observed inversion of these levels is explained by a calculated depression of 1755 cm^{-1} for the $J=1$ level and an upward perturbation of 979 cm^{-1} for the $J=2$ level, when the interaction with d^9s^2p is included.

The average purity of the d^9s^2p level compositions is 77% in the jj coupling scheme and 60% in the LS scheme. The purity of the $6s6p$ levels in the jj scheme (91% for the two levels having $J=1$) is slightly higher than their LS purity, but we retained the latter scheme for the compositions in Table VI.

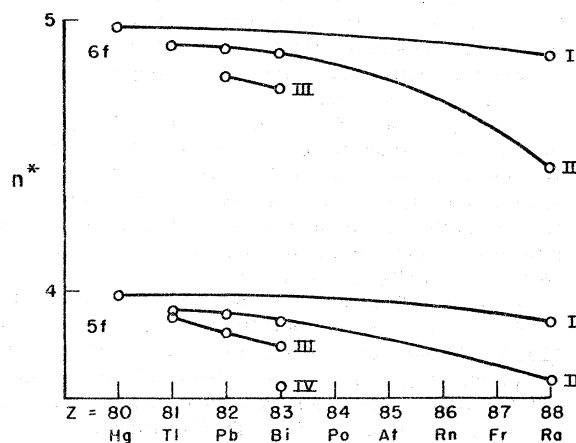


FIG. 2. Observed effective principal quantum numbers (n^*) for $5f$ and $6f$ electrons in the region $Z=80-88$. (n^* is related to the absolute-term value T by $T=RZ_c^2/n^{*2}$, where R is the Rydberg and Z_c is the net charge of the core.) Ionization stages are indicated by Roman numerals for the corresponding spectra.

¹C. E. Moore, *Atomic Energy Levels*, Vol. III, Natl. Bur. Std. (U.S.) Circ. No. 467 (1958) (U. S. GPO, Washington, D. C., 1958). Unless otherwise noted, experimental data quoted here are from this compilation.

²J. N. P. Hume and M. F. Crawford, *Phys. Rev.* **84**, 486 (1951). These authors showed that the interaction of $5d^9 6s^2 6p$ with $5d^{10} 6s 7p$ and $5d^{10} 6s 5f$ is very strong in Pb III. This appears to be the most complete previous calculation for any of these ions.

³E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U. P., Cambridge, England, 1951).

⁴J. S. Briggs, *Rev. Mod. Phys.* **43**, 189 (1971). See Eqs. 6.24 and 6.33.

⁵The computer codes were originally obtained from the Laboratoire Aimé Cotton, Orsay, France.

⁶G. Racah, *Bull. Res. Council Israel, Sect. F*, **8**, 1 (1959).

⁷C. Froese, *J. Chem. Phys.* **45**, 1417 (1966); C. Froese Fischer and M. Wilson, ANLR Report. No. 7404, 1968 (unpublished).

⁸A. G. Shenstone and H. N. Russell, *Phys. Rev.* **39**, 415 (1932).

⁹The increases in the integrals involving the $5f$ electron are much more rapid along the isoelectronic sequence in Table I than are the increases of the other interactions. This is explained by the relatively rapid contraction of the main part of the $5f$ wave function, which in Hg I is almost completely outside the core, to give a much increased overlap with the core functions (see the discussion of Bi IV).

¹⁰We thank R. D. Cowan for confirming this point with a self-consistent field calculation.

¹¹G. W. King and J. H. Van Vleck, *Phys. Rev.* **56**, 464 (1939). The λ parameter allows different radial wave functions for $sp^1 P$ and $^3 P$ in the spin-orbit matrix. It is equivalent in its effect for sp to the spin-other-orbit parameter η introduced by H. C. Wolfe [*Phys. Rev.* **41**, 443 (1932)]. The relation between these parameters is $\eta = \frac{1}{2}\xi(1 - \lambda)$.

¹²Z. B. Goldschmidt (unpublished). The exchange portion of the effective interaction of this type for sp is proportional to the η parameter. Similar interactions for equivalent electrons are discussed by A. Pasternak and Z. B. Goldschmidt [*Phys. Rev. A* **6**, 55 (1972)].

¹³Complete percentages in the jj coupling scheme are available from the authors.

¹⁴J. Blaise, *Ann. Phys. (Paris)* **3**, 1038 (1958). A table of the level shifts between isotopes 200 and 202 appears on p. 1043. The shift of the $d^9 s^2 p (\frac{5}{2}, \frac{3}{2})_2$ level at 78677 cm^{-1} is 0.239 cm^{-1} greater than the shift of the $6s 6p^3 P$ levels; this is the best experimental value for the difference in the shifts to be associated with the pure $5d^{10} 6s 6p$ and $5d^9 6s^2 6p$ configurations.

¹⁵G. Breit, *Phys. Rev.* **42**, 348 (1932); **44**, 418 (1933).

¹⁶(a) M. N. McDermott and W. L. Lichten, *Phys. Rev.* **119**, 134 (1960); (b) A. Lurio, *ibid.* **140**, A1505 (1965); (c) M. W. Swagel and A. Lurio, *ibid.* **169**, 114 (1968).

¹⁷The $6s 6p^3 P_1$ lifetime is now known to about $\pm 1 \text{ nsec}$; see, e.g., J. N. Dodd, W. J. Sandle, and O. M. Williams, *J. Phys. B* **3**, 256 (1970); J. S. Deech and W. E. Baylis, *Can. J. Phys.* **49**, 90 (1971). The value for the $^1 P_1$ lifetime [1.34(4) nsec] is an average quoted, with references, in Ref. 16(c).

¹⁸See, for example, B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Wiley, New York, 1965),

Chap. 3.

¹⁹The matrix of $S^{1/2}$, the square root of the line strength, was evaluated for the transitions from $5d^{10} 6s^2 ^1 S_0$ to the upper configurations in LS coupling (Ref. 18). The matrix has only three nonzero elements, $-\sqrt{2} I(6s, 6p)$, $2I(5d, 6p)$, and $-\sqrt{2} I(6s, 7p)$, for the transitions to $6s 6p^1 P$, $5d^9 6s^2 6p^1 P$, and $6s 7p^1 P$, respectively. This matrix was transformed (by multiplication by the matrix corresponding to the compositions in Table II) to obtain the predicted values of $S^{1/2}$ in intermediate coupling with CI. The value of $\tau(^3 P_1)/\tau(^1 P_1)$ was obtained from its equality to $2.582 S(^1 S_0 - ^1 P_1)/S(^1 S_0 - ^3 P_1)$, which depends only on the ratios of the above transition integrals, and the calculated coefficients. The quoted lifetime ratio results from use of the HF values of $I(6s, 6p)$, $I(5d, 6p)$, and $I(6s, 7p)$, which are -3.55 , 0.818 , and -0.282 a.u. , respectively. [The HF value for $|I(6s, 6p)|$ is definitely too large; the observed value of $\tau(^1 P_1)$ fixes $|I(6s, 6p)|$ at values near 2.0 a.u. If, for example, we fit this observed lifetime with our eigenvectors and the HF values of the integral ratios, we obtain $I(6s, 6p) = -2.07 \text{ a.u.}$]

²⁰A recalculation (with the wave functions in Table II) of the Hg I $6s 6p$ hyperfine structures [Ref. 16(a); also, A. Lurio, M. Mandel, and R. Novick, *Phys. Rev.* **126**, 1758 (1962); K. Murakawa, *J. Phys. Soc. Japan* **20**, 1094 (1965)] and of certain forbidden-line transition probabilities [R. H. Garstang, *J. Opt. Soc. Am.* **52**, 845 (1962)] would be of interest, but we have not done this.

²¹R. C. M. Learner and J. Morris, *J. Phys. B* **4**, 1236 (1971).

²²W. C. Martin, *J. Res. Natl. Bur. Std. (U.S.)* **75A**, 109 (1971).

²³K. Murakawa, *J. Phys. Soc. Japan* **14**, 1624 (1959).

²⁴J. P. Connerade, *Astrophys. J.* **172**, 213 (1972).

²⁵C. B. Ellis and R. A. Sawyer, *Phys. Rev.* **49**, 145 (1936).

²⁶P. Köhler, *Z. Physik* **113**, 306 (1939).

²⁷The ratio R^2/R^3 was fixed at 1.44, whereas the HF ratio is 1.51. The former value is the ratio of the corresponding HF integrals for the $5d^9 6s^2 6p - 5d^{10} 6s 6f$ interaction; we used it throughout the sequence before we noticed that the original HF calculation for Pb III had converged on the $6s 6f$ wave functions, instead of $6s 5f$. Even if the HF ratios were exact, the effect of this small difference on the calculations is well within the uncertainties due to other approximations.

²⁸Only the absolute values and relative signs of the configuration-interaction parameters are determined by the diagonalization and the level-fitting procedures. We reversed the signs of the parameter values (B, B' , and C) given by Hume and Crawford (Ref. 2) to obtain signs for the interaction integrals in agreement with the HF results.

²⁹W. C. Martin and J. Sugar, *J. Opt. Soc. Am.* **59**, 1266 (1969).

³⁰We use "rms error" to refer only to the level fit.

³¹The experimental uncertainty appears to be as large as $\pm 0.05 \text{ cm}^{-1}$ for some levels; see A. M. Crooker, *Can. J. Res.* **A14**, 115 (1936).

³²R. D. Cowan, *J. Opt. Soc. Am.* **58**, 924 (1968).

³³The observed terms in Table VI include five $5d^9 6s^2 6p$ levels from a recent extension of this analysis by C. M. Wu (unpublished). These are the levels of the $(\frac{3}{2}, \frac{3}{2})$ term, and the $(\frac{5}{2}, \frac{1}{2})_3$ level. We thank Professor A. M. Crooker for communicating these levels to us.

³⁴M. G. Mayer, Phys. Rev. **60**, 184 (1941).

³⁵D. C. Griffin, K. L. Andrew, and R. D. Cowan, Phys. Rev. **177**, 62 (1969). See particularly the discussion of Ba II $5p^6nf$ (near the lanthanide collapse). Similar effects occur in the higher ionizations well before each of the f -shell collapses.

³⁶In the neutral atoms coming after the collapse of the $4f$ shell ($Z \cong 58$) and before the beginning of the $5f$ -shell collapse, the energies of nf electrons with $n \geq 5$ are mainly determined by an outer well in the effective potential curve. A simple and basic argument shows that a quantum defect of approximately unity is expected for these excited nf electrons (Ref. 34) (Fig. 2). In the corresponding ions, the increased charge of the core (Z_c) contracts the outer well as $1/Z_c$, up to values of Z_c for which distortion of the well by overlap with core wave functions becomes important (Ref. 35). Thus the average value of the radial distance $\langle r \rangle_{nf}$ also varies as $1/Z_c$, and the quantum defect remains near unity, as long as the core overlap is small. This already rapid contraction is sufficient to explain most of the large increase in the electrostatic interactions involving the $5f$ electron in Table I. If core overlap of the outer well in Bi IV were negligible, $\langle r \rangle_{5f}$ would be equal to (hydrogenic $\langle r \rangle_{4f}$)/ $Z_c = \frac{18}{4}$ bohr. The overlap reduces this average radius from

4.5 to 3.46 bohr, according to our HF results. Thus the observed $5f$ quantum defect is increased from unity to 1.36 (Fig. 2). The effect on the quantum defects of the higher nf series members increases with n (Ref. 35), as shown by comparison of the $5f$ and $6f$ points for particular ions in Fig. 2. The $5f$ defect in Bi IV is almost the same as the $5f$ defect in Ra II; this suggests that the $6f$ defect in Bi IV is probably also near the value for $6f$ in Ra II (1.55), and thus considerably larger than the $5f$ defect. The position of Bi IV $6s5f$ in Fig. 1 is based on an assumed $6f$ defect of 1.50.

³⁷A. B. McLay and M. F. Crawford, Phys. Rev. **44**, 986 (1933). Note that the names of the d^3s^2p ($\frac{3}{2}, \frac{1}{2}$)₁ and ($\frac{5}{2}, \frac{3}{2}$)₁ levels in our Table VI are interchanged from the former designations. This change gives a separation of the two nominal d^3s^2p ($\frac{3}{2}, \frac{1}{2}$) levels that spans all the nominal $6s7p$ and $6s5f$ levels, as well as the four d^3s^2p ($\frac{5}{2}, \frac{3}{2}$) levels. Several of the conclusions of McLay and Crawford about interactions among the odd levels of Bi IV are verified by our calculation.

³⁸According to Ref. 37, the position of the $J=0$ level, without the hyperfine interaction, would be 224 586.1 cm^{-1} and the $J=1$ level would be at 224 606.5 cm^{-1} . The difference between either of these values and 224 600 cm^{-1} is small compared to the rms error of the level fit.

Effects of Multiple Ionization on the Fluorescence Yield of Carbon*

L. H. Toburen

Battelle Northwest Laboratory, Richland, Washington 99352

and

F. P. Larkins

Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168

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Estimated values for the fluorescence yields for various atomic configurations of the carbon atom and the calculated energy shifts of the x rays resulting from these initial configurations are presented. These results are used in conjunction with recent results concerning the probability of multiple ionization as a function of the incident proton energy to give a more detailed analysis of the variable fluorescence yield observed and presented in an earlier publication.

I. INTRODUCTION

A comparison of x-ray and Auger-electron emission cross sections measured for proton ionization of carbon targets has indicated a K -shell fluorescence yield which varies with the bombarding particle energy.¹ This increase in the fluorescence yield of carbon observed for proton energies increasing from 0.3 to 2.0 MeV was attributed to multiple ionization of the target atom. Recent experimental and theoretical work associated with multiple vacancy production and the dependence of the fluorescence yield on the degree of ionization provide a basis for a more detailed analysis of the observed energy dependence.

It was suggested by Toburen¹ that the observed

increase in the fluorescence yield of carbon with increasing proton energy may be due to a higher probability of producing multiple vacancies as the proton energy was increased. Recent measurements of multiple vacancy production as a function of proton energy by Stolterfoht² and by Knudson *et al.*,³ however, do not support this supposition. Stolterfoht's results for the variation in the intensity ratio of the Auger satellite to Auger diagram lines as a function of proton energy show that for the elements carbon, nitrogen, and oxygen the degree of multiple ionization decreases as the proton energy is increased from 0.05 to 0.5 MeV. Similarly, recent measurements of x-ray satellite lines by Knudson *et al.*³ for higher proton energies and for elements of somewhat higher atomic number