

RESONANCE TRANSITION PROBABILITIES IN INTERMEDIATE COUPLING FOR SOME NEUTRAL NON-METALS*

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ABSTRACT

Intermediate coupling calculations are made for the ground configuration and first excited s configuration of neutral Si, Ge, Sn, Pb, P, As, S, Se, Cl, Br, and I. The similar calculations for Si, Ge, Sn, and Pb by Khokhlov are confirmed. Tables of wavelengths, transition probabilities, and spin-orbit parameters are given. Experimental radiative lifetime data are used to provide an absolute scale and thus values of σ^2 . Some radiative lifetime measurements by the phase-shift method in Ge I, Si I, Sn I, Cl I, and I I are reported. The absolute scale accuracy is ± 20 per cent. The relative scale accuracy is thought to be about 10 per cent for strong lines, 31–100 per cent for intersystem lines.

I. INTRODUCTION

The most prominent lines in the ultraviolet spectra of the neutral non-metals are in the transition array: ground state np^m to $np^{m-1}(n+1)s$. We tabulate here dipole transition probabilities in these arrays for neutral Si, Ge, Sn, Pb, P, As, S, Se, Cl, Br, and I, calculated using an intermediate coupling theory (hereafter called "IC"). This theory and some examples are given by Condon and Shortley (1963, chap. xi; hereinafter cited as "TAS") and by Edlén (1964). Garstang (1961, 1962, 1964) and Garstang and Blerkhom (1965) have published outstanding examples of IC and more general calculations for forbidden lines. Calculations by Lurio (1966) for Pb I have been useful in verifying that a sign error was made by Helliwell (1961).

The calculation assumes that the only deviation from LS coupling is caused by the spin-orbit interaction. The matrices of this interaction are given in TAS, page 268, except for some sign conventions mentioned in § VI. The effect of the spin-orbit interaction is to mix levels of the configuration which have the same J . Thus a classification assignment of a level to an LS -coupling state simply names the largest component of the level. The coupling cases LS and JJ are limiting cases of IC. Essentially the same calculations have been done by Khokhlov (1961) for Si, Ge, Sn, and Pb. The inclusion of these transitions here is convenient, requires little extra effort, and allows examination of a change in the manner of determining the best fit. The present calculations yield the same line strengths within about 1 per cent for strong lines and about 5 per cent for weak lines. The elements B, C, N, O, and F are essentially in LS coupling in this context and are treated in the National Bureau of Standards tabulation for the first ten elements by Glennon, Smith, and Wiese (1966). In the s and p configurations of the boron column of the periodic table, there is no mixing of states due to the spin-orbit interactions so that the theory gives LS -coupling results. Some references to work on the neutral inert-gas resonance lines may be found in Anderson (1965) and Lincke and Griem (1966). The bibliography by Glennon and Wiese (1966) is recommended for other references.

II. PROCEDURE

a) Expansion in LS-Coupling Basis

The eigenvalue calculations and matrix multiplications were done numerically and were made practical by use of the matrix subroutines at the Princeton Computer Center.¹

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The Hamiltonian matrices used in the LS -coupling basis are taken to be $\delta_{ij}E_j + \zeta\lambda_{ij}$, where λ_{ij} is the spin-orbit matrix from TAS , $\zeta \equiv \zeta_p$ the spin-orbit parameter, and E_j the unperturbed energy of the j th LS -coupling level. Following Garstang (1964), we treat the E_j 's as independent parameters although in general the Slater integrals (TAS , p. 198) provide relations between them. Given a value of ζ , the E_j 's were found, where possible, by means of trace relationships for each of the J values. The analytical expressions for the diagonal elements in terms of the experimental energies are listed in § VI and also the separate procedure used for the configurations p^2s and p^3s .

Given a value of ζ , the form of the Hamiltonian matrix, and the experimental energies, the eigenvalues were calculated numerically. The rms error $\Delta\zeta$, between the experimental energies and the eigenvalues of the matrix was examined as a function of ζ and the ζ value for least-squares error found. In the few cases where approximate energies

TABLE 1
SPIN-ORBIT PARAMETERS

	Lower Config	$\Delta\zeta/\zeta$ (Per Cent)	ζ^* (cm ⁻¹)	ζ Other	Upper Config.	$\Delta\zeta/\zeta$ (Per Cent)	ζ^* (cm ⁻¹)	ζ Other§
Si.	3p ²	0.12	+ 148	+ 148†	3p4s	2.2	+ 214	178
Ge . .	4p ²	0 7	+ 920	+ 921 5‡	4p5s	0 06	+1110	1110
Sn. . .	5p ²	1 1	+2222	+2247‡	5p6s	0 3	+2650	2648
Pb	6p ²	1.4	+7315	+7355‡	6p7s	0 85	+8920	8908
P. . .	3p ³	0 5	− 325	+ 343†	3p ² 4s	0.2	+ 298	
As . .	4p ³	0 5	−1448	+1441‡	4p ² 5s	5 0	+1794	
S . . .	3p ⁴	0.5	− 387	− 389†	3p ³ 4s	0 4	− 484	
Se	4p ⁴	0 9	−1812	+1808‡	4p ³ 5s	3.2	−2015	
Cl	3p ⁵			..	3p ⁴ 4s	0 1	− 662	
Br.	4p ⁵				4p ⁴ 5s	0.6	−2714	
I	5p ⁵				5p ⁴ 6s	8 7	−5253	

* See § VI for a discussion of signs of ζ .

† Pasternack (1940).

‡ Garstang (1964).

§ Khokhlov (1961).

had to be included in the calculations, the eigenvalues resulting from their perturbation were left out of the comparison. This allows the poorly known level to give an approximate contribution to the mixing of states but eliminates an undue contribution to the mean square error. Table 1 lists the values of ζ obtained in the fit process and the values of the rms error divided by ζ .

b) Line Strengths

Given the “best” value of the spin-orbit parameter from the energy fit, the eigenvectors of the energy matrix form the transformation matrix, U between the LS -coupling basis and the energy states. The matrix of square roots of strengths of transitions between an upper and lower configuration is given by the unitary transformation

$$L_{ij} = U^{\dagger}_{ik} R_{kj} U_{ij}, \tag{1}$$

where R is the matrix of the total dipole moment in the LS -coupling basis. The R matrices are obtainable (with the proper signs) from the tables of Shore and Menzel (1965), which were prepared specifically for use in transformations of the form of equation (1).

The absolute line strengths are

$$S_{ij} = \sigma^2(4l_{>}^2 - 1) (L_{ij})^2, \tag{2}$$

where $(4l_{>}^2 - 1) = 3$ here and is not used by Shore and Menzel but is included in the definition of the usual radial factor σ^2

$$\sigma^2 = (4l_{>}^2 - 1)^{-1} \left(\int_0^\infty P_i P_f r dr \right)^2, \tag{3}$$

where P_i and P_f are the radial wavefunctions resulting from the choice of a (single) central potential.

III. TRANSITION PROBABILITY TABLES

From the line strengths, a value for σ^2 , the experimental energies, and the statistical weights, the transition probabilities given in Tables 2-5 were calculated. The wavelengths listed under the λ heading were calculated from the energies in Moore's tables

TABLE 2
TRANSITION PROBABILITIES, $ps-p^2$

TRANSITION	Si I		Ge I		Sn I		Pb I	
	λ	$A(\text{sec}^{-1})$	λ	$A(\text{sec}^{-1})$	λ	$A(\text{sec}^{-1})$	λ	$A(\text{sec}^{-1})$
$^1P_1-^1S_0$	3907	145(5)*	4228	131(5)	4526	143(5)	5007	130(5)
$^1D_2$	2882	181(6)	3040	172(6)	3263	174(6)	3574	124(6)
$^3P_2$	2453	608(3)	2590	169(4)	2791	517(3)	2578	569(5)
$^3P_1$	2444	700(3)	2534	656(4)	2662	145(5)	2403	258(5)
$^3P_0$	2440	747(3)	2499	573(4)	2547	946(4)	2023	606(4)
$^3P_2-^1D_2$	2968	224(2)	3126	104(4)	3332	897(4)	3741	299(5)
$^3P_2$	2514	124(6)	2652	129(6)	2841	131(6)	2664	118(6)
$^3P_1$	2505	418(5)	2593	464(5)	2707	561(5)	2477	832(5)
$^3P_1-^1S_0$	4104	157(3)	4687	868(3)	5633	875(3)	17181	989(1)
$^1D_2$	2989	222(4)	3270	146(5)	3802	150(5)	7231	410(3)
$^3P_2$	2529	673(5)	2755	656(5)	3176	748(5)	4059	560(5)
$^3P_1$	2520	405(5)	2692	360(5)	3010	308(5)	3641	188(5)
$^3P_0$	2515	545(5)	2652	531(5)	2864	565(5)	2834	719(5)
$^3P_0-^3P_1$	2525	163(6)	2710	163(6)	3035	159(6)	3685	101(6)

* Numbers in parentheses are powers of 10

(1949-1958) and may differ slightly from measured values. The numerical form of the formula connecting the Einstein A 's with the λ 's, L 's, and S_{ij} was taken from Allen (1963). The transitions are listed in groups with common upper levels to facilitate the computation of the radiative lifetimes and branching ratios.

IV. THE ABSOLUTE SCALE

The value of σ^2 chosen for each element is given in Table 6 along with the experimental data used. The choice is meant to correspond to reality, as determined largely by radiative lifetime measurements. Those lifetimes marked phase have been measured in our laboratory using the phase-shift method described in the references in the footnotes. Table 7 reports for the first time some phase shift determinations of lifetimes in Ge, Sn, Si, Cl, and I. A liberal estimate of maximum systematic error in these values is ± 20 per cent. The lifetime of the spin change line I 1, 1830 Å, is somewhat more uncertain because it suffers from cascading with a lifetime similar to its own upper level. The measurements in Table 7, except Si I, are for resolved lines of multiplets, whereas our previously reported lifetimes are for unresolved multiplets. It can be seen that as the spin-orbit interaction causes an expected difference of lifetimes in a multiplet, the wavelength splitting becomes resolvable with our 10 Å monochromator.

TABLE 3
TRANSITION PROBABILITIES, p^2s-p^3

TRANSITION	P I		As I		TRANSITION	P I		As I	
	λ	$A(\text{sec}^{-1})$	λ	$A(\text{sec}^{-1})$		λ	$A(\text{sec}^{-1})$	λ	$A(\text{sec}^{-1})$
p^2s-p^3					p^2s-p^3				
$^2S_{1/2}-^2P_{3/2}$	≈ 1951	215(6)	1860	160(6)	$^2P_{1/2}-^2P_{3/2}$	2556	300(5)	2900	298(2)
$^2P_{1/2}$	≈ 1950	112(6)	1845	106(6)	$^2P_{1/2}$	2554	714(5)	2369	250(4)
$^2D_{3/2}$	≈ 1705	335(3)	1618	259(4)	$^2D_{3/2}$	2150	318(6)	2351	151(3)
$^4S_{3/2}$	≈ 1429	689(1)	1381	172(2)	$^4S_{3/2}$	1728	148(3)	1882	126(6)
$^2D_{3/2}-^2P_{3/2}$	2155	173(5)	2372	346(5)	$^4P_{5/2}-^2P_{3/2}$	2660	41(0)	2920	612(4)
$^2P_{1/2}$	2154	485(5)	2346	191(5)	$^2D_{5/2}$	2224	881(2)	2881	305(5)
$^2D_{5/2}$	1859	226(5)	2004	104(4)	$^2D_{3/2}$	2223	536(1)	2364	174(6)
$^2D_{3/2}$	1859	254(6)	1991	131(6)	$^4S_{3/2}$	1775	217(6)	1890	459(4)
$^4S_{3/2}$	1535	815(1)	1644	387(3)	$^4P_{3/2}-^2P_{3/2}$	2678	130(3)	3034	120(4)
$^2D_{5/2}-^2P_{3/2}$	2155	579(5)	2370	253(5)	$^2P_{1/2}$	2676	274(2)	2992	256(3)
$^2D_{5/2}$	1859	264(6)	2003	144(6)	$^2D_{5/2}$	2236	617(3)	2457	563(4)
$^2D_{3/2}$	1859	232(5)	1990	220(5)	$^2D_{3/2}$	2236	128(3)	2438	777(3)
$^4S_{3/2}$	1535	440(2)	1644	218(4)	$^4S_{3/2}$	1783	214(6)	1938	115(6)
$^2P_{3/2}-^2P_{3/2}$	2536	951(5)	2781	441(5)	$^4P_{1/2}-^2P_{3/2}$	2689	406(2)	3121	608(3)
$^2P_{1/2}$	2535	200(5)	2746	151(5)	$^2P_{1/2}$	2687	391(2)	3076	872(3)
$^2D_{5/2}$	2137	283(6)	2289	163(6)	$^2D_{3/2}$	2243	403(3)	2494	108(5)
$^2D_{3/2}$	2136	211(5)	2272	783(2)	$^4S_{3/2}$	1788	213(6)	1973	108(6)
$^4S_{3/2}$	1719	263(3)	1831	225(4)					

* The $^2S_{1/2}$ energy for P I was estimated to be 70000 cm^{-1} .

TABLE 4
TRANSITION PROBABILITIES, p^3s-p^4

TRANSITION	S I		Se I		TRANSITION	S I		Se I	
	λ	$A(\text{sec}^{-1})$	λ	$A(\text{sec}^{-1})$		λ	$A(\text{sec}^{-1})$	λ	$A(\text{sec}^{-1})$
p^3s-p^4					p^3s-p^4				
$^1P_1-^1S_0$	1782	714(6)	1995	456(6)	$^3D_3-^1D_2$	1706	179(3)	1899	259(4)
$^1D_2$	1448	554(6)	1588	361(6)	$^3P_2$	1474	316(6)	1607	230(6)
$^3P_0$	1287	169(1)	1428	214(4)	$^3D_2-^1D_2$	1707	162(1)	1914	497(4)
$^3P_1$	1284	78(0)	1417	227(4)	$^3P_1$	1483	220(6)	1671	112(6)
$^3P_2$	1277	115(3)	1378	822(4)	$^3P_2$	1474	918(5)	1617	110(6)
$^3P_2-^1D_2$	1472	315(4)	1611	360(5)	$^3D_1-^1S_0$	2191	419(3)	2549	369(4)
$^3P_1$	1302	133(6)	1435	133(6)	$^1D_2$	1707	487(3)	1919	490(4)
$^3P_2$	1296	328(6)	1396	176(6)	$^3P_0$	1487	162(6)	1691	882(5)
$^3P_1-^1S_0$	1819	630(2)	2051	182(5)	$^3P_1$	1483	137(6)	1675	114(6)
$^1D_2$	1473	530(3)	1623	343(5)	$^3P_2$	1475	110(5)	1621	105(5)
$^3P_0$	1306	169(6)	1456	157(6)	$^3S_1-^1S_0$	3017	116(2)	3503	122(3)
$^3P_1$	1303	111(6)	1445	698(5)	$^1D_2$	2170	489(2)	2414	754(3)
$^3P_2$	1296	179(6)	1405	898(5)	$^3P_0$	1826	725(5)	2063	480(5)
$^3P_0-^3P_1$	1303	457(6)	1449	319(6)	$^3P_1$	1820	221(6)	2041	140(6)
$^1D_2-^1D_2$	1667	653(6)	1855	422(6)	$^3P_2$	1807	385(6)	1961	299(6)
$^3P_1$	1453	346(3)	1626	123(5)	$^5S_2-^1D_2$	2305	3(0)	2590	472(0)
$^3P_2$	1444	225(4)	1575	152(5)	$^3P_1$	1915	128(2)	2165	118(3)
					$^3P_2$	1900	447(2)	2076	768(3)

TABLE 5
TRANSITION PROBABILITIES, p^4s-p^5

TRANSITION p^4s-p^5	Cl I		Br I		I I	
	λ	$A(\text{sec}^{-1})$	λ	$A(\text{sec}^{-1})$	λ	$A(\text{sec}^{-1})$
$^2S_{1/2}-^2P_{1/2}$.	≈ 1122	381(5)	1385†	302(5)	1594	114(6)
$^2P_{3/2}$	≈ 1111	604(5)	1318†	239(5)	1421	138(4)
$^2D_{3/2}-^2P_{1/2}$	1201	209(6)	1358	156(6)	1702	205(6)
$^2P_{3/2}$	1189	282(5)	1293	461(4)	1507	177(5)
$^2D_{5/2}-^2P_{3/2}$	1189	243(6)	1294	174(6)	1515	205(6)
$^2P_{1/2}-^2P_{1/2}$	1352	326(6)	1532	195(6)	1799	211(6)
$^2P_{3/2}$	1336	174(6)	1450	134(6)	1583	207(6)
$^2P_{3/2}-^2P_{1/2}$	1364	708(5)	1575	199(5)	1845	692(4)
$^2P_{3/2}$.	1347	417(6)	1489	166(6)	1618	134(6)
$^4P_{1/2}-^2P_{1/2}$.	1390	173(4)	1583	820(4)	1876	287(4)
$^2P_{3/2}$.	1373	515(3)	1495	212(4)	1642	370(5)
$^4P_{3/2}-^2P_{1/2}$..	1397	107(4)	1634	100(5)	2062	296(4)
$^2P_{3/2}$	1380	909(4)	1541	128(6)	1783	271(6)
$^4P_{5/2}-^2P_{3/2}$	1390	226(3)	1577	191(4)	1830	160(5)

* The $^2S_{1/2}$ energy for Cl I was estimated to be 90000 cm^{-1}
† This classification of the $^2S_{1/2}$ level in Br I is questionable.

TABLE 6
SOURCES OF ABSOLUTE SCALE

Element	λ	Exper. τ (nsec)	σ^2 Exper.	σ^2 Adopted	σ^2 Other	τ Calculated
Si I	{2505 2514-15}	6 1* 6 0†	0 642} 0 646}	0 65	.	{ 6.02 6 02- 6 08
Ge I	{3040 2593}	4 4† 6 0†	0 913} 0 759}	0 8		{ 5.02 5 68
Sn I	{3176 3035 2707}	6 0† 6 0† 4 7†	1 03} 1.15} 1 19	1 1 ..	{1.03† 1 04† 0 90†	6.28 5 62 5 09
Pb I	{2833 2022}	5.75§ 4 99	1.47} 1 13}	1 25		{ 6.80 4 42
P I	{1859 1775 2136}	2.9* 4 0* 2.4*	0.605} 0 689} 0 594}	0 60		{ 2.89 4 60 2 38
As I				0 42#		
S I	{1807 1666}	1 5* 1 5*	0 490} 0.506}	0 50		{ 1 47 1 52
Se I.				0 48#		
Cl I .	1335	2 0†	0 202	0 202		2 0
Br I				0 19#		
I I	{1783 1830}	3 6† 80±30†	0 407 0 31±0 12}	0 40		{ 3 66 63

* Phase/life, Savage and Lawrence (1966). § Level crossing, Saloman and Happer (1966).
† Phase/life, Table 3 || Level crossing, Saloman (1966).
‡ Lawrence, Link, and King (1965). # Theoretical, Lawrence (1967).

The experimental values available for comparison with the calculations are clearly limited. However, general agreement is seen between calculated and measured relative lifetimes.

The lifetimes of the $^1P_1$ and $^3P_0$ states in Pb I are well known from level-crossing measurements as shown in Table 7. Comparing calculated and measured lifetimes, we find that

$$[\tau(^3P_1)/\tau(^1P_1)]_{\text{calc}}/[\tau(^3P_1)/\tau(^1P_1)]_{\text{meas}} = 1.34 \pm 0.06.$$

Thus for heavy atoms we may expect errors on the order of 30 per cent or more, though this may be an overgeneralization.

We have been unable as yet to measure the appropriate radiative lifetimes of As, Br, and Se because of technical difficulties. Values of σ^2 were calculated for these transition arrays using numerical solutions of the radial Schrodinger equation as described by Lawrence (1967). For third- and fourth-row elements these central field σ^2 values agree quite well with the experimental values determined here.

TABLE 7
PHASE-SHIFT LIFETIMES NOT REPORTED ELSEWHERE

El	Gas	λ	τ (nsec) ± 15 Per Cent	β/T	Nominal T
Si I	Si Cl ₄	2514-15*	6 0	0.01	100
Ge I	Ge Cl ₄	{ 3040	4 4	014	100
		{ 2593	6 0	01	100
Sn I	Sn Cl ₄	{ 3176	6 0	01	100
		{ 3034	6 0	015	100
		{ 2707	4 7	012	100
Cl I	C Cl ₄	{ 1335	2 0	0 013	50
		{ 1390	1500	Unknown	
I I	I F ₅	1783	3 6		50
I I	I F ₅	1830	90 $\pm$ 30	Unknown	

* Unresolved multiplet

V. ACCURACY

The $\Delta\zeta/\zeta$ values of Table 1 are the rms percentage residual error in the fit and generally indicate a good fit. The excited states seem to fit less well than the ground configurations. The comparison of ζ values with those of other authors, who use different weighting procedures, shows that the discrepancies are generally on the order of $\Delta\zeta$ or less. The strongest effect that the value of ζ itself has on the calculated line strengths is on the intersystem lines. Typically, $S \propto \zeta^2$ for these lines. Thus on the order of 2 per cent error is caused by the uncertainty in ζ , except for As, Se, and I.

However, several other perturbations on the central field, electrostatic, approximation have been neglected. The weak-line strengths are especially susceptible to admixture of "strong transition" states. The hook measurements of relative f -values in Si I and Ge I by Slavenas (1964) allow examination of this problem. If we multiply the hook values, f_{rel} , by 1.57×10^{-3} for Si I and by 1.61×10^{-3} for Ge I, the values for the non-spin-change lines agree with the present calculation within 5 per cent. On this scale, the measured f -values for the Ge I intersystem lines $\lambda 2590$, $\lambda 2534$, $\lambda 2499$, $\lambda 3126$, and $\lambda 3270$ are factors of 1.9, 0.9, 1.3, 1.8, and 1.2, respectively, larger than the present calculations.

Further, in these examples, the weaker the line, the larger the deviation. Thus the inter-system lines can be expected to have errors on the order of factors of 2.

Since the level lifetimes and hence the σ^2 values used here are determined mostly by the strong transitions, the absolute scale calibration will not suffer from problems with the weak lines.

VI. DIAGONAL MATRIX ELEMENTS

There are five separate Hamiltonian matrix forms involved in the cases treated here. The analytical forms of the diagonal elements are listed below in terms of the experimental energies.

In the matrices for p^3 and p^3s , the spin-orbit parameter does not appear on the diagonal and hence the eigenvalues are functions of ζ^2 . It follows from Garstang (1961), Obi and Yanagawa (1955), and Shore and Menzel (1965) that a consistent phase convention is obtained for these cases by using a negative ζ and the matrices of TAS , although ζ is usually defined as a positive quantity. Similarly, matrices involving more than half-filled shells, p^{6-m} , are formally the same as the corresponding partially filled shells, p^m , but with ζ replaced by $-\zeta$. The sign discrepancies in Table 1 are traceable to such sign conventions and the signs are consistent with the matrices used.

Let us denote the experimental energy of an assigned level by $E(^{2S+1}L_J)$ and the sum of energies over the levels of a given J by E_J . In the following, each LS -coupling level is in brackets along with the expression for the corresponding diagonal element, the level designation and the diagonal expression being separated by a comma.

a) p^2 or p^4

We call $E(^3P_1) \equiv E$. The diagonal expressions are $[^3P_1, E]$, $[^1D_2, E_2 - E - \zeta]$, $[^3P_2, E + \zeta]$, $[^3P_0, E - \frac{1}{2}\zeta]$, and $[^1S_0, E_0 - E + \frac{1}{2}\zeta]$.

b) ps

Note from *TAS*, page 270, that $\langle ^3P_1 | \zeta L \cdot S | ^1P_1 \rangle = -(\sqrt{2}/2)\zeta$. The diagonal expressions are $[^3P_1, E(^3P_0) + \frac{1}{2}\zeta]$, $[^1P_1, E_1 - E(^3P_0) - \frac{1}{2}\zeta]$, $[^3P_0, E(^3P_0)]$, and $[^3P_2, E(^3P_2)]$.

c) p^3

The diagonal expressions are $[^2P, E(^2P_{1/2})]$, $[^4S, E_{3/2} - E(^2P_{1/2}) - E(^2D_{5/2})]$, and $[^2D, E(^2D_{5/2})]$.

d) p^3s or p^4s

Two special problems occur with this matrix. There are four terms involved and only three trace relations. To handle this, the eigenvalues of the 2×2 submatrix for $J = \frac{5}{2}$ are expressed analytically, giving square-root expressions for the unperturbed energies. For the elements studied, the experimental value of $E(^2S_{1/2})$ was generally not available. An approximate value was put into the calculation by means of the Slater relations.

Let us call $2E \equiv E_{5/2} + \{[E(^2D_{5/2}) - E(^4P_{5/2})]^2 - 2\zeta^2\}^{1/2}$. The diagonal expressions are then $[^2D, E]$, $[^4P_{5/2}, E_{5/2} - E]$, $[^4P_{3/2}, E_{5/2} - E - 5/6\zeta]$, $[^2P_{3/2}, E_{3/2} - E_{5/2} + 5/6\zeta]$, $[^4P_{1/2}, E_{5/2} - E - 4/3\zeta]$, $[^2P_{1/2}, E_{3/2} - E_{5/2} - 1/6\zeta]$ and $[^2S_{1/2}, 7/2E - ^{1/2}E_{5/2} - ^{1/2}E_{3/2} + 1/4\zeta]$.

e) p^3s

Here, the diagonal elements do not depend on ζ . We can see that $E(^3D) = E(^3D_3)$ and $E(^3P) = E(^3P_0)$. The remaining term values, ^1D , ^5S , ^1P , and ^3S , have only two trace relations to restrain them. An iterative process was used to obtain the "best" values of these terms. Starting with the respective experimental values, numerical trial values of the terms were fed into the program and the resulting error used to iterate, subject to the trace constraints. For S and Se the process converged in three trials.

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