JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 69A, No. 5, September–October 1965

Matrices of Spin-Orbit Interaction in the Electron Configurations $p^2\, d$ and $p^4\, d$

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(May 27, 1965)

The matrices of spin-orbit interaction in the $p^2\, d$ and $p^4\, d$ electron configurations have been calculated in the LS representation. The matrices have been checked by showing that their eigenvalues, calculated by use of an IBM 7090, agree with the correct eigenvalues known from the theory of jj-coupling. For the sake of completeness, the energies of electrostatic interaction for these configurations are also given.

1. Introduction

In a previous paper [1] [3] one of us reported the complete energy matrices in the LS representation for the $p^2\, p$ and $p^4\, p$ electron configurations, in the approximation that includes both electrostatic and spin-orbit interactions. Each of the present authors had calculated independently, and for different purposes, the corresponding energy matrices for spin-orbit interaction in the $p^2\, d$ and $p^4\, d$ configurations. After intercomparing our results, we formed a final check of the matrices by using an IBM 7090 to determine their eigenvalues and showing them to agree with the correct eigenvalues easily calculated from the theory of jj-coupling [cf. 2, ch. 10]. In this paper we report the $n'\, d$ matrices in a form identical to that used earlier in the $n'\, p$ case (n' is the principal quantum number of the electron that is outside the p^2 or p^4 core).

The primary use of such interaction matrices is to obtain approximate predicted values for the energy levels of atomic systems as an aid in interpreting and understanding their spectra. The eigenvalues of the matrices represent the discrete energy levels of the atomic system. The eigenvectors of the matrices are useful in obtaining approximate wave functions of the actual levels in terms of the LS eigenfunctions. The eigenvectors also give directly the transformation matrices needed for the calculation of line strengths in intermediate coupling from the strengths in LS coupling, as done for example by one of us earlier for lines of astrophysical importance [3].

2. Spin-Orbit Interaction

The matrices of spin-orbit interaction for the configuration $p^2\, d$ are given in table 3. Since the energy matrix is diagonal in J, the nondiagonal elements occur only between levels having the same J value. There is thus one matrix for each possible value of J. The rows and columns of the matrices are specified by the name of the term in the notation of LS-coupling, the terms in parentheses denoting the parent terms in p^2. The elements of these matrices are linear combinations of the spin-orbit integrals ζ and ζ', where ζ stands for ζ_p of the core and ζ' stands for ζ_d of the external electron. Both these integrals are positive. Their coefficients were hand-calculated by well-known methods [cf. ref. 2, ch. 11, and ref. 4]. Although these coefficients have been thoroughly checked, it will be appropriate to write a simplified expression, in the notation of reference [4], by which any given matrix element may easily be recalculated if occasion arises. For this purpose, it can be shown that, in the configuration $p^2\, l$, the element

$$(\mathrm{S_1L_1}\tfrac{1}{2}l\mathrm{SLJ}||\zeta_p(\mathbf{S}_1\cdot\mathbf{L}_1)+\zeta_l(\mathbf{s}_l\cdot\mathbf{l})||\mathrm{S_1'L_1'}\tfrac{1}{2}l\mathrm{S'L'J})$$

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is given by

$$\sqrt{(2S+1)(2L+1)(2S'+1)(2L'+1)}\begin{Bmatrix} SS'1 \\ L'LJ \end{Bmatrix}\Big[(-1)^{S_1+S_1'+L_1+L_1+L+L'+J+l+\frac{1}{2}}$$

$$\times\sqrt{(2S_1+1)(2L_1+1)(2S_1'+1)(2L_1'+1)}\begin{Bmatrix} L_1L_1'1 \\ 1\ 1\ 1 \end{Bmatrix}\begin{Bmatrix} S_1S_1'1 \\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2} \end{Bmatrix}\begin{Bmatrix} SS'1 \\ S_1'S_1\frac{1}{2} \end{Bmatrix}\begin{Bmatrix} LL'1 \\ L_1'L_1 l \end{Bmatrix}6\zeta_p$$

$$+(-1)^{S+S'+J+l+\frac{1}{2}}\sqrt{l(l+1)(2l+1)}\begin{Bmatrix} SS'1 \\ \frac{1}{2}\frac{1}{2}S_1 \end{Bmatrix}\begin{Bmatrix} LL'1 \\ l\ lL_1 \end{Bmatrix}\sqrt{\frac{3}{2}}\zeta_l\Big],$$

where the subscript 1 indicates quantum numbers associated with the parent term of the core, and the $6-j$ symbols are equivalent to Racah's W coefficients. We have kept this expression literal in l since it holds for all l. It may thus be used also to recalculate any $p^2\,p$ element given in reference [1]. The values of the $6-j$ symbols can be found in reference [9].

The matrices for the $p^4\,d$ configuration are identical to the above except that in this case the sign of the spin-orbit coupling parameter ζ_p is reversed [2, p. 299].

TABLE 1. *Electrostatic energies for* $p^2\,d$

Parent	Term	Energy
(^{3}P)	^{4}F	$E-3F_2-2F_2'-4G_1'+3G_3'$
	^{4}D	$E-3F_2+7F_2'-4G_1'-42G_3'$
	^{4}P	$E-3F_2-7F_2'+6G_1'-42G_3'$
(^{1}D)	^{2}G	$E+3F_2+4F_2'-4G_1'+18G_3'$
	^{2}S	$E+3F_2+14F_2'+G_1'-42G_3'$

	(^{3}P) ^{2}F	(^{1}D) ^{2}F
(^{3}P) ^{2}F	$E-3F_2-2F_2'+5G_1'+30G_3'$	$-3\sqrt{6}G_1'+6\sqrt{6}G_3'$
(^{1}D) ^{2}F	$-3\sqrt{6}G_1'+6\sqrt{6}G_3'$	$E+3F_2-8F_2'+2G_1'+6G_3'$

	(^{3}P) ^{2}D	(^{1}D) ^{2}D	(^{1}S) ^{2}D
(^{3}P) ^{2}D	$E-3F_2+7F_2'+5G_1'+\frac{105}{2}G_3'$	$+\frac{15\sqrt{21}}{2}G_3'$	$-3\sqrt{3}G_1'+21\sqrt{3}G_3'$
(^{1}D) ^{2}D	$+\frac{15\sqrt{21}}{2}G_3'$	$E+3F_2-3F_2'+3G_1'-\frac{27}{2}G_3'$	$+4\sqrt{7}F_2'-\sqrt{7}G_1'-3\sqrt{7}G_3'$
(^{1}S) ^{2}D	$-3\sqrt{3}G_1'+21\sqrt{3}G_3'$	$+4\sqrt{7}F_2'-\sqrt{7}G_1'-3\sqrt{7}G_3'$	$E+12F_2$

	(^{3}P) ^{2}P	(^{1}D) ^{2}P
(^{3}P) ^{2}P	$E-3F_2-7F_2'+\frac{105}{2}G_3'$	$+3G_1'+\frac{63}{2}G_3'$
(^{1}D) ^{2}P	$+3G_1'+\frac{63}{2}G_3'$	$E+3F_2+7F_2'+2G_1'-\frac{63}{2}G_3'$

3. Electrostatic Interaction

To obtain the complete energy matrices in intermediate coupling, the electrostatic matrices must be added to the spin-orbit matrices of table 3. The matrices of electrostatic interaction in Russell-Saunders coupling are well-known for the $p^2\,d$ and $p^4\,d$ configurations, and we give them here in tables 1 and 2 for the sake of completeness. The elements of the matrices are expressed as linear combinations of the usual Slater parameters F_k and G_k, which are defined as certain integrals over radial wave functions [2, p. 177.] We calculated the coefficients of these parameters from the general tables [4] given by Slater [5, vol. II, appendix 21]. We have checked them in the manner outlined by Racah [6].

Following Slater, the energies are stated in terms of the average energy, $E_{\mathrm{av}}=E$, which represents the center of gravity of the terms of the configuration, each term being assigned the weight (2S+1)(2L+1). The energy expressions can easily be converted, if desired, so as to

[4] A typographical error exists in Slater's tables. The nondiagonal matrix element for $p^4\,l$ $((^3P)\ ^2(l+1)|H|(^1D)\ ^2(l+1))$ should read: $-3(2l+1)\sqrt{3l(l+2)}$. This quantity multiplies $G^{l+1}(pl)/2(2l+1)(2l+3)^2$.

TABLE 2. *Electrostatic energies for* $p^4\,d$

Parent	Term	Energy
(^{3}P)	^{4}F	$E-3F_2+2F_2'-2G_1'-21G_3'$
	^{4}D	$E-3F_2-7F_2'-2G_1'-21G_3'$
	^{4}P	$E-3F_2+7F_2'-2G_1'-21G_3'$
(^{1}D)	^{2}G	$E+3F_2-4F_2'-2G_1'+24G_3'$
	^{2}S	$E+3F_2-14F_2'+8G_1'-21G_3'$

	(^{3}P) ^{2}F	(^{1}D) ^{2}F
(^{3}P) ^{2}F	$E-3F_2+2F_2'-2G_1'+69G_3'$	$-15\sqrt{6}G_3'$
(^{1}D) ^{2}F	$-15\sqrt{6}G_3'$	$E+3F_2+8F_2'-2G_1'-6G_3'$

	(^{3}P) ^{2}D	(^{1}D) ^{2}D	(^{1}S) ^{2}D
(^{3}P) ^{2}D	$E-3F_2-7F_2'+\frac{23}{2}G_1'+42G_3'$	$+\frac{3}{2}\sqrt{21}G_1'-3\sqrt{21}G_3'$	$+3\sqrt{3}G_1'-21\sqrt{3}G_3'$
(^{1}D) ^{2}D	$+\frac{3}{2}\sqrt{21}G_1'-3\sqrt{21}G_3'$	$E+3F_2+3F_2'+\frac{3}{2}G_1'-18G_3'$	$-4\sqrt{7}F_2'+\sqrt{7}G_1'+3\sqrt{7}G_3'$
(^{1}S) ^{2}D	$+3\sqrt{3}G_1'-21\sqrt{3}G_3'$	$-4\sqrt{7}F_2'+\sqrt{7}G_1'+3\sqrt{7}G_3'$	$E+12F_2$

	(^{3}P) ^{2}P	(^{1}D) ^{2}P
(^{3}P) ^{2}P	$E-3F_2+7F_2'+\frac{11}{2}G_1'-21G_3'$	$+\frac{15}{2}G_1'$
(^{1}D) ^{2}P	$+\frac{15}{2}G_1'$	$E+3F_2-7F_2'+\frac{11}{2}G_1'-21G_3'$

conform to the usage of Condon and Shortley. In this case, E is replaced in the energy expressions by the following quantities:

Configuration	E
$p^2\,d$	$(F_0+2F_0')-2F_2-2G_1'-21G_3'$
$p^4\,d$	$(6F_0+4F_0')-12F_2-4G_1'-42G_3'$

Here as in tables 1 and 2 the parameters without primes refer to the (p, p) interactions while those with primes refer to the (p, d) interactions. In accordance with Condon and Shortley, the subscripted parameters are defined in terms of the superscripted parameters as follows:

$$F_2(p, p)=(1/25)F^2(p, p), \qquad F_2(p, d)=(1/35)F^2(p, d),$$
$$G_1(p, d)=(1/15)G^2(p, d), \qquad G_3(p, d)=(1/245)G^3(p, d).$$

4. Conclusion

The complete energy matrices in the approximation that includes electrostatic and spin-orbit interactions are now available, in several coupling schemes, for most electron configurations of the types $p^2\,l$ and $p^4\,l$. The $p^2\,s$ and $p^4\,s$ cases are treated by Condon and Shortley [2, pp. 198 and 268] in the LS scheme. Our $n'\,p$ and $n'\,d$ results are also built in the LS scheme. Möller [7] calculated the matrices of $p^4\,l$ electrostatic interaction in the $J_c\,l$ repre-

TABLE 3. *Matrices of spin-orbit interaction for the configuration* p² d

$J=\frac{9}{2}$	$(^1D)\ ^2G$	$(^3P)\ ^4F$
$(^1D)\ ^2G$	$+\zeta'$	$+\frac{\sqrt{2}}{2}\zeta$
$(^3P)\ ^4F$	$+\frac{\sqrt{2}}{2}\zeta$	$+\frac{1}{2}(\zeta+2\zeta')$

$J=\frac{7}{2}$	$(^1D)\ ^2G$	$(^3P)\ ^4F$	$(^3P)\ ^2F$	$(^1D)\ ^2F$	$(^3P)\ ^4D$
$(^1D)\ ^2G$	$-\frac{5}{4}\zeta'$	$+\frac{\sqrt{2}}{4}\zeta$	$-\frac{\sqrt{6}}{4}\zeta$	$-\frac{3}{4}\zeta'$	0
$(^3P)\ ^4F$	$+\frac{\sqrt{2}}{4}\zeta$	0	$-\frac{\sqrt{3}}{6}(\zeta-4\zeta')$	$+\frac{\sqrt{2}}{4}\zeta$	$+\frac{\sqrt{6}}{6}(\zeta-\zeta')$
$(^3P)\ ^2F$	$-\frac{\sqrt{6}}{4}\zeta$	$-\frac{\sqrt{3}}{6}(\zeta-4\zeta')$	$+\frac{1}{3}(\zeta-\zeta')$	$+\frac{\sqrt{6}}{12}\zeta$	$+\frac{\sqrt{2}}{6}(\zeta+2\zeta')$
$(^1D)\ ^2F$	$-\frac{3}{4}\zeta'$	$+\frac{\sqrt{2}}{4}\zeta$	$+\frac{\sqrt{6}}{12}\zeta$	$+\frac{3}{4}\zeta'$	$+\frac{\sqrt{3}}{3}\zeta$
$(^3P)\ ^4D$	0	$+\frac{\sqrt{6}}{6}(\zeta-\zeta')$	$+\frac{\sqrt{2}}{6}(\zeta+2\zeta')$	$+\frac{\sqrt{3}}{3}\zeta$	$+\frac{1}{6}(\zeta+5\zeta')$

$J=\frac{5}{2}$	$({}^3P)\ {}^4F$	$({}^3P)\ {}^2F$	$({}^1D)\ {}^2F$	$({}^3P)\ {}^4D$	$({}^3P)\ {}^2D$	$({}^1D)\ {}^2D$	$({}^1S)\ {}^2D$	$({}^3P)\ {}^4P$
$({}^3P)\ {}^4F$	$-\frac{7}{18}(\zeta+2\zeta')$	$-\frac{\sqrt{5}}{9}(\zeta-4\zeta')$	$+\frac{\sqrt{30}}{18}\zeta$	$+\frac{8\sqrt{5}}{45}(\zeta-\zeta')$	$-\frac{\sqrt{70}}{45}(\zeta+2\zeta')$	$+\frac{\sqrt{30}}{45}\zeta$	$-\frac{2\sqrt{210}}{45}\zeta$	0
$({}^3P)\ {}^2F$	$-\frac{\sqrt{5}}{9}(\zeta-4\zeta')$	$-\frac{4}{9}(\zeta-\zeta')$	$-\frac{\sqrt{6}}{9}\zeta$	$+\frac{1}{9}(\zeta+2\zeta')$	$+\frac{\sqrt{14}}{18}(2\zeta+\zeta')$	$+\frac{\sqrt{6}}{18}\zeta$	$-\frac{\sqrt{42}}{9}\zeta$	0
$({}^1D)\ {}^2F$	$+\frac{\sqrt{30}}{18}\zeta$	$-\frac{\sqrt{6}}{9}\zeta$	$-\zeta'$	$+\frac{\sqrt{6}}{9}\zeta$	$-\frac{\sqrt{21}}{9}\zeta$	$-\zeta'$	0	0
$({}^3P)\ {}^4D$	$+\frac{8\sqrt{5}}{45}(\zeta-\zeta')$	$+\frac{1}{9}(\zeta+2\zeta')$	$+\frac{\sqrt{6}}{9}\zeta$	$-\frac{1}{36}(\zeta+5\zeta')$	$-\frac{\sqrt{14}}{36}(\zeta-10\zeta')$	$+\frac{7\sqrt{6}}{36}\zeta$	$+\frac{\sqrt{42}}{9}\zeta$	$+\frac{\sqrt{105}}{20}(\zeta-\zeta')$
$({}^3P)\ {}^2D$	$-\frac{\sqrt{70}}{45}(\zeta+2\zeta')$	$+\frac{\sqrt{14}}{18}(2\zeta+\zeta')$	$-\frac{\sqrt{21}}{9}\zeta$	$-\frac{\sqrt{14}}{36}(\zeta-10\zeta')$	$+\frac{1}{18}(2\zeta-5\zeta')$	$+\frac{\sqrt{21}}{18}\zeta$	$+\frac{2\sqrt{3}}{9}\zeta$	$+\frac{\sqrt{30}}{20}(\zeta+2\zeta')$
$({}^1D)\ {}^2D$	$+\frac{\sqrt{30}}{45}\zeta$	$+\frac{\sqrt{6}}{18}\zeta$	$-\zeta'$	$+\frac{7\sqrt{6}}{36}\zeta$	$+\frac{\sqrt{21}}{18}\zeta$	$+\frac{1}{2}\zeta'$	0	$+\frac{\sqrt{70}}{20}\zeta$
$({}^1S)\ {}^2D$	$-\frac{2\sqrt{210}}{45}\zeta$	$-\frac{\sqrt{42}}{9}\zeta$	0	$+\frac{\sqrt{42}}{9}\zeta$	$+\frac{2\sqrt{3}}{9}\zeta$	0	$+\zeta'$	$-\frac{\sqrt{10}}{5}\zeta$
$({}^3P)\ {}^4P$	0	0	0	$+\frac{\sqrt{105}}{20}(\zeta-\zeta')$	$+\frac{\sqrt{30}}{20}(\zeta+2\zeta')$	$+\frac{\sqrt{70}}{20}\zeta$	$-\frac{\sqrt{10}}{5}\zeta$	$-\frac{1}{4}(\zeta-3\zeta')$

$J=\frac{3}{2}$	$({}^3P)\ {}^4F$	$({}^3P)\ {}^4D$	$({}^3P)\ {}^2D$	$({}^1D)\ {}^2D$	$({}^1S)\ {}^2D$	$({}^3P)\ {}^4P$	$({}^3P)\ {}^2P$	$({}^1D)\ {}^2P$
$({}^3P)\ {}^4F$	$-\frac{2}{3}(\zeta+2\zeta')$	$+\frac{\sqrt{70}}{30}(\zeta-\zeta')$	$-\frac{\sqrt{70}}{30}(\zeta+2\zeta')$	$+\frac{\sqrt{30}}{30}\zeta$	$-\frac{\sqrt{210}}{15}\zeta$	0	0	0
$({}^3P)\ {}^4D$	$+\frac{\sqrt{70}}{30}(\zeta-\zeta')$	$-\frac{1}{6}(\zeta+5\zeta')$	$-\frac{1}{12}(\zeta-10\zeta')$	$+\frac{\sqrt{21}}{12}\zeta$	$+\frac{\sqrt{3}}{3}\zeta$	$+\frac{\sqrt{5}}{5}(\zeta-\zeta')$	$-\frac{1}{4}(\zeta+2\zeta')$	$+\frac{1}{4}\zeta$
$({}^3P)\ {}^2D$	$-\frac{\sqrt{70}}{30}(\zeta+2\zeta')$	$-\frac{1}{12}(\zeta-10\zeta')$	$-\frac{1}{12}(2\zeta-5\zeta')$	$-\frac{\sqrt{21}}{12}\zeta$	$-\frac{\sqrt{3}}{3}\zeta$	$+\frac{\sqrt{5}}{20}(\zeta+2\zeta')$	$+\frac{1}{4}(2\zeta+\zeta')$	$+\frac{1}{4}\zeta$
$({}^1D)\ {}^2D$	$+\frac{\sqrt{30}}{30}\zeta$	$+\frac{\sqrt{21}}{12}\zeta$	$-\frac{\sqrt{21}}{12}\zeta$	$-\frac{3}{4}\zeta'$	0	$+\frac{\sqrt{105}}{60}\zeta$	$-\frac{\sqrt{21}}{12}\zeta$	$-\frac{\sqrt{21}}{4}\zeta'$
$({}^1S)\ {}^2D$	$-\frac{\sqrt{210}}{15}\zeta$	$+\frac{\sqrt{3}}{3}\zeta$	$-\frac{\sqrt{3}}{3}\zeta$	0	$-\frac{3}{2}\zeta'$	$-\frac{\sqrt{15}}{15}\zeta$	$+\frac{\sqrt{3}}{3}\zeta$	0
$({}^3P)\ {}^4P$	0	$+\frac{\sqrt{5}}{5}(\zeta-\zeta')$	$+\frac{\sqrt{5}}{20}(\zeta+2\zeta')$	$+\frac{\sqrt{105}}{60}\zeta$	$-\frac{\sqrt{15}}{15}\zeta$	$+\frac{1}{6}(\zeta-3\zeta')$	$+\frac{\sqrt{5}}{12}(\zeta+6\zeta')$	$+\frac{\sqrt{5}}{4}\zeta$
$({}^3P)\ {}^2P$	0	$-\frac{1}{4}(\zeta+2\zeta')$	$+\frac{1}{4}(2\zeta+\zeta')$	$-\frac{\sqrt{21}}{12}\zeta$	$+\frac{\sqrt{3}}{3}\zeta$	$+\frac{\sqrt{5}}{12}(\zeta+6\zeta')$	$-\frac{1}{12}(2\zeta+3\zeta')$	$+\frac{1}{4}\zeta$
$({}^1D)\ {}^2P$	0	$+\frac{1}{4}\zeta$	$+\frac{1}{4}\zeta$	$-\frac{\sqrt{21}}{4}\zeta'$	0	$+\frac{\sqrt{5}}{4}\zeta$	$+\frac{1}{4}\zeta$	$+\frac{1}{4}\zeta'$

$J=\frac{1}{2}$	$({}^3P)\ {}^4D$	$({}^3P)\ {}^4P$	$({}^3P)\ {}^2P$	$({}^1D)\ {}^2P$	$({}^1D)\ {}^2S$
$({}^3P)\ {}^4D$	$-\frac{1}{4}(\zeta+5\zeta')$	$+\frac{1}{4}(\zeta-\zeta')$	$-\frac{\sqrt{2}}{4}(\zeta+2\zeta')$	$+\frac{\sqrt{2}}{4}\zeta$	0
$({}^3P)\ {}^4P$	$+\frac{1}{4}(\zeta-\zeta')$	$+\frac{5}{12}(\zeta-3\zeta')$	$+\frac{\sqrt{2}}{12}(\zeta+6\zeta')$	$+\frac{\sqrt{2}}{4}\zeta$	$+\frac{\sqrt{3}}{3}\zeta$
$({}^3P)\ {}^2P$	$-\frac{\sqrt{2}}{4}(\zeta+2\zeta')$	$+\frac{\sqrt{2}}{12}(\zeta+6\zeta')$	$+\frac{1}{6}(2\zeta+3\zeta')$	$-\frac{1}{2}\zeta$	$+\frac{\sqrt{6}}{6}\zeta$
$({}^1D)\ {}^2P$	$+\frac{\sqrt{2}}{4}\zeta$	$+\frac{\sqrt{2}}{4}\zeta$	$-\frac{1}{2}\zeta$	$-\frac{1}{2}\zeta'$	$-\frac{\sqrt{6}}{2}\zeta'$
$({}^1D)\ {}^2S$	0	$+\frac{\sqrt{3}}{3}\zeta$	$+\frac{\sqrt{6}}{6}\zeta$	$-\frac{\sqrt{6}}{2}\zeta'$	0

sentation. (Here J_c refers to the total angular momentum of the core.) These expressions are especially valuable in the analysis of configurations where the $J_c\,l$ coupling is very pure and hence the spin-orbit contribution can be neglected. To make the $J_c\,l$ matrices complete, however, Källén has calculated the spin-orbit elements and reports them in reference [8] together with the complete $p^4\,l$ matrices built in the $J_c\,j$ scheme.

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(Paper 69A5–361)