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Matrix Elements of the Spin-Spin Interaction for the f^3 Electron Configuration

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The spin-spin matrix elements for the f^3 electron configuration are computed by a method developed by Innes and checked by another method developed by Trees. A few irregularities have been noted.

I. INTRODUCTION

ENERGY-LEVEL structures showing deviations from the Landé interval rule for complex spectra can be explained in part by the consideration of the Heisenberg¹ spin-spin interaction operator. Araki² and Trees³ suggest that this interaction may be very appreciable in discussing the spectra of atoms that have large atomic numbers.

The spin-spin interaction for the f^3 electron configuration has been computed by two independent methods, a recurring tensor method developed by Trees,³ and a

method developed by Innes⁴ which expresses the submatrix element directly in the $l^n\alpha vSLJM$ scheme.

II. MATRIX ELEMENTS OF THE SPIN-SPIN INTERACTION

From the tensor equation in Racah,⁵ Eq. (38), it can be shown that the spin-spin interaction is given by

$$(l^n\alpha SLJM | H_m^{11} | l^n\alpha' S'L'JM) = (-)^{S+L'-J} W(SLS'L'; J2) \times (l^n\alpha SL \| T^{(22)} \| l^n\alpha' S'L'), \quad (1)$$

where $(l^n\alpha SL \| T^{(22)} \| l^n\alpha' S'L')$ is given by Eq. (9) in Ref. 3 when $p=q=2$; namely,

$$\begin{aligned} (l^n\alpha SL \| T^{(22)} \| l^n\alpha' S'L') &= (-)^{L+S-L+7/2} [n/(n-2)] [(2S+1)(2L+1)(2S'+1)(2L'+1)]^{1/2} \\ &\times \sum_{\alpha_1 S_1 L_1, \alpha_2 S_2 L_2} (-)^{L_2+S_2} (l^n\alpha SL \{ | l^{n-1}(\alpha_1 S_1 L_1) lSL (l^{n-1}\alpha_1 S_1 L_1 \| T^{(22)} \| l^{n-1}\alpha_2 S_2 L_2) \\ &\quad \times l^{n-1}(\alpha_2 S_2 L_2) lS'L' | \} l^n\alpha' S'L') W(S_1 S_2 S'; \frac{1}{2} 2) W(L_1 L_2 L'; l2). \end{aligned} \quad (2)$$

This submatrix element is the coefficient of M^t in Marvin's⁶ notation.

Innes⁴ in Eq. (18) expresses this submatrix element directly in the $l^n\alpha vSLJM$ scheme so that the coefficient of M^t is given by

$$\begin{aligned} (l^n\alpha vSL \| \mu_t \| l^n\alpha' vS'L') &= -2(5)^{1/2} [(2t+5)!/(2t)!]^{1/2} (l \| C^{(t+2)} \| l) (l \| C^{(t)} \| l) \sum_{\alpha'' S'' L''} (l^n\alpha vSL \| V^{(1,t+2)} \| l^n\alpha'' vS''L'') \\ &\quad \times (l^n\alpha'' vS''L'' \| V^{(1,t)} \| l^n\alpha' vS'L') W(1S1S'; S'2) W(t+2L2L'; L'2). \end{aligned} \quad (3)$$

¹ W. Heisenberg, Z. Physik **39**, 499 (1926).

² G. Araki, Progr. Theoret. Phys. (Kyoto) **3**, 152 (1948).

³ R. E. Trees, Phys. Rev. **82**, 683 (1951).

⁴ F. R. Innes, Phys. Rev. **91**, 31 (1953).

⁵ G. Racah, Phys. Rev. **62**, 438 (1942).

⁶ H. H. Marvin, Phys. Rev. **71**, 102 (1947).

For f electrons, $l=f=3$, so that in Eq. (3)

$$(f\|C^{(t)}\|f) = -7V(fft; 000); \quad V(ft; 000) = 0 \quad (2f+t, \text{ odd}),$$

$$V(ft; 000) = (-)^g \left[\frac{(2f-t)!(t!)^2}{(2f+t+1)!} \right]^{1/2} \frac{g!}{[(g-f)!]^2(g-t)!} \quad (2f+t=2g, \text{ even}). \quad (4)$$

When $n=3$,

$$(f^3\alpha v SL \| V^{(1,t)} \| f^3\alpha' v' S' L') = (-)^{t-5/2-S'-L'} [3(6)^{1/2}/2] [(2S+1)(2L+1)(2S'+1)(2L'+1)]^{1/2}$$

$$\times \sum_{S_1 L_1} (f^3\alpha v SL \{ | f^2(S_1 L_1) f S L f^2(S_1 L_1) f S' L' | \} f^3\alpha' v' S' L') W(\frac{1}{2}S_2^1 S'; S_1 1) W(3L3L'; L_1 t), \quad (5)$$

and when $n=2$ the coefficients of fractional parentage are unity so that

$$(f^2 S L \| V^{(1,t)} \| f^2 S' L') = (-)^{t+1-S'-L'} 6^{1/2} [(2S+1)(2L+1)(2S'+1)(2L'+1)]^{1/2} W(\frac{1}{2}S_2^1 S'; S_1 1) W(3L3L'; L_1 t). \quad (6)$$

W is a Racah coefficient given in Ref. 7. Since t is restricted to the even numbers ranging from 0 to $2l-2$, we have, for f electrons, $t=0, 2, 4$. The spin-spin interaction is diagonal in v , as this interaction breaks up into products of one-particle tensors of odd degree and these are known to be diagonal in v .

The submatrix element in Eq. (3) was checked by Trees's recurring tensor method [see Eq. (2)] for $l=f$ and $n=3$; namely,

$$(f^3\alpha S L \| T^{(22)} \| f^3\alpha' S' L') = (-)^{L+S+1/2} 3 [(2S+1)(2L+1)(2S'+1)(2L'+1)]^{1/2} \sum_{S_1 L_1, S_2 L_2} (f^3\alpha S L \{ | f^2(S_1 L_1) f S L$$

$$\times (f^2 S_1 L_1 \| T^{(22)} \| f^2 S_2 L_2) f^2(S_2 L_2) f S' L' | \} f^3\alpha' S' L') W(S_1 S S_2 S'; \frac{1}{2}2) W(L_1 L L_2 L'; 32), \quad (7)$$

where $(f^2 S_1 L_1 \| T^{(22)} \| f^2 S_2 L_2)$ is evaluated by Eq. (3) when $l=f$ and $n=2$; namely,

$$(f^2 S_1 L_1 \| T^{(22)} \| f^2 S_2 L_2) = -2(5)^{1/2} [(2t+5)!(2t)!]^{1/2} (f\|C^{(t+2)}\|f) (f\|C^{(t)}\|f)$$

$$\times \sum_{S'' L''} (f^2 S_1 L_1 \| V^{(1,t+2)} \| f^2 S'' L'') (f^2 S'' L'' \| V^{(1,t)} \| f^2 S_2 L_2) W(1S_1 1S_2; S'' 2) W(t+2L_1 t L_2; L'' 2), \quad (8)$$

where use is made of Eq. (6).

Table I gives the spin-spin interaction of the f^3 electron configuration for the various J levels, where the following definitions for the various integrals M^t are used:

$$M_0 = M^0/15, \quad M_2 = M^2/225, \quad M_4 = M^4/1089.$$

The common multiple of each interaction is placed at the head of the column of the interaction with the values of the coefficients of M_0 , M_2 , and M_4 directly below. For example, for $J=\frac{1}{2}$ the spin-spin interaction gives

$${}^3P_{11} - {}^3D_{20} = 3(10)^{1/2} (M_0 + 90M_2 - 990M_4).$$

It can be seen from this table that in most cases the value of the coefficient of M_t increases as the value of t increases. The exceptional cases are given in Table II with respect to the J values. These irregularities are due to the linear combination of the coefficients of fractional parentage used in Eq. (2).

⁷ T. Ishidzu *et al.*, *Tables of the Racah Coefficients* (Pan-Pacific Press, Tokyo, 1960).

TABLE I. Spin-spin interaction of f^3 electrons for various J levels.

		$J = \frac{1}{2}$	$J = \frac{3}{2}$	$J = \frac{5}{2}$	$J = \frac{7}{2}$	$J = \frac{9}{2}$		
		$^3P_{11}$	$^3D_{20}$	$^3S_{00}$	$^3P_{11}$	$^3D_{20}$	$^3F_{10}$	
$^3P_{11}$	M_0	0	$3(10)^{1/2}$					
	M_2	0	1					
	M_4	0	90	-990				
$^3D_{20}$	M_0	$3(10)^{1/2}$	2					
	M_2	1	34					
	M_4	90	-690	-4785				
		$J = \frac{3}{2}$	$J = \frac{5}{2}$	$J = \frac{7}{2}$	$J = \frac{9}{2}$	$J = \frac{11}{2}$	$J = \frac{13}{2}$	
		$^3D_{20}$	$^3D_{21}$	$^3D_{20}$	$^3D_{21}$	$^3D_{20}$	$^3F_{10}$	
$^3S_{00}$	M_0	0	$2(210)^{1/2}$	$90(770)^{1/2}$	$4(30)^{1/2}$			
	M_2	0	7	77				
	M_4	0	-300	13	-2	0	0	
$^3P_{11}$	M_0	0	0	0	-1	2		
	M_2	0	0	0	-90	-95		
	M_4	0	0	0	990	715		
$^3D_{20}$	M_0	$2(210)^{1/2}$			$(7)^{1/2}$	$(42)^{1/2}$		
	M_2	7			7	7		
	M_4	-300	0	0	67	16		
$^3D_{21}$	M_0	7	0	0	30	465		
	M_2	-300	0	0	660	-10 065		
	M_4	2310	0	0				
$^3D_{21}$	M_0	$90(770)^{1/2}$			$6(231)^{1/2}$	$9(154)^{1/2}$		
	M_2	77			77	7		
	M_4	-77	0	0	11	1		
$^3D_{20}$	M_0	$4(30)^{1/2}$	$3(5)^{1/2}$	$(7)^{1/2}$	$6(231)^{1/2}$	$2(6)^{1/2}$		
	M_2	-2	-1	7	77			
	M_4	-30	-90	67	11	8		
$^3F_{10}$	M_0	825	990	30	-635	-105		
	M_2			660	2200	1650		
	M_4							
$^3D_{20}$	M_0	$3(30)^{1/2}$		$(42)^{1/2}$	$9(154)^{1/2}$	12		
	M_2	0	2	7	7			
	M_4	0	-95	16	1	-2		
$^3F_{10}$	M_0	0	715	465	40	-30		
	M_2			-10 065	-185	825		
	M_4							
		$J = \frac{5}{2}$	$J = \frac{7}{2}$	$J = \frac{9}{2}$	$J = \frac{11}{2}$	$J = \frac{13}{2}$	$J = \frac{15}{2}$	
		$^3D_{20}$	$^3D_{21}$	$^3D_{20}$	$^3F_{10}$	$^3F_{21}$	$^3F_{10}$	$^3G_{20}$
$^3D_{20}$	M_0	0	0	$(2)^{1/2}$		$(42)^{1/2}$	$(110)^{1/2}$	
	M_2	0	0	-67	0	0	44	
	M_4	0	0	-30	0	-465	155	
$^3D_{21}$	M_0	0	0	$6(66)^{1/2}$		$9(154)^{1/2}$	$(30)^{1/2}$	
	M_2	0	0	77		7	77	
	M_4	0	0	-11	0	-1	341	
$^3D_{21}$	M_0	0	0	635	0	0	14 860	
	M_2	0	0	-2200	0	0	27 775	
	M_4	0	0					

TABLE I. (continued).

			$J = \frac{5}{2}$						
			${}^3D_{20}$	${}^3D_{21}$	${}^3D_{20}$	${}^1F_{10}$	${}^3F_{21}$	${}^3F_{10}$	${}^3G_{20}$
			$(2)^{1/2}$	$6(66)^{1/2}$	10		$2(2310)^{1/2}$	$4(21)^{1/2}$	$4(55)^{1/2}$
${}^3D_{20}$	M_0	-67		-11	-34	0	22	8	8
	M_2	-30		635	690	0	705	-105	95
	M_4	-660		-2200	4785	0	165	1650	-535
${}^1F_{10}$	M_0	0		0	0	0	0	0	0
	M_2	0		0	0	0	0	0	0
	M_4	0		0	0	0	0	0	0
			$2(2310)^{1/2}$			$3(110)^{1/2}$			$5(42)^{1/2}$
${}^3F_{21}$	M_0	0		0	22	0	0	-11	33
	M_2	0		0	705	0	0	210	-3 790
	M_4	0		0	165	0	0	5115	-30 745
			$(42)^{1/2}$	$9(154)^{1/2}$	$4(21)^{1/2}$		$3(110)^{1/2}$	3	$5(1155)^{1/2}$
${}^3F_{10}$	M_0	-16		-1	8	0	-11	2	22
	M_2	-465		-40	-105	0	210	30	-630
	M_4	10 065		185	1650	0	5115	-825	2475
			$(110)^{1/2}$	$(30)^{1/2}$	$4(55)^{1/2}$		$5(42)^{1/2}$	$5(1155)^{1/2}$	5
${}^3G_{20}$	M_0	44		341	8	0	154	77	77
	M_2	155		14 860	95	0	-3 790	-630	-14 970
	M_4	60 005		27 775	-535	0	-30 745	2475	-14 025
			$J = \frac{7}{2}$						
			${}^3D_{20}$	${}^1F_{10}$	${}^3F_{21}$	${}^3F_{10}$	${}^3G_{20}$	${}^3G_{21}$	${}^3G_{20}$
			4		$(1155)^{1/2}$	$3(70)^{1/2}$	$2(330)^{1/2}$	$15(13)^{1/2}$	$5(66)^{1/2}$
${}^3D_{20}$	M_0	34		0	-22	-8	-11	-26	8
	M_2	-690		0	-705	105	985	-2 015	95
	M_4	-4785		0	-165	-1650	-21 065	-10 835	-535
${}^1F_{10}$	M_1	0		0	0	0	0	0	0
	M_2	0		0	0	0	0	0	0
	M_4	0		0	0	0	0	0	0
			$(1155)^{1/2}$			$5(66)^{1/2}$			$9(70)^{1/2}$
${}^3F_{21}$	M_0	-22		0	0	11	0	0	-33
	M_2	-705		0	0	-210	0	0	3 790
	M_4	-165		0	0	-5115	0	0	30 745
			$3(70)^{1/2}$		$5(66)^{1/2}$	10	$10(231)^{1/2}$	$3(910)^{1/2}$	$2(1155)^{1/2}$
${}^3F_{10}$	M_0	-8		0	11	2	-11	13	22
	M_2	105		0	-210	30	-405	-4030	-630
	M_4	-1650		0	-5115	-825	7425	-6325	2475
			$2(330)^{1/2}$			$10(231)^{1/2}$			$10(5)^{1/2}$
${}^3G_{20}$	M_0	-11		0	0	-11	0	0	-11
	M_2	985		0	0	-405	0	0	1083
	M_4	-21 065		0	0	7425	0	0	3729

TABLE I. (continued).

$J = \frac{7}{2}$						
${}^3D_{20}$		${}^1F_{10}$	${}^3F_{21}$	${}^3F_{10}$	${}^3G_{20}$	${}^3G_{21}$
				3 (910) $^{1/2}$		(858) $^{1/2}$
		15 (13) $^{1/2}$		364		4004
		91				
${}^3G_{21}$	M_0	-26	0	0	13	0
${}^3G_{21}$	M_2	-2 015	0	0	-4030	0
${}^3G_{21}$	M_4	-10 835	0	0	-6325	0
${}^3G_{20}$	M_0	5 (66) $^{1/2}$		9 (70) $^{1/2}$	2 (1155) $^{1/2}$	10 (5) $^{1/2}$
${}^3G_{20}$	M_2	7		308	77	77
${}^3G_{20}$	M_4	8	0	-33	22	-11
${}^3G_{20}$	M_2	95	0	3 790	-630	1083
${}^3G_{20}$	M_4	-535	0	30 745	2475	3729
$J = \frac{9}{2}$						
${}^3F_{10}$		${}^3G_{20}$	${}^3G_{21}$	${}^3G_{20}$	${}^3H_{11}$	${}^3H_{21}$
		4 (231) $^{1/2}$	3 (910) $^{1/2}$	(3) $^{1/2}$	(22) $^{1/2}$	(10 010) $^{1/2}$
		5	77	910	11	715
${}^3F_{10}$	M_0	-2	11	-13	-22	143
${}^3F_{10}$	M_2	-30	405	4030	630	-780
${}^3F_{10}$	M_4	825	-7425	6325	-2475	-13 035
${}^3G_{20}$	M_0	4 (231) $^{1/2}$			20 (77) $^{1/2}$	4 (3003) $^{1/2}$
${}^3G_{20}$	M_2	77			847	11 011
${}^3G_{20}$	M_4	11	0	0	11	0
${}^3G_{20}$	M_2	405	0	0	-1083	0
${}^3G_{20}$	M_4	-7425	0	0	-3729	0
${}^3G_{21}$	M_0	3 (910) $^{1/2}$			(2730) $^{1/2}$	6 (70) $^{1/2}$
${}^3G_{21}$	M_2	910			10 010	5005
${}^3G_{21}$	M_4	-13	0	0	-4 433	0
${}^3G_{21}$	M_2	4030	0	0	-1 170	0
${}^3G_{21}$	M_4	6325	0	0	102 465	544 775
${}^3G_{20}$	M_0	(3) $^{1/2}$	20 (77) $^{1/2}$	(2730) $^{1/2}$	7	3 (66) $^{1/2}$
${}^3G_{20}$	M_2		847	10 010	121	121
${}^3G_{20}$	M_4		-22	-4 433	22	-88
${}^3G_{20}$	M_2	630	-1083	-1 170	14 970	-3 825
${}^3G_{20}$	M_4	-2475	-3729	102 465	14 025	62 865
${}^3H_{11}$	M_0	(22) $^{1/2}$			3 (66) $^{1/2}$	7 (286) $^{1/2}$
${}^3H_{11}$	M_2	11			121	121
${}^3H_{11}$	M_4	-44	0	0	-88	0
${}^3H_{11}$	M_2	1 635	0	0	-3 825	0
${}^3H_{11}$	M_4	-13 035	0	0	62 865	0
${}^3H_{21}$	M_0	(10 010) $^{1/2}$			3 (30 030) $^{1/2}$	2 (770) $^{1/2}$
${}^3H_{21}$	M_2	715			7865	7865
${}^3H_{21}$	M_4	143	0	0	-143	0
${}^3H_{21}$	M_2	-780	0	0	12 480	0
${}^3H_{21}$	M_4	-15 675	0	0	1 815	0
${}^3I_{20}$	M_0	4 (3003) $^{1/2}$			6 (70) $^{1/2}$	4 (3003) $^{1/2}$
${}^3I_{20}$	M_2	11 011			5005	11 011
${}^3I_{20}$	M_4	0	1 001	-2 002	1573	1573
${}^3I_{20}$	M_2	0	-29 770	-44 005	121	121
${}^3I_{20}$	M_4	0	107 030	544 775	-6270	-6270
${}^3I_{20}$	M_0	0			-1144	-1144
${}^3I_{20}$	M_2				210	210
${}^3I_{20}$	M_4				115 635	115 635
${}^3I_{20}$	M_0				145 200	145 200
${}^3I_{20}$	M_2				-122 595	-122 595
${}^3I_{20}$	M_4					

TABLE I. (continued).

			$J = \frac{1}{2}$		
			${}^3G_{20}$	${}^3H_{11}$	${}^3H_{21}$
			4	$(110)^{1/2}$	$(2002)^{1/2}$
			121	121	1573
${}^3G_{20}$	M_0	-22		88	143
	M_2	-14 970		3 825	-12 480
	M_4	-14 025		-62 825	-1 815
			$(110)^{1/2}$		$2(910)^{1/2}$
			121		1573
${}^3H_{11}$	M_0	88		0	0
	M_2	3 825		0	0
	M_4	-62 865		0	0
			$(2002)^{1/2}$		$5(1001)^{1/2}$
			1573		121
${}^3H_{21}$	M_0	143		0	0
	M_2	-12 480		0	0
	M_4	-1 815		0	0
			$(10 010)^{1/2}$		$5(11)^{1/2}$
			1573		1573
${}^3I_{20}$	M_0	-286		0	0
	M_2	-3 445		0	0
	M_4	40 205		0	0
			$2(910)^{1/2}$		40
			1573	121	1573
${}^3I_{20}$	M_0	-1 144		-11	2 431
	M_2	18 785		-210	-115 635
	M_4	113 465		6270	-145 200
			$5(1001)^{1/2}$		$5(11)^{1/2}$
			1573	121	1573
${}^3I_{20}$	M_0	-1 144		-11	2 431
	M_2	18 785		-210	-115 635
	M_4	113 465		6270	-145 200
			$2(55)^{1/2}$		-1859
			1573	121	1573
${}^3K_{21}$	M_0	1 859		0	0
	M_2	-117 390		0	0
	M_4	642 840		0	0
			$(70)^{1/2}$		
			1001		
${}^3I_{20}$	M_0	0	1 859	0	
	M_2	0	-117 390	0	
	M_4	0	642 840	0	
			$(70)^{1/2}$		
			1001	143	1001
${}^3I_{20}$	M_0	1 859	-286	143	
	M_2	-117 390	11 310	-5 460	
	M_4	642 840	122 595	-10 131	
			$60(14)^{1/2}$		
			1001		
${}^3K_{21}$	M_0	0	143	0	
	M_2	0	-5 460	0	
	M_4	0	-10 131	0	
			$J = \frac{1}{2}$		
			${}^3I_{20}$	${}^3K_{21}$	${}^3L_{21}$
			4	15	$(255)^{1/2}$
			143	143	143
${}^3I_{20}$	M_0	286	-143	143	
	M_2	-11 310	5 460	-780	
	M_4	-122 595	10 131	-15 675	

TABLE I. (*continued*).

			$J = \frac{15}{2}$
			$J = 17/2$
			$J = 17/2$
${}^3I_{20}$			${}^3K_{21}$
${}^3L_{21}$			${}^3L_{21}$
		15	
		<u>143</u>	
${}^3K_{21}$	M_0	−143	0
	M_2	5 460	0
	M_4	10 131	0
		<u>(255)$^{1/2}$</u>	
		143	
${}^3L_{21}$	M_0	143	0
	M_2	−780	0
	M_4	−15 675	0
			${}^3L_{21}$

TABLE II. Exceptional cases of the spin-spin interaction for f^3 electrons.

J	Spin-spin configuration	J	Spin-spin configuration
$\frac{3}{2}$	${}^3D_{20} - {}^3D_{20}$	$\frac{9}{2}$	${}^3G_{21} - {}^3G_{20}$
$\frac{5}{2}$	${}^3D_{20} - {}^3D_{20}$ ${}^3D_{20} - {}^3F_{21}$ ${}^3G_{20} - {}^3G_{20}$	$\frac{11}{2}$	${}^3G_{20} - {}^3G_{20}$ ${}^3G_{20} - {}^3H_{21}$
$\frac{7}{2}$	${}^3D_{20} - {}^3F_{21}$ ${}^3G_{21} - {}^3G_{20}$ ${}^3G_{20} - {}^3G_{20}$		

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