The Low Even Configurations of Hf II†

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The experimental energy levels and g values of the low even configurations ds^2, d^2s, and d^3 of Hf II, are compared with the theoretical formulas for intermediate coupling with configuration interaction. The energy levels are in good agreement, while the mean error is less than 0.7 percent of the configuration width; the agreement between calculated and observed g values is satisfactory.

1. INTRODUCTION

THE experimental data on the spectrum of Hf II show that the Landé g values depart strongly from the LS values. The comparison between theory and experiment needs, therefore, to be made in intermediate coupling.

For the electrostatic energy of the configurations d^2s and d^3 we used the formulas given by Condon and Shortley;[1] for the electrostatic interaction between configurations we used the formulas of Ufford,[2] and for the spin-orbit interaction, the matrices of Marvin.[3]

Our purpose is to fit formulas to the experimental values[4] by the method of least squares. However, as the formulas are not linear,[1] we need "starting" parameters.

2. THE ELECTROSTATIC ENERGY PARAMETERS

Since other spectra in the neighborhood of hafnium have not been theoretically investigated, we have first determined the electrostatic parameters by a least squares fitting of the center of gravity of the known terms with the Condon and Shortley formulas,[1] which are linear. In this state of the calculation we neglected $d^3\ ^2P$, as not all levels are known.

The results are given in Table I, column A. The mean error defined by $[\sum_i \Delta_i^2/(n-m)]^{\frac{1}{2}}$ (where Δ is the difference between observed and calculated values, n is the number of equations, and m is the number of parameters) is 1072, i.e., 2.9 percent of the configuration width.

The largest deviation was caused by the term $d^2s\ ^2P$. As this term has the largest configuration interaction ($315\frac{1}{3}H_2$), and we have neglected this interaction in our

TABLE I. The configurations ds^2, d^2s, and d^3 of Hf II in the LS approximation.

Level			Calculated		Mean level values	Obs.-Calc.		
Conf.	Term	Obs.	A	B	C	A	B	C
$5d6s^2$	$a\ ^2D$	1831	...	...	1865	...	...	−34
$5d^26s$	$a\ ^4F$	6371	7123	6648	6529	−752	−277	−158
$5d^26s$	$a\ ^4P$	13 042	12 861	13 063	13 204	+181	−21	−162
$5d^26s$	$a\ ^2F$	13 793	12 655	13 942	14 471	+1138	−149	−678
$5d^26s$	$b\ ^2D$	16 165	15 085	15 128	15 770	+1080	+1037	+395
$5d^26s$	$a\ ^2P$	16 972	18 393	...	16 528	−1421	...	+444
$5d^26s$	$a\ ^2G$	17 532	17 763	18 121	17 312	−231	−589	+220
$5d^3$	$b\ ^4F$	21 463	21 513	21 310	21 160	−50	+153	+303
$5d^3$	$b\ ^4P$	27 868	27 251	27 725	27 835	+617	+143	+33
$5d^3$	$b\ ^2G$	28 262	29 351	28 885	29 445	−1089	−623	−1183
$5d^3$	$a\ ^2H$	31 367	31 264	31 023	30 552	+103	+344	+815
$5d^3$	$c\ ^2D$	(32 778)	...	...	32 749	...	...	+29
$5d^3$	$b\ ^2P$	(36 883)	...	...	36 138	...	...	+745
$5d^3$	$b\ ^2F$	37 422	37 002	37 439	38 198	+420	−17	−776
Parameters:		$F_0(ds^2)$	...	...	6748			
		$F_0(d^2s)$	16 815	17 669	18 543			
		$F_0(d^3)$	36 084	35 937	35 378			
		$F_2(d^2)$	683.430	707.285	701.570			
		$F_4(d^2)$	60.086	55.857	51.314			
		$G_2(ds)$	1844	2431	2970			
		$H_2(dd;ds)$	...	...	513			

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[2] C. W. Ufford, Phys. Rev. **44**, 732 (1933).

[3] H. H. Marvin, Phys. Rev. **47**, 522 (1935).

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calculation, we expect to obtain more reliable values of the parameters by neglecting the $d^2s\ ^2P$ term. Repeating this calculation without $d^2s\ ^2P$, we have obtained much better agreement (see Table I, column B), the mean error being 644, i.e., 1.7 percent of the configuration width.

3. THE CONFIGURATION INTERACTION PARAMETER

From the deviations between the experimental and theoretical values we have estimated the parameter $H_2=500$; and taking this value and the values of Table I, column B, as starting values, we fitted by least squares all terms, comprising the "nonlinear" term $d^3\ ^2D$, the fundamental term $ds^2\ ^2D$, and a roughly estimated value of $d^3\ ^2P$. The results are given in Table I, column C, and the mean error is 777, i.e., 2.2 percent of the configuration width.

4. THE LEVEL VALUES CALCULATION

From the splitting of the quadruplets we have estimated the spin interaction parameter, $a=1250$, and calculated the complete matrices with this value and those of Table I, column C. With the help of Many's electrical network for diagonalization of matrices[5,6] we have found the eigenvalues and eigenvectors of these matrices. Using these eigenvectors, we calculated by the method of Racah[7] the derivatives of the eigenvalues with respect to the parameters, and were then able to adjust the parameters by least squares.

The final results are given in Table II; the mean error is 257, i.e., 0.7 percent of the configuration width. With the help of these parameters we have computed also all the remaining levels, which have not yet been found experimentally (Table II).

5. THEORETICAL CALCULATION OF THE g's

In order to obtain the splitting factors g, we have used the eigenvectors from the last calculation and applied them to the diagonal matrices for the Landé g values. The calculated g values were, however, not in satisfactory agreement with the observed values.

As the eigenvectors used for the calculation were obtained from the diagonalization of the matrices with provisional parameters, we repeated the diagonalization with the final parameters; the new g values obtained for these eigenvectors were in satisfactory agreement with the observed g values (see Table II).

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TABLE II. The configurations ds^2, d^2s, and d^3 of Hf II in intermediate coupling.

Conf.	Level Term	J	Energy levels Obs.	Calc.	Diff.	g values Obs.	Calc.
$5d\ 6s^2$	$a\ ^2D$	3/2	0000	95	−95	0.80	0.79
$5d\ 6s^2$	$a\ ^2D$	5/2	3051	2928	+123	1.18	1.19
$5d^26s$	$a\ ^4F$	3/2	3645	3988	−343	0.45	0.43
$5d^26s$	$a\ ^4F$	5/2	4905	5093	−188	1.06	1.05
$5d^26s$	$a\ ^4F$	7/2	6344	6622	−278	1.23	1.24
$5d^26s$	$a\ ^4F$	9/2	8362	8590	−228	1.33	1.33
$5d^26s$	$a\ ^4P$	1/2	11 952	11 741	+211	2.61	2.62
$5d^26s$	$a\ ^4P$	3/2	12 921	12 690	+231	1.69	1.66
$5d^26s$	$a\ ^4P$	5/2	13 486	13 429	+57	1.42	1.34
$5d^26s$	$a\ ^2F$	5/2	12 071	12 154	−83	0.98	1.05
$5d^26s$	$a\ ^2F$	7/2	15 084	15 067	+17	1.11	1.10
$5d^26s$	$b\ ^2D$	3/2	14 360	14 556	−196	1.03	1.01
$5d^26s$	$b\ ^2D$	5/2	17 369	17 056	+313	1.29	1.26
$5d^26s$	$a\ ^2P$	1/2	15 254	15 558	−304	0.74	0.73
$5d^26s$	$a\ ^2P$	3/2	17 830	17 987	−157	1.12	1.13
$5d^26s$	$a\ ^2G$	9/2	17 389	17 024	+365	1.13	1.13
$5d^26s$	$a\ ^2G$	7/2	17 711	17 349	+362	0.92	0.94
$5d^3$	$b\ ^4F$	3/2	18 898	18 455	+443	0.46	0.46
$5d^3$	$b\ ^4F$	5/2	20 135	19 926	+209	1.01	1.04
$5d^3$	$b\ ^4F$	7/2	21 638	21 550	+88	1.23	1.23
$5d^3$	$b\ ^4F$	9/2	23 146	23 129	+17	1.29	1.29
$5d^3$	$b\ ^4P$	1/2	26 997	26 925	+72		2.62
$5d^3$	$b\ ^4P$	3/2	27 285	27 454	−169	1.76	1.63
$5d^3$	$b\ ^4P$	5/2	28 547	28 536	+11	1.51	1.57
$5d^3$	$b\ ^2G$	9/2	28 105	27 898	+207	1.05	1.01
$5d^3$	$b\ ^2G$	7/2	28 458	28 240	+218	0.92	0.90
$5d^26s$	$a\ ^2S$	1/2		30 295			1.91
$5d^3$	$a\ ^2H$	11/2	30 942	30 886	+56	1.10	1.09
$5d^3$	$a\ ^2H$	9/2	31 878	32 011	−133	1.05	1.04
$5d^3$	$c\ ^2D$	3/2		30 692			0.92
$5d^3$	$c\ ^2D$	5/2	32 778	33 122	−344	1.15	1.21
$5d^3$	$b\ ^2P$	1/2		35 034			0.81
$5d^3$	$b\ ^2P$	3/2	37 325	37 429	−104		1.27
$5d^3$	$b\ ^2F$	5/2	37 399	37 565	−166		0.90
$5d^3$	$b\ ^2F$	7/2	37 440	37 580	−140		1.14
$5d^3$	$d\ ^2D$	5/2		46 113			1.18
$5d^3$	$d\ ^2D$	3/2		46 250			0.81
Parameters:			$F_0(ds^2)$	6599			
			$F_0(d^2s)$	18 044			
			$F_0(d^3)$	34 663			
			$F_2(d^2)$	653.570			
			$F_4(d^2)$	43.714			
			$G_2(ds)$	2818			
			$H_2(dd;ds)$	482			
			$\zeta(d)$	1336			

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