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Hyperfine structure in the atomic spectrum of niobium

II: Theoretical analysis of the even configurations

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Abstract. A parametric analysis of the fine and the hyperfine structure for the three even configurations $4d^45s$, $4d^45s^2$ and $4d^5$ has been performed. Effective one-electron parameters $a_{nl}^{k_sk_l}(k_sk_l = 01, 12$ and $10)$ and b_{nl}^{02} were determined for these three configurations. Extremely large ratios a_{4d}^{10}/a_{4d}^{01} were found. Theoretical predictions for the hyperfine structure constants A and B for all levels of the configurations $4d^45s$, $4d^45s^2$ and $4d^5$ have been determined from experimental data. Additionally, the fine and hyperfine structure for the two energetically high lying even configurations $4d^46s$ and $4d^35s6s$ are discussed. The results presented here call into doubt the existence of the fine structure levels $4d^35s6s\ ^6\mathrm{F}_{11/2}$ at an energy of 39 408.88 cm^{-1} and $4d^35s5p\ ^6\mathrm{G}_{13/2}$ at 18 876.46 cm^{-1} given in the Moore tables.

PACS. 31.30.Gs Hyperfine interactions and isotope effects, Jahn-Teller effect – 32.10.Fn Fine and hyperfine structure

1 Introduction

Niobium with the ground configuration $4d^45s$ belongs to the transition elements. Up to now, parametric analyses of the hyperfine structure of Nb I existed only for the two even configurations $4d^45s$ and $4d^35s^2$ (Büttgenbach and Dicke [1]). Their analysis is based on the experimental data of nine levels belonging to the two lowest multiplets $4d^45s\ ^6$D and $4d^35s^2\ ^4$F, Büttgenbach *et al.* [2].

In the preceding paper, Bouzed *et al.* [3], experimental results on the hyperfine structure of atomic Nb are compiled. Experimental hyperfine structure constants A and B for 41 energy levels of even parity are currently known. Due to this large quantity of data, the parametric investigation of the hyperfine structure needs to be improved.

Here we report on a parametric fine and hyperfine structure analysis in the three even configurations $4d^45s$, $4d^35s^2$ and $4d^5$. Additionally, the fine and hyperfine structure for the two high lying even configurations $4d^35s6s$ and $4d^46s$ are investigated.

2 Fine structure

As a basis for the interpretation of the hyperfine structure, a parametric analysis of the fine structure has been performed using the program code of Cowan [4]. The experimental basis of our fine structure calculation is given by the the list of atomic energy levels from Moore [5]. A description of the parameters can be found in Cowan [4]. All calculations have been performed in successive SL-coupling schema.

2.1 Configurations $4d^45s$, $4d^35s^2$ and $4d^5$

The three configurations $4d^45s$, $4d^35s^2$ and $4d^5$ are comprised of 63, 19 and 37 theoretical fine structure levels, respectively. In the list of atomic energy levels by Moore [5] 50 of these 119 levels are already identified. One further even level, 18 332.04 cm^{-1}, $J = 11/2$, is classified as *miscellaneous* by Moore. We included this level in our fit.

For the parametric fine structure calculations 19 parameters are required (see Tab. 1), five each for $4d^35s^2$ and $4d^5$, six for the configuration $4d^45s$ and three configuration interaction parameters.

Since only one level (11 344.70 cm^{-1}, $J = 5/2$) is assigned predominantly to the configuration $4d^5$, it was not possible to fit more than one parameter of this configuration. For this reason the parameters $F^2(4d^2)$, $F^4(4d^2)$ and ζ_{4d} of this configuration are held at a constant ratio to the corresponding parameter of the other configurations according to

$$P(4d^5)/P(4d^45s) = P(4d^45s)/P(4d^35s^2)\,,$$

where P is any one of the parameters. Additionally, the parameter α for this configuration remains fixed. The two

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Table 1. Fine structure parameters for the even parity configurations $4d^3\,5s^2$, $4d^4\,5s$ and $4d^5$ of Nb I in cm^{-1} together with values from Büttgenbach and Dicke [1]; f: parameter is held at a fixed value, r: parameter is held in a constant ratio with the same parameter in the configurations $4d^3 5s^2$ and $4d^4\,5s$.

parameter	value	reference [1]
$4d^4 5s$:		
$E_{\rm av}$	17 170 (60)	
$F^2(4d^2)$	32 750 (190)	31 649 (254)
$F^4(4d^2)$	19 900 (200)	18 921 (272)
ζ_{4d}	425 (15)	393 (24)
$G^2(4d, 5s)$	9 100 (80)	8 551 (71)
α	34 (3)	50 (4)
$4d^3 5s^2$:		
$E_{\rm av}$	12 810 (70)	
$F^2(4d^2)$	37 400 (300)	37 925 (500)
$F^4(4d^2)$	23 100 (300)	25 572 (434)
ζ_{4d}	494 (20)	515 (35)
α	28 (5)	−7 (7)
$4d^5$:		
$E_{\rm av}$	30 060 (120)	
$F^2(4d^2)$	28 680 r	
$F^4(4d^2)$	17 140 r	
ζ_{4d}	366 r	
α	30 f	
$4d^4 5s - 4d^3 5s^2$:		
$R^2(4d^2, 4d5s)$	−12 600 (300)	−14 406 (202)
$4d^4 5s - 4d^5$:		
$R^2(4d5s, 4d^2)$	−10 700 (600)	
$4d^3 5s^2 - 4d^5$:		
$R^2(5s^2, 4d^2)$	10 600 r	
number of fitted levels	51	49
standard deviation	70	109

configuration interaction parameters $R^2(4d5s, 4d^2)$ and $R^2(5s^2, 4d^2)$, describing the interaction of the configurations $4d^4 5s$ and $4d^3 5s^2$ with $4d^5$, respectively, are held in the constant ratio of their HF values as calculated by the Cowan Program [4].

Using all 51 experimental energy levels in a least squares fit with 14 free parameters, a standard deviation of 70 cm^{-1} was achieved. The fitted parameters are compared to those from Büttgenbach and Dicke [1] in Table 1 and show a reasonable agreement as expected if one uses the same input data. Nevertheless, some deviation occurs which are due to the fact that we include the $4d^5$ configuration in our calculation.

A comparison between experimental and calculated energies shows good agreement without excluding any levels from the fit, Table 2. With a few exceptions, the agreement between experimental and calculated g-factors is also very good. Where deviations occur between experimental and calculated g-factors generally two or three adjacent levels far away from SL limit are affected, *i.e.* the contribution of the leading component is less than 50%. For these levels, the atomic states are not well represented by the eigenvectors, even though the agreement between experimental and calculated energies is good.

The level 18 332.04 cm^{-1}, $J = 11/2$, which is indicated as *miscellaneous* by Moore [5] is assigned predominately to the configuration $4d^4 5s$. Unfortunately no g-factor is given to confirm the classification.

For the levels lying below 40 000 cm^{-1} the uncertainty of the calculated energies for the configurations $4d^4 5s$ and $4d^3 5s^2$ is estimated to be less than 100 cm^{-1}. This value is considerably higher for the $4d^5$ configuration. The few levels above 40 000 cm^{-1} are possibly disturbed by unknown levels of the configurations $4d^4 6s$ and $4d^3 5s 6s$.

In most cases the SL-purity of the levels is very low, which can be seen by the percentage of the leading eigenvector components. Additionally the configuration mixing is very strong, so that assignment of certain levels to a single configuration is not meaningful. For a few energetic high lying levels of $J = 3/2$ and $J = 5/2$ even the leading component is not part of the strongest configuration.

2.2 Configurations $4d^4 6s$

The configuration $4d^4 6s$ consists of 63 fine structure levels, only five of which are known experimentally [5]. These five constitute the lowest multiplet $[4d^4(^5\mathrm{D})6s]\,^6\mathrm{D}$ and lie in the energy range from 37 400 cm^{-1} to 38 600 cm^{-1}. From our fine structure calculation, there are no levels of the three configurations $4d^4 5s$, $4d^3 5s^2$ and $4d^5$ in this energy region, see Table 2. For this reason a separate treatment of this configuration is warrantable.

Since levels from just one multiplet are available, only the value for the spin-orbit interaction parameter ζ_{4d} can be determined. With the exception of the average energy of the configuration, all other fine structure parameters were fixed to constant values. These values have practically no influence on the result for ζ_{4d}. The average energy of the configuration $E_{\rm av}$ is needed to adjust the average energy of the ^{6}D multiplet.

A fit of the five experimental energy levels of this configuration with ζ_{4d} and $E_{\rm av}$ as free parameters leads to very good agreement between experimental and calculated energies as shown by a standard deviation of less than 1 cm^{-1}, Table 4. The fitted value of

$$\zeta_{4d}(4d^4 6s) = 463\,(1)\ \mathrm{cm}^{-1}$$

is of the same order of magnitude as the ζ_{4d} value of the configuration $4d^4 5s$. The purity of the levels of the ^{6}D multiplet, which are listed in Table 3, is in SL coupling about 99%. However, no g-factors are given by Moore [5] to confirm these results.

2.3 Configurations $4d^3 5s 6s$

For the configuration $4d^3 5s 6s$, which consists of 74 fine structure levels, similar conditions are found as for $4d^4 6s$: Here, six of these energy levels are known experimentally

Table 2. List of levels of the even parity configurations $4d^4\,5s$, $4d^3\,5s^2$ and $4d^5$ of Nb I with experimental values $E_{\rm exp}$ and $g_{\rm exp}$ according to [5], calculated values $E_{\rm calc}$ and $g_{\rm calc}$ and the respective deviations, leading eigenvector component and percentage distribution over the configurations, experimental and best fitted hyperfine constants A and B and the respective deviations. Levels with ΔA or ΔB in parentheses were excluded from the corresponding fit. Energies in $\rm cm^{-1}$, A and B in MHz.

$E_{\rm exp}$	$E_{\rm calc}$	ΔE	$g_{\rm exp}$	$g_{\rm calc}$	Δg	Leading component			percentage distribution			$A_{\rm exp}$	$A_{\rm calc}$	ΔA	$B_{\rm exp}$	$B_{\rm calc}$	ΔB
						config.	term	%	$4d^4\,5s$	$4d^3\,5s^2$	$4d^5$						
$J = 1/2$																	
0.00	−41	41	3.323	3.328	−0.005	$4d^4\,5s$	^{5}D ^{6}D	98.5	100	0	0	1 868	1 915	−47			
4 998.17	4 970	28	2.650	2.652	−0.002	$4d^3\,5s^2$	^{4}P	51.0	44	52	4	539	570	−31			
8 410.90	8 436	−26	0.06	0.063	−0.003	$4d^4\,5s$	^{5}D ^{4}D	88.0	93	4	3	1 999	2 022	−23			
10 126.06	10 161	−35	0.66	0.638	0.022	$4d^3\,5s^2$	^{2}P	66.5	33	67	1	324	1 137	(−813)			
13 629.15	13 623	6	2.64	2.611	0.029	$4d^3\,5s^2$	^{4}P	38.4	61	38	0	2 923	915	(2008)			
15 460.77	15 429	31	0.04	0.015	0.025	$4d^4\,5s$	^{3}D ^{4}D	91.9	94	1	5		−1 159				
	17 509			1.653		$4d^4\,5s$	^{1}S ^{2}S	48.5	83	11	5		4 949				
	18 564			1.051		$4d^4\,5s$	^{3}P ^{2}P	33.7	80	17	3		2 182				
	23 788			2.643		$4d^5$	^{4}P	72.0	20	7	73		−342				
	26 087			0.089		$4d^5$	^{4}D	88.9	11	0	89		1 168				
	27 114			2.595		$4d^4\,5s$	^{3}P ^{4}P	36.9	74	1	25		2 300				
	29 940			0.674		$4d^4\,5s$	^{3}P ^{2}P	54.2	94	0	6		661				
	35 643			2.001		$4d^5$	^{2}S	88.3	11	0	89		141				
	48 086			0.669		$4d^5$	^{2}P	92.3	6	1	93		365				
	48 768			2.002		$4d^4\,5s$	^{1}S ^{2}S	72.2	96	0	4		6 115				
$J = 3/2$																	
154.19	116	38	1.863	1.866	−0.003	$4d^4\,5s$	^{5}D ^{6}D	99.0	100	0	0	853	812	41	−65	−65	0
1 142.79	1 166	−24	0.402	0.404	−0.002	$4d^3\,5s^2$	^{4}F	91.6	6	93	1	644	674	−29	33	34	−1
5 297.92	5 259	38	1.721	1.723	−0.002	$4d^3\,5s^2$	^{4}P	52.6	41	55	5	497	447	50	60	56	4
8 705.32	8 737	−32	1.197	1.202	−0.005	$4d^4\,5s$	^{5}D ^{4}D	93.4	96	1	3	−141	−126	−15	−10	2	−12
9 439.08	9 417	22	0.953	0.953	0.000	$4d^3\,5s^2$	^{2}D	43.4	23	74	3	389	336	53	74	−5	(79)
11 318.09	11 351	−33	1.175	1.189	−0.014	$4d^3\,5s^2$	^{2}P	51.4	28	71	2	167	233	−66	−6	64	(−70)
12 288.25	12 288	0	0.402	0.406	−0.004	$4d^4\,5s$	^{3}F ^{4}F	69.1	94	6	0		−599			23	
14 211.30	14 226	−15	1.71	1.715	−0.005	$4d^4\,5s$	^{3}P ^{4}P	37.1	63	37	0	1 414	500	(914)	30	16	14
15 439.25	15 397	42	1.21	1.207	0.003	$4d^4\,5s$	^{3}D ^{4}D	90.7	95	1	5		683			6	
	19 097			1.302		$4d^4\,5s$	^{3}P ^{2}P	44.2	74	24	1		−234			−18	
	19 251			0.802		$4d^4\,5s$	^{3}D ^{2}D	38.8	87	3	11		−186			−34	
	21 492			0.834		$4d^4\,5s$	^{3}D ^{2}D	29.5	59	36	5		329			7	
	23 708			1.715		$4d^5$	^{4}P	67.2	22	8	73		99			19	
	25 011			0.417		$4d^4\,5s$	^{3}F ^{4}F	72.3	96	1	3		−607			−82	
	26 021			1.270		$4d^5$	^{4}D	75.4	23	1	76		341			34	
	26 882			1.653		$4d^4\,5s$	^{3}P ^{4}P	30.4	60	1	39		931			−1	
	28 095			0.812		$4d^5$	^{2}D	31.9	17	29	54		321			−46	
	29 220			1.322		$4d^4\,5s$	^{3}P ^{2}P	53.2	92	1	7		−854			−52	
	30 402			0.414		$4d^5$	^{4}F	94.0	2	3	95		716			−15	
	34 029			0.799		$4d^5$	^{2}D	30.2	20	42	38		403			−62	
	35 386			0.800		$4d^5$	^{2}D	51.7	40	7	54		−48			37	
	41 628			0.800		$4d^4\,5s$	^{1}D ^{2}D	42.2	56	3	41		−337			67	
	47 969			1.322		$4d^5$	^{2}P	90.8	6	1	93		−56			−33	
	50 546			0.811		$4d^5$	^{2}D	71.1	1	4	95		476			21	
$J = 5/2$																	
391.99	357	34	1.652	1.656	−0.004	$4d^4\,5s$	^{5}D ^{6}D	99.3	100	0	0	719	683	36	−48	−46	−2
1 586.90	1 607	−21	1.029	1.031	−0.002	$4d^3\,5s^2$	^{4}F	91.6	7	92	1	372	342	30	33	34	−1

Table 2. *Continued.*

$E_{\rm exp}$	$E_{\rm calc}$	ΔE	$g_{\rm exp}$	$g_{\rm calc}$	Δg	Leading component			percentage distribution			$A_{\rm exp}$	$A_{\rm calc}$	ΔA	$B_{\rm exp}$	$B_{\rm calc}$	ΔB
						config.	term	%	$4d^4\,5s$	$4d^3\,5s^2$	$4d^5$						
5 965.45	5 903	62	1.596	1.600	−0.004	$4d^3\,5s^2$	^{4}P	55.7	39	56	5	343	435	−92	−80	−76	−4
9 043.14	9 058	−15	1.360	1.363	−0.003	$4d^4\,5s$	^{5}D ^{4}D	91.5	94	2	4	−408	−394	−14	35	46	−11
10 237.51	10 189	48	1.206	1.207	−0.001	$4d^3\,5s^2$	^{2}D	57.1	30	66	4	296	319	−23	37	36	1
11 344.70	11 342	2	1.99	2.000	−0.010	$4d^5$	^{6}S	99.5	0	0	100	−642	−643	1	−0.1	0	0
12 018.25	12 093	−75	0.742	0.800	−0.058	$4d^4\,5s$	^{3}G ^{4}G	48.3	95	3	2	−101	−4	−97		49	
12 692.12	12 770	−78	0.852	0.805	0.047	$4d^4\,5s$	^{3}F ^{4}F	46.3	94	3	2		−179			−2	
13 404.77	13 499	−95	0.860	0.863	−0.003	$4d^4\,5s$	^{3}F ^{2}F	40.5	61	32	7	304	577	(−273)	−44	−37	−7
14 899.26	14 917	−18	1.54	1.541	0.001	$4d^4\,5s$	^{3}P ^{4}P	29.3	72	27	1		734			−59	
15 467.08	15 423	44	1.42	1.424	−0.004	$4d^4\,5s$	^{3}D ^{4}D	68.7	89	7	4		922			33	
	19 461			0.920		$4d^4\,5s$	^{1}F ^{2}F	25.6	76	14	9		230			11	
	19 840			1.142		$4d^4\,5s$	^{3}D ^{2}D	32.7	82	8	10		465			−90	
	21 295			1.201		$4d^4\,5s$	^{2}D	29.9	56	39	5		479			−20	
	23 048			0.577		$4d^5$	^{4}G	93.7	5	0	95		516			6	
	23 577			1.581		$4d^5$	^{4}P	57.9	29	10	61		142			−11	
	24 870			1.016		$4d^4\,5s$	^{3}F ^{4}F	61.8	87	8	5		431			−79	
	25 626			0.891		$4d^4\,5s^2$	^{2}F	33.6	54	34	12		−118			−89	
	25 847			1.449		$4d^5$	^{4}D	50.8	41	1	58		384			45	
	26 580			1.496		$4d^5$	^{4}D	34.5	37	1	62		341			−89	
	27 564			0.971		$4d^5$	^{2}F	28.9	45	8	47		382			−68	
	28 311			1.096		$4d^5$	^{2}D	18.4	33	25	43		348			−108	
	30 372			1.031		$4d^5$	^{4}F	93.7	2	2	96		210			−28	
	32 439			0.906		$4d^5$	^{2}F	35.4	30	13	57		438			30	
	33 979			1.145		$4d^5$	^{2}D	28.4	16	35	50		197			−81	
	34 953			1.013		$4d^5$	^{2}F	28.4	35	4	61		461			−30	
	35 642			1.056		$4d^5$	^{2}D	30.8	37	2	62		544			−25	
	41 698			1.200		$4d^5$	^{2}D	41.3	55	3	42		850			85	
	50 465			1.200		$4d^5$	^{2}D	73.0	1	4	95		61			−1	
$J = 7/2$																	
695.25	661	34	1.582	1.586	−0.004	$4d^4\,5s$	^{5}D ^{6}D	99.0	100	0	0	690	666	24	20	22	−2
2 154.11	2 166	−12	1.235	1.240	−0.005	$4d^3\,5s^2$	^{4}F	90.8	8	91	1	292	242	50	45	46	−1
8 827.00	8 814	13	0.885	0.895	−0.010	$4d^3\,5s^2$	^{2}G	83.7	14	84	1	420	429	−9	−49	−37	−12
9 497.52	9 492	5	1.420	1.419	0.001	$4d^4\,5s$	^{5}D ^{4}D	93.2	95	1	4	−477	−496	19	127	123	4
10 922.74	10 963	−41	0.690	0.690	0.000	$4d^4\,5s$	^{3}H ^{4}H	92.6	99	1	0		−244			−19	
12 136.86	12 198	−62	1.081	1.104	−0.023	$4d^4\,5s$	^{3}G ^{4}G	41.3	94	4	2		371			32	
12 982.38	13 062	−80	1.120	1.099	0.021	$4d^4\,5s$	^{3}G ^{4}G	48.9	94	3	3		394			−11	
13 515.20	13 586	−71	1.130	1.147	−0.017	$4d^4\,5s$	^{3}F ^{2}F	38.2	60	34	6	137	222	−85	−49	−52	3
15 282.35	15 231	51	1.43	1.424	0.006	$4d^4\,5s$	^{3}D ^{4}D	91.9	95	1	5	957	882	75		−21	
16 918.78	16 801	117	0.88	0.895	−0.015	$4d^4\,5s$	^{1}G ^{2}G	53.4	94	1	5		−195			55	
	18 997			0.950		$4d^4\,5s$	^{3}G ^{2}G	57.9	81	16	3		415			18	
	19 900			1.081		$4d^4\,5s$	^{3}F ^{2}F	28.4	81	14	5		382			−54	
	23 098			0.986		$4d^5$	^{4}G	94.4	5	0	95		234			10	
	24 790			1.226		$4d^4\,5s$	^{3}F ^{4}F	62.6	87	8	5		693			−110	
	25 787			1.159		$4d^4\,5s$	^{1}F ^{2}F	37.6	58	32	10		539			−119	
	26 085			1.416		$4d^5$	^{4}D	86.2	12	0	88		−72			12	
	27 438			1.142		$4d^4\,5s$	^{3}F ^{2}F	40.5	58	0	42		132			−89	
	29 425			0.902		$4d^4\,5s$	^{1}G ^{2}G	52.0	75	2	23		−178			−58	
	30 348			1.228		$4d^5$	^{4}F	90.7	5	1	94		30			−25	

Table 2. *Continued.*

$E_{\rm exp}$	$E_{\rm calc}$	ΔE	$g_{\rm exp}$	$g_{\rm calc}$	Δg	Leading component			percentage distribution			$A_{\rm exp}$	$A_{\rm calc}$	ΔA	$B_{\rm exp}$	$B_{\rm calc}$	ΔB
						config.	term	%	$4d^4\,5s$	$4d^3\,5s^2$	$4d^5$						
	32 299			1.135		$4d^5$	^{2}F	35.7	28	6	66		98			44	
	33 255			0.902		$4d^5$	^{2}G	69.8	25	0	75		176			24	
	35 487			1.141		$4d^5$	^{2}F	56.8	30	0	70		110			−131	
	41 143			0.890		$4d^5$	^{2}G	96.5	2	1	97		340			−13	
$J = 9/2$																	
1 050.26	1 011	39	1.549	1.553	−0.004	$4d^4\,5s$	^{5}D ^{6}D	98.2	99	1	0	692	684	8	133	131	−2
2 805.36	2 801	4	1.330	1.334	−0.004	$4d^3\,5s^2$	^{4}F	88.8	9	90	1	270	218	52	64	67	−3
9 328.88	9 302	26	1.103	1.103	0.000	$4d^3\,5s^2$	^{2}G	79.1	14	85	1	359	284	75	−61	−46	−15
11 044.08	11 085	−41	0.984	0.990	−0.006	$4d^4\,5s$	^{3}H ^{4}H	90.4	99	1	0		196			−6	
12 102.12	12 130	−28	0.93	0.926	0.004	$4d^3\,5s^2$	^{2}H	71.4	22	75	3	385	474	−89	−163	−174	11
12 357.70	12 401	−44	1.23	1.247	−0.017	$4d^4\,5s$	^{3}F ^{4}F	40.1	92	7	2		597			21	
13 145.71	13 221	−76	1.224	1.227	−0.003	$4d^4\,5s$	^{3}G ^{4}G	54.9	93	4	3		673			−13	
16 828.52	16 728	100	1.04	1.056	−0.016	$4d^4\,5s$	^{1}G ^{2}G	38.9	89	8	3		754			18	
18 035.97	18 007	28	0.97	0.972	−0.002	$4d^4\,5s$	^{3}H ^{2}H	57.9	86	12	2	708	603	105	18	−53	(71)
	19 530			1.110		$4d^4\,5s$	^{3}G ^{2}G	77.2	85	12	3		113			4	
	23 137			1.172		$4d^5$	^{4}G	95.0	5	0	95		112			9	
	24 916			1.333		$4d^4\,5s$	^{3}F ^{4}F	78.5	98	1	1		795			−164	
	29 170			1.121		$4d^4\,5s$	^{1}G ^{2}G	49.4	69	2	29		686			−51	
	30 388			1.319		$4d^5$	^{4}F	90.2	9	1	90		40			−15	
	31 479			0.919		$4d^5$	^{2}H	92.2	4	2	94		338			3	
	33 477			1.107		$4d^5$	^{2}G	69.7	25	0	75		322			−9	
	41 102			1.111		$4d^5$	^{2}G	97.3	2	1	97		155			7	
$J = 11/2$																	
11 247.88	11 284	−37	1.12	1.141	−0.021	$4d^4\,5s$	^{3}H ^{4}H	93.7	100	0	0		461			−24	
12 502.97	12 496	6	1.10	1.093	0.007	$4d^3\,5s^2$	^{2}H	76.1	21	76	3		304			−192	
13 012.20	13 130	−118	1.26	1.262	−0.002	$4d^4\,5s$	^{3}G ^{4}G	88.2	94	2	5		672			−11	
17 476.22	17 357	119	1.01	0.973	0.037	$4d^4\,5s$	^{1}I ^{2}I	69.8	93	7	0		−117			−120	
18 332.04	18 233	99		1.042		$4d^4\,5s$	^{3}H ^{2}H	57.9	87	12	0		35			−104	
	23 134			1.272		$4d^5$	^{4}G	94.6	5	0	95		55			1	
	27 763			0.928		$4d^5$	^{2}I	96.8	0	0	99		295			4	
	31 686			1.087		$4d^5$	^{2}H	93.9	0	3	97		175			−11	
$J = 13/2$																	
11 524.65	11 546	−22	1.22	1.230	−0.010	$4d^4\,5s$	^{3}H ^{4}H	99.3	100		0		669			−66	
	17 643			1.078		$4d^4\,5s$	^{1}I ^{2}I	98.8	100		0		750			−131	
	27 870			1.077		$4d^5$	^{2}I	99.6	0		100		187			−1	

Table 3. Experimental and best fitted hyperfine constants A and B and differences in between in MHz for the levels of the $[4d^4(^5\mathrm{D})6s]\,^6\mathrm{D}$ multiplet of Nb I.

E/cm^{-1}	J	A_{exp}	A_{calc}	ΔA	B_{exp}	B_{calc}	ΔB
37 410.17	1/2	−986	−985	−1			
37 578.72	3/2	−199	−204	5	−70	−63	−7
37 842.36	5/2	−86	−83	−3	−47	−45	−2
38 177.65	7/2	−37	−33	−4	42	21	21
38 567.85	9/2	5	2	3	119	127	−8

and constitute the lowest multiplet $\{[4d^3(^4\mathrm{F})5s]^5\mathrm{F}\,6s\}\,^6\mathrm{F}$. These levels lie in the energy range from 37 800 cm^{-1} to 39 400 cm^{-1}. From our fine structure calculation there are no levels of the three configurations $4d^45s$, $4d^35s^2$ and $4d^5$ in this energy region (see Tab. 2) and a separate treatment of this configuration is warrantable.

As for the previous configuration ζ_{4d} and E_{av} are choosen as free fit parameters. The other parameters were fixed to constant values having virtually no influence on the result for ζ_{4d}.

However, a problem occurs for the configuration $4d^35s6s$: a fit with all six energy levels given in [5] shows very bad agreement between experimental and calculated energies. Excluding the $^6\mathrm{F}_{11/2}$ level re-establishes good agreement as indicated by the standard deviation of 5 cm^{-1} achieved by fitting the remaining five experimental energy levels $^6\mathrm{F}_{1/2\,-\,9/2}$. The fitted value of the spin-orbit interaction parameter is

$$\zeta_{4d}(4d^35s6s) = 500\,(2)\ \mathrm{cm}^{-1}$$

which is in good agreement with the ζ_{4d} value of the configuration $4d^35s^2$.

The levels of the $^6\mathrm{F}$ multiplet are listed in Table 4. They are nearly pure SL states and, as for the configuration $4d^46s$, no g-factors are given in [5].

As a result of this fit of the five levels $^6\mathrm{F}_{1/2\,-\,9/2}$, an energy of 39 633 cm^{-1} is calculated for the level $^6\mathrm{F}_{11/2}$ instead of 39 408.88 cm^{-1} as given by Moore [5]. The difference of 224 cm^{-1} between this two energy values is too high to be explained as deviation of fit results. The level 39 408.88 cm^{-1} is specified with two spectral lines only in the visible spectral range. In the experimental investigations of the hyperfine structure of Nb I, summarized in [3], no transition to this level is measured. Therefore, we assume that the level $^6\mathrm{F}_{11/2}$ is not existent at the energy given by Moore [5]. Currently the calculated energy is given for the $^6\mathrm{F}_{11/2}$ level in Table 4.

As a consequence of this, the energy of the low lying odd level $4d^35s5p\ ^6\mathrm{F}_{13/2}$ given with 18 976.46 cm^{-1} by Moore [5] is also questionable, because it is reachable in the visible spectral range only as transition from the levels $^6\mathrm{F}_{11/2}$, whose energy is called into doubt just now.

Table 4. Experimental and calculated hyperfine constants A and B and differences in between in MHz for the levels of the $\{[4d^3(^4\mathrm{F})5s]^5\mathrm{F}\,6s\}\,^6\mathrm{F}$ multiplet of Nb I. The differences between experimental and calculated B's are given in parentheses to indicate that this is not a result of a fit (see text). For the level with $J = 11/2$ the calculated fine structure energy is given (see comment in Sect. 2.3).

E/cm^{-1}	J	A_{exp}	A_{calc}	ΔA	B_{exp}	B_{calc}	ΔB
37 871.30	1/2	−1 750	−1 750	0			
38 021.41	3/2	548	552	−4	−24	−9	(−15)
38 276.59	5/2	872	868	4	−10	−2	(−8)
38 638.47	7/2	959	958	1	−59	15	(−74)
39 100.73	9/2	982	983	−1	67	42	(25)
39 633	11/2		979			78	

3 Hyperfine structure

The hyperfine structure investigation is based on the experimental data from the preceding paper, Bouzed *et al.* [3]. In general, the mean value is taken for the fit if two or more values are given for one energy level. Where the B constant of a level is determined by atomic beam magnetic resonance technique [2] or laser radiofrequency double resonance technique [6], only these values are considered. A further exception is for the 14 211.30 cm^{-1}, $J = 3/2$ level, where a very large deviation is found between our A and B values [3] and those given by Singh *et al.* [7]. In this case our values were taken, as the results have proved to be consistent using the result of two different spectral lines.

According to the effective operator formalism introduced by Sandards and Beck [8], the experimental hyperfine structure constants A_{exp} and B_{exp} can be expressed as a linear combination of effective one-electron hyperfine parameters. For the magnetic dipole hyperfine structure, there are three parameters, a^{01}_{4d}, a^{12}_{4d} and a^{10}_{4d}, for the $4d$ shell of each configuration plus one parameter, a^{10}_{ns}, for each open ns shell. For the electric quadrupole hyperfine structure, three parameters, b^{02}_{4d}, b^{11}_{4d} and b^{13}_{4d}, for the $4d$ shell of each configuration are found. We determined the one-electron hyperfine structure parameters by a least squares fit of the experimental hyperfine constants A and B. The angular coefficients, $\alpha^{k_sk_l}_{nl}$ and $\beta^{k_sk_l}_{nl}$, are calculated with a numerical implementation of the Racah algebra method [9]. This takes into account the admixtures given by the fine structure calculation.

3.1 Configurations $4d^45s$, $4d^35s^2$ and $4d^5$

For the configurations $4d^45s$, $4d^35s^2$ and $4d^5$ ten effective one-electron hyperfine parameters $a^{k_sk_l}_{nl}$ occur for the magnetic dipole hyperfine structure and nine one-electron parameters $b^{k_sk_l}_{nl}$ for the electric quadrupole hyperfine structure. It should be noted that further hyperfine parameters, which result from non diagonal matrix elements between the configurations, are neglected here.

For the analysis of these configurations, 31 experimental A and 24 experimental B constants were available from literature [3]. Although the systems of equations are well overdetermined it is not possible to fit all parameters independently.

For the configuration $4d^5$, only one level is assigned predominantly to this configuration. According to the fine structure calculation (see Sect. 2.1) this level (11 344.70 cm^{-1}, $J = 5/2$) is 99.5% pure $4d^5\,{}^6$S. For a $^{2S+1}$S state the only parameter, which contributes to A is a^{10}_{4d}. Due to the very small deviation of this state from the SL limit, the angular coefficients of all other parameters are almost equal to zero and the contributions of these parameters are negligible. The angular coefficient of a^{10}_{4d} is approximately 1; and in the SL limit it is exactly 1. Therefore the parameter

$$a^{10}_{4d} \approx A_{\rm exp}(4d^5\,{}^6{\rm S}) = -642 \text{ MHz}$$

is reliably determined.

It is not possible to fit more than this one parameter for the configuration $4d^5$, so the two other parameters a^{01}_{4d} and a^{12}_{4d} have to be fixed or held at a constant ratio with another parameter. There exist two possibilities to do this: firstly to hold all three parameters of this configuration at a constant ratio based on the ratios of the relativistic hyperfine integrals as calculated from the OHFS (Optimized Hartree-Fock-Slater) method given in [10], or secondly to hold the two parameters a^{01}_{4d} and a^{12}_{4d} at a constant ratio with the corresponding parameters of another configuration (*e.g.* $4d^45s$) based on the ratio of the fine structure spin-orbit parameter, ζ_{4d}, of the relevant configurations. First attempts indicated that the ratios a^{10}_{4d}/a^{01}_{4d} and a^{10}_{4d}/a^{12}_{4d} are clearly different from what is expected from OHFS calculations. We therefore decided to use the second option. Additionally, the ratio of the two parameters a^{12}_{4d} of the configurations $4d^45s$ and $4d^35s^2$ is set to the ratio of the corresponding fine structure spin-orbit parameters.

This leads finally to a fit for the magnetic dipole hyperfine structure with four free parameters and 31 experimental A constants. Under exclusion of four levels a standard deviations of 52 MHz is achieved which corresponds to approximately 8% of the mean absolute value of the A constants.

All four levels excluded from the fit are levels which are strongly mixed between the configurations, hence the strong deviations between experimental and calculated A constants of these levels may be due to neglecting the matrix elements of the hyperfine structure operator between different configurations. For other levels, which are also strongly mixed between the configurations, the hyperfine interaction between different configurations seems to be not so influential.

Two of these levels, 10 126.06 cm^{-1} and 13 629.15 cm^{-1}, are levels which additionally show high deviations between experimental and calculated g-factors indicating the inaccuracy of the eigenfunctions.

The experimental and the best fitted A values as well as calculated A constants for all levels with unknown $A_{\rm exp}$ are listed in column 13 to 15 of Table 2. The resulting effective one-electron hyperfine parameters are summarized in Table 5.

Table 5. Magnetic dipole hyperfine structure parameters for the even parity configurations $4d^45s$, $4d^35s^2$, $4d^5$, $4d^46s$ and $4d^35s6s$ of Nb I in MHz together with values from Büttgenbach and Dicke [1].

	parameter	this work	reference [1]
$4d^45s$	a^{01}_{4d}	280 (30)	351.67 (0.58)
	a^{12}_{4d}	210 (100)	276.08 (2.17)
	a^{10}_{4d}	−370 (40)	−511 (30)
	a^{10}_{5s}	6 390 (160)	6 700 (118)
$4d^35s^2$	a^{01}_{4d}	380 (30)	395.39 (0.25)
	a^{12}_{4d}	250	338.34 (3.19)
	a^{10}_{4d}	−300 (60)	−225.84 (1.97)
$4d^5$	a^{01}_{4d}	240	
	a^{12}_{4d}	180	
	a^{10}_{4d}	−650 (60)	
number of fitted A's		27	9
standard deviation		52	
$4d^46s$	a^{01}_{4d}	310 (6)	
	a^{12}_{4d}	135 (30)	
	$4\,a^{10}_{4d} + a^{10}_{6s}$	−1 303 (12)	
number of fitted A's		5	
standard deviation		4	
$4d^35s6s$	a^{01}_{4d}	366 (8)	
	a^{12}_{4d}	−980 (100)	
	$4\,a^{10}_{4d} + a^{10}_{6s}$	8 854 (18)	
number of fitted A's		5	
standard deviation		3	

Concerning the electric quadrupole hyperfine structure, for the only level assigned predominantly to the configuration $4d^5$, ^{6}S$_{5/2}$ at 11 344.70 cm^{-1}, all angular coefficients are approximately zero. The experimental result

$$B_{\rm exp}(4d^5\,{}^6{\rm S}) = -0.061\,(92) \text{ MHz}$$

agrees with this. Hence, this levels is inapplicable for the determination of the one-electron parameters of the configuration $4d^5$. Because the admixture of $4d^5$ is very small for all other levels with experimentally known B constants it is not at all possible to determine the parameters of this configuration. Therefore all three parameters b^{02}_{4d}, b^{11}_{4d} and b^{13}_{4d} of the configuration $4d^5$ were held at a constant ratio with the corresponding parameters of the configuration $4d^45s$ based on the ratio of the fine structure spin-orbit parameter of the relevant configurations.

A fit of the electric quadrupole hyperfine structure with six free parameters, three each for the configurations

Table 6. Electric quadrupole hyperfine structure parameters for the even parity configurations $4d^4 5s$, $4d^3 5s^2$, $4d^5$ and $4d^4 6s$ of Nb I in MHz together with values from Büttgenbach and Dicke [1].

	parameter	this work	reference [1]
$4d^4 5s$	b_{4d}^{02}	−231 (8)	−232.04 (0.17)
$4d^3 5s^2$	b_{4d}^{02}	−273 (9)	−263.58 (2.85)
$4d^5$	b_{4d}^{02}	−199	
number of fitted B's		21	8
standard deviation		7	
$4d^4 6s$	b_{4d}^{02}	−220 (20)	
number of fitted B's		4	
standard deviation		13	

$4d^4 5s$ and $4d^3 5s^2$ leads to reasonable standard deviation but to uncertainties of the parameters b_{4d}^{11} and b_{4d}^{13} which are of the same order of magnitude as the values themselves. The same facts are found if additionally the parameters of $4d^3 5s^2$ are coupled to the corresponding parameters of $4d^4 5s$ using the ratio of the fine structure spin-orbit parameters. This is due to the high uncertainty of some of the experimental B values associated with relatively small coefficients of the parameters b_{4d}^{11} and b_{4d}^{13}.

If instead of the coupling the parameters of the configurations $4d^3 5s^2$ and $4d^4 5s$, the ratio of all three parameters of each one configuration is held in a constant ratio following the relativistic hyperfine integrals from the OHFS [10], the standard deviation doesn't change significantly. The values of the remaining two free fit parameters, b_{4d}^{02} for the two configurations $4d^4 5s$ and $4d^3 5s^2$, concur for all fit variations mentioned above in the range of tolerance, which means that the influence of the parameters b_{4d}^{11} and b_{4d}^{13} is negligible. Even in the non-relativistic limit, which means $b_{4d}^{11} = 0$ and $b_{4d}^{13} = 0$, the best fit values of the parameters b_{4d}^{02} and the standard deviations remained similar.

In all different fit versions three levels have been excluded from the fit because of strong deviations between experimental and best fitted values. The results of the non-relativistic fit version are listed in Table 6. The standard deviation of the fit was 7 MHz which corresponds to 13% of the mean absolute value of the B constants. The experimental and the best fitted B values as well as calculated B constants for all levels with unknown B_{exp} are listed in column 16 to 18 of Table 2.

For comparison, one-electron parameter values from previous parametric investigations done by Büttgenbach and Dicke [1] are given in Tables 5 and 6. In the model space of Büttgenbach and Dicke the configuration $4d^5$ was not included. Using only nine experimental A constants and eight experimental B constants belonging to the lowest two multiplets, they fitted seven and six parameters, respectively. So, the degree of overdetermination of their fits is very low. Nevertheless their results for the magnetic dipole hyperfine structure are similar to our results. The values for the electric quadrupole hyperfine structure even agree with our results within the limits of error.

3.2 Configuration $4d^4 6s$

In the configuration $4d^4 6s$ for all five known fine structure levels the hyperfine structure constants are measured [3]. The experimental magnetic dipole hyperfine structure constants A_{exp} can be expressed as a linear combination of the four effective one-electron hyperfine parameters a_{4d}^{01}, a_{4d}^{12}, a_{4d}^{10} and a_{6s}^{10}. Following the fine structure calculation (Sect. 2.2) the states are nearly pure in SL coupling. Because of the very small departure of the states from the SL limit, distinction between a_{4d}^{10} and a_{6s}^{10} is difficult if only one multiplet is given as experimental basis. If the states are assumed to be pure SL states, the angular coefficients α_{4d}^{10} and α_{6s}^{10} of the parameters a_{4d}^{10} and a_{6s}^{10} are linearly dependent for all levels of the multiplet ^{6}D:

$$\alpha_{4d}^{10} = 4\alpha_{6s}^{10}.$$

Therefore only the linear combination $(4\,a_{4d}^{10} + a_{6s}^{10})$ can be determined in a fit of the experimental A constants. So, we get a fit with three free parameters and five experimental A values. The fitted parameters are listed in Table 5. The agreement between experimental and the best fitted hyperfine structure constants A, tabulated in Table 3, is good, shown by a standard deviation of 4 MHz.

The fitted value of $(4\,a_{4d}^{10} + a_{6s}^{10})$ is –1 303 (12) MHz. If we assume that the ratio of $a_{6s}^{10}(4d^4 6s)/a_{5s}^{10}(4d^4 5s)$ lies between 5 and 20, with

$$a_{5s}^{10}(4d^4 5s) \approx 6\,500 \text{ MHz}$$

it follows

$$325 \text{ MHz} < a_{6s}^{10}(4d^4 6s) < 1\,300 \text{ MHz}.$$

Consequently, from

$$4\,a_{4d}^{10} + a_{6s}^{10} = -1\,303\,(12) \text{ MHz}$$

follows

$$-650 \text{ MHz} < a_{4d}^{10}(4d^4 6s) < -400 \text{ MHz}.$$

Hence, as for the other even configurations, for this configuration the value of a_{4d}^{10} is according to amount of same order of magnitude than the value of a_{4d}^{01}.

For the electric quadrupole hyperfine structure four experimental constants B_{exp} are available [3]. The experimental uncertainty of these values is rather high, on average about 30%. Following Sandars and Beck [8] three one-electron parameters b_{4d}^{02}, b_{4d}^{13} and b_{4d}^{11} occur to describe the experimental B values. A fit of all three parameters leads to an uncertainty of the parameters b_{4d}^{13} and b_{4d}^{11} in the same order of magnitude as the value itself. The difference between best fitted and experimental values is much smaller than the uncertainty of the experimental values. So the results of this fit are not significant.

If the ratios b^{02}_{4d}/b^{11}_{4d} and b^{02}_{4d}/b^{13}_{4d} calculated from OHFS by Olsson and Rosén [10] for the configuration $4d^4 5s$ are adopted for the configuration $4d^4 6s$ and are fixed during the fit (*i.e.* only one free parameter), the value of the parameter b^{02}_{4d} changes only within the limits of error. The standard deviation becomes higher but is still smaller than the uncertainty of the experimental values.

Also a fit in the non-relativistic limit, which means $b^{13}_{4d} = 0$ and $b^{11}_{4d} = 0$, doesn't change the value of b^{02}_{4d} and the standard deviation significantly.

The resulting value of the non-relativistic fit for the parameter b^{02}_{4d} is given in Table 6. The experimental and the best fitted hyperfine structure constants B are listed in Table 3.

3.3 Configuration 4d^{3}5s6s

For the configuration $4d^3 5s6s$ the hyperfine structure constants are measured for five of six fine structure levels belonging to the lowest multiplet ^{6}F [3].

The experimental magnetic dipole hyperfine structure constants $A_{\rm exp}$ can be expressed as a linear combination of the five effective one-electron hyperfine parameters a^{01}_{4d}, a^{12}_{4d}, a^{10}_{4d}, a^{10}_{5s} and a^{10}_{6s}. Following the fine structure calculation (Sect. 2.3) the states are nearly pure in SL coupling. As consequence – as for the lowest multiplet of the configuration $4d^4 6s$ – distinction between the parameters a^{10}_{4d}, a^{10}_{5s} and a^{10}_{6s} is difficult if only one multiplet is given as experimental basis. If the states are assumed to be pure SL states we found for the lowest multiplet ^{6}F:

$$\alpha^{10}_{4d} = 3\alpha^{10}_{5s} = 3\alpha^{10}_{6s}.$$

A fit with the three free parameters a^{01}_{4d}, a^{12}_{4d} and $(3\,a^{10}_{4d} + a^{10}_{5s} + a^{10}_{6s})$ (case of pure SL coupling) and five experimental A constants leads to a good agreement between experimental and fitted A values (standard deviation of 3 MHz). But the fitted value for a^{12}_{4d} is $-980\,(100)$ MHz, which is of opposite sign and much higher than would be expected. Following our results for the other even configurations the ratio of the parameters a^{01}_{4d}/a^{12}_{4d} lies between 1.3 and 2.2. On the other hand, following the OHFS values from Olsson and Rosén [10] for the even configuration $4d^4 5s$, $4d^3 5s^2$ and $4d^5$ the ratios a^{01}_{4d}/a^{12}_{4d} should be between 0.91 and 0.94.

A few trials have been performed with fixed values for the ratio of these two parameters with the following results: The fitted value of $(3\,a^{10}_{4d} + a^{10}_{5s} + a^{10}_{6s})$ is not influenced very much by this additional reduction of free fit parameters. It varies from 8 720 MHz (for the ratio $a^{01}_{4d}/a^{12}_{4d} = 0.9$) to 8 850 MHz (for a fit with all parameters free), which is an uncertainty of about 1.5%. The value of a^{01}_{4d} is of course affected by the ratio a^{01}_{4d}/a^{12}_{4d} and varies from 480 MHz (for the ratio $a^{01}_{4d}/a^{12}_{4d} = 0.9$) to 370 MHz (for a fit with all parameters free).

If one deviates from pure SL coupling and takes into account the very small contribution of the other levels of this configuration, the angular coefficients are changing perceptibly. Especially for the coefficients of the parameter a^{12}_{4d}, whose absolute value is very small, the influence is strong. Additionally the linear dependence of the three parameters a^{10}_{nl} is overrided by the consideration of the small contribution of the other basis states. The system responds very sensitively to changes in the eigenvectors. However, because one multiplet is known only for this configuration, no reliable prediction can be given for the eigenvectors. Hence, no satisfying results can be found for a parametric fit of the magnetic dipole hyperfine structure constants A.

Nevertheless the best fitting values of the fit in pure SL coupling with three free parameters are listed in Table 4, particularly to show the calculated value of the ^{6}F$_{11/2}$ level, the A constant of which is experimentally unknown up to now.

Also the parametric fit of the electric quadrupole hyperfine structure for the configuration $4d^3 5s6s$ gives trouble. Four experimental constants $B_{\rm exp}$ are available. The absolute value of these constants are small, the relative uncertainty consequently rather high, up to more than 100%. Following Sandards and Beck [8], three one-electron parameters b^{02}_{4d}, b^{13}_{4d} and b^{11}_{4d} occur. A fit of all three parameters leads to an uncertainty of all three parameters in the same order of magnitude as the value it self. The difference between experimental and best fitting B values is high, but still smaller than the uncertainty of the experimental values. So the results of this fit are not significant. Even a fit in the non-relativistic limit ($b^{13}_{4d} = 0$ and $b^{11}_{4d} = 0$) does not yield better results.

To give an impression of the order of magnitude of the B's, approximate values are calculated using the value of the b^{02}_{4d} parameter of the configuration $4d^3 5s^2$. They are listed together with the experimental values in Table 6. With exception of the level ^{6}F$_{7/2}$ at 38 638.47 cm^{-1} at least the trend of the experimental values is represented correctly by the calculated ones.

4 Discussion

For all configurations under investigation the values determined for the contact parameter a^{10}_{4d} for the magnetic dipole hyperfine interaction are very much larger than would be expected from Optimized Hartree-Fock-Slater calculations done by Olsson and Rosén [10]. This may arise from the contribution of the spin to the core polarization. Following our suggestion *ab initio* calculations of the hyperfine structure parameter a^{10}_{4d} for ^{93}Nb have been done by Loginov and Tupitsin [11] in various approximations applying non-relativistic Hartree-Fock-Sturm equations as well as relativistic Hartree-Fock-Dirac-Sturm equations. The results of these calculations for the configuration $4d^5$ lie between $a^{10}_{4d} = -650$ MHz and $a^{10}_{4d} = -492$ MHz using methods which take into account configuration interaction and all orders of the perturbation theory. These results are in good agreement with our result.

From our interpretations of the electric quadrupole interaction it is to be seen that the influence of relativistic effects represented by the parameters b^{13}_{4d} and b^{11}_{4d} is small, especially by comparison with the uncertainty of some of

the experimental B values. Therefore, for all configurations the results from the non relativistic approach are given. The standard deviation achieved is inside the experimental uncertainties of Doppler limited optical measurements. In contrast to us, Büttgenbach and Dicke [1] were able to determine parameters values for b^{13}_{4d} and b^{11}_{4d}. This is due to the high accuracy of the eight experimental B constants they used and due to the fact that the eigenvectors for all these states are very close to the SL limit.

5 Conclusion

For the three configurations $4d^45s$, $4d^45s^2$ and $4d^5$ as well as for the two energetically high lying configurations $4d^46s$ and $4d^35s6s$, a parametric analysis of the fine structure and the hyperfine structure has been performed. Effective one-electron parameters a^{01}_{4d}, a^{12}_{4d}, a^{10}_{4d}, a^{10}_{5s} and b^{02}_{4d} are determined. A very large value for the contact parameter a^{10}_{4d} has been ascertained. This is in good agreement with results from *ab initio* calculations done by Loginov and Tupitsin [11].

Theoretical predictions for the fine structure energies as well as for the hyperfine structure constants A and B for all levels of the configurations $4d^45s$, $4d^45s^2$ and $4d^5$ with experimentally unknown values are given.

For the configuration $4d^35s6s$ the parametric interpretation of the fine structure leads to the deduction that the energy of the fine structure levels $4d^35s6s\ ^6\mathrm{F}_{11/2}$ given in the Moore tables is not correct. As a consequence, the energy of the level $4d^35s5p\ ^6\mathrm{G}_{13/2}$ is called into doubt. Experiments to scrutinize these energies are in progress.

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