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Studies of electronic configurations in the emission spectra of lanthanides and actinides: application to the interpretation of Es I and Es II, predictions for Fm I

Jean-Francois Wyart[a,*], Jean Blaise[a], Earl F. Worden[b]

[a]*Laboratoire Aimé Cotton, CNRS, Batiment 505, Centre Universitaire, FR-91405 Orsay Cedex, France*
[b]*Physics and Advanced Technologies Directorate, Lawrence Livermore National Laboratory, L-044, Livermore, CA 94550, USA*

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Abstract

The interpretation of the spectra of free atoms and gaseous ions in the $4f^N$ and $5f^N$ periods became less active after critical compilations of energy levels appeared. However, several spectra are still under study and the application of the Racah–Slater and HFR methods to extended sets of configurations leads to revisions and additions. In doubly charged ions of lanthanides, the treatment of configuration interaction by means of effective parameters and by extension of the basis of states are both important. Concerning actinides, calculations of several observables (Landé factors and isotope shifts in Pu I, hyperfine constants, transition probabilities) prove the quality of eigenfunctions. The classification of Es I and Es II has been extended and radial parameters for fine and hyperfine structures have been derived. Level predictions for the next element fermium are supported by parameter extrapolations.

Keywords: Atomic spectra; Racah–Slater theory; Hyperfine structure; Isotope shift; Praseodymium; Plutonium; Californium; Einsteinium; Fermium

1. Introduction

The present contribution has several purposes which are bound with the continuous interest of Carnall for the parametric interpretation of energy levels. First a survey of recent works giving experimental energy levels of lanthanide ions produced by sparks, and a comment on excited configurations in Pr^{3+}; second, a progress report on the analysis of Es I and Es II, and predictions for Fm I by means of Racah–Slater parametric method with extrapolated radial integrals. Major advances in the spectra of atoms and gaseous free ions were performed in the period 1965–1975 owing to: (a) systematic observations of visible and ultraviolet, emission and absorption spectra on the 9.15 m Paschen–Runge spectrograph at Argonne for nearly all *f*-elements, (b) Fourier Transform spectra initiated in the infrared at Orsay and continued in many other places. At the same time parametric calculations of various configurations guided the search for new levels.

Besides difficulties specific to each element, radial parameters pertaining to the Hamiltonian operator show regular trends as a function of atomic number, so that *f*-periods benefit from findings in any of their members. Carnall had a prominent role in the description of those regularities [1]. Later, the large distribution of LANL computer codes by Cowan which coupled the Slater–Racah method with Hartree–Fock (HFR) evaluations of radial integrals stimulated calculations of mixed configurations and of their gA transition probabilities [2]. The comparison of gA with observed intensities resulted in checks and improvements of the identifications for several lanthanide ions, as reviewed in Section 2.

*Corresponding author. Fax: +33 1 69 35 21 00.
E-mail address: jean-francois.wyart@lac.u-psud.fr (J.-F. Wyart).

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The strong resonance lines in the spectra of neutral and ionized einsteinium have been classified in Ref. [3], but the lowest levels of the first excited configurations in Es I have been interpreted only recently by parametric calculations. The present status of Es I and Es II is sketched in Section 3. In as much as $_{100}$Fm I cannot be studied by the same conventional spectroscopic means as $_{98}$Cf I and $_{99}$Es I, i.e. energy levels derived from line rich emission spectra, predictions bound with parametric studies of lower-Z elements are welcome. New studies of $5f^N7s^2$ and $5f^N7s$ levels and hyperfine effects are collected in Section 4 and extrapolations for Fm I in Section 5.

Finally, it seems worth mentioning that the critical compilation of Atomic Energy Levels and Spectra of Actinides [4] was made available on the website of laboratoire Aime Cotton (www.lac.u-psud.fr/Database/Contents.html) in 2002.

2. Status of the analysis and parametric studies in lanthanide spark spectra

Until 1976 when the Atomic Spectroscopy group at NBS ended the compilation *Atomic Energy Levels—The Rare Earth Elements* [5], almost all elements La till Lu were actively studied. Further revisions and additions in Pr II [6], Nd II [7], Yb II [8] are not reported in the NIST database which is built from Ref. [5]. In Nd II, Blaise et al. corrected their initial value of the lowest odd parity levels given in Ref. [5]. The status of the classification for lanthanides singly charged ion spectra strongly depends on the element. For some reasons (hyperfine structure of the lines, lack of theoretical studies for the largest $4f^{N-2}5d^2$ configurations, weak population of high levels in light sources), the "second" system of transitions with lower configurations $4f^{N-2}(5d+6s)^2$ has not yet been detected in Pm II, Sm II, Eu II, Ho II.

Global knowledge for doubly charged lanthanides is still worse than for second spectra and the presence of such ions in outer layers of some chemically peculiar stars observed from Hubble Space Telescope [9] leads to resume the interpretation of laboratory spectra. Fourier Transform spectrometers (FTS) fulfil the wavelength accuracy requirements of the stellar spectra from HST. However FTS needs light sources of stable intensities which do not excite well high-energy levels needed for extended analyses. In absence of new observations from sparks with VUV high-resolution spectrographs, old spectral plates and line lists keep an unsurpassed interest. This was true for the analysis of Dy III, missing spectrum in Ref. [5], whose first energy levels were issued in 1997 [10]. Another source of data are the numerous lists of lines (classified and unclassified) from which new levels may be obtained, as done in Ce III [11], Tb III [12], Er III [13] and Yb III [14]. In all those spectra, the application of the Racah–Slater parametric method leads to average deviations $\Delta E = E_{\rm exp} - E_{\rm th}$ of the order of 10^{-3} of the interpreted energy range, when configuration interaction (CI) effects are taken into account simultaneously by Slater integrals connecting states of the multiconfiguration bases and by effective parameters for far configuration effects. It is worth noticing in a preliminary report on the Pr III [15] extended analysis that, for $4f^3$, the two-particle, 2nd-order parameters α, β, γ, of the usual correction $\alpha L(L+1)+\beta G(G2)+\gamma G(R7)$ [16] converge in a 20 configurations basis assumption to smaller values than in a strictly effective process of CI effects [17].

The present status for trivalent gaseous free ion energy levels is not different from that given by Martin et al. [5], except for Yb IV, in which the number of classified lines was doubled, the number of known levels was increased from 111 in Ref [18] to 193, the $4f^{12}$ core parameters were improved, and the lowest terms of $4f^{12}7s$ and -$6d$ were established [19]. For other lanthanides, the published line lists are limited to classified lines with intensities. This prevents any search for levels but allows checks of the designations by means of calculated transition probabilities. The Cowan codes used for Ce III [11] are applied here to the isoelectronic spectrum of Pr IV. This spectrum had been analyzed by Crosswhite [20] and Sugar [21,22] who agreed for all strong classified lines as commented in Ref. [5]. Parametric studies of single configurations $4f^2$, $4f5d$, $4f6s$, $4f6p$, $4f6d$ and $4f5f$ ended with small $E_{\rm exp}-E_{\rm th}$ deviations, in average smaller than $30\,{\rm cm}^{-1}$ for all twelve levels of $4f6p$. In the energy range of $4f6p$, a few experimental levels were attributed empirically to $5d^2$ without support of parametric studies. For several reasons derived from the application of the Slater–Racah and HFR methods, other identifications are needed for these levels:

(a) In the isoelectronic spectrum of Ce III [11] very strong fp–d^2 repulsions and mixings are noticed, preventing any acceptable description of $4f6p$ on a 'single' configuration basis. Therefore, it is unlikely that, the HFR values of the R^1 (fp,dd) and R^3 (fp,dd) integrals being, respectively, 3379 and $467\,{\rm cm}^{-1}$ in Pr IV and 4048 and $961\,{\rm cm}^{-1}$ in Ce III, $4f6p$ may be not perturbed in the former case by the overlapping configuration $5d^2$; actually, attempts to determine an acceptable parameter set and small ΔE deviations for $(4f6p+5d^2)$ cannot be obtained as long as any of the levels at 139,711, 139,784, 144,343 and $145{,}362\,{\rm cm}^{-1}$ is forced to a $5d^2$ identification.

(b) The correspondence between line intensities and transition probabilities is very good for $4f6p$, as seen in the column gA (a) of Table 1; it does not fit at all for the assumed $5d^2$ levels, which are predicted by RCN/RCG codes above $152{,}000\,{\rm cm}^{-1}$. As the four

Table 1
Comparison of observed intensities (I1 from Ref. [20] and I2 from Ref. [21,22]) with transition probabilities (gA in $10^7\,s^{-1}$) for selected even levels of Pr IV decaying to 4*f*5*d* and 4*f*6s. The transition probabilities gA (a) are calculated with two-electron configurations only, for gA (b) the configuration $5p^5 4f^3$ is added. In the latter case, the radial parameters given in Table 2 lead to calculated energies 140,219 cm^{-1} for 4*f*6*p* 140,225 and 139,838 cm^{-1} for $5p^5 4f^3$ 139,784 cm^{-1}. Wavelengths (in air above 2000 Å) are derived from the level energies

Odd level	E (cm^{-1})	J	Wavelength (Å)	I1	I2	gA (a)	gA (b)	Wavelength (Å)	I1	gA (b)	Note
			139,875.31 4*f*6*p* (7/2,1/2)3					139,710. 81 $5p^5 4f^3$			[a]
4*f*5*d*	61,170.95	4	1270.578	5	300	41		1273.239	—		
4*f*5*d*	61,457.48	2	1275.220	—	3	4					
4*f*5*d*	63,355.94	3	1306.859	7	300	68		1309.674	—		
4*f*5*d*	63,580.59	4	1310.707	3	200	27		1313.539	—		
4*f*5*d*	64,123.54	3	1320.101	10	500	179		1322.974	5		
4*f*5*d*	65,321.67	2	1341.316	5	200	25		1344.282	—		
4*f*5*d*	65,639.95	4	1347.067	25	1000	218		1350.059	?		[b]
4*f*5*d*	66,518.01	4	1363.191	10	100	30		1366.255	3		
4*f*5*d*	68,411.51	2	1399.310	30	1000	177		1402.538	5		
4*f*5*d*	68,495.57	3	1400.958	25	1000	116		1404.194	3		
4*f*5*d*	71,724.77	3	1467.340	—	40	12					
4*f*5*d*	72,185.10	2	1477.319	5	200	41		1480.917	—		
4*f*6*s*	100,258.48	2	2523.420	—	1	9					[c]
4*f*6*s*	100,543.85	3	2541.730	—	—	18					[c]
4*f*6*s*	103,271.38	4	2731.138	7	100	134		2743.469	2		[c]
4*f*6*s*	103,753.75	3	2767.612	20	200	105		2780.274	3		[c]
			140,225.92 4*f*6*p* (7/2,1/2)4					139,784.48 $5p^5 4f^3$			[a]
4*f*5*d*	61,170.95	4	1264.943	5	5	34	36	1272.046	—	0	
4*f*5*d*	63,355.94	3	1300.898	—	100	22	19	1308.412	—	2	
4*f*5*d*	63,580.59	4	1304.711	10	200	106	102	1312.269	—	3	
4*f*5*d*	64,123.54	3	1314.019	3	100	41	39	1321.686	—	2	
4*f*5*d*	65,239.39	5	1333.573	30	5000	376	332	1341.470	10	36	
4*f*5*d*	65,639.95	4	1340.735	10	1000	287	266	1348.717	2	17	
4*f*5*d*	66,518.01	4	1356.706	—	20	12	13	1364.881	—	0	
4*f*5*d*	67,899.32	5	1382.617	15	1000	172	173	1391.108	—	2	
4*f*5*d*	68,495.57	3	1394.110	20	300	81	79	1402.743	—	2	
4*f*5*d*	71,724.77	3	1459.830	—	—	1	1	1469.298	—	0	
4*f*5*d*	75,265.66	5	1539.403	15	15	81	80	1549.935	-	1	
4*f*6*s*	100,543.85	3	2519.272	—	—	10	7	2547.614	20	6	[c]
4*f*6*s*	103,271.38	4	2705.225	20	500	220	212	2737.933	3	8	[c]
4*f*6*s*	103,753.75	3	2741.01	20	100	116	108	2774.590	3	5	[c]
			144,925.33 4*f*6*p* (7/2,3/2)4					145,362.7 $5p^5 4f^3$			
4*f*5*d*	61,170.95	4	1193.967	—	100	76		1187.765	—		
4*f*5*d*	63,355.94	3	1225.950	—	10	6					
4*f*5*d*	63,580.59	4	1229.336	—	—	14		1222.761	—		
4*f*5*d*	64,123.54	3	1237.596	—	10	9					
4*f*5*d*	65,239.39	5	1254.927	—	—	8		1248.076	—		
4*f*5*d*	65,639.95	4	1261.267	1	200	53					
4*f*5*d*	66,518.01	4	1275.391	5	200	297		1268.316	1		
4*f*5*d*	67,899.32	5	1298.263	5	200	132		1290.933	3		
4*f*5*d*	68,495.57	3	1308.400	—	50	13					
4*f*5*d*	71,724.77	3	1366.110	15	100	80		1357.996	5		
4*f*5*d*	75,265.66	5	1435.551	45	5000	559		1426.594	15		
4*f*6*s*	100,543.85	3	2252.494	—	20	27					[c]
4*f*6*s*	103,271.38	4	2400.002	20	100	158		2375.062	2		[c]
4*f*6*s*	103,753.75	3	2428.123	60	500	307		2402.598	—		[c]

[a] Transitions for the levels 139,710 and 139,784 have not been reported by Sugar [21,22].
[b] Silicon is seen to be an impurity in the light source of Ref. [20]. The Si II strong line λ1350.057 Å may mask the Pr IV transition 65,639–139,711 with probable I~5.
[c] Wavelengths to 4*f*6*s* are for the center of gravity of the hyperfine structure.

levels have enough transitions to be considered as real, another interpretation has to be found. By resuming the Pr IV study with the core-excited configuration $5p^5 4f^3$ added to the previous set of 'two-electron' ones, it is found that $5p^5 4f^3$ extends from 136,000 to 243,000 cm^{-1} with some uncertainty

bound with its average energy E_{av} relative to the ground and with the unknown scaling factor of the HFR radial integrals with $5p$ electron. Although the LS coupling is broken by the large spin–orbit splitting of $5p^5$, the lowest levels of $5p^54f^3$ have a dominant quintet character, and they do not interact directly with the close LS terms of $4f6p$. The CI effects $5p^54f^3$–$5p^64f6p$ have been evaluated by introducing (or removing) the Slater integrals $R^k(4f4f,5p6p)$ (HFR values $R^1 = 7070\,\mathrm{cm}^{-1}$ and $R^3 = 6203\,\mathrm{cm}^{-1}$) in the parameter sets. The shifts on the 12 levels of $4f6p$ are in the range -142 to $-202\,\mathrm{cm}^{-1}$, due to higher singlet and triplet terms in $5p^54f^3$. In a parametric study of $4f6p$ alone, such small shifts can be taken in account by its own parameters, mainly E_{av}. The configuration $5p^54f^3$ is metastable in absence of CI effects, the lower levels in odd parity ($5p^64f5d$, $5p^64f6s$) differing from $5p^54f^3$ by two electrons. For levels of $5p^54f^3$ with an assumed small component $4f6p$ in their wavefunctions, the branching ratios of radiative decay to $5p^64f5d$ and $5p^64f6s$ should be similar to the one of a $5p^64f6p$ close perturber. This fact is verified empirically for the couples of levels reported in Table 1 and the parameters proposed in Table 2 support our assumptions. If the value of E_{av} ($5p^54f^3$) is lowered in such a way that the second lowest level $J = 4$ in $5p^54f^3$ (which shows the largest mixing propensity) becomes coincident with $E_{exp} = 139,784\,\mathrm{cm}^{-1}$, then all five observed decay lines of this level correspond to the highest calculated transition probabilities (column gA (b) in Table 1). At least nine parameters are necessary for describing $5p^54f^3$ levels. This prevents a firm identification of the $5p^54f^3$ levels as long as the Pr IV analysis is not extended.

In the odd parity, the $5d6p$ levels predicted by the RCN/RCG codes are much higher (about $50{,}000\,\mathrm{cm}^{-1}$) in energy than levels 195,917 and $202{,}487\,\mathrm{cm}^{-1}$ tentatively labeled in Ref. [5] and a mixing of $5p^54f^25d$, $5p^64f6d$ and $5p^64f7s$ configurations probably occurs in the odd parity range 190,000–$203{,}000\,\mathrm{cm}^{-1}$. The presence of unclassified lines with Pr IV character noticed by Sugar [22] and the unknown level $4f^2\ {}^1S_0$ [5] should be reasons for resuming the analysis of Pr IV spark spectra.

3. Interpretation of the einsteinium spectra

After the initial determination of ground state and low-energy level intervals in Es I and Es II [3], the magnetic dipole A and electric quadrupole B hyperfine constants were investigated by Crosswhite owing to measurements of spectral plates [23] on an automatic comparator, but this did not lead to new energy levels. In the systematic study of $5f^N7s^2$ and $5f^N7s$ configurations of I and II spectra with the support of global fits of radial parameters from all relevant E_{exp} values of the actinides [24], a few additional levels were derived from the short line list of Ref. [3]. One of the reasons for the slow advances is that the infrared region of the Es emission spectrum is still unobserved and should contain transitions to $5f^{11}6d7s$ (first excited, odd parity configuration), to excited levels of the ground configuration $5f^{11}7s^2$ and also the $5f^{10}7s^27p$–$5f^{10}6d7s^2$ transitions. However, the level search from the line list of Refs. [3,23], corrected by measurements of the plates on the semi-automatic densitometer at Paris-Meudon observatory, led recently to several new levels (center of gravities and total hyperfine widths). The J-undeterminacy of some of the levels with few transitions, is removed by unraveling the hyperfine structure of each classified line, A_{upper}, B_{upper}, A_{lower} and B_{lower} constants being least-squares fitted from the wavenumbers of the hyperfine components of the line. The accuracy of atomic beam resonance method being about three orders of magnitude better than spectral plate measurements, but limited to the ground state $5f^{11}7s^2\ {}^4I_{15/2}$, the stepwise derivation of the hfs constants starts from resonance lines with fixed values $A = 27.2573\,\mathrm{mK}$ and $B = -143.9747\,\mathrm{mK}$ ($1\,\mathrm{mK} = 10^{-3}\,\mathrm{cm}^{-1}$) for $5f^{11}\ {}^4I_{15/2}$ [25]. For most of the analyzed hfs patterns, the

Table 2
Radial parameters used for $5p^64f6p$ and $5p^54f^3$ in Pr IV. All values in cm^{-1}

	Empirical	HFR	Empirical/HFR
$5p^64f^2$			
E_{av}	10,304	0	
$5p^64f6p$			
E_{av}	143,540	125,702	
ζ_{4f}	859	951	0.903
ζ_{6p}	3224	2796	1.153
$F^2(4f,6p)$	8486	10,059	0.844
$G^2(4f,6p)$	2677	2543	1.053
$G^4(4f,6p)$	2464	2340	1.053
$5p^54f^3$			
E_{av}	170,700	166,831	
F^2 $(4f,4f)$	72,273	92,272	0.78
F^4 $(4f,4f)$	50,910	57,606	0.88
F^6 $(4f,4f)$	32,660	41,359	0.79
ζ_{4f}	780	780	1
ζ_{6p}	17,000	14,953	1.14
F^2 $(5p,4f)$	45,591	50,656	0.90
G^2 $(5p,4f)$	23,527	29,409	0.80
G^4 $(5p,4f)$	17,768	22,210	0.80
R^2 $(5p6p,4f4f)$	6010	7070	0.85
R^4 $(5p6p,4f4f)$	5272	6203	0.85

Table 3
Selected energy levels of Es I (in cm^{-1}) and hyperfine constants (in $10^{-3}\,cm^{-1}$)

Term	J	E_{exp}	E_{th}	ΔE	A	B
$5f^{11}7s^2$						
^4I	15/2	0.00	52	−52	27.257	−143.975
^2H	11/2	8759.24	8708	52	29.11	4
$5f^{11}$ ($^4I_{15/2}$)$7s7p$						
$sp\ ^3P_0$	15/2	17,802.87	17,874	−71	68.31	
$sp\ ^3P_1$	17/2	19,209.02	19,126	83	93.87	−205
	15/2	19,367.92	19,541	−173	−4.20	6
	13/2	19,788.22	19,615	173	−42.85	−150
$sp\ ^3P_2$	19/2	23,333.05	23,275	58	88.55	0
	17/2	23,934.19	24,026	−92	(76.2)	
	15/2	24,338.29	24,463	−124	(51.1)	
	11/2	24,390.58	24,378	12	(-64.3)	
	13/2	24,489.42	24,562	−73	(3.3)	
$sp\ ^1P_1$	13/2	28,118.58	28,528	[−410]	44.4	88
	17/2	28,578.71	28,624	−46	-4.42	−65
	15/2	29,159.28	29,116	43	(18.6)	
$5f^{10}6d7s^2$ ($^5I_8$,$^2D_{3/2}$)						
	15/2	20,162.56			28.16	−52
	13/2	20,817.85			(32.4)	
	17/2	20,871.30			27.44	
$5f^{10}6d7s7p$ ($^5I_8$,$^2D_{3/2}$)15/2, $sp\ ^3P_0$)						
	15/2	37,485.58			69.00	
($5f^{11}$ ($^4I_{15/2}$)$7s$) $J1$, $7d\ j2$						
($J1$,$j2$)	J					
(8,3/2)	13/2	40,478.25	40,459	20	133.41	
(8,3/2)	15/2	40,536.93	40,564	−27	117.11	
(8,3/2)	19/2	40,704.55	40,722	−18	97.16	
(8,3/2)	17/2	40,744.46	40,729	15	106.35	
(8,5/2)	21/2	40,862.81	40,862	1	(89.1)	
(8,5/2)	19/2	40,977.22	40,974	3	96.57	
(8,5/2)	17/2	41,101.95	41,097	5	103.94	
(7,5/2)	17/2	41,602.40	41,588	14	−49.82	
(7,5/2)	15/2	41,682.02	41,657	25	(−48.2)	
(7,5/2)	19/2	41,819.18	41,839	−20	−44.6	
(7,5/2)	17/2	41,907.59	41,879	65	−50.53	
(7,5/2)	15/2	41,910.78	41,956	−45	−19.7	

relatively high J-values (from 11/2 to 19/2) lead to eight well-resolved components, eventually supplemented by weak and less accurate 'off-diagonal' components. This part of the work is still in progress and, for the selected levels reported in Table 3, the errors are about 0.15 mK for the A constants derived from the detailed analysis of the hfs patterns and close to 0.50 mK for the approximate A values in parentheses derived from the total width of the levels, the quadrupole constants B being neglected. The present status of Es I and Es II may be summarized as follows:

(a) The resonance transitions with $\lambda > 400$ nm have firmly established upper levels which in turn are lower levels of $5f^{11}7s8s$–$5f^{11}7s7p$, $5f^{11}7s7d$–$5f^{11}7s7p$ and also $5f^{10}6d7s7p$–$5f^{10}6d7s^2$ transitions. So far, only three lines of moderate intensity pertain to the latter type of transitions which makes Es I markedly different from the corresponding spectrum Ho I in lanthanides [26,27]. The lowest $5f^{10}6d7s7p$ level is in agreement with Brewer's predictions [28], only 13,873 cm^{-1} below the first ionization limit at 51,358 cm^{-1} [29]. By taking into account missing levels of $5f^{11}7s^2$, the first level ($^5I_8$,$^2D_{3/2}$) 8 of $5f^{10}6d7s^2$ is the 13th excited level whereas in Ho I the equivalent level of $4f^{10}5d6s^2$ is only the fourth highest in the level scheme.

(b) The isolated ground level $^4I_{15/2}$ within $4f^{11}$ leads to clear coupling conditions: in spite of marked differences in radial parameter values, the relationship $G^1(s,p) > \zeta_p > F^2(f,p)$, $G^k(f,p)$ holds for $f^N sp$ configurations at the end of f^N periods; it lead to similar multiplets in [J_{core}, (sp) $^{3,1}P_{J2}$] coupling

Table 4
Radial parameters used in Es I and Es II. Parameter values are followed by their uncertainties when they are fitted from experimental data without constraint. Parameters fixed according to HFR calculations or empirical trends in actinides are noted 'fix'. The parameters noted '*r*' are constrained to keep a constant ratio with the previous parameter in the same column. All values are in cm^{-1}

Parameter	Es I $5f^{11}7s7p$		Es I $5f^{11}7s7d$		Es II $5f^{11}7s$	
E^1	4213.6	fix	4301	fix	4301	72
E^2	19.1	fix	18.5	fix	18.5	0.6
E^3	415.0	fix	401.5	fix	401.5	3.9
$F^2(f,p)$	5954	867				
$G^2(f,p)$	958	r				
$G^4(f,p)$	1987	r				
$F^2(f,d)$			1159	258		
$F^4(f,d)$			872	r		
$G^1(f,d)$			726	63		
$G^3(f,d)$			680	r		
$G^5(f,d)$			396	r		
$G^3(f,s)$	1927	42	2105	69	2371	161
$G^1(p,s)$	8521	r				
$G^2(d,s)$			486	204		
$\alpha_{L(L+1)}$			2.6	0.7		
ζ_{5f}	3780	fix	3780	fix	3783	16
ζ_{7p}	3902	65				
ζ_{7d}			113	fix		
r.m.s. $\langle \Delta E \rangle$	138		35		64	
Magnetic hyperfine structure (all values in $10^{-3}\,cm^{-1}$)						
$a^{10}f$	−1.65	fix	−1.65	fix	−1.65	fix
$a^{01}f$	34.84	1.6	34.93	0.9	38.55	1.9
$a^{12}f$	38.96	r	39.06	r	43.11	r
$a^{01}d = a^{12}d$			6.8	3.6		
$a^{10}p$	−1.5	fix				
$a^{01}p$	73.27	10.5				
$a^{12}p$	102.58	r				
$a^{10}s$	1164	28	1455	12	1508	19
r.m.s. $\langle \Delta A \rangle$	3.8		1.9		4.8	

scheme for Es I $5f^{11}7s7p$ and for the similar Ho I $4f^{11}6s6p$ [26]. Also the trends of hfs constants A versus J in the multiplets are comparable.

(c) In the energy range 40,478–42,000 cm^{-1}, eleven levels have hyperfine widths slightly smaller than $5f^{11}7s$ $(^4I_{15/2},^2S_{1/2})$ $J = 8$ of Es II, whereas seven others have negative widths, similarly to the first excited level of Es II $(^4I_{15/2},^2S_{1/2})$ $J = 7$. The attribution of those high odd levels to the $5f^{11}(^4I_{15/2})$ $7s7d$ sub-configuration, obeying $(5f^{11}7s)7d$ coupling conditions was checked in two ways: (a) by the parametric study of the energies and of the hyperfine constants as it was done for Ho I [27,30] and (b) by deriving the transition probabilities of $7d$–$7p$ transitions by means of the computer codes by Cowan [2]. A close perturber of $5f^{11}7s7d$ should be $5f^{11}7p^2$ and not all levels are interpreted so far in that energy range.

(d) The classification of Es II is limited to transitions from more than 60 even parity levels, many of them with ambiguous J-values, to sixteen low odd levels of $5f^{11}7s$ and $5f^{11}6d$, which are discriminated in two ways: for $5f^{11}7s$, large positive and negative values of hfs widths for the pairs $(5f^{11}(\alpha J_1),7s\ ^2S_{1/2})$ $J = J_1 + 1/2$ and $J = J_1 - 1/2$ respectively, transitions $7s$–$7p$ occurring in the ultraviolet; for $5f^{11}6d$, average positive values of hfs widths and lines in the red region ($7p$–$6d$ transitions). The twelve known levels of $5f^{11}7s$ lead to six fitted parameters, three others being fixed. All parameter values derived so far in Es I and Es II are collected in Table 4.

The eigenfunctions in intermediate coupling have been used in a determination of the monoelectronic hyperfine structure parameters $a^{\kappa k}{}_{\rm nl}$ following the Sandars and Beck formalism [31]. Few similar studies have been performed in other $5f$ elements, in particular ^{235}U I [32] and ^{239}Pu I, II [33]. Whereas the $a_{\rm f}$ parameters are very close in $5f^{11}7s7p$, $5f^{11}7s7d$ and $5f^{11}7s$, the $a_{\rm s}^{10}$ parameter has significantly different values, the one for $5f^{11}7s7d$ being closer to the Es II $5f^{11}7s$ value than to Es I $5f^{11}7s7p$.

Table 5
Identified energy levels of $5f^6 7s^2$ in Pu I (in cm^{-1}). Isotope shifts (240–239) are in mK (1 mK = 10^{-3} cm^{-1}). All experimental data are from Ref. [40]

	E_{exp}	E_{calc}	ΔE	g_{exp}	g_{calc}	IS_{exp}	IS_{calc}
$J = 0$							
	0.000	−128	128	—	—	465	464.6
	9772.532	9851	−79	—	—	483	483.7
		22,154		—	—		508.8
$J = 1$							
	2203.606	2203	1	1.495	1.498	468	467.1
	13,677.903	13,752	−74	1.442	1.445	498	490.7
	24,323.884	24,203	121	0.800	0.355	460	512.9[a]
		27,970			1.402		520.8
	29,182.445	29,255	−72		1.619	468	523.1[b]
		34,531			1.722		533.4
$J = 2$							
	4299.659	4369	−70	1.482	1.484	470	470.1
	17,305.142	17,352	−47		1.408	499	497.8
	17,776.429	17,730	47	0.565	0.697	498	501.0
	22,339.429	22,288	51	1.049	1.070	481	509.9[c]
		25,919			0.844	516	516.0
		26,807			1.049		519.1
		31,693			0.979		527.1
		32,667			1.352		529.7
	33,920.944	33,908	13	1.040	1.117	455	515.9
		34,790			1.167		519.1
$J = 3$							
	6144.515	6220	−75	1.473	1.473	472	473.2
	18,652.287	18,613	40	0.822	0.879	519	502.0[d]
	20,402.369	20,444	−42		1.328	515	504.0
	22,974.132	22,906	68	1.147	1.190	514	510.1
	23,966.450	23,944	23	0.765	0.848	494	510.5[e]
		26,958			1.063		517.5
	27,976.883	27,997	−20	1.080	1.149	515	521.2
		30,636			0.895		525.5
	32,803.205	32,868	−65	0.825	0.830	493	529.3
	33,354.592	33,358	−3		1.043	498	529.8
		34,383			1.341		533.7
$J = 4$							
	7774.653	7805	−30	1.463	1.465	475	476.0
	19,307.447	19,511	−204		1.004	515	502.9
	22,081.891	22,100	−18		1.210	508	507.9
		24,357			0.941		511.3
	24,753.684	24,668	86	0.975	1.012	481	512.3
	25,605.707	25,670	−64	1.160	1.208	474	514.4
		28,442			1.074		520.9
$J = 5$							
	9179.262	9118	61	1.454	1.455	478	478.6
	19,317.922	19,394	−76		1.075	501	501.9
	23,168.176	23,107	61	1.115	1.159	478	510.8[f]
		24,688			1.027		511.6
	24,921.670	24,912	10	1.034	0.976	555	512.9
	27,805.163	27,724	81	1.024	1.054	513	517.0
	28,906.153	28,798	108	1.105	1.167	434	521.4[g]
		30,526			1.060		524.4
		32,558			1.012		527.9
		33,965			1.050		531.7
$J = 6$							
	10,238.473	10,036	202	1.431	1.431	479	480.8
	16,604.786	16,644	−39	0.950	0.963	494	495.7
		20,700			1.050		501.8
		24,663			1.119		511.4

Table 5 (*continued*)

	E_{exp}	E_{calc}	ΔE	g_{exp}	g_{calc}	IS_{exp}	IS_{calc}
	27,106.673	27,128	−21	1.040	1.105	544	515.8[h]
	27,523.650	27,567	−44	1.080	1.023	548	517.5
		28,795			1.074		518.8
$J = 7$							
		20,416			1.003		501.2
		24,221			1.147		508.5
	27,505.248	27,689	−184		1.104	518	517.1
	30,324.858	30,324	0	1.170	1.126	532	521.3
		31,855			1.134		525.6
	33,362.705	33,280	82	1.140	1.122	475	528.8
		35,380			1.021		532.5
$J = 8$							
		22,751			1.060		504.6
	27,510.909	27,446	65		1.187	515	514.9
		28,395			1.084		518.3
	31,586.283	31,527	59	1.045	0.997	566	522.8
		35,078			1.002		530.8
$J = 9$		24,148			1.119		506.8
$J = 10$		24,188			1.148		508.8
$J = 11$		33,988			1.035		523.8
$J = 12$		35,531			1.062		525.6

[a]Close perturber $5f^6 6d7s$ $E = 24,488.770\,cm^{-1}$ (IS = 327 mK).
[b]Close perturbers 29,048.255 cm^{-1} (IS = 391 mK) and 29,269.059 cm^{-1} (IS = 457 mK).
[c]Close perturber $5f^6 6d7s$ $E = 22,409.753\,cm^{-1}$ (IS = 251 mK).
[d]Close perturber $5f^5 7s^2 7p$ $E = 17,897.919\,cm^{-1}$ (IS = 698 mK, $g = 0.45$).
[e]Close perturber $5f^6 6d7s$ $E = 23,618.964\,cm^{-1}$ (IS = 265 mK).
[f]Close perturber $5f^6 6d7s$ $E = 23,129.429\,cm^{-1}$ (IS = 295 mK).
[g]Close perturber $E = 28,834.535\,cm^{-1}$ ($IS = 501$ mK) $5f^5 7s^2 7p$?
[h]Close perturber $5f^5 7s^2 7p$ $E = 26,873.930\,cm^{-1}$ (IS = 610 mK).

4. Interpretation of $5f^N 7s^m$ configurations and isotope shifts

The last sections of this article are devoted to the determination of radial parameters of the core $5f^N$ in some favorable cases of the highest-Z elements. In Pu and beyond, the configurations $5f^N 7s^2$ in neutral atoms have a lower part free of overlap with others of the same parity, from which least-squares fitted values of the radial integrals F^k, ζ_{5f} and effective α, β, γ parameters are to be derived. A successful application of the parametric method requires a number N_{lev} of E_{exp} experimental energies well above the number N_p of adjustable parameters. When the analysis of first and second spectra of transplutonium elements started, a first attempt of systematic determination of radial parameters was performed [24]. For that purpose we increased the ratio N_{lev}/N_p by means of generalized-least-squares (GLS) techniques of fitting, all electrostatic parameters involved being assumed to depend on N number of $5f^N$-core electrons as $P = P_0 + P1(N-7) + P_2(N-7)^2$. This led to average values of α, β, γ in $5f^N 7s^2$ and $5f^N 7s$. In that application of the GLS method, the experimental levels had been selected from their energies and Landé g-factor known in 1978. Further measurements of isotope shifts and Landé factors led to reject some of these attributions in the ranges of overlap with $5f^N 6d7s$, $5f^{N-1} 6d7s7p$ and $5f^{N-1} 7s^2 7p$. The revised versions of individual studies of Pu I $5f^6 7s^2$, Cm I $5f^8 7s^2$, Cf I $5f^{10} 7s^2$ and Cm II $5f^8 7s$ are given in Tables 5–8 for the energies and Table 9 for the parameters.

In cases of Pu I and Cm I, extended isotope shift (IS) measurements had served for configuration assignments. The phenomenological interpretation of level IS values following Bauche and Champeau [34] tells that, the normal mass shift contribution being removed, the residual IS values in a configuration f^N, may be described by two parameters: (1) an additive constant occurring from 1st order of perturbation of specific mass shift (SMS) and field shift (FS), (2) a z_f parameter having the same angular dependence as the spin–orbit ζ_f (1st order in SMS and 2nd order in FS). One additional parameter per Russell–Saunders term involved, T(αSL), appears at 2nd order of SMS and 3rd order of FS. In the present applications, this allowance for a term dependence was taken into account by $e1$, $e2$, $e3$ parameters

Table 6
Identified energy levels of $5f^8 7s^2$ in Cm I (in cm^{-1}). Isotope shifts (246–244) are in mK ($1\,mK = 10^{-3}\,cm^{-1}$). All experimental data are from Ref. [41]

	E_{exp}	E_{calc}	ΔE	g_{exp}	g_{calc}	IS_{exp}	IS_{calc}
$J=0$	8887.265	8974	−87	—	—	−260	−256.0
		23,019			—		−229.2
$J=1$	8696.688	8757	−60	1.463	1.469	−262	−256.5
		25,709			0.860		−224.4
		28,332			0.848		−219.3
	30,882.019	30,994	−112	2.110	1.738	−292	−214.8[a]
		34,534			1.699		−207.8
$J=2$	7521.122	7638	−117	1.457	1.462	−257	−258.7
	18,945.133	18,837	108		1.412	−230	−237.4
		22,091			0.480		−232.8
		25,923			1.431		−224.5
	27,263.194	27,290	−27	1.279	1.205	−285	−221.6[b]
		31,812			1.322		−213.2
$J=3$	7208.827	7203	7	1.465	1.466	−251	−259.6
		20,710			0.911		−235.7
		23,381			1.342		−229.4
	26,107.218	26,183	−66		1.437		−223.5
	28,464.320	28,481	−17	0.980	1.014	−242	−220.6
	28,629.204	28,620	9	1.006	0.971	−267	−220.3
	31,655.785	31,497		1.308	1.200	−198	−214.5[c]
		33,980			1.022		−209.5
		35,578			0.841		−206.5
	36,972.302	36,857	115		1.107	−245	−204.2
$J=4$	4877.610	4986	−108	1.450	1.451	−263	−264.0
	14,521.027	14,355	166	1.424	1.425	−236	−246.4
	18,491.582	18,621	−129		1.076	−250	−239.8
		23,944			1.242		−228.3
	26,730.227	26,778	−48	0.883	0.871	−234	−224.8
		27,853			0.940		−222.8
$J=5$	5136.50	4954	183	1.463	1.467	−262	−263.9
	19,584.14	19,579	5		1.148	−278	−237.9[d]
	22,954.72	22,892	63	1.332	1.266	−379	−231.1[e]
	25,316.43	25,238	78	1.180	1.136	−238	−227.6
		28,292			0.991		−221.9
$J=6$	1214.18	1133	81	1.452	1.456	−275	−271.3
	15,302.54	15,350	−48	1.140	1.154	−256	−246.3
		22,048			0.950		−234.9
$J=7$		20,072			1.127		−238.5
	24,725.95	24,724	2		1.067	−235	−230.2

[a]Close perturber $5f^7 6d7s7p$ $E = 31,264\,cm^{-1}$ (IS = −380 mK).
[b]Close perturber $5f^7 6d7s7p$ $E = 27,266\,cm^{-1}$ (IS = −405 mK).
[c]Close perturber $5f^7 7s^2 7p$ $E = 31,493\,cm^{-1}$ (IS∼0).
[d]Close perturber $5f^8 6d7s$ $E = 19,824\,cm^{-1}$ (IS = −565 mK).
[e]Close perturber $5f^8 6d7s$ $E = 23,057\,cm^{-1}$ (IS = −463 mK).

with same angular coefficients as E^1, E^2 and E^3 and was varied in the ratio of the fitted parameters E^n in the fine structure study. In case of an $f^N s$ configuration, the $g^3(f,s)$ parameter with same coefficients as Slater exchange integral $G^3(f,s)$ arises from the 2nd order in both SMS and FS. Starting from the eigenfunctions of the fine structure studies, we have applied this formalism to the shift values in Pu I, Cm I, Cm II $5f^8 7s$ and IS parameters have well-defined, consistent values (Table 9) provided that upper levels presumably perturbed by close configurations are discarded from the fit (IS values not underlined in Tables 5–8). Then the root mean squares deviation $\langle \Delta(IS) \rangle$ is similar to average experimental errors on IS.

Table 7
Identified energy levels of $5f^{10}7s^2$ in Cf I (in cm^{-1}). Levels followed by 'N' had not been reported in Ref. [36]

	E_{exp}	E_{calc}	ΔE	g_{exp}	g_{calc}
$J=0$		28,501			—
$J=1$		19,581			0.391
$J=2$					
	10,589.25	10,604	−15	1.295	1.296
	17,591.48	17,557	34	1.545	1.534
	21,898.93 N	21,802	96	0.870	0.845
		27,642			1.178
$J=3$					
	18,684.08	18,710	−26	1.240	1.237
		23,387			1.022
$J=4$					
	13,965.75	14,016	−50	1.275	1.270
	15,375.47	15,370	6	0.920	0.932
	18,002.22	18,030	−28		1.105
	22,438.97 N	22,546	−107		1.126
		30,192			1.089
$J=5$					
	8516.38	8544	−28	1.220	1.223
	15,846.15	15,844	3	1.060	1.066
	19,891.98 N	19,788	103		1.257
		26,094			
$J=6$					
	11,074.39	11,025	49	1.135	1.143
	16,820.39	16,833	−13	1.235	1.237
		25,196			1.146
$J=7$					
	9078.15	9081	−4	1.155	1.163
	23,961.67	24,009	−48		1.034
$J=8$					
	0.00	−9	9	1.213	1.219
	17,690.40 N	17,656	34		1.097
$J=9$		23,715			1.095
$J=10$		27,913			1.092

5. Energy level predictions in neutral fermium (Fm I)

The resonance transitions of $_{100}$Fm I have been investigated on the short-lived ^{255}Fm isotope ($t_{1/2} = 20.1$ h) by means of resonance ionization spectroscopy [35,36]. From the ground level $5f^{12}7s^2\ ^3H_6$, the lowest odd parity configurations $5f^{12}7s7p$ and $5f^{11}6d7s^2$ may be reached in one step and the studies of $5f^N7s7p$ and $5f^{N-1}6d7s^2$ performed in lighter elements lead to parameter extrapolations for fermium. The average energies of both configurations are chosen in such a way that the lowest level $5f^{12}(^3H_6)\mathrm{sp}(^3P_0)$ $J=6$ fits the extrapolated $7s^2$–$7s7p$ jump at 18,300 cm^{-1} and that $5f^{11}(^4I_{15/2})6d7s^2$ $(^2D_{3/2})$ $J=6$ at 21,000 cm^{-1} fits Brewer's prediction [28] corrected from systematic deviations found in Bk, Cf and Es after 1971. The radial parameters defining the levels of both configurations were scaled HFR integrals, assumed to have the same scaling factors as for Cf I $5f^{10}7s7p$ and $5f^96d7s^2$ calculated for level assignments in Ref. [37]. They are given in Table 10 and all predicted odd parity levels of Fm I up to 30,000 cm^{-1} are collected in Table 11. The codes RCN/RCG of Cowan were used for this determination and this leads also to transition probabilities and lifetimes. Three levels of the multiplet $(^3H_6,^3P_2)$ may fit the resonance transitions at 25,099.8 and 25,111.8 cm^{-1} reported by Sewtz et al. [36] and from lifetime consideration we agree that they should be $J=5$ and 6. There is no other possible identification in $f^{12}sp$, the less accurately predicted $f^{11}ds^2$ levels being far

Table 8
Identified energy levels of Cm II $5f^8 7s$ (in cm^{-1}). Isotope shifts (246–244) are in $10^{-3}\,cm^{-1}$ units. Experimental data are from Ref. [42]

	E_{exp}	E_{calc}	ΔE	g_{exp}	g_{calc}	IS_{exp}	IS_{calc}
$J = 1/2$							
	9801.31	9905	−104	3.740	3.735	−729	−726.9
	11,978.44	12,073	−94	−0.420	−0.420	−760	−759.7
$J = 3/2$							
	9127.85	9240	−112	1.834	1.844	−733	−732.5
	11,250.89	11,348	−97	1.167	1.159	−759	−759.0
$J = 5/2$							
	8436.10	8513	−77	1.656	1.655	−733	−731.7
	10,433.78	10,486	−52	1.300	1.304	−763	−763.0
		20,584			1.542		−736.7
		22,482			0.780		−732.6
		24,669			0.750		−744.4
		25,927			1.294		−730.7
	27,625.72	27,884	−208	1.596	1.554	−717	−731.3[a]
		28,975			1.393		−730.4
	29,477.20	29,412	65	1.389	1.411	−738	−735.3
		30,390			0.492		−716.9
		31,435			1.180		−739.2
	33,670.00	33,767	−97		1.375	−893	−721.7
$J = 7/2$							
	7067.13	7127	−60	1.485	1.488	−748	−747.5
	9073.57	9093	−19	1.444	1.440	−753	−753.9
	17,126.59	17,037	88	1.34	1.350	−750	−749.9
	20,544.78	20,627	−82		1.001	−885	−743.2[b]
		22,934			1.069		−741.9
		25,196			1.414		−722.4
		26,455			1.202		−735.6
	28,232.67	28,077	156	1.543	1.487	−741	−726.9
		28,773			0.736		−724.9
		29,712			0.866		−722.1
		30,519			1.397		−723.8
		31,426			0.823		−734.4
		32,441			1.086		−731.7
	33,576.60	33,609	−32	1.318	1.328	−722	−722.5
		34,577			1.095		−719.6
	36,415.10	36,360	55	1.05	1.046	−723	−724.9
	36,618.28	36,526	92		1.098	−708	−728.8
$J = 9/2$							
	5919.26	5933	−14	1.527	1.527	−736	−738.8
	8144.31	8046	99	1.400	1.403	−765	−764.8
	15,918.05	15,768	150	1.489	1.491	−731	−731.5
		20,330			1.190		−739.2
		22,058			1.066		−747.4
	25,436.47	25,301	135	1.240	1.244	−726	−737.0[c]
		26,087			1.253		−741.9
	27,446.76	27,510	−63		1.085	−903	−732.7[d]
$J = 11/2$							
	3941.44	3860	82	1.424	1.429	−765	−766.0
	6347.90	6195	153	1.500	1.496	−744	−741.1
	17,511.40	17,600	−89	1.160	1.071	−867	−755.6[e]
$J = 13/2$							
	2093.87	1961	133	1.500	1.498	−738	−742.2
	16,938.94	16,950	−11	1.225	1.233	−750	−746.2
$J = 15/2$							
		21,741			1.197		−736.5
$J = 17/2$							
		23,526			1.163		−730.6

Table 8 (*continued*)

E_{exp}	E_{calc}	ΔE	g_{exp}	g_{calc}	IS_{exp}	IS_{calc}
$J = 19/2$						
	22,868			1.138		−741.4
$J = 21/2$						
	21,872			1.207		−731.6
$J = 23/2$						
	37,053			1.088		−718.7
$J = 25/2$						
	37,746			1.106		−717.7

[a]Probable perturber $5f^7 7s7p$ $E = 2,7980.08$ IS $= -513$, $g = 2.024$.
[b]Probable perturber $5f^8 6d$ $E = 20,340.960$ IS $= -1007$.
[c]Possible perturber $5f^7 7s7p$ $E = 25,579.725$ IS $= -485$.
[d]Probable perturber $5f^8 6d$ $E = 27,539.800$ IS $= -1002$.
[e]Probable perturber $5f^8 6d$ $E = 17,468.095$ IS $= -1070$.

Table 9
Radial parameters for the configurations $5f^N 7s^2$ of Pu I, Cm I, Bk I and Cf I and $5f^8 7s$ of Cm II and isotope shifts (240–239) in Pu and (246–244) in Cm (all fine structure parameters and their uncertainties are in cm^{-1})

	Pu I[a]		Cm I[b]		Bk I		Cf I		Cm II[c]	
E^1	2967	80	3530	31	3739	53	3970	56	3573	10
E^2	14.48	0.3	15.88	0.5	16.31	1.4	17.91	0.58	16.51	
E^3	289.4	5.2	344.6	6.9	338.6	18	374.6	4.5	352.7	5
α	38.8	3.4	38.9	2.6	42.8	f	41.5	3.6	38.8	4
β	−1103	204	−915	275	−1078	f	−1026	10	−780	f
γ	1737	427	1694	f	1694	f	1470	313	1723	f
ζ_{5f}	2068.6	10	2559.2	23	3027.7	35	3369.2	17	2625	24
$G^3(f,s)$									2100	70
$\langle \Delta E \rangle$	91		109		156		68		111	
N_{lev}	38		22		14		17		28	
N_{par}	8		7		5		8		6	
Isotope shift parameters (in $10^{-3}\,cm^{-1}$)										
a	480.8	2	−255	10					−747.9	1.8
e^1	7.02	0.3	6.96	6.0					2.23	0.23
e^2	0.034	r	0.032	r					0.010	r
e^3	0.681	r	0.69	r					0.22	r
z_f	3.73	0.3	4.90	2.3					5.54	0.4
g^3 (f,s)									−31.05	1.3
$\langle \Delta IS \rangle$	2.6		5.9						2.1	
N_{IS}	19		7						20	
N_{par}	3		3						4	

f—fixed value; r—held in a constant ratio with parameter above.
[a]IS $= 0.465\,cm^{-1}$ for $5f^6 7s^2\ ^7F_6$ ground state.
[b]IS $= 0$ for $5f^7 6d7s^2\ ^9D_2$ ground state.
[c]IS $= 0$ for $5f^7 7s^2\ ^8S_{7/2}$ ground state.

above and below. Once again the (J_{core}, *sp* $^3P_{J2}$) J coupling scheme leads to multiplets well separated in energy. The sensitivity of the calculated energies to parameter changes was checked for the CI. The results in Table 11 are obtained with $R^1(5f7p,6d7s) = -4883\,cm^{-1}$ and $R^3(5f7p,7s6d) = -1297\,cm^{-1}$, corresponding to 60% of the HFR values and large mixing effects are noticed between f^{12} *sp* ($^3H_6$,$^1P_1$) levels and $f^{11}ds^2$ ($^4I_{15/2}$,$^2D_{5/2}$) which both contain $^3I_7$, $^3H_6$ and $^3G_5$ components in their wavefunctions. By decreasing the scaling factors of the CI integrals from 0.60 to 0.15 dramatic effects are noticed at $E > 26,000\,cm^{-1}$; in the range

Table 10
Fitted radial parameters in Cf I from separate studies of $5f^{10}7s7p$ and $5f^{9}6d7s^2$ and estimated parameters in Fm I. All parameters and uncertainties are in cm^{-1}

	Cf I		Cf I		Fm I	Fm I
	$5f^{10}7s7p$		$5f^{9}6d7s^2$		$5f^{12}7s7p$	$5f^{11}6d7s^2$
E^1	4141	27	4521	51		
E^2	18.1	0.4	19.6	1.1		
E^3	389	3.6	461	18		
F^2 (5*f*,5*f*)	58,986		66,368		62,909	70,447
F^4 (5*f*,5*f*)	47,222		53,944		50,516	57,418
F^6 (5*f*,5*f*)	32,724		31,627		35,011	33,677
F^2 (5*f*,7*p*)	5558	503			5256	
G^2 (5*f*,7*p*)	893	186			837	
G^4 (5*f*,7*p*)	1844	416			1722	
F^2 (5*f*,6*d*)			17,156	399		16,722
F^4 (5*f*,6*d*)			11,126	690		8078
G^1 (5*f*,6*d*)			4981	270		4489
G^3 (5*f*,6*d*)			5214	750		4744
G^5 (5*f*,6*d*)			6301	760		5753
G^3 (5*f*,7*s*)	1780	182			1703	
G^1 (7*p*,7*s*)	7584	108			7577	
ζ_{5f}	3349	15	3601	26	4064	4342
ζ_{7p}	3757	40			4033	
ζ_{6d}			1574	44		1639
r.m.s. $\langle \Delta E \rangle$	127		140			
Known levels used	69		56			

18,000–26,000 cm^{-1}, energies are almost unaffected, but the lifetimes of both levels ($^3H_6$,$^3P_2$) $J = 5$ and 6 become almost twice larger. The present work confirms the identifications of Sewtz et al. [36] who used the MCDF method but it reminds us that beyond 26,000 cm^{-1} the influence of the second even configuration $5f^{11}6d7s^2$ cannot be ignored.

6. Conclusions

The grounds of the atomic structure theory were set long ago and were readily applied to relatively simple cases. The interpretation of the most complex spectra followed the advances in computer capabilities and there are still open problems in elements close to half-filled *f*-subshells. Spontaneous emission spectra in lanthanides and actinides gaseous ions lead to the lowest terms of some low configurations. From those limited numbers of experimental levels, not all radial parameters relevant for f^N can be derived with a good accuracy. It is regretted that the recent development of orthogonal operators for f^N configurations [38,39] does not meet the abundant data needed for applications in atomic emission spectra. Until now few attention has been paid to the correlation between both ways of describing configuration mixing (effective or explicit). Important effects on fitted parameters remarked in Pr^{2+} should be investigated in trivalent ions also. The case of Pr^{3+} reminds us that many experimental levels tabulated in the literature have just empirical designations (if any) and that critical compilation activities supported by theoretical calculations of configurations, should be continued.

In spite of approximations and computational limitations, it is shown that the Racah–Slater method applies well to the highest-*Z* atoms and first ions, and the eigenfunctions in intermediate coupling are supported by the parametric studies of hyperfine structures and isotope shifts. Although the number of known levels is still small, the parametric interpretation of Es I and Es II is possible owing to the parameter trends along actinides, in particular for $5f^N7s7p$. These trends are not as smooth as for $5f^N$ in trivalent ions, however the Racah–Slater and HFR methods seem adapted to resonance transitions of $_{100}$Fm, the first element which cannot be studied from conventional light sources.

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Table 11
Predicted energies and lifetimes of Fm I odd parity levels. Mutual mixings affect levels denoted P1, P2 and P3

Multiplet	J	E (cm^{-1})	τ (ns)	
$5f^{12}7s7p$ ($^3H_6$,$^3P_0$)	6	18,300	366	
$5f^{12}7s7p$ ($^3H_6$,$^3P_1$)	6	19,426	76	
$5f^{12}7s7p$ ($^3H_6$,$^3P_1$)	7	19,471	45	
$5f^{12}7s7p$ ($^3H_6$,$^3P_1$)	5	19,642	41	
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{3/2}$)	6	21,000	30,200	
$5f^{12}7s7p$ ($^3F_4$,$^3P_0$)	4	21,504	1253	
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{3/2}$)	7	21,882	50,400	
$5f^{12}7s7p$ ($^3F_4$,$^3P_1$)	5	22,376	46	
$5f^{12}7s7p$ ($^3F_4$,$^3P_1$)	4	22,501	56	
$5f^{12}7s7p$ ($^3F_4$,$^3P_1$)	3	22,568	50	
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{3/2}$)	9	22,733	M	
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{3/2}$)	8	23,434	M	
$5f^{12}7s7p$ ($^3H_6$,$^3P_2$)	8	23,928	M	
$5f^{12}7s7p$ ($^3H_6$,$^3P_2$)	4	24,777	567	
$5f^{12}7s7p$ ($^3H_6$,$^3P_2$)	7	24,946	718	
$5f^{12}7s7p$ ($^3H_6$,$^3P_2$)	5	25,020	74	
$5f^{12}7s7p$ ($^3H_6$,$^3P_2$)	6	25,115	179	
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{5/2}$)	10	25,399	M	
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{5/2}$)	6	26,179	10	P1
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{5/2}$)	5	26,332	10	P2
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{5/2}$)	7	26,421	7	P3
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{5/2}$)	9	26,663	M	
$5f^{12}7s7p$ ($^3F_4$,$^3P_2$)	5	27,535	357	
$5f^{12}7s7p$ ($^3F_4$,$^3P_2$)	2	27,567	3200	
$5f^{12}7s7p$ ($^3F_4$,$^3P_2$)	6	27,607	3400	
$5f^{12}7s7p$ ($^3F_4$,$^3P_2$)	4	27,707	7300	
$5f^{12}7s7p$ ($^3H_6$,$^1P_1$)	5	27,726	4.6	P2
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{5/2}$)	8	27,731	M	
$5f^{12}7s7p$ ($^3F_4$,$^3P_2$)	3	27,736	441	
$5f^{12}7s7p$ ($^1D_2$,$^3P_0$)	2	29,431	812	
$5f^{11}6d7s^2$($^4F_{9/2}$,$^2D_{3/2}$)	4	29,579	1100	
$5f^{12}7s7p$ ($^3H_6$,$^1P_1$)	7	29,682	3.5	P3
$5f^{12}7s7p$ ($^1D_2$,$^3P_1$)	1	29,820	82	
$5f^{11}6d7s^2$($^4I_{15/2}$,$^2D_{5/2}$)	6	29,878	4.2	P1
$5f^{12}7s7p$ ($^1D_2$,$^3P_1$)	3	29,943	6.3	P

P means perturbed by CI, M means metastable.

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