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ABSTRACT

The 119 electrostatic energy levels for an nf^6 configuration have been calculated for three different sets of Slater F_k ratios: $4f^6$ hydrogenic-- $F_4/F_2 = 0.1381$, $F_6/F_2 = 0.01511$; $5f^6$ hydrogenic-- $F_4/F_2 = 0.1422$, $F_6/F_2 = 0.0161$; and $5f^6$ based on a Hartree-Fock calculation for the normal uranium atom-- $F_4/F_2 = 0.159$, and $F_6/F_2 = 0.0204$. A tentative theoretical analysis of the absorption spectra of Eu IV can be made by using $\zeta = 1360 \text{ cm}^{-1}$ and $F_2 = 370 \text{ cm}^{-1}$. The results of our work show clearly that the intermediate field matrices are essential to a quantitative analysis of the Eu IV and Am IV spectra, and that Zeeman studies are needed to identify certain levels.

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INTRODUCTION

The absorption and fluorescence spectra of Eu IV and Am IV have been reported in a number of papers.¹⁻⁵ However, a theoretical analysis of the absorption-spectra data (arising from $4f \longrightarrow 4f$ transitions) has not been attempted, and only a complete analysis of the $7F$ ground term and $5D$ term by B. R. Judd⁶ has been made from the fluorescence data of Sayre and Freed.³ As a start in analyzing the absorption spectra, we have evaluated the 119 pure electrostatic energy levels for an nf^6 configuration. Tentative theoretical assignments can then be made for Eu IV and Am IV based on several assumptions.

When the calculation of pure electrostatic energy levels for configurations with more than two f electrons is carried out following the methods outlined by Condon and Shortley, we find the work exceedingly tedious and laborious.⁷ However, the necessary theory to handle such a problem is available in the papers of Racah who has shown how states of f^n may be classified by group-theoretical methods.⁸ Several papers are now available which describe how Racah's theory can be used.⁹

Elliott, Judd, and Runciman have re-evaluated all the pure electrostatic energy levels from f^2 to f^4 and the two lowest multiplicities of the f^5 and f^6 configurations.⁹ Also B. G. Wybourne has calculated the doublet electrostatic energy matrices for f^5 and triplet and singlet matrices for f^6 .¹⁰ In this paper, a complete evaluation of the f^6 configuration energy matrices has been made independently by the authors, and actual energy levels in terms of F_2 , the Slater radial integral, are presented on the assumption of various Slater F_k ratios.

Electrostatic Energy Levels

Three different Slater F_k ratios were used in our calculations. For $4f^6$, the $4f$ hydrogenic radial-distribution function yields, $F_4/F_2 = 0.1381$ and $F_6/F_2 = 0.01511$; for $5f^6$ the $5f$ hydrogenic radial distribution function yields $F_4/F_2 = 0.1422$, and $F_6/F_2 = 0.01610$; and from Cohen's relativistic Hartree-Fock calculation for the normal uranium atom, Marrus et al. obtained from an IBM-704 program, $F_4/F_2 = 0.159$ and $F_6/F_2 = 0.0204$.¹¹ The additional assumption is made that the F_k ratios obtained from the Hartree-Fock calculation will not change appreciably in going from the uranium atom with three f electrons to the AmIV, $5f^6$, for example. However, one should expect the probability-density-distribution function to become sharper in going from an atom to the ion, which has only a partly filled f shell of electrons, but the question of whether the F_k ratios will become larger or smaller cannot be answered simply. A Hartree-Fock calculation for an actinide ion is sorely needed. Thus, the use of these uranium-atom ratios may be open to error, but at least it will give us some indication of the shift of the pure electrostatic energy-level spectrum as we go from the $4f^6$ to the $5f^6$ configuration.

The energy matrices are in terms of the parameters E^0 , E^1 , E^2 , and E^3 , which Racah has defined as:

$$E^0 = F_0 - 10F_2 - 33F_4 - 286F_6 \quad (1)$$

$$E^1 = \frac{1}{9} [70F_2 + 231F_4 + 2002F_6] \quad (2)$$

$$E^2 = \frac{1}{9} [F_2 - 3F_4 + 7F_6] \quad (3)$$

$$E^3 = \frac{1}{3} [5F_2 + 6F_4 - 91F_6]. \quad (4)$$

We can divide Eqs. (1) through (4) by F_2 , substitute the proper set of F_k ratios, and obtain numerical secular equations which can be solved by an IBM-650 program.

The theoretical results are given in Tables I, II, and III. Each table gives the configuration considered and the assumption made for that calculation. It should be noted that several numerical errors were found under the f^6 column in Table III of Elliott et al. These errors have been corrected and all other energy levels for nf^6 rechecked.

TABLE I

Pure Electrostatic Energy Levels for the $4f^6$ configuration.Assumption: $4f$ hydrogenic radial distribution function.Energy levels in terms of F_2 .

Term	Energy	Term	Energy	Term	Energy	Term	Energy	Term	Energy
$7F$	0	$1I$	114.5	$3H$	148.3	$3H$	181.7	$3H$	250.4
$5D$	51.70	$3D$	114.6	$5F$	148.6	$1L$	183.6	$1G$	251.4
$5L$	57.64	$1N$	117.5	$1M$	148.7	$1H$	185.0	$3G$	253.6
$5G$	60.69	$3H$	118.2	$3D$	151.3	$3M$	186.7	$1I$	257.7
$5H$	68.93	$3G$	118.9	$1I$	151.6	$3L$	194.3	$3G$	268.3
$5I$	78.03	$3M$	121.7	$1F$	153.4	$3I$	198.8	$3P$	269.1
$5F$	78.89	$3K$	121.8	$1G$	154.5	$3K$	199.3	$1S$	269.7
$5K$	88.05	$1L$	122.6	$1K$	155.8	$3P$	200.0	$1D$	277.2
$3P$	88.57	$3I$	126.7	$3I$	157.6	$1G$	202.6	$1L$	277.6
$3O$	95.37	$1G$	126.8	$3K$	162.3	$1L$	203.4	$1G$	277.7
$5G$	96.52	$3L$	128.2	$3F$	163.6	$3G$	204.0	$3D$	278.7
$3M$	97.67	$3H$	130.1	$1F$	164.5	$1N$	208.2	$1F$	279.4
$3K$	99.56	$1M$	130.8	$3H$	167.1	$3F$	213.4	$3F$	300.4
$5D$	99.73	$3F$	131.2	$1S$	168.4	$1F$	221.7	$1D$	304.4
$3F$	101.2	$5S$	132.2	$1G$	170.1	$1P$	222.5	$1G$	322.8
$3H$	101.4	$3P$	132.7	$3P$	170.6	$3H$	222.8	$1H$	325.5
$3I$	101.5	$1H$	133.2	$1D$	171.4	$3D$	228.3	$3F$	334.3
$5P$	104.5	$3I$	135.6	$3D$	174.9	$1H$	233.9	$3P$	337.2
$3N$	106.7	$3L$	136.1	$3G$	175.0	$1D$	236.4	$1I$	337.4
$3G$	107.5	$1D$	136.7	$5G$	177.3	$3I$	237.5	$3H$	337.9
$5H$	110.1	$3F$	137.7	$3F$	178.6	$3F$	241.1	$1G$	372.3
$3K$	112.6	$1I$	142.1	$5D$	180.7	$1I$	241.3	$1D$	395.3
$1S$	113.9	$5I$	144.4	$1K$	180.9	$3K$	242.6	$1S$	462.2
$1Q$	114.1	$3G$	145.7	$1I$	181.4	$1K$	246.5		

TABLE II

Pure electrostatic energy levels for the $5f^6$ configuration.

Assumption: $5f$ hydrogenic radial distribution function.

Energy levels in terms of F_2 .

Term	Energy	Term	Energy	Term	Energy	Term	Energy	Term	Energy
$7F$	0	$1S$	120.2	$5F$	150.8	$1L$	188.1	$1G$	255.1
$5D$	54.76	$1I$	120.5	$3H$	151.7	$1H$	189.3	$3G$	255.7
$5L$	60.04	$3H$	122.6	$1M$	152.9	$3M$	190.4	$1I$	261.8
$5G$	63.56	$3G$	122.9	$3D$	154.7	$3L$	197.7	$3G$	270.9
$5H$	71.03	$1N$	123.2	$1I$	156.4	$3I$	202.0	$3P$	272.6
$5I$	80.21	$3K$	125.6	$1F$	158.4	$3P$	203.8	$1S$	273.8
$5F$	81.29	$3M$	125.7	$1G$	159.2	$3K$	204.4	$1D$	280.7
$5K$	90.06	$1L$	127.9	$1K$	160.7	$1G$	206.5	$3D$	280.7
$3P$	94.53	$3I$	130.5	$3I$	161.0	$3G$	207.6	$1L$	281.0
$5G$	98.73	$1G$	131.9	$3K$	166.5	$1L$	207.7	$1G$	282.0
$3O$	99.50	$3L$	132.0	$3F$	167.3	$1N$	212.4	$1F$	282.1
$5D$	101.8	$3H$	133.8	$1F$	168.5	$3H$	216.6	$3F$	303.8
$3M$	102.0	$3F$	134.7	$3H$	170.7	$1S$	172.6	$1D$	307.5
$3K$	104.0	$5S$	135.0	$1S$	172.6	$3P$	173.9	$1P$	225.6
$3I$	105.7	$1M$	135.3	$3P$	173.9	$1G$	174.4	$3H$	226.0
$3F$	105.8	$3P$	136.6	$1G$	174.4	$1D$	175.4	$3D$	231.3
$5P$	106.1	$1H$	137.6	$1D$	175.4	$3G$	178.1	$1H$	238.1
$3H$	106.2	$3I$	139.6	$3G$	178.1	$3D$	178.3	$3I$	240.0
$3N$	110.6	$3L$	140.1	$3D$	178.3	$5G$	178.7	$1D$	240.7
$5H$	111.8	$3F$	141.6	$5G$	178.7	$5D$	181.7	$3K$	243.5
$3G$	112.0	$1D$	142.4	$5D$	181.7	$3F$	181.8	$3F$	244.1
$3K$	115.8	$1I$	147.0	$3F$	181.8	$1K$	184.5	$1I$	244.8
$3D$	118.5	$5I$	147.0	$1K$	184.5	$3H$	185.4	$1K$	250.0
$1Q$	119.0	$3G$	148.9	$1I$	185.4	$1I$	185.4	$3H$	253.4

TABLE III

Pure electrostatic energy levels for the $5f^6$ configuration.

Assumption: Slater ratios from Hartree-Fock calculation for the normal uranium atom.

Energy levels in terms of F_2 .

Term	Energy	Term	Energy	Term	Energy	Term	Energy	Term	Energy
$7F$	0	$3H$	140.4	$3H$	166.3	$1I$	205.9	$1K$	266.5
$5D$	67.21	$3G$	140.6	$1I$	168.0	$3M$	206.9	$3H$	266.9
$5L$	70.14	$3K$	141.2	$3D$	169.6	$1L$	207.6	$1G$	272.0
$5G$	72.24	$3M$	142.8	$1M$	171.4	$1H$	208.0	$1I$	280.0
$5H$	80.01	$1I$	144.8	$3I$	176.0	$3L$	213.1	$3G$	283.6
$5I$	89.52	$1S$	145.5	$1I$	176.7	$3I$	216.7	$3P$	288.5
$5F$	91.36	$3I$	146.2	$1F$	179.0	$3K$	217.5	$3D$	291.3
$5K$	98.83	$1N$	147.2	$1G$	179.6	$3P$	220.5	$1S$	292.7
$5G$	108.4	$5S$	147.6	$3K$	180.2	$3G$	223.5	$1F$	295.1
$5D$	111.2	$3L$	147.9	$1K$	181.9	$1G$	223.9	$1D$	296.7
$5P$	113.4	$3F$	149.8	$3F$	183.1	$1L$	226.7	$1L$	296.8
$3O$	116.8	$3H$	149.9	$5G$	185.3	$3F$	231.0	$1G$	301.3
$3P$	118.5	$1L$	149.9	$3H$	185.7	$1N$	231.5	$3F$	319.6
$5H$	119.4	$3P$	152.5	$1F$	186.2	$1P$	239.8	$1D$	322.6
$3M$	119.9	$1G$	153.1	$5D$	187.7	$3H$	240.6	$1H$	342.0
$3I$	123.5	$1M$	154.2	$3P$	188.2	$1F$	240.6	$1G$	343.6
$3K$	123.5	$1H$	156.2	$1S$	191.1	$3D$	244.7	$3F$	347.3
$3F$	124.5	$3I$	157.3	$3G$	192.1	$3I$	252.2	$3P$	348.5
$3H$	125.5	$3L$	157.5	$1D$	192.6	$1H$	256.8	$3H$	357.8
$3N$	127.0	$3F$	158.5	$3D$	193.0	$3F$	257.7	$1I$	359.7
$3G$	130.4	$5I$	158.7	$1G$	193.3	$3I$	259.4	$1G$	387.6
$3K$	131.6	$5F$	160.7	$3F$	195.8	$1D$	259.8	$1D$	418.2
$3D$	134.6	$3G$	162.8	$1K$	201.3	$1I$	260.6	$1S$	494.6
$1Q$	139.9	$1D$	166.3	$3H$	202.0	$3G$	266.0		

From Figs. 1 through 6, which show the electrostatic energy-level spectra, we note the marked change in position of terms as we go from a $4f^6$ configuration to a $5f^6$ configuration. The spectrum on the right is that of a $5f^6$ configuration, based on the uranium atom Hartree-Fock, (H-F), F_k ratios. All spectra are normalized to the ground term, ${}^7F = 0$. In general, as we go from $4f^6$ to $5f^6$, the energy spectrum moves in the direction of greater F_2 . In many cases, quintets, triplets, and singlets appear in different order from the ground term.

TERM ANALYSIS

An attempt has been made to use the electrostatic energy levels as an aid in term assignments. Judd has indicated that for Eu IV, L-S coupling is reasonably well-obeyed for the lower terms.⁶ It is remarkable how well the Landé-interval rule holds qualitatively for many J levels in the Eu IV spectra. We have found the $5f$ hydrogenic ratios to give the best results in our calculations. From a least-squares fit, Wybourne in his analysis of Nd IV, $4f^3$ also obtained Slater ratios close to the $5f$ hydrogenic ratios.¹² With these assumptions and using $\zeta = 1360 \text{ cm}^{-1}$ and $F_2 = 370 \text{ cm}^{-1}$, we have plotted the L-S case for Eu IV on the left-hand side of Fig. 7. The experimental values of Sayre and Freed are plotted on the right, and have been corrected for the depression of the 7F_0 below the center of gravity of the 7F multiplet.^{3,13} Judd has calculated the depression of the 7F_0 by the 5D_0 and obtains 1324 cm^{-1} .¹³ This correction has also been taken into account. It can be seen that a limited number of assignments can be made to groups of lines, and that Zeeman experiments must be carried out in order to unequivocally identify the levels. In addition, part of the analysis problem includes intermixing of crystal quantum levels of different J values. Several points are brought out in this type of comparison. The most important is that L-S coupling is not followed quantitatively, and before better agreement can be expected, the intermediate-field calculations will have to be considered. The second point is that the F_k ratios should be determined from the experimental data.

The right-hand side of Fig. 7 represents Am IV using values of 2600 cm^{-1} for ζ and 225 cm^{-1} for F_2 .¹³ The depression of the 7F_0 level was taken into account in plotting the experimental data. The experimental infrared energy levels are unpublished work of the authors; other levels shown are from Stover and Conway.⁵ It is apparent that nothing can be derived from the L-S model

even in the ground state for Am IV, and that the intermediate field calculations are essential. However, the L-S consideration shows the limited number of multiplets that are important in Zeeman experiments and absorption-spectra studies of americium salts.

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MUB-432

Fig. 1. Pure electrostatic energy level spectra based on the $4f$ and $5f$ hydrogenic F_k ratios, and the $5f$ F_k ratios obtained from a Hartree-Fock calculation for the normal uranium atom. Energy levels are in terms of F_2 .

MUB-433

Fig. 2. Pure electrostatic energy level spectra based on the 4f and 5f hydrogenic F_k ratios, and the 5f F_k ratios obtained from a Hartree-Fock calculation for the normal uranium atom. Energy levels are in terms of F_2 .

MUB-434

Fig. 3. Pure electrostatic energy level spectra based on the $4f$ and $5f$ hydrogenic F_k ratios, and the $5f$ F_k ratios obtained from a Hartree-Fock calculation for the normal uranium atom. Energy levels are in terms of F_2 .

MUB-435

Fig. 4. Pure electrostatic energy level spectra based on the $4f$ and $5f$ hydrogenic F_k ratios, and the $5f$ F_k ratios obtained from a Hartree-Fock calculation for the normal uranium atom. Energy levels are in terms of F_2 .

Fig. 5. Pure electrostatic energy level spectra based on the $4f$ and $5f$ hydrogenic F_k ratios, and the $5f$ F_k ratios obtained from a Hartree-Fock calculation for the normal uranium atom. Energy levels are in terms of F_2 .

MUB-437

Fig. 6. Pure electrostatic energy level spectra based on the $4f$ and $5f$ hydrogenic F_k ratios, and the $5f$ F_k ratios obtained from a Hartree-Fock calculation for the normal uranium atom. Energy levels are in terms of F_2 .

Fig. 7. Comparison of the L-S, Landé energy levels with experimental levels for Eu IV and Am IV.

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