

Hyperfine Structure of Americium-241*

RICHARD MARRUS, WILLIAM A. NIERENBERG, AND JOSEPH WINOCUR
Lawrence Radiation Laboratory, University of California, Berkeley, California

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Atomic-beam measurements on Am^{241} have confirmed that the nuclear spin is $I = \frac{5}{2}$, and have established that the electronic ground state is characterized by an angular momentum $J = \frac{7}{2}$ and a Landé splitting factor $g_J = -1.9371(10)$. In addition, the magnetic-dipole and electric-quadrupole hyperfine-structure coupling constants have been found to be, respectively, $A = \pm 17.144(8)$ Mc/sec and $B = \mp 123.82(10)$ Mc/sec. It is hypothesized that these values arise from a state that is primarily formed from the Hund's rule term 8S of the configuration $(5f)^7(7s)^2$. However, important contributions to the measured g_J , A , and B values are shown to come from the admixture of other terms in the ground state by means of the spin-orbit interaction, and also from the excitation of s electrons in the core to higher s states.

INTRODUCTION

RECENT investigations of Am^{241} have thrown much light on the structure of the electronic and nuclear ground states of this isotope. Optical spectroscopic investigations have established the nuclear spin as $I = \frac{5}{2}$,^{1,2} and the nuclear magnetic dipole and electric quadrupole moments as, respectively, $+1.4$ nuclear magnetons and $+4.9$ barns.¹ These measurements have shown, in addition, that the configuration of the electronic state of Am is $(5f)^7(7s)^2$,¹ thus supporting chemical evidence bearing on this point.³

The atomic-beam research described herein was undertaken to measure the g_J value of the electronic ground state of americium and to determine the magnetic dipole (A) and electric quadrupole (B) hyperfine-structure coupling constants in the electronic ground state. These measurements yield detailed information concerning coupling of the electrons in the ground state. In addition, the measured A and B values taken together with the optically measured moments can serve as the basis for determination of the moments of other americium isotopes.

Measurements on other elements containing $5f$ electrons, specifically Pa, Np, Pu, and Cm,⁴ have all indicated that pure L - S coupling to the Hund's-rule ground state is an excellent approximation to the actual coupling. Most striking, and most relevant to the situation in americium, are the curium data. The ground-state configuration of Cm is $(5f)^7(6d)^1(7s)^2$, giving rise to four J states whose g_J values can be very well fitted on the assumption of pure L - S coupling among the $5f$ electrons to the Hund's-rule ground state.

Hence, it is expected that a similar situation should prevail in americium, and that the electronic ground state ought to be $^8S_{7/2}$, giving rise to a pure spin g_J value and no hyperfine structure. Perturbations whose sources are discussed in the text cause deviations from these values.

BEAM PRODUCTION AND DETECTION

Americium-241 can be obtained in a weak HCl solution from the AEC stockpile. The procedure used to produce a beam of atomic americium was to reduce the oxide in the oven. Americium oxide can be produced by adding concentrated NH_4OH to americium chloride, boiling the material down, and then heating the residue. The residue easily decomposes to leave americium oxide.

Barium, carbon, and lanthanum reductions were all tried; lanthanum yielded the only satisfactory beam. The barium reduction was altogether unsuccessful because at the temperature at which the reduction takes place barium has such a high vapor pressure that it boils out of the oven too quickly for the reaction to go. The carbon reduction yields an atomic beam, but at such high temperatures (about 1500°C) that there is appreciable interaction between the americium and the tantalum oven, and only about 10% of the activity is recovered in the beam. With lanthanum as a reducing agent, beams of atomic americium of useful intensity are formed at about 1000°C .

The materials involved in americium beam production are suitably contained by a molybdenum oven with a sharp-edged inner liner to prevent creep. The oven is heated to the beam temperature by electron bombardment.

The radioactive americium beam is collected by deposition on uncooled platinum foils at the detector end of the apparatus. The collection efficiency of platinum for americium is found to be at least 20% and very highly reproducible. After exposure of the foil to the americium beam, the deposition is measured by placing the foil in low-background 2π alpha counters (about 0.1 count/min). Resonance counting rates are typically of the order of 1 to 5 counts/min.

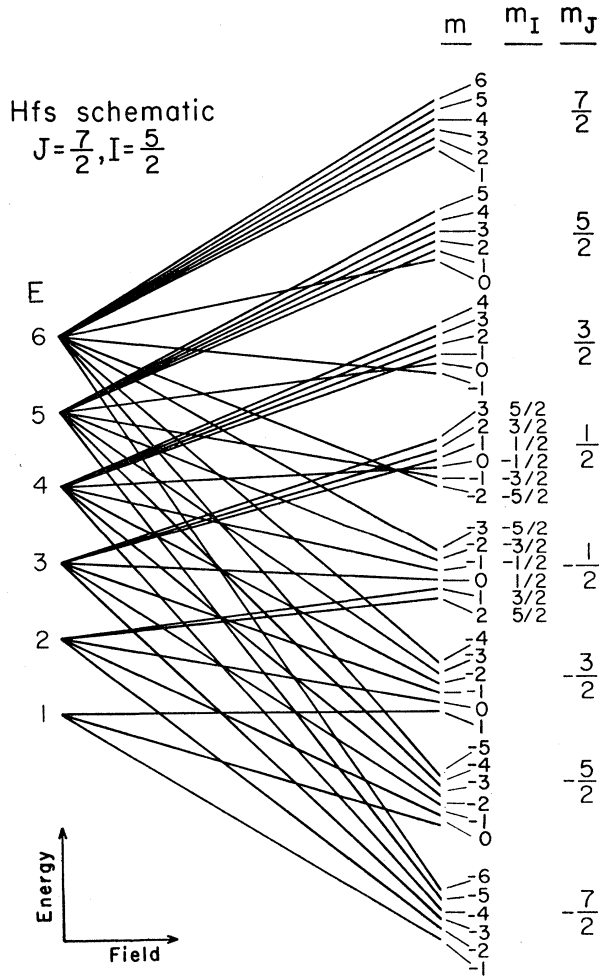
* This work was done under the auspices of the U. S. Atomic Energy Commission.

¹ T. E. Manning, M. Fred, and F. S. Tompkins, Phys. Rev. **102**, 1108 (1956).

² R. P. Thorne, Nature **178**, 484 (1956).

³ See the article by I. Perlman and K. Street, Jr., in *The Actinide Elements*, edited by G. T. Seaborg and J. J. Katz (McGraw-Hill Book Company, Inc., New York, 1954), 1st ed.

⁴ J. C. Hubbs and R. Marrus, Phys. Rev. **110**, 287 (1958); J. C. Hubbs, R. Marrus, W. A. Nierenberg, and J. L. Worcester, Phys. Rev. **109**, 390 (1958); J. C. Hubbs, R. Marrus, and J. Winocur, Phys. Rev. **114**, 586 (1959); J. C. Hubbs and J. Winocur, Bull. Am. Phys. Soc. **3**, 319 (1958).

FIG. 1. Hyperfine structure of the electronic ground state of Am^{241} .

HYPERFINE STRUCTURE

The qualitative features of a hyperfine-structure system with $I = \frac{5}{2}$ and $J = \frac{7}{2}$ and normal ordering of the states of total angular momentum F are shown in Fig. 1. It can be seen that in an atomic beam machine with flop-in magnet geometry, four transitions of the type $\Delta F = 0$, $\Delta m_J = \pm 1$ can be refocused. The quantum numbers of the states between which these transitions take place, as well as those for the transitions of the type $\Delta m_I = 0, \pm 1$; $\Delta m_J = 0, \pm 1$ are given in Table I. The Hamiltonian that gives the energy of these states in a low field or I, J, F, m_f representation is

$$\mathcal{H} = A \mathbf{I} \cdot \mathbf{J} + \frac{B}{2IJ(2I-1)(2J-1)} [3(\mathbf{I} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I} \cdot \mathbf{J}) - I(I+1)J(J+1)] - g_J \mu_0 \mathbf{J} \cdot \mathbf{H} / h. \quad (1)$$

Here octupole and higher order multipole moment terms and a field-dependent term in the nuclear magnetic moment have been neglected.

The small value of the hyperfine structure means that elements of the operator $g_J \mu_0 \mathbf{J} \cdot \mathbf{H}$ that are off-diagonal in F become important at relatively low fields (about 1 gauss), and a scheme for solving the secular equation for a state of given m_f is needed. Approximate solutions obtained from the lowest orders of perturbation theory soon break down, and it is therefore found most useful to employ an electronic computer in the determination of the energy levels. A step-wise technique employing the Newton method for solving the secular equation for the desired root was used. This technique is described elsewhere.⁵

A feature of the hyperfine structure useful in determining an accurate g_J independent measure of the constant A can be obtained from the high-field limit of the Hamiltonian—i.e., in the limit in which I, J, m_I, m_J are good quantum numbers. In this limit, the approximate Hamiltonian has the form

$$\mathcal{H} = A m_I m_J + \frac{B}{4IJ(2I-1)(2J-1)} [3m_I^2 - I(I+1)] \times [3m_J^2 - J(J+1)] - g_J \mu_0 m_J H / h. \quad (2)$$

Each of the observable transitions occurs between states in which m_I is the same for both states and m_J changes sign only (Table I). Since the term in B is quadratic in m_I and m_J , it contributes nothing to the transition energy, which becomes

$$\nu = A m_I - g_J \mu_0 H / h. \quad (3)$$

Since successive transitions differ by $m_I = \pm 1$, the energy difference between two resonances is

$$\nu_F - \nu_{F \pm 1} = A. \quad (4)$$

Examples of such transitions are shown in Fig. 2.

EXPERIMENTAL DATA AND OBSERVATIONS

An initial search for resonances made at a low field of ≈ 1 gauss yielded a set of four resonances. These were ascribed to the four flop-in transitions arising from the system $I = \frac{5}{2}, J = \frac{7}{2}$. The positions of these resonances indicated deviations from the Zeeman frequencies; the deviations were verified by a search at 3 gauss. The

TABLE I. Observable transitions in an atomic beam apparatus with flop-in type magnet geometry.

Single-quantum transitions ($\Delta F = 0$)							
F	m_F	m_I	m_J	F	m_F'	m_I'	m_J'
(6)	-2	$-\frac{5}{2}$	$\frac{1}{2}$	(6)	-3	$-\frac{5}{2}$	$-\frac{1}{2}$
(5)	-1	$-\frac{3}{2}$	$\frac{1}{2}$	(5)	-2	$-\frac{3}{2}$	$-\frac{1}{2}$
(4)	0	$-\frac{1}{2}$	$\frac{1}{2}$	(4)	-1	$-\frac{1}{2}$	$-\frac{1}{2}$
(3)	1	$\frac{1}{2}$	$\frac{1}{2}$	(3)	0	$\frac{1}{2}$	$-\frac{1}{2}$

⁵ H. L. Garvin, T. M. Green, E. Lipworth, and W. A. Nierenberg, Phys. Rev. **116**, 393 (1959). See also W. A. Nierenberg, University of California Radiation Laboratory Report UCRL-3816, June, 1957 (unpublished).

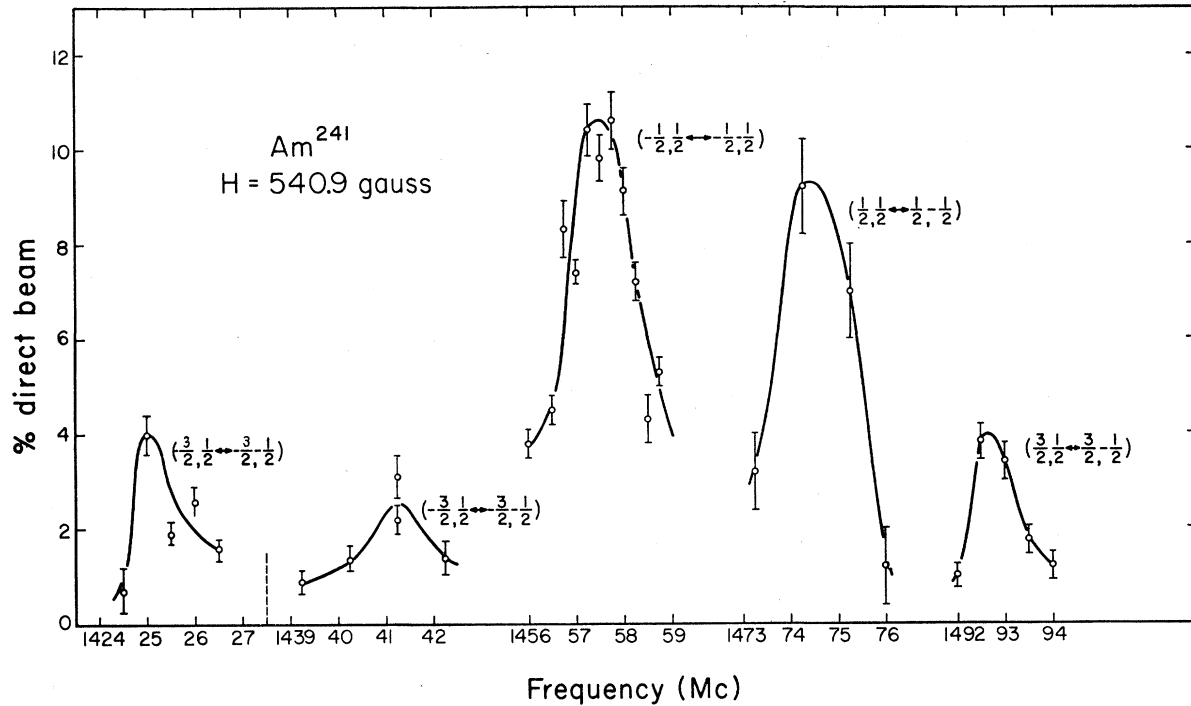


FIG. 2. Transitions of the type $(m_I, m_J = \frac{1}{2}) \leftrightarrow (m_I, m_J = -\frac{1}{2})$ observed in the Paschen-Back region of hyperfine structure.

existence of such shifts confirmed our *a priori* expectation of a small hyperfine structure.

Since resonant frequencies in the intermediate-field region depend critically on all three parameters g_J , A , and B , we decided to follow the most intense of these lines through intermediate field into the high-field region. Here the energy levels are linear, and the g_J value can be accurately obtained from the slope of the curve for resonance frequency vs field. The searches in intermediate field were very difficult because we had only very crude information for g_J , A , and B . In addition, the energy-level diagram is extremely complicated, with the feature that in intermediate field the curves for resonance frequency vs field in the $F=5$ and $F=6$ states cross. This led to a misidentification of the transition under observation.

The observations made in high field on the transition $(m_I = -\frac{1}{2}; m_J = \frac{1}{2}) \leftrightarrow (m_I = -\frac{1}{2}, m_J = -\frac{1}{2})$ were fitted by a straight line governed by Eq. (3). The value of g_J was obtained from the slope, and the product Am_I was determined from the frequency intercept. A search at a field of 540.9 gauss (Fig. 2) yielded five equally spaced resonances, which yielded the value of A according to Eq. (3). A crude value of B was then determined from all the existing data, and a search of the $\Delta F = \pm 1$ transitions was undertaken. All the observations are listed in Table II.

The final values obtained from the data are $g_J = -1.9371(10)$; $A = \pm 17.144(8)$ Mc/sec, and $B = \mp 123.82(10)$ Mc/sec. These were obtained from an

IBM 704 routine designed to choose g_J , A , and B so that the root-mean-square error in the data is an extreme. This routine is similar to one described elsewhere⁶ but has the additional feature that g_J is variable. A description of the g_J modification is given

TABLE II. Fit of the Am^{241} data based on the indicated hyperfine-structure constants. $I = \frac{5}{2}$, $J = \frac{7}{2}$, $g_J = -1.9371(10)$, $A = \pm 17.144(8)$ Mc/sec, $B = \mp 123.82(10)$ Mc/sec.

Data No.	H (gauss)	ν_{obs} (Mc/sec)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (Mc/sec)	$X'n$
1	8.248(40)	14.08(67)	-0.016	<i>b</i>
2	12.150(38)	21.95(10)	-0.012	<i>c</i>
3	20.754(35)	42.35(25)	0.152	<i>a</i>
4	20.754(35)	39.86(10)	0.003	<i>c</i>
5	26.517(44)	56.30(20)	-0.184	<i>a</i>
6	36.198(41)	82.40(20)	-0.244	<i>a</i>
7	46.077(47)	110.45(25)	0.050	<i>a</i>
8	71.628(39)	181.85(30)	-0.022	<i>a</i>
9	93.043(40)	240.80(40)	-0.129	<i>a</i>
10	121.670(42)	319.10(50)	-0.189	<i>a</i>
11	169.074(59)	448.50(60)	0.062	<i>a</i>
12	250.442(81)	669.60(60)	0.086	<i>a</i>
13	540.903(146)	1425.00(80)	-0.200	<i>c</i>
14	540.903(146)	1441.20(100)	0.409	<i>b</i>
15	540.903(146)	1457.50(100)	0.063	<i>a</i>
16	540.903(146)	1474.50(60)	-0.138	(3, 1 \leftrightarrow 3, 0)
17	540.903(146)	1492.70(60)	0.351	(3, 2 \leftrightarrow 2, 1)
18	1.418(28)	90.10(10)	-0.010	(3, 1 \leftrightarrow 2, 1)
19	1.418(28)	96.84(12)	-0.000	(4, 0 \leftrightarrow 3, 0)
20	1.418(28)	81.45(10)	-0.007	(5, -1 \leftrightarrow 4, -1)
21	1.418(28)	39.75(05)	0.001	(6, -2 \leftrightarrow 5, -2)

$a \equiv (4, 0 \leftrightarrow 4, -1)$; $b \equiv (5, -1 \leftrightarrow 5, -2)$; $c \equiv (6, -2 \leftrightarrow 6, -3)$

⁶ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1957).

in the Appendix. The error in g_J is chosen to be about one part in 2000 of the measured g_J in order to include the possibility of systematic errors in the apparatus, which are proportional to the field. The errors in A are about 2.5 times the rms error. By using the chosen and B values of A , B , and g_J , the frequency for each transition was calculated at the field of observation. These frequencies, and the difference between the calculated and experimental frequencies, are given in Table II.

EFFECT OF BREAKDOWN OF L - S COUPLING

The observed deviations of the g_J , A , and B values from the values expected for a pure $^8S_{7/2}$ ground state indicate considerable perturbation. A contribution to these deviations can come from the admixing, by the spin-orbit interaction, of terms other than 8S into the ground state. The order of the perturbation required to mix a given term into the ground state is determined from the selection rule that the spin-orbit interaction can directly couple only those states with $\Delta L=0, \pm 1$; $\Delta S=0, \pm 1$; and $\Delta J=0$. Thus, of all the terms that can arise from the configuration f^7 , only $^6P_{7/2}$ is coupled by first-order perturbation into the ground state. However, as shall be seen, the quadrupole interaction vanishes for a wave function that is a mixture of $^8S_{7/2}$ and $^6P_{7/2}$ only. In order to explain the large observed quadrupole interaction, it is necessary to go at least to second order and include $^6D_{7/2}$ as well. To this approximation, the angular part of the ground-state wave function is

$$|J=\frac{7}{2}, m_J\rangle = [1-\alpha^2-\beta^2]^{\frac{1}{2}} |^8S_{7/2}, m_J\rangle + \alpha |^6P_{7/2}, m_J\rangle + \beta |^6D_{7/2}, m_J\rangle, \quad (5)$$

where α and β are coefficients determined from the diagonalization of the matrix of the spin-orbit plus electrostatic energies. The matrix elements of the electrostatic energy can be determined by the procedure outlined in Condon and Shortley utilizing the diagonal sum rule.⁶ Such a calculation has been carried out to yield

$$\begin{aligned} \langle ^8S | C | ^8S \rangle &= 0, \\ \langle ^6P | C | ^6P \rangle &= 15F_2 + 165F_4 + 3003F_6, \\ \langle ^6D | C | ^6D \rangle &= 41F_2 + 297F_4 + 1001F_6, \end{aligned} \quad (6)$$

where C is the Coulomb interaction $\sum_{i>j} e^2/r_{ij}$ and the F_k 's are the Slater radial integrals. The ratios of the radial integrals have been calculated from hydrogenic functions⁷ and also from relativistic wave functions for uranium.⁸ These yields $F_4/F_2=0.142$, $F_6/F_2=0.0161$ from hydrogenic functions, and $F_4/F_2=0.159$, $F_6/F_2=0.0204$ from the relativistic functions. For the electrostatic energies, we obtain:

⁷ J. P. Elliott, B. R. Judd, and W. A. Runciman, Proc. Roy. Soc. (London) A240, 509 (1957).

⁸ Stanley Cohen, University of California Radiation Laboratory Report, UCRL-8633, February, 1960 (unpublished).

	Hydrogenic	Relativistic Hartree
$\langle ^8S C ^8S \rangle$	0	0
$\langle ^6P C ^6P \rangle$	$86.8F_2$	$102.3F_2$
$\langle ^6D C ^6D \rangle$	$99.3F_2$	$108.5F_2$

The values derived from the relativistic functions are used in the following calculations, since they are expected to be a more accurate approximation to the actual wave functions.

The spin-orbit matrix elements are derived by expanding the wave functions for the state in terms of the single-particle states and then evaluating the spin-orbit operator $\Lambda = \sum_i a_{5f} \mathbf{l}_i \cdot \mathbf{s}_i$ in a straightforward way. The results are

$$\begin{aligned} \langle ^8S_{7/2} | \Lambda | ^6P_{7/2} \rangle &= (14)^{\frac{1}{2}} a_{5f}, \\ \langle ^6P_{7/2} | \Lambda | ^6D_{7/2} \rangle &= -(9/10)(5)^{\frac{1}{2}} a_{5f}, \\ \langle ^6P_{7/2} | \Lambda | ^6P_{7/2} \rangle &= \langle ^6D_{7/2} | \Lambda | ^6D_{7/2} \rangle = 0. \end{aligned}$$

When these values are used, the energy matrix that determines the ground state is of the form

$$W = \begin{matrix} & \begin{matrix} ^8S & ^6P & ^6D \end{matrix} \\ \begin{matrix} ^8S \\ ^6P \\ ^6D \end{matrix} & \begin{pmatrix} 0 & +(14)^{\frac{1}{2}}x & 0 \\ (14)^{\frac{1}{2}}x & 102.3 & -(9/10)(5)^{\frac{1}{2}}x \\ 0 & -(9/10)(5)^{\frac{1}{2}}x & 108.5 \end{pmatrix} \end{matrix},$$

where $x = a_{5f}/F_2$. The diagonalization of the matrix W and the computation of the unitary matrix which transforms it into diagonal form was performed on an IBM 704 for different values of the parameter x . In this way, the coefficients of the wave function (5) could be calculated as a function of x , and the g_J value determined from the formula

$$g_J = (1-\alpha^2-\beta^2)g_J(^8S_{7/2}) + \alpha^2 g_J(^6P_{7/2}) + \beta^2 g_J(^6D_{7/2}).$$

That value of x was chosen which gives best agreement with the observed g_J . The value corresponding to $g_J = -1.937(1)$ is $x = 17.7(2)$, and the ground-state wave function that this yields is

$$|\frac{7}{2}, \frac{7}{2}\rangle = 0.882 |^8S_{7/2}, \frac{7}{2}\rangle - 0.457 |^6P_{7/2}, \frac{7}{2}\rangle - 0.114 |^6D_{7/2}, \frac{7}{2}\rangle. \quad (7)$$

The eigenvalues of the energy matrix for $x=17.7$ are 0, $123F_2$, and $203F_2$ for the states that go adiabatically, in the limit of $x=0$, to $^8S_{7/2}$, $^6P_{7/2}$, and $^6D_{7/2}$, respectively.

A value of a_{5f} of about 2700 cm^{-1} has been observed by Conway for Am^{+3} in LaCl_3 .⁹ This can be combined with the value $x=17.7$ to yield $F_2=153$ and $^6P=123F_2=18\,800 \text{ cm}^{-1}$. This is in reasonable agreement with the value of $27\,000 \text{ cm}^{-1}$ observed for the energy of the $^6P_{7/2}$ state of Cm^{+3} in LaCl_3 ,¹⁰ since it is expected that the effect of the crystalline field is to increase the energy above that for the free atom.

⁹ John G. Conway, Lawrence Radiation Laboratory (private communication).

¹⁰ J. G. Conway, J. C. Wallmann, B. B. Cunningham, and G. V. Shalimoff, J. Chem. Phys. 27, 1416 (1957).

Calculation of Quadrupole Interaction Constant B

The quadrupole interaction constant B is determined by the expectation value of the operator $B = -e^2 Q \sum_i \{ (3 \cos^2 \theta - 1)/r^3 \}_i$ in the ground state of Am^{241} . Here e is the electronic charge, Q is the quadrupole moment of Am^{241} , and the sum runs over all 5f electrons. If the wave function is separable, the angular part of the operator can be evaluated independently of the radial part. The procedure used for evaluating the expectation value $\sum_i \langle 3 \cos^2 \theta - 1 \rangle_i$ is to expand the wave function (7) into the m_l and m_s quantum numbers of the individual electrons according to the techniques of Condon and Shortley, and to evaluate the contributions from the individual electrons according to the formula

$$\langle l s m_l m_s | (3 \cos^2 \theta - 1) | l s m_l m_s \rangle = -\frac{2}{(2l-1)(2l+3)} [3m_l^2 - l(l+1)]. \quad (8)$$

It is found in this way that the only nonvanishing contribution to this expectation value arises from a matrix element that is off-diagonal in the term, that is, between the states 6D and 6P , and has the value

$$\langle {}^6D_{7/2} | \sum_i (3 \cos^2 \theta - 1) | {}^6P_{7/2} \rangle = -(2/15)\sqrt{5}. \quad (9)$$

A value $\langle 1/r^3 \rangle = 3.9/\alpha_0^3$, based on the relativistic uranium wave functions of Cohen, was used, and the value of the quadrupole moment $Q = 4.9$ barns was taken from the optical spectroscopic measurements. By using these values the quadrupole interaction constant was found to be $B = +145$ Mc/sec, to be compared with the measured $B = \mp 123.82(10)$ Mc/sec. The relativistic correction factors of Casimir¹¹ were neglected in this calculation.

Calculation of Magnetic Dipole Interaction Constant A

A contribution to the magnetic dipole hyperfine structure arises from the breakdown of L - S coupling. For evaluation of this contribution, the matrix elements of the magnetic field \mathbf{H} must be found; the classical expression for \mathbf{H} is given by

$$\mathbf{H} = \sum_i \left[\frac{e \mathbf{r} \times \mathbf{v}}{c} - \frac{\mathbf{u}(\mathbf{r})^2 - 3\mathbf{r}(\mathbf{u} \cdot \mathbf{r})}{r^5} \right]_i. \quad (10)$$

This is the field due to a point particle of charge e and magnetic dipole moment \mathbf{u} located at the point \mathbf{r} with respect to which the field is being calculated. Writing, for electrons, $\mathbf{u} = -2\mu_0 \mathbf{s}$ and $m\mathbf{r} \times \mathbf{v} = \hbar \mathbf{l}$, one obtains the

¹¹ H. B. G. Casimir, *On the Interaction Between Atomic Nuclei and Electrons* (Teylers Tweede Genootschap, Haarlem, 1936).

quantum-mechanical form of the z component of this field:

$$H_z = \sum_i (H_z)_i = -2\mu_0 \sum_i \frac{1}{r_i^3} \left[l_z - s_z + \frac{3}{2r^2} [z(\mathbf{s} \cdot \mathbf{r}) + (\mathbf{s} \cdot \mathbf{r})z] \right]_i. \quad (11)$$

For the wave function (7), the expectation value of this operator has contributions that are diagonal in the term and that are off-diagonal in the term. The only nonvanishing contribution that is diagonal in the term is $\langle {}^6P_{7/2} | H_z | {}^6P_{7/2} \rangle$. Evaluation of this matrix element was performed in the same way as the evaluation of the quadrupole interaction matrix element, making use of the formula

$$\langle l s m_l m_s | (H_z)_i | l s m_l m_s \rangle = -2\mu_0 \left\langle \frac{1}{r^3} \right\rangle \left[m_l - \frac{2m_s}{(2l-1)(2l+3)} [3m_l^2 - l(l+1)] \right]_i. \quad (12)$$

In this way, we obtain

$$\langle {}^6P_{7/2} | H_z | {}^6P_{7/2} \rangle = -(8/5)\mu_0 \langle 1/r^3 \rangle. \quad (13)$$

The nonvanishing contribution that is off-diagonal in the term is $\langle {}^6D_{7/2} | H_z | {}^8S_{7/2} \rangle$. It is found that if the single-particle expression for the wave function is used, then matrix elements of the form

$$\langle l s m_l + 1 m_s - 1 | (H_z)_i | l s m_l m_s \rangle$$

must be evaluated. This reduces to

$$-\frac{3}{2}\mu_0 \left\langle \frac{1}{r^3} \right\rangle \left\langle l s m_l + 1 m_s - 1 \left| \frac{z(s_{-}r_{+}) + (r_{+}s_{-})z}{r^2} \right| l s m_l m_s \right\rangle,$$

where $s_{-} = s_x - is_y$; $r_{+} = x + iy = r \sin \theta e^{i\phi}$; $z = r \cos \theta$; therefore

$$\langle (H_z)_i \rangle = -3\mu_0 \langle 1/r^3 \rangle \langle l m_l + 1 | \cos \theta \sin \theta e^{i\phi} | l m_l \rangle.$$

The angular part of the matrix element can be expressed as the product of three spherical harmonics, where, for the case at hand, $l=3$. From Condon and Shortley¹² one has

$$\langle l=3, m_l+1 | \cos \theta \sin \theta e^{i\phi} | l=3, m_l \rangle = -(1/45)(2m_l+1)[(4+m_l)(3-m_l)]^{1/2}. \quad (14)$$

Use of this formula yields

$$\langle {}^6D_{7/2} | H_z | {}^8S_{7/2} \rangle = (2/3)(14/5)^{1/2}\mu_0 \langle 1/r^3 \rangle, \quad (15)$$

$$\langle H_z \rangle = -0.41\mu_0 \langle 1/r^3 \rangle.$$

Now,

$$A = -(1/IJ)\langle \mu_I \rangle \langle H_z \rangle. \quad (16)$$

Using the optical spectroscopic value of μ_I and the value of $\langle 1/r^3 \rangle$ from the uranium wave functions, one

¹² See reference 6, p. 176.

obtains $A = +16.6$ Mc/sec, to be compared with a measured value $A = \pm 17.144(8)$ Mc/sec.

Summary of Effect of L - S Coupling Breakdown

If a value of the parameter $x = (a_{5f}/F_2)$ is chosen which is in good agreement with related experimental quantities and which gives the correct g_J value, good numerical agreement is also obtained between the absolute values of the calculated and measured A and B values. However, the sign (B/A) is calculated as positive, whereas the measured sign is negative. Therefore, for at least one of these quantities an effect more important than the breakdown of L - S coupling plays a role.

It is known that in many elements the effect of configuration interaction, exercises a considerable influence on the magnetic dipole constant A .¹³ The excitation is of a type in which one electron of an s -electron pair in the ground state is raised to a higher s state. The excited electron then recouples with the unexcited member to form either the singlet or triplet spin state. This state then recouples with each of the admixed terms of the core in such a way that the L , S , and J values are all unchanged. Therefore, both the g_J and B values are unaffected, but the admixture of an excited s electron gives rise to a net spin density of the electronic system at the nucleus and hence a resultant magnetic dipole hyperfine structure.

CALCULATION OF CONFIGURATION INTERACTION

Since many of the parameters entering the calculation can be only crudely extrapolated from existing data, this calculation is performed in the spirit of obtaining an order-of-magnitude estimate for the effect. The ground state of americium is therefore taken as the pure spherically symmetric state $|^8S_{7/2,7/2}\rangle$, which is denoted by $\alpha_{7/2}{}^{7/2}$. The unperturbed state is written as $\psi_u = \alpha_{7/2}{}^{7/2}0^+0^-$, where the notation 0^+0^- indicates an electron pair in an unexcited s state, both having $m_l = 0$, one with spin up (+), the other with spin down (-). Antisymmetrization of the wave function is assumed throughout, and to avoid sign difficulties, we adhere to the notation of Condon and Shortley.

For the singlet state, the wave function is

$$\psi(1) = \alpha_{7/2}{}^{7/2}(1/\sqrt{2})[0^+0^- - 0^-0^+], \quad (17)$$

where the bold-face notation indicates an electron in the excited $8s$ state. With the same notation, the wave function for the triplet state is

$$\psi(2) = (1/3\sqrt{2})[7^{1/2}\alpha_{7/2}{}^{7/2}(0^+0^- + 0^-0^+) - 2\alpha_{7/2}{}^{5/2}0^+0^+], \quad (18)$$

and for the ground-state wave function,

$$\psi = (1 - \gamma^2 - \delta^2)^{1/2}\psi_u + \gamma\psi(1) + \delta\psi(2). \quad (19)$$

¹³ A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) A230, 169 (1955).

The hyperfine structure in this state (A) is given by

$$A = \frac{4}{3}(\mu_n/I)\mu_0\langle\chi\rangle, \quad (20)$$

where χ is an operator defined by Abragam *et al.*¹³ and is related to the net spin density at the nucleus,

$$\chi = (4\pi/S) \sum_k \delta(\mathbf{r})_{kS_{kz}}. \quad (21)$$

Evaluation of χ for the stated wave function yields a nonvanishing term linear in the perturbation amplitude

$$\langle\chi\rangle_{\text{linear}} = -\frac{16\pi\delta}{3(14)^{1/2}}|\psi_{ns}(0)| |\psi_{8s}(0)|,$$

and two terms quadratic in the amplitude,

$$\begin{aligned} \langle\chi\rangle_{\text{quadratic}} = & \frac{8\pi(7)^{1/2}\gamma\delta}{21}\{|\psi_{ns}(0)|^2 - |\psi_{8s}(0)|^2\} \\ & + \frac{8\pi\gamma^2}{63}\{|\psi_{ns}(0)|^2 + |\psi_{8s}(0)|^2\}, \end{aligned}$$

where n is the principal quantum number of the state being excited.

To calculate the coefficients γ and δ , it is necessary to evaluate the noncentral part of the Coulomb interaction (c') coupling the unperturbed state with excited states. Such a noncentral interaction arises from exchange integrals and can be calculated in a straightforward way,

$$\begin{aligned} \gamma &= \frac{\langle\psi_u|c'|\psi(1)\rangle}{E_u - E(1)} = -\frac{R^3}{\sqrt{2}[E_u - E(1)]}, \\ \delta &= \frac{\langle\psi_u|c'|\psi(2)\rangle}{E_u - E(2)} = \frac{3R^3}{(14)^{1/2}[E_u - E(2)]}, \end{aligned}$$

where R^3 is a Slater radial integral given by

$$R^3 = e^2 \int_0^\infty \int_0^\infty \frac{r_<^3}{r_>^4} R_1^*(ns) R_2^*(5f) R_1(5f) R_2(8s) dr_1 dr_2,$$

where $r_<$ is the smaller of r_1 and r_2 , $r_>$ is the larger of r_1 and r_2 , and R_1 and R_2 are radial wave functions for the indicated states. The wave functions used in this calculation are the relativistic wave functions of Cohen. It was necessary, however, to extrapolate the $8s$ wave function from the wave functions for the other s orbits. Such an extrapolation could be reasonably performed, since the nodes and peaks of the ns wave function coincide with those of the $(n+1)s$ wave function. This radial integral was calculated for $n=7$ and was found to be $R^3 = 2000 \text{ cm}^{-1}$.

For $7s$ electrons, the quantity $|\psi_{7s}(0)|$ can be taken from the optically measured hyperfine-structure constant $A(7s) = 0.666 \text{ cm}^{-1}$, and the energy separations can be estimated from the optical work to be about $32\,000 \text{ cm}^{-1}$. From the optical data on the hyperfine-structure widths of the term $^{10}S_{9/2}$ and $^6S_{5/2}$ arising from the configurations $(5f)^7(7s)(8s)$, we have inferred a value $A(8s) \approx 0.024 \text{ cm}^{-1}$.

Using these values, one finds the perturbation amplitudes

$$\gamma = \frac{1}{16\sqrt{2}} = 0.044, \quad \delta = \frac{1}{16} \frac{3}{(14)^{\frac{1}{2}}} = 0.050,$$

and the contribution to the hyperfine structure is $A_{\text{linear}} \approx +70$ Mc/sec and $A_{\text{quadratic}} \approx -13$ Mc/sec.

It is seen that the effect of the above correction is to enhance the discrepancy between the measured value and the value obtained from the breakdown of L - S coupling. However, this treatment cannot be regarded as complete, since the effect of electrons from inner s orbits has been neglected owing to lack of information concerning the parameters involved. It is also possible that a calculation of the radial integrals with more accurate wave functions might improve the agreement. It is felt that the importance of s -electron excitation for the hyperfine structure of americium is clearly demonstrated, although its treatment must still be regarded as an open question.

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APPENDIX. DETERMINATION OF A , B , AND g_J FROM THE EXPERIMENTAL DATA

The problem is to minimize the function

$$Q(A, B, g_J) = \sum_i \left[(f_{\text{obs}}^i - \frac{(M_1 - M_2)g_I H^i}{h} - X_1^i + X_2^i)^2 \right] w^i. \quad (\text{A1})$$

Here f_{obs}^i is the i th of a set of measured resonance frequencies corresponding to a transition between the states X_1 and X_2 with magnetic quantum numbers M_1 and M_2 , whose energies are X_1^i and X_2^i for the particular value of the field H^i at which the observation was made. The term in g_I is a correction for the nuclear moment, and the quantity w^i is a weight factor related to the error in the frequency and field measurements by

$$w^i = \{ (\Delta f_{\text{obs}}^i)^2 + [(\partial f / \partial H)^i \Delta H^i]^2 \}^{-1}.$$

The extreme points of Q [commonly called χ^2] are determined from the condition $\delta Q = 0$, where

$$\delta Q = (\partial Q / \partial A) \delta A + (\partial Q / \partial B) \delta B + (\partial Q / \partial g_J) \delta g_J = 0,$$

and so the equations

$$\partial Q / \partial A = \partial Q / \partial B = \partial Q / \partial g_J = 0 \text{ must be solved.} \quad (\text{A2})$$

The procedure is to compute energies X_1 and X_2 (see reference 5 for the method) for some initial starting values of A , B , and g_J and then to calculate improved values A' , B' , and g_J' by the Newton method,

$$A' = A + \delta A, \quad B' = B + \delta B, \quad g_J' = g_J + \delta g_J.$$

The increments are determined from the three simultaneous equations

$$\begin{aligned} \frac{\partial^2 Q}{\partial A^2} \delta A + \frac{\partial^2 Q}{\partial A \partial B} \delta B + \frac{\partial^2 Q}{\partial A \partial g_J} \delta g_J &= -\frac{\partial Q}{\partial A}, \\ \frac{\partial^2 Q}{\partial B \partial A} \delta A + \frac{\partial^2 Q}{\partial B^2} \delta B + \frac{\partial^2 Q}{\partial B \partial g_J} \delta g_J &= -\frac{\partial Q}{\partial B}, \\ \frac{\partial^2 Q}{\partial g_J \partial A} \delta A + \frac{\partial^2 Q}{\partial g_J \partial B} \delta B + \frac{\partial^2 Q}{\partial g_J^2} \delta g_J &= -\frac{\partial Q}{\partial g_J}. \end{aligned} \quad (\text{A3})$$

By treating the partial derivatives as numbers to be determined from (A1), one can conveniently program the systems of Eqs. (A3) for a computer.