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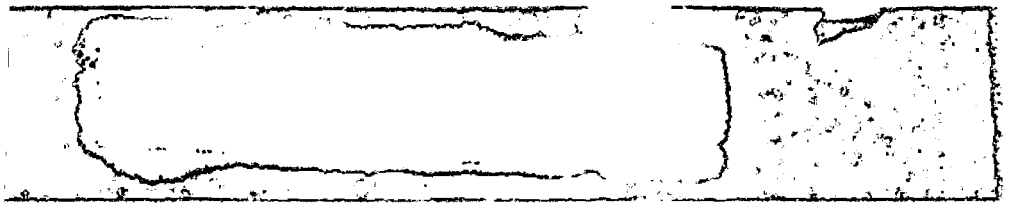

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ABSTRACT

By means of the atomic-beam magnetic resonance method using radioactive detection, the hyperfine structure of $_{91}Pa^{233}$ ($T_{1/2} = 27.4$ days) has been investigated. Three low-lying states are found to be present in the beam, characterized by electronic angular momenta $J = 11/2$, $9/2$, and $7/2$, and g values $g_J = -0.8141(4)$, $-0.8062(15)$, and $-0.7923(15)$ respectively. From these results it is inferred that the ground-state configuration of protactinium is almost certainly $(5f)^2\,(6d)^1\,(7s)^2$. The nuclear spin is measured and found to be $I = 3/2$ and the magnetic dipole and electric quadrupole hyperfine structure coupling constants are measured to be $A = \pm 595(40)$ Mc and $B = \mp 2400(300)$ Mc respectively. From a direct measurement, the nuclear moment is found to be $\mu_I = +\ 3.4(1.2)$ nm. From the hyperfine-structure constants and detailed calculations involving the electronic wave functions, the quadrupole moment is inferred to be $Q = -3.0$ barns.

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INTRODUCTION

The subject of the ground-state electronic configurations of the elements after actinium in the periodic table is of great interest, since they constitute a series with transition-type electronic structure in the same sense as the elements after lanthanum. To date, measurements by either optical spectroscopy or atomic beams have established the ground configuration of all elements from $_{90}$Th to $_{96}$Cm with the exception of $_{91}$Pa.[1] The measurements reported here complete our knowledge for all elements in this range, and effectively verify the large body of chemical evidence supporting the hypothesis of an actinide transition series.[2] Table I gives the ground-state configuration for each element and the observed value of total angular momentum J characterizing the ground state.

From the point of view of nuclear physics, interest in Pa^{233} centers about the fact that the ground-state rotational band is characterized by $K = 1/2$.[3] Calculations based on the Nilsson model indicate also that the deformation δ is positive, and therefore the charge distribution about the nuclear symmetry axis is prolate. If these considerations are correct, then the measured quadrupole moment should be negative.

The beta decay scheme of Pa^{233} indicates that $I = 3/2$.[4] In addition, there is evidence that the level scheme of Pa^{231} is similar to that of Pa^{233},

hence these states are described by the same orbitals. Optical spectroscopic measurements on Pa^{231} indicate that I = 3/2.[5]

BEAM PRODUCTION

Production of Pa^{233} is via the reaction $Th^{232} + n \rightarrow Th^{233} \rightarrow Pa^{233} + e^-$. $[T_{\frac{1}{2}} = 23.5 \text{ min.}]$

Two grams of thorium metal were bombarded for 10 days at a flux of 2×10^{14} neutrons/cm^2-sec to yield about 50 curies of Pa. This quantity provided about one month of running time.

The initial attempt to form a Pa beam was by heating irradiated thorium in a small tantalum oven and boiling out the Pa. However, this procedure yielded a molecular rather than an atomic beam. Carbon and lanthanum were then added to the oven in order to reduce the Pa. This reduction failed, apparently because of interference from the Th. The Th was removed by an ion-exchange method, and the separated Pa was oxidized and placed in a small tantalum oven with an excess of carbon. Removal of the Th ensures the success of the reduction, and at a temperature of 3000°C a beam of Pa atoms is formed. Incidentally, it is found that ovens made from a 90% tantalum-10% tungsten alloy give the best service at these high temperatures.

Collection of the protactinium beam is successfully accomplished by condensation on freshly flamed, uncooled platinum discs. The radioactivity deposited is measured by placing the foil in a methane proportional counter.

EXPERIMENTAL DATA AND OBSERVATIONS

At low magnetic fields, i.e., at fields at which the nuclear spin (I) and the electronic angular momentum (J) are tightly coupled to a total angular momentum (F), resonances are observed at frequencies given by

$$\nu = \frac{1}{2F(F+1)} \left[(g_J + g_I) F (F+1) + (g_J - g_I) \left\{ J(J+1) - I(I+1) \right\} \right] \frac{\mu_0 H}{h} \quad , \quad (1)$$

where g_J is the spectroscopic splitting factor of the electronic system, g_I is the nuclear g factor, H is the applied magnetic field, and (μ_0/h) is the Bohr magneton divided by Planck's constant. For Pa^{233} g_I turns out to be about 1/700 g_J, and although its effect at low field may be neglected, the influence on the intermediate-field data is measurable.

Since none of the parameters entering into (1) was known prior to this experiment, a search was made at a low field to detect all observable resonances. The resonances were then observed at several fields up to a maximum of 20.8 gauss (Fig. 1). In all, eight transitions were observed. They are most plausibly fitted to the assumption that three electronic states are present in the beam, characterized by J=7/2, 9/2, and 11/2 and that the nuclear spin is I=3/2. From the observed resonances intensities it is inferred that the ordering of the electronic energy levels is probably inverted. All data taken at low magnetic field are given in Table II, along with the mean values of g_J.

HYPERFINE-STRUCTURE MEASUREMENTS

In order to obtain information about the magnetic-dipole (A) and electric-quadrupole (B) hyperfine-structure coupling constants, the transitions in the three highest F states arising from J = 11/2 and I = 3/2 were followed up in field (see Fig. 2 for a hyperfine-structure diagram of the system). The data obtained were fitted to the Hamiltonian

$$\mathcal{H} = A\vec{I} \cdot \vec{J} + B \frac{1}{2IJ(2I-1)(2J-1)} \left[3(\vec{I} \cdot \vec{J})^2 + 3/2 \ (\vec{I} \cdot \vec{J}) - I(I+1)J(J+1) \right]$$

$$- g_J \mu_0 J_z H - g_I \mu_0 I_z H \quad (2)$$

by means of an IBM 704 routine designed to give the best values of A, B, and g_J for a fixed value of g_I. In Table III we give the best values of g_J, A, and B determined from the routine for different values of g_I, and the value of χ^2, which is a measure of goodness of fit. In Table IV, we give the fit to the data for the best set of parameters, $g_J = -0.8141(4)$, $A = \pm 600(40)$ Mc, $B = \pm 2400(300)$ Mc, and $g_I = +12.5(4.5) \times 10^{-4}$. The errors quoted for A and B are about three times the rms error for the data. The error in g_J is chosen to be 1 part in 2000, to allow for the possibility of systematic errors present in the apparatus which are proportional to the magnetic field. The error in g_I is chosen from Fig. 3 so that the probability of the true value lying outside the stated error is less than 0.02.

ELECTRONIC STRUCTURE

On the basis of available chemical evidence, it has been postulated[6] that the ground-state configuration of $_{91}$Pa is either $(5f)^2 (6d)^1 (7s)^2$ or $(5f)^1 (6d)^2 (7s)^2$. No plausible fit to the data can be made with $(5f)^1(6d)^2(7s)^2$ as the ground state. In contrast, if it is assumed that the ground-state configuration of Pa is $(5f)^2(6d)^1(7s)^2$, the data are very well fitted by the same model as has given agreement with the observed g_J and J values in other actinide elements containing both 5f and 6d electrons. This model assumes that the electrons in each shell couple independently to the Hund's Rule ground state, and that there is pure J_1-J_2 coupling between the shells. The Hund's Rule state for the configuration $(5f)^2$ is $^3H_4$ with $g_J = -0.800$, and for $(6d)^1$ it is $^2D_{3/2}$, also with $g_J = -0.800$. In the limit of pure J_1-J_2 coupling between shells, four levels are predicted, characterized by J = 11/2, 9/2, 7/2, and 5/2, with $g_J = -0.800$ for all of them. On the other hand, the calculated values of the g factors for pure L-S coupling among all electrons are

$g_J(^4K_{11/2}) = -0.769$, $g_J(^4I_{9/2}) = -0.727$, and $g_J(^4H_{7/2}) = -0.702$.

The observed g values deviate from those predicted according to the simple model described above because of the spin-orbit interactions of the 5f and 6d electrons and because of the breakdown of J of each of the shells due to the electrostatic interaction between them. The problem of determining the exact ground state would involve the diagonalization of the matrix of the spin-orbit energy plus electrostatic energy for all terms giving rise to a state with J = 11/2. Such a calculation would involve the determination of several hundred integrals of the electrostatic energy.

We have attempted an alternative approach based on the J_1-J_2 scheme as a starting approximation. In performing this calculation it is easiest to determine the energy in the L- S scheme and then to transform the energy matrix into the J_1 - J_2 scheme.

The L-S matrix elements of the electrostatic energy have the form

$$\left\langle (\ell_1)^2 L_1 S_1;\ \ell_2;\ LS \left| \frac{e^2}{r_{12}} \right| (\ell_1)^2\ L_1' S_1';\ \ell_2;\ L\ S \right\rangle , \tag{3}$$

where the subscripts 1 and 2 refer to the configurations $(5f)^2$ and $(6d)^1$ respectively. Thus $\ell_1 = 3$ and $\ell_2 = 2$. The matrix element may be written as the sum over the Slater radial integrals $F^k(5f, 6d)$ and $G^k(5f, 6d)$:

$$\left\langle L\ S \left| \frac{e^2}{r_{12}} \right| L\ S \right\rangle = \sum_{k=2,4} f^k F^k + \sum_{k=1,3,5} g^k G^k . \tag{4}$$

The interaction among the $(5f)^2$ electrons is independent of L and S and merely adds a constant term to Eq. (3).

A general expression for the coefficients f^k and g^k has been derived by Judd[7] for the case of a d electron interacting with n equivalent f electrons. For n = 2 these expressions become

$$f^k = (2\ell_1 + 1)(2\ell_2 + 1)\,\delta(S_1, S_1')\left[(2L_1 + 1)(2L_1' + 1)\right]^{1/2}$$

$$\times \begin{pmatrix} \ell_1 & k & \ell_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_2 & k & \ell_2 \\ 0 & 0 & 0 \end{pmatrix} \left[1 + (-1)^{L_1 + L_1'}\right] (-1)^{k + \ell_1 + L} \begin{Bmatrix} k & \ell_1 & \ell_1 \\ \ell_1 & L_1' & L_1 \end{Bmatrix} \begin{Bmatrix} L_1 & k & L_1' \\ \ell_2 & L & \ell_2 \end{Bmatrix}, \quad (5a)$$

$$g^k = 2(2\ell_1+1)(2\ell_2+1) \begin{pmatrix} \ell_2 & k & \ell_1 \\ 0 & 0 & 0 \end{pmatrix}^2 (-)^{S_1 + S_1'} \left[(2S_1+1)(2S_1'+1)(2L_1+1)(2L_1'+1)\right]^{1/2}$$

$$\times \begin{Bmatrix} 1/2 & 1/2 & S_1' \\ 1/2 & S & S_1 \end{Bmatrix} \begin{Bmatrix} \ell_1 & \ell_1 & L_1' \\ \ell_1 & k & \ell_2 \\ \ell_1 & \ell_2 & L \end{Bmatrix} . \quad (5b)$$

In this calculation we concern ourselves only with the ^3H ground term of the configuration f^2. Therefore, $L_1 = L_1' = 5$ and $S_1 = S_1' = 1$, only. Tables of the 3-j and 6-j symbol as well as the definition of the 9-j symbol are all found in Edmonds.[8] The coefficients f^k and g^k for all quartet terms are given in Table V. Coefficients for the doublet terms can be obtained from this table by leaving f^k unchanged and multiplying g^k by - 1/2.

No experimental or theoretical values of the radial integrals are available for protactinium. However, Racah[9] has calculated the values of the radial integrals which give best agreement with the observed optical spectrum of Th(III). Another set of radial integrals has been obtained by us from the relativistic wave functions for the normal uranium atom of Cohen.[10] Since there is no preference for either set of integrals, we have calculated the electrostatic energy from both and give the results in Table VI. It is encouraging to note the similarity between the level ordering predicted from the two sets.

We now proceed to obtain the electrostatic energy in the J_1 - J_2 coupling scheme. The LS - J_1J_2 transformation coefficient is given by[8]

$$\left\langle (L_1 L_2)\ \ L,\ (S_1 S_2)\ S,\ J \,\middle|\, (L_1 S_1)\ J_1,\ (L_2 S_2)\ J_2,\ J \right\rangle$$

$$= \left[(2L+1)(2S+1)(2J_1+1)(2J_2+1) \right]^{1/2} \begin{Bmatrix} L_1 & L_2 & L \\ S_1 & S_2 & S \\ J_1 & J_2 & J \end{Bmatrix} . \qquad (6)$$

The smallest argument appearing in the 9-j symbol is $S_2 = 1/2$. Therefore, the formula for the 9-j symbol can be simplified to an expression involving the sum of only two 6-j symbols.

The ^3H ground term of $(5f)^2$ is split by the spin-orbit interaction into the levels $J_1 = 4, 5$, and 6; the 6d ^2D term is split into $J_2 = 3/2$ and 5/2. The electrostatic interaction between these two systems gives rise to the following states in the $J_1 J_2 J$ scheme: 4(3/2)J, 4(5/2)J, 5(3/2)J, 5(5/2)J, 6(3/2)J, and 6(5/2)J. Neither the electronic g-factor operator nor the hyperfine structure interaction operator couples the last three states with the 4(3/2)J ground state. Since they do not produce any first-order effects, these states are neglected. Using formula (6), we find for the electrostatic energy in the J_1 - J_2 scheme:

$J = 11/2$

	4(3/2)	5(3/2)	4(5/2)
4(3/2)	-6455	1507	-2489
5(3/2)	1507	-4513	-1915
4(5/2)	-2489	-1915	-3287

$cm.^{-1}$

	4(3/2)	5(3/2)	4(5/2)
4(3/2)	-8768	1867	-3052
5(3/2)	1867	-6889	-2681
4(5/2)	-3052	-2681	-5159

$cm.^{-1}$

$$J = 9/2$$

$$\begin{array}{c} 4(3/2) \\ 5(3/2) \\ 4(5/2) \end{array} \begin{pmatrix} -5290 & 865 & -1174 \\ 865 & -1011 & 296 \\ -1174 & 296 & -3699 \end{pmatrix} \text{cm.}^{-1} \begin{pmatrix} -7689 & 1249 & -1634 \\ 1249 & -1733 & 369 \\ -1634 & 369 & -5633 \end{pmatrix} \text{cm.}^{-1}$$

$$J = 7/2$$

$$\begin{array}{c} 4(3/2) \\ 5(3/2) \\ 4(5/2 \end{array} \begin{pmatrix} 264 & 1213 & -1574 \\ 1213 & 646 & -1044 \\ -1574 & -1044 & -1284 \end{pmatrix} \text{cm.}^{-1} \begin{pmatrix} 104 & 1955 & -2413 \\ 1955 & 1515 & -1620 \\ -2413 & -1620 & -2038 \end{pmatrix} \text{cm.}^{-1}$$

The matrices in the first column are calculated from Racah's values of the radial integrals; the matrices in the second column are calculated from the uranium radial integrals.

To complete the energy matrix, the spin-orbit energy must be added. This is

$$S = \begin{array}{c} \\ 4(3/2) \\ 5(3/2) \\ 4(5/2) \end{array} \begin{array}{c} \begin{array}{ccc} 4(3/2) & 5(3/2) & 4(5/2) \end{array} \\ \begin{pmatrix} 0 & & \\ & (5/2)a_{5f} & \\ & & (5/2)a_{5f} \end{pmatrix} \end{array} \tag{7}$$

The matrix of the total energy may be written in the form

$$W = S + \lambda E, \tag{8}$$

where W is the sum of the spin-orbit matrix S plus the electrostatic matrix E multiplied by a parameter λ. The justification for introducing λ rests on the expectation that the ratios of the F and G integrals are approximately correct even though their strength may not be.

A more accurate representation of the J = 4 state of the f^2 configuration can be obtained if we allow for the admixture by the spin-orbit interaction of terms different from ^3H. The allowed terms of $(f)^2$ that can give rise to a state $J_1 = 4$ are ^1G and ^3F. The matrix of the total energy has been calculated, and is of the form

	^3H	^1G	^3F
^3H	$-3a_{5f}$	$-(10/3)^{1/2}a_{5f}$	
^1G	$-(10/3)^{1/2}a_{5f}$	G	$(11/3)^{1/2}a_{5f}$
^3F		$(11/3)^{1/2}a_{5f}$	$F + 3/2\, a_{5f}$

(9)

Where F and G, the electrostatic energies of the ^3F and ^1G term with respect to the ^3H terms, are given in Condon and Shortley.[11] We have used the values for the ratios F^4/F^2 and F^6/F^2 from the uranium wave functions,[12] and obtained in this way $G = 20.3F_2$ and $F = 12.3F_2$. It has been found that $F_2 = 153\ cm^{-1}$ gives the best fit with the observed g_J of americium.[12] We have found by extrapolation that, for Pa, the value of F_2 ought to be about $137\ cm^{-1}$. For a_{5f} we have used the value of $1300\ cm^{-1}$ obtained by Judd in fitting the energy levels of U(I).[7] For these values of the parameters we obtain, for the ground state of f^2,

$$\left| J = 4 \right) = -0.939 \left| {}^3H_4 \right) - 0.323 \left| {}^1G_4 \right) + 0.095 \left| {}^3F_4 \right) . \qquad (10)$$

The electronic g factor g_J is defined by

$$g_J m_J = \left\langle J\, m_J \left| \sum_i (-\ell_z + g_S s_z)_i \right| J\, m_J \right\rangle . \qquad (11)$$

Here $g_S = -2.0023$ is the electron spin g factor; ℓ_z and s_z are the z components of the orbital and spin angular momenta. The g_J matrix in the J_1-J_2 scheme can be obtained by a transformation of the diagonal g_J matrix in the

L-S scheme using the transformation coefficients determined from formula (6). It can also be calculated directly by considering the angular momenta as tensors of rank one, and using tensor methods. We here omit the details of this calculation and state the result

$$g_J=11/2 \qquad \begin{array}{c} \\ 4(3/2) \\ 5(3/2) \\ 4(5/2) \end{array} \begin{array}{c} \begin{array}{ccc} 4(3/2) & 5(3/2) & 4(5/2) \end{array} \\ \begin{pmatrix} 0.8185 & 0.0388 & -0.0572 \\ 0.0388 & 1.0023 & 0 \\ -0.0572 & 0 & 0.9363 \end{pmatrix} \end{array} (-1) \tag{11}$$

$$g_J=9/2 \qquad \begin{array}{c} \\ 4(3/2) \\ 5(3/2) \\ 4(5/2) \end{array} \begin{array}{c} \\ \begin{pmatrix} 0.8211 & 0.0586 & -0.0904 \\ 0.0586 & 1.0405 & 0 \\ -0.0909 & 0 & 0.9089 \end{pmatrix} \end{array} (-1)$$

$$g_J=7/2 \qquad \begin{array}{c} \\ 4(3/2) \\ 5(3/2) \\ 4(5/2) \end{array} \begin{array}{c} \\ \begin{pmatrix} 0.8260 & 0.0714 & -0.1266 \\ 0.0714 & 1.1114 & 0 \\ -0.1266 & 0 & 0.8568 \end{pmatrix} \end{array} (-1)$$

The eigenvalues and eigenvectors of the energy matrices W were calculated on an IBM 704 computer. The g_J matrices were then transformed with the same unitary matrix which brings the energy matrix into diagonal form. The elements occurring along the diagonal of the g_J matrix are characteristic g factors.

Figure 4 shows how g_J varies with λ for the lowest three J states. The observed g_J values are indicated by the arrows. There is no

single value of λ for which the observed and calculated g factors are in satisfactory agreement. Thus it appears necessary to go to higher order and to include those states not directly coupled to the ground state by the g_J and hyperfine operators. Since these states have larger g_J values than the ground state, it is expected that including them will improve the agreement with the experimental values.

HYPERFINE STRUCTURE

The evaluation of the nuclear moments from the measured hyperfine structure depends on the choice of the angular part of the wave function. In the preceding section, we showed that first-order calculations employing the J-J coupling model were inadequate to explain the observed electronic g factors. However, there is much less need for an accurate wave function for the hyperfine-structure calculations, since uncertainties introduced in the values of $\left\langle \frac{1}{r^3} \right\rangle$ are expected to be larger in any case. Therefore, the wave function we use admits the same states as in the calculation of the g values, with the $J_1=4$ state of the $(f)^2$ configuration assumed to be an admixture of ^3H and ^1G only (Eq. (10)).

The ground state is the eigenvector of the W matrix for an appropriate value of λ. Judd has found that the observed spectrum of U(I) can be fitted if the radial integrals of Racah are multiplied by $\lambda = 1/2$.[7] Using this value for protactinium, we obtain, for the ground-state wave function,

$$\left| J=11/2 \right\rangle = -0.976 \left| 4(3/2)\,11/2 \right\rangle + 0.124 \left| 5(3/2)\,11/2 \right\rangle - 0.178 \left| 4(5/2)\,11/2 \right\rangle . \tag{12}$$

On the basis of this wave function, we now proceed with the calculation of the nuclear moments. The magnetic dipole moment (μ_I) can be obtained from the magnetic dipole hyperfine structure according to the relation

$$A = -(1/IJ)\mu_I \left\langle \bar{H} \right\rangle_{J_1 m_J = J} , \tag{13}$$

where $\bar{H}$ is the magnetic field at the nucleus due to the orbital electrons. The quantum mechanical expression for this field is

$$\bar{H} = -2\mu_0 \sum_i \left(\frac{1}{r^3}\right)_i \left\{ \bar{\ell} - \bar{s} + \frac{3}{2} \frac{(\bar{s}\cdot\bar{r})\bar{r} + \bar{r}(\bar{s}\cdot\bar{r})}{r^2} \right\}_i , \tag{14}$$

where $\bar{\ell}$ and $\bar{s}$ are the orbital and spin angular momenta of the individual electrons, and $\bar{r}$ is the radius vector. The sum is over-all electrons. Trees has noted that this operator can be written in a form which better exhibits its spherical tensor character,[13]

$$\bar{H} = -2\mu_0 \sum_i \left(\frac{1}{r^3}\right)_i \left\{ \bar{\ell}_i - \sqrt{10}\, \bar{X}_i \right\} , \tag{15}$$

where $\bar{X}$ is a spherical tensor of rank one formed from the tensor composition of the spin $(\bar{s})$ with the spherical harmonic of rank two $(C^{(2)})$.

$$\bar{X}^m_1 = \sum_{m_1} s^{m_1}_1 \, C^{(2)}_{m-m_1} (1\, m_1;\ 2\, m-m_1 \mid 1\ 2\ 1\ m) \tag{16}$$

$(1m_1;\ 2\ m-m_1 \mid 1\ 2\ 1\ m)$ is the Clebsch-Gordan coefficient arising in the coupling of an angular momentum of one unit with another of two units to form a resultant of one unit.

When this form of the operator is used, the theorems concerning the evaluation of matrix elements of spherical tensor operators may be applied. The matrix elements arising from the wave function (12) have the form $\left\langle j_1' \ j_2' \ Jm_J = J \left| \bar{H} \right| j_1 \ j_2 \ Jm_J = J \right\rangle$. For the wave function (12) the appropriate matrix elements are:

$$\left\langle {}^3H_4\ {}^2D_{3/2}\ 11/2 \left| \bar{H} \right| {}^3H_4\ {}^2D_{3/2}\ 11/2 \right\rangle = -\frac{8}{5}\mu_0 \left[\frac{296}{45} \left\langle \frac{1}{r^3} \right\rangle_{5f} + 3 \left\langle \frac{1}{r^3} \right\rangle_{6d} \right]$$

$$\left\langle {}^1G_4\ {}^2D_{3/2}\ 11/2 \left| \bar{H} \right| {}^1G_4\ {}^2D_{3/2}\ 11/2 \right\rangle = -\frac{8}{5}\mu_0 \left[5 \left\langle \frac{1}{r^3} \right\rangle_{5f} + 3 \left\langle \frac{1}{r^3} \right\rangle_{6d} \right]$$

$$\left\langle {}^3H_5\ {}^2D_{3/2}\ 11/2 \left| \bar{H} \right| {}^3H_5\ {}^2D_{3/2}\ 11/2 \right\rangle = -\frac{8}{65}\mu_0 \left[\frac{3472}{45} \left\langle \frac{1}{r^3} \right\rangle_{5f} + 19 \left\langle \frac{1}{r^3} \right\rangle_{6d} \right] \tag{17}$$

$$\left\langle {}^3H_4\ {}^2D_{5/2}\ 11/2 \left| \bar{H} \right| {}^3H_4\ {}^2D_{5/2}\ 11/2 \right\rangle = -\frac{8}{65}\mu_0 \left[\frac{3478}{45} \left\langle \frac{1}{r^3} \right\rangle_{5f} + 21 \left\langle \frac{1}{r^3} \right\rangle_{6d} \right]$$

$$\left\langle {}^3H_4\ {}^2D_{5/2}\ 11/2 \left| \bar{H} \right| {}^3H_4\ {}^2D_{3/2}\ 11/2 \right\rangle = \frac{4}{65}\sqrt{26}\,\mu_0 \left\langle \frac{1}{r^3} \right\rangle_{6d}$$

$$\left\langle {}^3H_5\ {}^2D_{3/2}\ 11/2 \left| \bar{H} \right| {}^3H_4\ {}^2D_{3/2}\ 11/2 \right\rangle = -\frac{14}{25}\sqrt{\frac{11}{26}}\,\mu_0 \left\langle \frac{1}{r^3} \right\rangle_{5f}$$

The values of $\left\langle \frac{1}{r^3} \right\rangle$ were obtained from the relativistic wave functions for uranium:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{2a, a_0} \int r^{-2} FG\,dr \qquad \begin{array}{l} = 3.9/a_0^3 \text{ for 5f electrons,} \\ = 2.0/a_0^3 \text{ for 6d electrons.} \end{array} \tag{18}$$

Thus, the value for the field is -3.0×10^6 gauss, and, from Eq. (13), $A = 277\ \mu_N(\text{nm})$ Mc. Using the experimental value $A = 595$ Mc, we obtain

$$\mu_N = 2.1\text{nm}.$$

We have neglected in this calculation the effect on the magnetic hyperfine structure of excitation of core electrons to excited s states. Although this effect can be substantial, we take the agreement of the calculated moment with the value obtained from direct measurement as evidence for the essential correctness of our assumptions concerning the electronic structure.

Calculation of the quadrupole interaction proceeds from the formula

$$B = -e^2 Q \sum_i \left(\frac{1}{r^3}\right)_i \left\langle 3\cos^2\theta_i - 1 \right\rangle_{J,\, m_J = J} . \tag{19}$$

The evaluation of the sum is easily accomplished by using spherical tensor methods. An alternative approach is to expand the wave function (12) into the single-particle quantum numbers, and to evaluate B directly. However, the spherical tensor method has the property of exhibiting the addition of two quadrupole interactions B_1 and B_2 arising from systems with two angular momenta J_1 and J_2 coupled together to a resultant J.

Thus:

$$B = \frac{\left[3C_1 (C_1 - 1) - 4 J_1 (J_1 + 1) J (J + 1)\right]}{J_1 (2J_1 - 1)(2J + 2)(2J + 3)} B_1 + \frac{\left[3C_2 (C_2 - 1) - 4 J_2 (J_2 + 1) J (J + 1)\right]}{J_2 (2J_2 - 1)(2J + 2)(2J + 3)} B_2 , \tag{20}$$

where $C_1 = J(J + 1) + J_1 (J_1 + 1) - J_2(J_2 + 1)$,

$C_2 = J(J + 1) + J_2 (J_2 + 1) - J_1(J_1 + 1)$.

Applying this formula to the diagonal matrix elements arising from the wave function (12) we obtain, for the matrix elements of

$$q = \sum_i \left(\frac{1}{r^3}\right)_i \left\langle 3\cos^2\theta_i - 1 \right\rangle_{J_1 m_J = J} ,$$

$$\left\langle {}^3H_4\ {}^2D_{3/2}\ 11/2 \left| q \right| {}^3H_4\ {}^2D_{3/2}\ 11/2 \right\rangle = -\frac{4}{5}\left[\frac{364}{495}\left\langle \frac{1}{r^3}\right\rangle_{5f} + \frac{1}{2}\left\langle \frac{1}{r^3}\right\rangle_{6d}\right]$$

$$\left\langle {}^1G_4\ {}^2D_{3/2}\ 11/2 \left| q \right| {}^1G_4\ {}^2D_{3/2}\ 11/2 \right\rangle = -\frac{4}{5}\left[\frac{2}{11}\left\langle \frac{1}{r^3}\right\rangle_{5f} + \frac{1}{2}\left\langle \frac{1}{r^3}\right\rangle_{6d}\right]$$

$$\left\langle {}^3H_5\ {}^2D_{3/2}\ 11/2 \left| q \right| {}^3H_5\ {}^2D_{3/2}\ 11/2 \right\rangle = -\frac{28}{65}\left[\frac{6}{5}\left\langle \frac{1}{r^3}\right\rangle_{5f} - \frac{1}{2}\left\langle \frac{1}{r^3}\right\rangle_{6d}\right] \qquad (21)$$

$$\left\langle {}^3H_4\ {}^2D_{5/2}\ 11/2 \left| q \right| {}^3H_4\ {}^2D_{5/2}\ 11/2 \right\rangle = -\frac{4}{5}\left[\frac{259}{495}\left\langle \frac{1}{r^3}\right\rangle_{5f} + \frac{17}{91}\left\langle \frac{1}{r^3}\right\rangle_{6d}\right]$$

$$\left\langle {}^3H_4\ {}^2D_{5/2}\ 11/2 \left| q \right| {}^3H_4\ {}^2D_{3/2}\ 11/2 \right\rangle = -\frac{24}{35}\sqrt{\frac{2}{13}}\left\langle \frac{1}{r^3}\right\rangle_{6d}$$

$$\left\langle {}^3H_5\ {}^2D_{3/2}\ 11/2 \left| q \right| {}^3H_4\ {}^2D_{3/2}\ 11/2 \right\rangle = \frac{52}{825}\sqrt{\frac{22}{13}}\left\langle \frac{1}{r^3}\right\rangle_{5f}$$

The values of $\frac{1}{r^3}$ are taken from the wave functions for uranium:

$$\frac{1}{r^3} = \int (F^2 + G^2)\ \frac{1}{r^3}\, dr \qquad \begin{aligned} &= 3.99/a_0^3 \text{ for 5f electrons,} \\ &= 2.39/a_0^3 \text{ for 6d electrons.} \end{aligned} \qquad (22)$$

The value for the quadrupole interaction is thus found to be:

$$B = 802\ Q \text{ (barns) Mc.} \qquad (23)$$

The sign of B is determined experimentally to be opposite that of A. Since the A value predicted from the calculated magnetic field and the experimentally measured positive moment is positive, we take for B the negative sign and

$$Q = -2400/802 = -3.0 \text{ barns.} \qquad (24)$$

SECOND-ORDER ELECTRONIC PERTURBATION

So far we have assumed that J is a good quantum number. This assumption is valid so long as the second-order contribution to the energy,

$$W_F = \left| \left\langle J \pm 1 \; IF \; m_f \right| -\bar{\mu}_I \cdot \bar{H} - 4e^2 \frac{r_n^2}{r_e^3} \left[C^2_{(n)} \cdot C^2_{(e)} \right] + \mathcal{H}_{mag} \left| I \; J \; F m_f \right\rangle \right|^2 / (E_J - E_{J\pm 1}), \tag{25}$$

is negligible in comparison with the first-order energy. If it is not, then the second-order field-dependent energy terms, which can not be distinguished experimentally from the first-order terms, affect the computed value of g_I, and-- to a smaller extent—A, B, and g_J. We will show, however, that for Pa, the effect of this perturbation is negligible.

The second-order dipole and quadrupole interactions calculated by means of the tensor method are, for J=11/2 and I= 3/2

$$\left\langle (J-1 \; IF \; m_f \left| -\bar{\mu}_I \cdot \bar{H} \right| J \; I \; F \; m_f \right\rangle = \frac{32 \mu_0 \mu_I}{495 \sqrt{5}} \left[(F+8)(7-F)(F+4)(F-3) \right]^{1/2}$$

$$\left[-\frac{37}{15} \left\langle \frac{1}{r^3} \right\rangle_{5f} + 3 \left\langle \frac{1}{r^3} \right\rangle_{6d} \right]$$

and $$\left\langle (J-1) I \; F \; m_f \left| -4e^2 \frac{r_n^2}{r_e^3} \left[C^{(2)}_{(n)} \cdot C^{(2)}_{(e)} \right] \right| J \; I \; F \; m_f \right\rangle = \frac{8e^2 Q}{45(55)\sqrt{3}} \left[F(F+1) - 33 \right]$$

$$\left[(F+8)(7-F)(F+4)(F-3) \right]^{1/2} \left[91/165 \left\langle \frac{1}{r^3} \right\rangle_{5f} - \left\langle \frac{1}{r^3} \right\rangle_{6d} \right] .$$

The matrix elements of the magnetic field interaction,

$\mathcal{H}_{mag} = \sum_i -(\ell_z + 2s_z)_i \frac{\mu_0 H_z}{h}$, may be written:

$$\left\langle J-1 \; I \; F \; m_f \left| \mathcal{H}_{mag} \right| J \; I \; F \; m_f \right\rangle = f(F, m_f) \left\langle J-1 \left\| \sum_i (-\ell_z + g_s s_z)_i \right\| J \right\rangle \mu_0 H_z / h$$

where

$$f(F_1 m_f) = \frac{m_f}{4\sqrt{165}F(F+1)} \left[(F+8)(F+4)(7-F)(F-3)\right]^{1/2} .$$

There are no matrix elements of the hyperfine structure that are off-diagonal in F.

It is not sufficient to calculate the matrix element in pure J-J coupling, because it vanishes in lowest order:

$$\left\langle 4(\tfrac{3}{2})\ \tfrac{9}{2} \right\| \sum_i (-\ell_z + g_s s_z)_i \left\| 4(\tfrac{3}{2})\ \tfrac{11}{2} \right\rangle = -\frac{12}{\sqrt{11}} (g_{J_2} - g_{J_1}) = 0.$$

We must therefore evaluate matrix elements between the ground state and states that are admixed by the electrostatic interaction. These are

$$\left\langle {}^3H_4\ {}^2D_{3/2}\ \tfrac{9}{2} \right\| \sum_i (-\ell_z + g_s s_z)_i \left\| {}^3H_5\ {}^2D_{3/2}\ \tfrac{11}{2} \right\rangle = 36\sqrt{26}\ (g_s+1)\ /55,$$

$$\left\langle {}^3H_4\ {}^2D_{3/2}\ \tfrac{9}{2} \right\| \sum_i (-\ell_z + g_s s_z)_i \left\| {}^3H_4\ {}^2D_{5/2}\ \tfrac{11}{2} \right\rangle = (6/5)\sqrt{\frac{26}{11}}\ (g_s+1),$$

$$\left\langle {}^3H_5\ {}^2D_{3/2}\ \tfrac{9}{2} \right\| \sum_i (-\ell_z + g_s s_z)_i \left\| {}^3H_4\ {}^2D_{3/2}\ \tfrac{11}{2} \right\rangle = -\frac{6}{55}\ (g_s+1),$$

$$\left\langle {}^3H_4\ {}^2D_{5/2}\ \tfrac{9}{2} \right\| \sum_i (-\ell_z + g_s s_z)_i \left\| {}^3H_4\ {}^2D_{3/2}\ \tfrac{11}{2} \right\rangle = -(2/5)\sqrt{\frac{14}{11}}\ (g_s+1).$$

The electronic wave function of the $J = 11/2$ state is given by Eq. (12). For the $J = 9/2$ state, it is (for $\lambda = 1/2$)

$$\left| J = 9/2 \right\rangle = 0.990 \left| 4(\tfrac{3}{2})\tfrac{9}{2} \right\rangle - 0.081 \left| 5(\tfrac{3}{2})\tfrac{9}{2} \right\rangle + 0.115 \left| 4(\tfrac{5}{2})\tfrac{9}{2} \right\rangle .$$

The coefficients $f(F, m_f)$ for observed transitions are

$$f(7, m_f) = 0.$$

$$f(6, 0) \leftrightarrow f(6, -1) = (1/12)(1/77)^{1/2} ,$$

and

$$f(4, 2) \leftrightarrow f(4, 1) = (1/20)(6/55)^{1/2} .$$

The separation of the $J = 9/2$, $J = 11/2$ levels is calculated to be 700 cm^{-1}. Using this value for the separation, and the above matrix elements, we find that the second-order perturbation at a magnetic field of 500 gauss is less than 100 cps for any state F, and may therefore be neglected.

NUCLEAR STRUCTURE

Mottelson and Nilsson[3] have noted that the similarity of the lowest levels of Pa^{231} and Pa^{233} suggests that the spin of Pa^{233} is 3/2, and that the odd proton belongs to the orbital 1/2-(530). The irregularities in the spacing of the levels of the ground-state rotational multiplet suggest that they are characterized by $K = 1/2$, and a fit to the spacings has been obtained by assuming for the moment of inertia $\frac{\hbar^2}{2\mathcal{I}} = 6$ kev, and for the decoupling parameter $d = -1.3$.

An expression for the nuclear dipole moment μ_N, in terms of the coefficients $a_{\ell\Lambda}$ of the eigenvectors of the odd nucleon, has been given by Nilsson. For $K = 1/2$, it is

$$\mu_I = \frac{1}{I+1}\left\{(g_s - g_\ell)\left[\frac{1}{4}\sum_\ell (a^2_{\ell 0} - a^2_{\ell 1}) + (-1)^{I-\frac{1}{2}+\ell}\,\frac{1}{2}\,(I+\tfrac{1}{2})\sum_\ell a^2_{\ell 0}\right]\right.$$

$$\left. + (g_\ell - g_R)\left[\frac{1}{4} + (-1)^{I-\frac{1}{2}}\,\frac{1}{2}\,(I+\tfrac{1}{2})d\right] + g_R\, I(I+1)\right\} .$$

For an odd proton, $g_s = 5.585$ and $g_\ell = 1.0$. The g factor of the core g_R is taken as $Z/A = 0.4$ for a uniformly charged nucleus. The nuclear moment, μ_I, was calculated from the revised wave functions of Mottelson and Nilsson.

The results for d = -1.3 are

δ	0	0.1	0.2	0.3
μ_I (nm)	2.09	2.32	2.63	2.77

where δ is a parameter that characterizes the eccentricity of the nuclear potential. The value of δ may be estimated from the measured nuclear Q. The intrinsic quadrupole moment Q_0, is approximately

$$Q_0 = (4/5)\, Z R_0^2\, \delta\, (1 + \tfrac{1}{2}\delta).$$

Here $R_0 \approx 1.2 \times 10^{-13} A^{1/3}$ cm is the mean charge radius of the nucleus. The relation between Q and Q_0 is

$$Q = \frac{3K^2 - I(I+1)}{(I+1)(2I+3)}\, Q_0 .$$

For K = 1/2 and I = 3/2, we have $Q_0 = -5Q$. The measured Q is -3.0 barns; therefore Q_0 is + 15 barns, and δ is 0.3. The predicted value of the nuclear moment corresponding to $\delta = 0.3$ is $\mu_I = 2.77$ nm. For a nuclear spin I = 3/2, the measured Q can be negative only for K = 1/2. Thus the observed sign and magnitude of Q are in agreement with the configuration assignment 1/2-(530) for the odd proton.

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Table I. Ground-state configurations for the actinide transition-series elements.

Element	Ground configuration	Ground-state J
$_{90}Th$	$(6d)^2 (7s)^2$	2
$_{91}Pa$	$(5f)^2 (6d)^1 (7s)^2$	11/2
$_{92}U$	$(5f)^3 (6d)^1 (7s)^2$	3
$_{93}Np$	$(5f)^4 (6d)^1 (7s)^2$	11/2
$_{94}Pu$	$(5f)^6 (7s)^2$	0
$_{95}Am$	$(5f)^7 (7s)^2$	7/2
$_{96}Cm$	$(5f)^7 (6d)^1 (7s)^2$	2

Table II. Pa^{233} low-field data

J	H (gauss)	ν(Mc) g_J			
		F = 7	F = 6	F = 5	F = 4
11/2	2.819(30)	2.512(35) 0.810(11)			
	5.567(30)		5.582(50) 0.813(7)	6.535(50) 0.812(6)	
	10.865(30)	9.700(50) 0.8117(40)	10.912(35) 0.8144(28)	12.812(35) 0.8152(22)	16.112(50) 0.8150(25)
	20.755(30)	18.590(25) 0.8144(11)	20.812(50) 0.8132(20)	24.450(60) 0.8145(20)	30.800(60) 0.8155(16)
9/2	2.819(30)		2.400(35) 0.811(11)		
	10.865(30)		9.162(50) 0.8033(43)	10.412(35) 0.8055(27)	12.560(60) 0.8058(40)
	20.755(30)		17.575(30) 0.8067(15)	19.912(50) 0.8065(20)	24.000(50) 0.8060(17)
7/2	10.865(30)			8.425(50) 0.7914(48)	
	20.755(30)			16.115(30) 0.7924(15)	

Table III. Pa^{233} data analysis

$g_I \times 10^4$	g_J	a(Mc)	b(Mc)	χ^2
5.66	-0.81391	566	-2086	3.85
7.65	-0.81396	574	-2172	2.56
9.71	-0.81401	582	-2267	1.68
11.84	-0.81406	592	-2370	1.26
12.39	-0.81408	595	-2396	1.227
12.94	-0.81409	597	-2423	1.231
14.06	-0.81412	603	-2483	1.34
16.38	-0.81418	614	-2608	1.99
18.83	-0.81424	628	-2750	3.31
21.40	-0.81431	643	-2911	5.41

Table IV. Pa^{233} hfs data

Data No.	H (gauss)	$\nu_{obs.}$ (Mc)	$\nu_{obs.} - \nu_{calc.}$	Transition
1	20.754(18)	18.590(12)	+0.008	a
2	55.192(21)	49.470(50)	+0.017	a
3	105.804(24)	94.910(75)	-0.002	a
4	156.142(29)	140.230(40)	-0.010	a
5	225.371(42)	202.770(40)	-0.009	a
6	318.227(58)	287.010(40)	-0.042	a
7	450.668(74)	408.120(30)	+0.031	a
8	149.713(30)	150.330(40)	+0.018	b
9	207.147(39)	208.025(40)	+0.014	b
10	308.464(58)	309.840(30)	-0.010	b
11	99.548(25)	147.800(25)	-0.003	c
12	144.665(30)	214.980(50)	+0.011	c
13	207.147(39)	308.160(50)	-0.006	c
14	258.908(48)	385.460(63)	-0.018	c

[a] $(7, -1 \leftrightarrow 7, -2)$

[b] $(6, 0 \leftrightarrow 6, -1)$

[c] $(4, 2 \leftrightarrow 4, 1)$

Table V. Calculations of f^k and g^k for Pa.

	f^2	f^4	g^1	g^3	g^5
^4K:	2/21	-4/693	-4/7	-2/21	-10/2541
^4I:	-11/105	8/231	-6/35	-44/315	-205/7,623
^4H:	-1/9	-8/99	6/35	-38/945	-1,975/22,869
^4G:	0	26/297	-1/15	-88/945	-575/3267
^4F:	52/315	-26/693	3/245	316/6,615	-41,605/160,083.

Table VI. Term energies in cm^{-1}

Term	From Th	From U
^4K	-7976	-10645
^4I	-6219	- 9267
^2H	-4091	- 6412
^4G	-2460	- 3612
^4H	-2266	- 3682
^2I	788	214
^4F	1196	2432
^2G	3287	4461
^2F	3460	6265
^2K	6702	10120

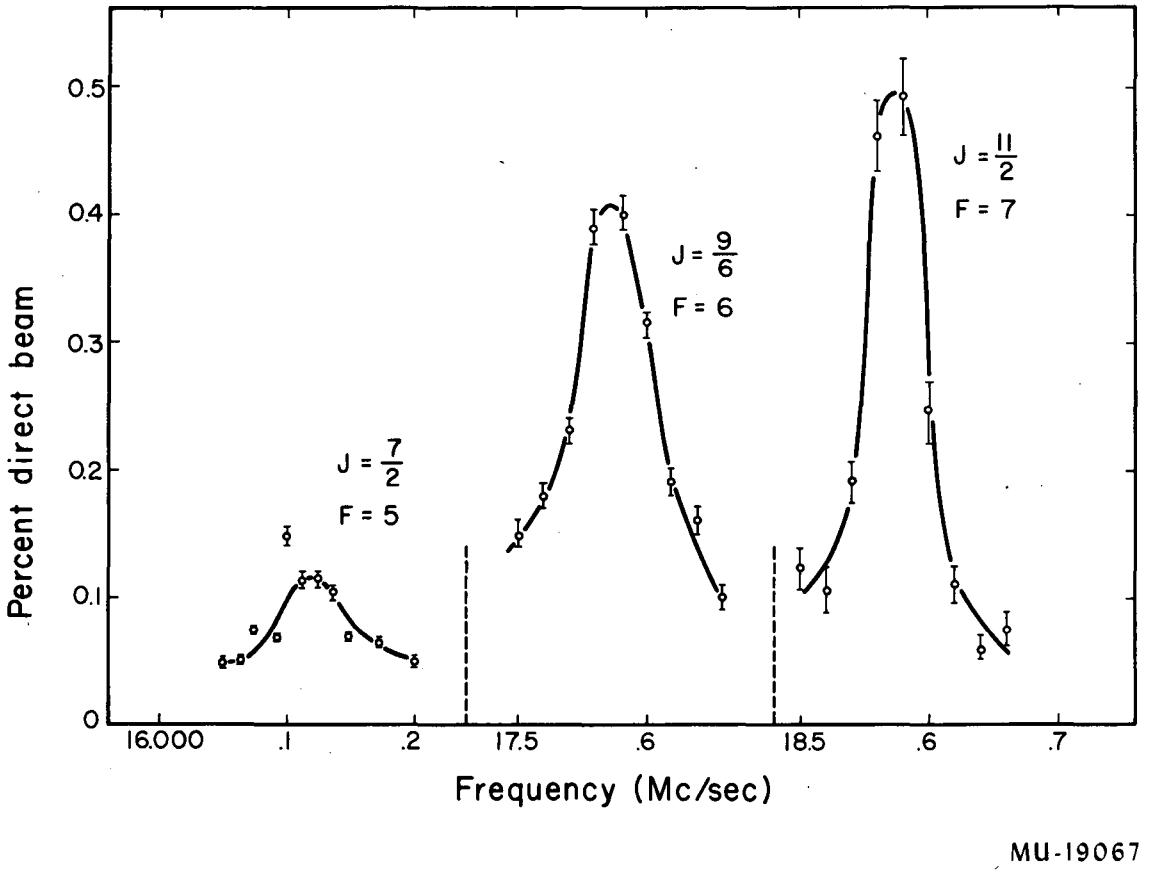

Fig. 1. Three of the observed transitions in Pa^{233}.

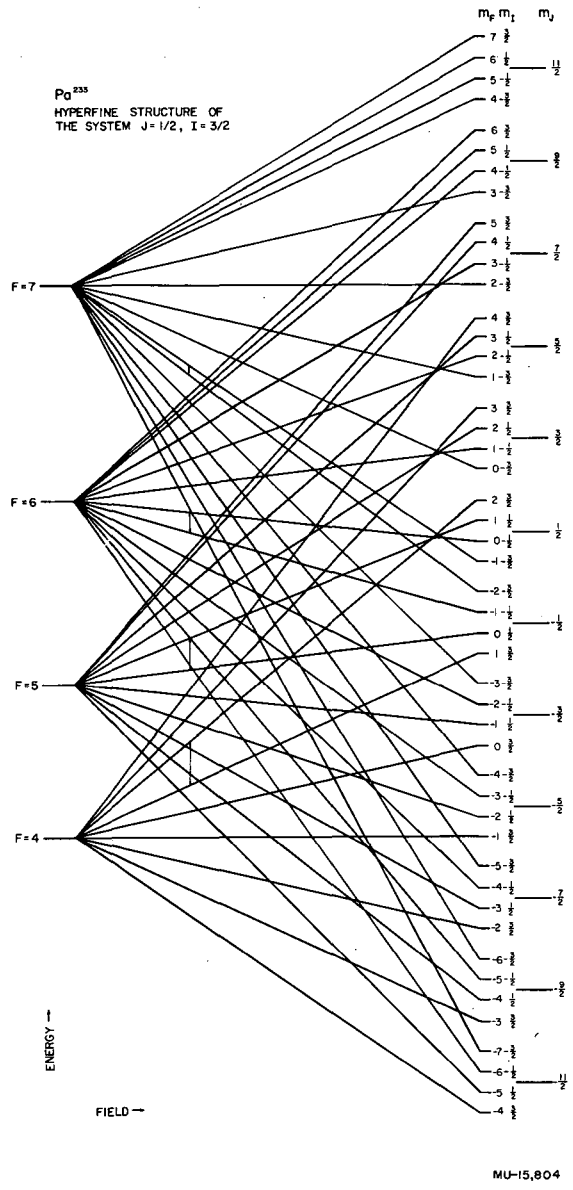

Fig. 2. Schematic diagram of hyperfine-structures levels of Pa^{233} in a magnetic field.

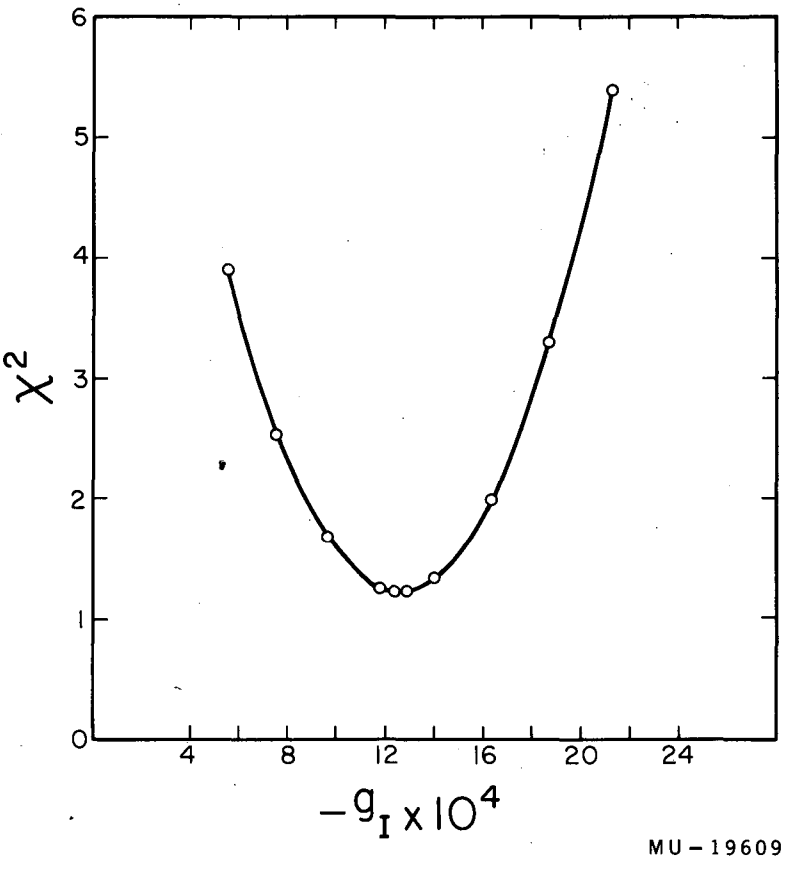

Fig. 3. Plot of χ^2 vs. g_I for Pa^{233}.

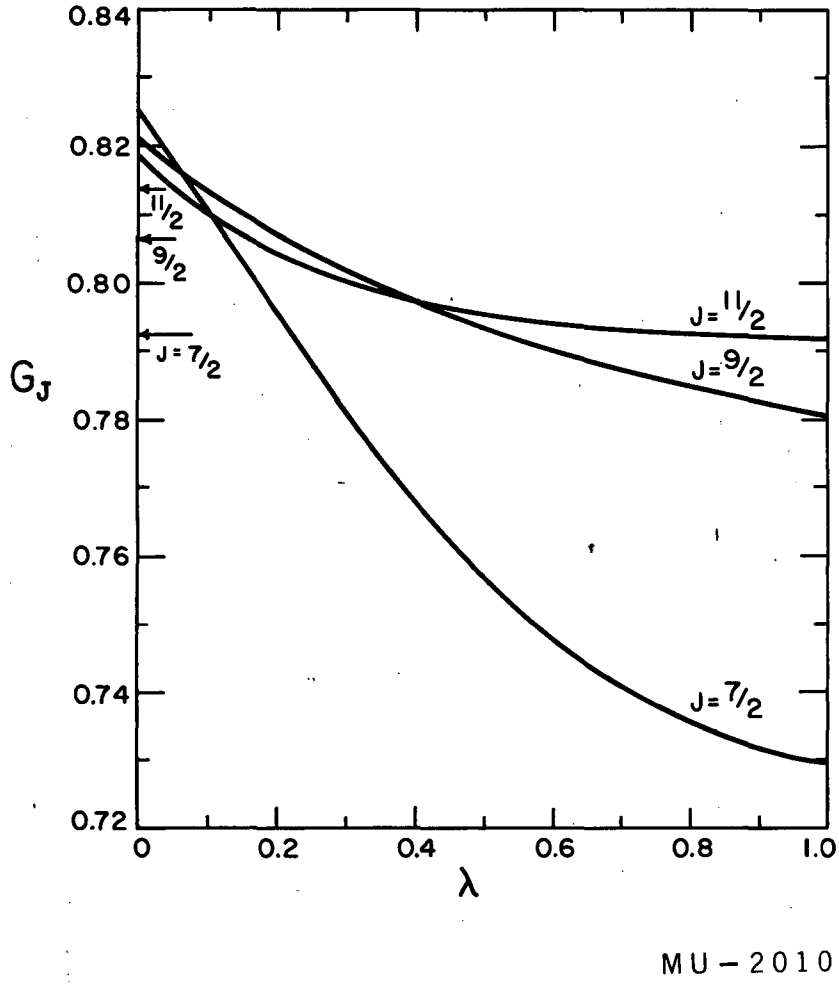

Fig. 4. Calculated g_I factors of the levels J=11/2, 9/2 and 7/2 of Pa as a function of the strength of the electrostatic interaction.