which $C_j=0$ as would be required. In this connection, it is interesting to observe that the "ferromagnetic case" can be included in the assumptions of Eqs. (8) by letting $M_2=0$. Then both (5) and (11) lead to the same frequency H_0+H_A, if one first assumes a sphere in (5), and then neglects demagnetizing effects as was done in (11).

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The Effects of Configuration Interaction on the Atomic Hyperfine Structure of Gallium*†

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The effects on the hyperfine structure of the mixing of higher configurations with the ground configuration $(4s)^2 4p$ of gallium is studied. It is found that the only configuration which need be considered is the $4s4p5s$. A Hartree wave function for the excited $5s$-state of gallium is calculated, and the extent of the mixing of this excited configuration with the ground configuration is determined. The coupling constants for magnetic and electric quadrupole hyperfine structure are computed with the use of the wave function for the ground state of gallium including the excited configuration. The determination of quadrupole moments from atomic hyperfine structure measurements is discussed and various methods of making this calculation compared. Beside the determination of the quadrupole moments of gallium, the quadrupole moments of aluminum, indium, and chlorine are estimated.

I. INTRODUCTION

THE splitting of the fine structure levels of an atom due to the hyperfine interactions can be written (in units of sec^{-1}) as[1]

$$\left(\frac{E}{h}\right)_F=\frac{aC}{2}+b\left\{\frac{(3/4)C(C+1)-I(I+1)J(J+1)}{2IJ(2I-1)(2J-1)}\right\},\qquad(1)$$

where

$$C=F(F+1)-I(I+1)-J(J+1).$$

Here J is the total electronic angular momentum, I is the nuclear spin, and F is the total angular momentum of the nucleus and the electrons. The first term in Eq. (1) arises from the interaction of the magnetic dipole moment of the nucleus and the magnetic field at the nucleus because of the surrounding electrons. The second term arises from the interaction of the electric field at the nucleus, due to the electrons, and the electric quadrupole moment of the nucleus. The quantities a and b are two coupling constants which measure the strength of the interaction between the nucleus and the atomic electrons. They are given by[2]

$$a=-(\mu/IJ)\langle\textstyle\sum_i H_{iz}\rangle_{\mathrm{Av}}\qquad(2)$$

$$b=-e^2Q\langle\textstyle\sum_i(3\cos^2\theta_i-1)/r_i^3\rangle_{\mathrm{Av}}.\qquad(3)$$

Here μ is the magnetic moment of the nucleus, and H_{iz} is the z component of the magnetic field at the nucleus caused by the ith electron. The summation extends over all the atomic electrons. Q is the quadrupole moment of the nucleus and θ_i, ϕ_i, and r_i are the spherical coordinates of the ith electron. The average values which appear in these formulas are to be taken for the electrons in the state $m_J=J$. If we assume that our electronic wave function arises from a single configuration, and that this configuration contains one electron outside of closed shells, we find that[2]

$$a=(\mu\mu_0/I)[2L(L+1)/J(J+1)]\langle 1/r^3\rangle_{\mathrm{Av}}\mathcal{F}\qquad(4)$$

where $\mu_0=eh/4\pi mc$. Here L is the orbital angular momentum of the electron outside the closed shells and the average value is taken with respect to this electron's wave function. $\mathcal{F}$ is a small relativistic correction (~1) given by Casimir.[2] The constant b is given by[2]

$$b=e^2Q(2L/2L+3)\langle 1/r^3\rangle_{\mathrm{Av}}\mathcal{R},\qquad(5)$$

if we assume that the wave function is separable into a product of a radial and an angular part. $\mathcal{R}$ is another small relativistic correction given by Casimir. For the atoms with one p-electron outside of closed shells, we

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[1] H. Kopfermann, *Kernmomente* (Akademische Verlagsgesellschaft M.B.H., Leipzig, 1940), Chapter I.

[2] H. B. G. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (Teylers Tweede Genootschap, Haarlem, 1936).

find, on the basis of Eqs. (4) and (5), (setting $J=\frac{3}{2}$) that the quadrupole moment can be expressed in terms of the experimentally measured value of the ratio of a to b.

$$Q=(8/3)(b/a)(\mu\mu_0/e^2I)(\mathcal{F}/\mathcal{R}). \tag{6}$$

These equations also predict that

$$(a_{\frac{1}{2}})/(a_{\frac{3}{2}})=5(\mathcal{F}_{\frac{1}{2}})/(\mathcal{F}_{\frac{3}{2}}). \tag{7}$$

The use of Eq. (6) to determine the quadrupole moment was first suggested by Davis, Feld, Zabel, and Zacharias,[3] who also noticed that for aluminum, gallium, and indium the ratio in Eq. (7) differed considerably from the value predicted. This leads one to suspect that the assumptions underlying the use of Eq. (6) to determine the quadrupole moments of substances may be in error. The aspect which we shall investigate is the assumption that the ground-state wave function of these atoms can be taken as though it arises from a single configuration. In particular, we shall consider the effect of configuration interactions on the ground states of gallium. Fermi and Segrè[4] first carried out a calculation of configuration interaction for thallium, which shows similar anomalies.

II. CALCULATION OF THE MIXING OF CONFIGURATIONS

The mixing of configurations is caused by the electrostatic interactions between electrons. The Hamiltonian for the electrons in an atom, neglecting magnetic interactions, is given by

$$H=\sum_i -\nabla_i^2-\frac{2Z}{r_i}+\frac{1}{2}\sum_{i\neq j}\frac{2}{r_{ij}}, \tag{8}$$

where r_{ij} represents the distance between two electrons and Z is the atomic number of the atom. The units in the equation are atomic units.[5] There exist matrix elements of this Hamiltonian between different configurations. The choice of gallium for a calculation of configuration interaction was governed by the existence of numerical wave functions for the ground configuration of this atom[6] and of accurate hyperfine structure measurements in both the $^2P_{\frac{1}{2}}$ and the metastable $^2P_{\frac{3}{2}}$ states. Matrix elements of the Hamiltonian [Eq. (8)] vanish if the states arising from the two configurations differ in either multiplicity, total orbital angular momentum (L), total angular momentum (J), or parity. Since the ground state of gallium is a ^2P-state, we need only consider ^2P-states arising from excited configurations as being mixed with the ground configuration. (The ground configuration of gallium is $(1s)^2(2s)^2(2p)^6$-$(3s)^2(3p)^6(3d)^{10}(4s)^24p$.) In our choice of an excited configuration, we are also limited to those which are strongly coupled to the nucleus and which are energetically close to the $(4s)^24p$ configuration. The $4s4p5s$ configuration has all the desired properties. It can produce relatively great hyperfine structure splittings since it contains two s electrons outside of closed shells which need no longer, because of the exclusion principle, have paired spins. The only other nearby configuration which has the desired properties is the $4s4p4d$ configuration. We shall not include it in our calculations since it does not interact as strongly with the $(4s)^24p$ configuration[7] and also because it is further removed in energy from the $(4s)^24p$ configuration than is the $4s4p5s$ configuration. The $4s4p5s$ configuration can give rise to two different ^2P-states, depending on how the spins of the $4s$, $4p$, and $5s$ electrons are combined to give a system of angular momentum $S=\frac{1}{2}$. Let us denote these two states by $\Psi^1(^2P_J)$ and $\Psi^2(^2P_J)$. The $(4s)^24p$ ^2P-state we shall denote by $\Psi^0(^2P_J)$. Our ground-state wave function must be written, if configuration interaction is included, as

$$\Phi(^2P_J)=\alpha_0\Psi^0(^2P_J)+\alpha_1\Psi^1(^2P_J)+\alpha_2\Psi^2(^2P_J). \tag{9}$$

The α's are calculated by minimizing the expectation value of the Hamiltonian [Eq. (8)] subject to the constraint

$$\alpha_0^2+\alpha_1^2+\alpha_2^2=1. \tag{10}$$

Details of this calculation, along with the specific forms of the wave functions $\Psi^i(^2P_J)$ for $J=\frac{3}{2}$, $\frac{1}{2}$ in terms of one electron wave functions, are contained in Appendix I. There we find that

$$\alpha_0=0.995;\quad \alpha_1=0.0307;\quad \alpha_2=-0.102 \tag{11}$$

for both $J=\frac{1}{2}$ and $J=\frac{3}{2}$.

III. EFFECT ON THE HYPERFINE COUPLING CONSTANTS

The effect that this mixture of configurations has on the magnetic hyperfine coupling constant, a, is now sought. The coupling constants for the states $J=\frac{1}{2}$ and $J=\frac{3}{2}$ will be given by

$$\begin{aligned} a_{\frac{1}{2}}&=-(\mu/IJ)\int\Phi^*(^2P_{\frac{1}{2}},m_J=\tfrac{1}{2})\\ &\qquad\times\textstyle\sum_i H_{iz}\Phi(^2P_{\frac{1}{2}},m_J=\tfrac{1}{2})d\tau_1\cdots d\tau_{31}\\ a_{\frac{3}{2}}&=-(\mu/IJ)\int\Phi^*(^2P_{\frac{3}{2}},m_J=\tfrac{3}{2})\\ &\qquad\times\textstyle\sum_i H_{iz}\Phi(^2P_{\frac{3}{2}},m_J=\tfrac{3}{2})d\tau_1\cdots d\tau_{31}. \end{aligned} \tag{12}$$

These integrals can be reduced to a sum of integrals over one electron coordinates by use of the explicit

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[3] Davis, Feld, Zabel, and Zacharias, Phys. Rev. **76**, 1076 (1949).

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[5] D. R. Hartree, Reports on Progress in Physics **11**, 113 (1946–1947). The unit of energy is *Rhc*. *R* is the Rydberg.

[6] Hartree, Hartree, and Manning, Phys. Rev. **59**, 299 (1941).

[7] The off-diagonal terms for the matrix of the interaction of this configuration with the ground configuration are about 1/20 of the similar terms for the $4s4p5s$ configuration. This result was obtained by using Slater's analytic wave functions [J. C. Slater, Phys. Rev. **36**, 57 (1930)].

forms of $\Psi^i({}^2P_J)$ in Appendix I. For the integrals of single electron wave functions with $l=1$, we shall use as the operator for the magnetic field at the nucleus due to a single electron[8]

$$\mathbf{H}_i = -(2\mu_0/r_i^3)\{\mathbf{L}_i - \mathbf{S}_i + [3(\mathbf{S}_i\cdot\mathbf{r}_i)/r_i^2]\mathbf{r}_i\}. \quad (13)$$

For the expectation values involving s electrons, use of this operator would not yield finite results. Instead we shall use the relativistic expression for the magnetic field at the nucleus[8]

$$\mathbf{H}_i = e(\boldsymbol{\alpha}\times r_i)/r_i^3. \quad (14)$$

Here α_x, α_y, and α_z are the well-known matrices appearing in the Dirac equation.[9] For a four-component wave function, we shall use the approximation of a Dirac wave function by a Schrödinger wave function for a central field given by Darwin.[8,10]

$$\psi_{4s}(\text{Dirac}) = \left[\left(\frac{ih}{4\pi mc}\right)\cos\theta\frac{\partial}{\partial r}\psi_{4s};\ \left(\frac{ih}{4\pi mc}\right)(\sin\theta)e^{i\varphi}\frac{\partial}{\partial r}\psi_{4s};\ \psi_{4s;0}\right]. \quad (15)$$

This expression will replace $\psi_{4s}\alpha$.

Table I. Quadrupole moments of Al, Ga, and In (all quadrupole moments in units of 10^{-24} cm^2).[a]

Nucleus	Z	Z_i	I	II	III	IV
Al^{27}	13	10.0	0.156	0.153	0.155	
Ga^{69}	31	27.4	0.232	0.178	0.186	0.189
Ga^{71}	31	27.4	0.146	0.112	0.118	0.119
In^{115}	49	45.1	1.17	0.759	0.834	
In^{113}	49	45.1	1.15	0.746	0.820	

[a] The shielding correction (see reference 15, Table II) would increase the values of the quadrupole moments by a factor of 1.105 for Al, 1.032 for In, and 1.046 for Ga.

If we use the explicit forms of the angular parts of our one-electron wave functions as given in Condon and Shortley,[11] we can evaluate the integrals (12) using the s wave function (15) and the form of the magnetic field at the nucleus given in Eqs. (13) and (14). We find

$$\begin{aligned} a_{\frac{3}{2}} = -(2\mu\mu_0/3I)\{&\alpha_0^2[-(8/5)\mathfrak{F}\langle 1/r^3\rangle] \\ &+\alpha_2^2[-(8/5)\mathfrak{F}\langle 1/r^3\rangle] \\ &+\alpha_1^2[-(16\pi/9)\{s^2(0)+\sigma^2(0)\}-(32/15)\mathfrak{F}\langle 1/r^3\rangle] \\ &+2\alpha_1\alpha_2[(1/3)^{\frac{1}{2}}(8\pi/3)\{s^2(0)-\sigma^2(0)\}] \\ &\qquad +2\alpha_1\alpha_0[(1/6)^{\frac{1}{2}}(16\pi/3)s(0)\sigma(0)]\} \\ a_{\frac{1}{2}} = -(2\mu\mu_0/I)\{&\alpha_0^2[-(8/3)\mathfrak{F}\langle 1/r^3\rangle] \\ &+\alpha_2^2[-(8/3)\mathfrak{F}\langle 1/r^3\rangle] \\ &+\alpha_1^2[(16\pi/27)\{s^2(0)+\sigma^2(0)\}-(8/3)\mathfrak{F}\langle 1/r^3\rangle] \\ &+2\alpha_1\alpha_2[-(1/3)^{\frac{1}{2}}(8\pi/9)\{s^2(0)-\sigma^2(0)\}] \\ &\qquad +2\alpha_1\alpha_0[-(1/6)^{\frac{1}{2}}(16\pi/9)s(0)\sigma(0)]\}. \end{aligned} \quad (16)$$

In these equations, $s(0)$ represents the value of the $4s$ wave function at $r=0$ and $\sigma(0)$ represents the value of the $5s$ wave function at $r=0$. We have also that

$$\langle 1/r^3\rangle = \int_0^\infty [P_{4p}^2(r)/r^3]dr.$$

We notice that terms in addition to that appearing in Eq. (4) have appeared in the coupling constant arising from the unpaired spins in the excited configuration.

The quadrupole coupling constant will be given by

$$b = -e^2Q\int\Phi^*({}^2P_{\frac{3}{2}}, m_J=\tfrac{3}{2})\textstyle\sum_i[(3\cos\theta_i - 1)/r_i^3] \times\Phi({}^2P_{\frac{3}{2}}, m_J=\tfrac{3}{2})d\tau_1\cdots d\tau_{31}. \quad (17)$$

Performing the indicated integrations, we find that

$$b = e^2Q(2/5)\langle 1/r^3\rangle(\alpha_0^2+\alpha_1^2+\alpha_2^2)\mathfrak{R}. \quad (18)$$

This yields, by use of the normalization condition [Eq. (10)], that

$$b = e^2Q(2/5)\mathfrak{R}\langle 1/r^3\rangle.$$

This is exactly the same form which the coupling constant would have if the configuration interaction were neglected ($\alpha_1=\alpha_2=0$; $\alpha_0=1$). The excited configuration differs from the ground configuration only in that one of the $4s$ electrons is excited to a $5s$ state. The s electrons, because of their spherical symmetry, do not contribute to the quadrupole interaction energy. In this way we can understand this result.

IV. QUADRUPOLE MOMENT OF GALLIUM

In order to determine the quadrupole moment of gallium from the measured value of b, we need the value of $\langle 1/r^3\rangle$. We shall determine the value of this quantity from the measured value of $a_{\frac{1}{2}}$ by estimating $s(0)$ and $\sigma(0)$. We can estimate these quantities by two means. They are given directly from the Hartree $4s$ and $5s$ functions for gallium. This gives the values $s(0)=2.70a_0^{-\frac{3}{2}}$ cm$^{-\frac{3}{2}}$ and $\sigma(0)=0.956a_0^{-\frac{3}{2}}$ cm$^{-\frac{3}{2}}$. a_0 is the Bohr radius. We can also determine these quantities from the formula of Fermi and Segrè[4]

$$[\psi_{ns}^0(0)]^2 = \frac{1}{a_0^3\pi}\frac{Z}{n^{*3}}\frac{dn^*}{dn}\left[\frac{1}{1-\beta^2Z^2}\right]^2. \quad (19)$$

Here β is the fine structure constant and n^* is defined by the equation

$$E_n = -(R/n^{*2})\ \text{cm}^{-1},$$

where E_n is the term energy of the electron under consideration, and R is the Rydberg. Using the Hartree energies for E_n and the estimate of dn^*/dn given by Kopfermann,[1] we find that $s(0)=2.82a_0^{-\frac{3}{2}}$ cm$^{-\frac{3}{2}}$ and $\sigma(0)=1.07a_0^{-\frac{3}{2}}$ cm$^{-\frac{3}{2}}$. These values are in good agreement with those obtained from the Hartree functions.

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[8] E. Fermi, Z. Physik **60**, 320 (1930).

[9] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949).

[10] C. G. Darwin, Proc. Roy. Soc. (London) **118**, 654 (1928).

[11] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935).

If we insert the Hartree values along with the values of α_0, α_1, and α_2 that we have determined into Eq. (16), we obtain

$$\begin{aligned} a_{\frac{1}{2}} &= -(2\mu\mu_0/I)[-0.280a_0^{-3}-2.67\mathfrak{F}_{\frac{1}{2}}\langle 1/r^3\rangle] \\ a_{\frac{3}{2}} &= -(2\mu\mu_0/3I)[0.837a_0^{-3}-1.61\mathfrak{F}_{\frac{3}{2}}\langle 1/r^3\rangle]. \end{aligned} \tag{20}$$

We notice the effect of the configuration interaction is smaller in the $J=\frac{1}{2}$ state. This is a reflection of the fact that in the $J=\frac{1}{2}$ state the probability of finding an s electron with spin "up" is more nearly equal to the probability of finding it with spin "down" than it was in the $J=\frac{3}{2}$ state. The smaller correction resulting from configuration interaction in this state provides the reason for calculating $\langle 1/r^3\rangle$ from the $J=\frac{3}{2}$ rather than the $J=\frac{3}{2}$ state. For gallium, we have the values[12–14]

Ga^{69}:

$$a_{\frac{1}{2}}=1338.78 \text{ Mc/sec}, \quad a_{\frac{3}{2}}=190.790 \text{ Mc/sec},$$
$$\mu=2.001 \text{ (in nuclear magnetons)}, \quad I=\tfrac{3}{2},$$
$$b=62.518 \text{ Mc/sec}.$$

Ga^{71}:

$$a_{\frac{1}{2}}=1701.05 \text{ Mc/sec}, \quad a_{\frac{3}{2}}=242.424 \text{ Mc/sec},$$
$$\mu=2.543 \text{ nm}, \quad I=\tfrac{3}{2}, \quad b=39.398 \text{ Mc/sec}.$$

Using these values in Eq. (20) for the $J=\frac{1}{2}$ state we find that $\langle 1/r^3\rangle=3.46a_0^{-3}$ cm^{-3} for Ga^{69}. Substituting this value into the formula for the coupling constant for the $J=\frac{3}{2}$ state in (20), we find $a_{\frac{3}{2}}=201$ Mc/sec. Neglecting the configuration interaction, we had $a_{\frac{1}{2}}/a_{\frac{3}{2}}=5.41$. Including the configuration interaction, we find $a_{\frac{1}{2}}/a_{\frac{3}{2}}=6.67$, while the experimental value of this ratio is 7.02.

From the experimental value of b and the value of $\langle 1/r^3\rangle$ that we have determined, we calculate the quadrupole moments of gallium to be[15]

$$Q(Ga^{69})=0.190\times 10^{-24} \text{ cm}^2$$
$$Q(Ga^{71})=0.120\times 10^{-24} \text{ cm}^2.$$

V. QUADRUPOLE MOMENTS OF OTHER NUCLEI

We have four possible ways that we can use to estimate the quadrupole moments of nuclei in other elements with an electronic structure similar to that of gallium.

Method I: From the measured value of $b/a_{\frac{3}{2}}$

$$Q=(8/3)(b/a_{\frac{3}{2}})(\mu\mu_0/e^2I)(\mathfrak{F}_{\frac{3}{2}}/\mathfrak{R}). \tag{21}$$

Method II: From the measured value of $b/a_{\frac{1}{2}}$

$$Q=(40/3)(b/a_{\frac{1}{2}})(\mu\mu_0/e^2I)(\mathfrak{F}_{\frac{1}{2}}/\mathfrak{R}). \tag{22}$$

Method III: The theoretical formula for the fine structure splitting, δ, will be unaffected by this type of configuration interaction. The reason for this is that s electrons do not contribute to the fine structure separations. Exciting an s electron by raising it to an s state with principal quantum number increased by one will, therefore, not change the formula for this splitting. Calculation of the fine structure coupling constant for our many configuration wave function bears out this result. We have that

$$\delta=(3\mu_0^2/e)\langle(1/r)(dV/dr)\rangle\mathfrak{H}. \tag{23}$$

V is the potential in which the electron outside of the spherically symmetric shells moves, and

$$\langle(1/r)(dV/dr)\rangle=\int_0^\infty P_{np}^2(r)(1/r)(dV/dr)dr$$

for elements with one p electron outside of closed shells. $\mathfrak{H}$ is a small relativistic correction given by Casimir.[2] We can define a quantity Z_i by the relation

$$\langle(1/r)(dV/dr)\rangle=Z_i\langle 1/r^3\rangle \tag{24}$$

TABLE II. Quadrupole moments of the chlorine isotopes.[a, b]

Nucleus	Z	Z_i	I	II	III′
Cl^{35}	17	13.7	−0.0789	−0.0778	−0.0782
Cl^{37}	17	13.7	−0.0621	−0.0612	−0.0616

[a] The values of the coupling constants used in this calculation were obtained from a private communication from V. Jaccarino and J. G. King and also from V. Jaccarino and J. G. King, Phys. Rev. **83**, 471 (1951).

[b] The shielding correction (see reference 15, Table III) would increase the values of the quadrupole moments of Cl by a factor of 1.079.

Z_i can be determined from the formula of Casimir[2]

$$\delta/R=(dn^*/dn)[Z_i^2/n^{*3}L(L+1)]\beta^2, \quad E_n=-n^{*-2}. \tag{25}$$

Here E_n is expressed in Rydbergs and the fine structure splitting in cm^{-1}. From the term values of the configurations $(4s)^2np$ ($n=4, 5, 6, \cdots$) values of n^* and dn^*/dn are estimated. From the measured value of δ for each of these terms a value of Z_i is calculated by use of Eq. (25). To determine the quadrupole moment, we use the formula

$$Q=(b/\delta)(\mu_0^2/e^2)(15/2)(\mathfrak{H}/\mathfrak{R})Z_i.$$

The values of Z_i for the higher values of n are used in this formula, since the uncertainties in the values of dn^*/dn disappear because this ratio approaches unity as n increases. This method was applied by Renzetti[12] to gallium.

Method IV: This method is the method carried out for gallium in this paper and involves the calculation of the mixing of configurations.

Table I contains the values of the quadrupole moments of elements in the same column of the periodic table as gallium along with the values of Z_i determined by the use of Eqs. (25).

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[12] N. A. Renzetti, Phys. Rev. **57**, 753 (1940).

[13] G. E. Becker and P. Kusch, Phys. Rev. **73**, 584 (1948).

[14] J. E. Mack, Revs. Modern Phys. **22**, 64 (1950).

[15] Values of the quadrupole moments in this article do not include shielding corrections of the type considered by R. Sternheimer, Phys. Rev. **84**, 244 (1951); **80**, 102 (1950). This correction, on the basis of Sternheimer's Thomas-Fermi calculation, increases the values of the quadrupole moments of gallium by a factor 1.046.

If we assume that these elements undergo the same type of configuration interaction as gallium, we can expect that method I will yield a value too large whereas method II will yield a value too small. This we can see by noticing that the sign of the correction terms in Eq. (31) is different from the $J=\frac{3}{2}$ state than it is for the $J=\frac{1}{2}$ state.

In Table II are given the quadrupole moments of the chlorine isotopes. Chlorine has one electron missing from a closed p shell, so that all of the methods except method III are applicable except for those changes of sign arising from the fact that we are considering a missing p electron.[3] Method III is not applicable since there is nothing in chlorine similar to the series $(4s)^2np$. Instead of method III, we used a method III′. In this method, we determined the value of Z_i for chlorine by interpolation between the values we obtained for aluminum, gallium, and indium.

VI. CONCLUSION

In gallium, we have seen that the only type of configuration interaction that we must consider is the type in which one of the $4s$ electrons is excited to a $5s$ state. This type of mixing has a large effect on the theoretical value of the magnetic hyperfine coupling constant. In the $J=\frac{3}{2}$ state of the atom, it decreases the value of the coupling constant below the value computed without the inclusion of the interaction. In the $J=\frac{1}{2}$ state, it increases the value of the coupling constant. The inclusion of this type of mixing of configurations does not change the form of either the fine structure or electric quadrupole coupling constants. This mixing of states is able to explain in a quantitative manner the deviation of the measured value of $a_{\frac{1}{2}}/a_{\frac{3}{2}}$ from the theoretical value calculated without the mixing.

We can also draw the conclusion that the hope that $\langle 1/r^3\rangle$ will cancel from the ratio of either $a_{\frac{1}{2}}$ to b or $a_{\frac{3}{2}}$ to b is not realized. The quadrupole moments calculated on the basis of this assumption will be in error. If $a_{\frac{3}{2}}$ is used, a value of the quadrupole moment too large will be obtained. If $a_{\frac{1}{2}}$ is used a value will be obtained which is too small. Since the correction is smaller in the $\frac{1}{2}$ state the value of Q obtained by method II will be more reliable.

Calculation of $\langle 1/r^3\rangle$ from the magnetic hyperfine structure with the inclusion of configuration interaction affords the most reliable method of evaluating this quantity and from it the quadrupole moment of the nucleus. We have also seen that, in the case of gallium, the calculation of $\langle 1/r^3\rangle$ from the observed doublet separation, through the use of Z_i, affords a method which gives a result in good agreement with the value obtained using the configuration interaction.

Since we might expect that the type of configuration interaction will be the same for all elements in the same column of the periodic table, some of the conclusions we have derived for gallium can be applied to these elements. The effect of the configuration interaction is greater the higher the nuclear charge. This we judge from the increase of the deviation of $a_{\frac{1}{2}}/a_{\frac{3}{2}}$ from the value predicted by Eq. (7). We conclude that, in the absence of a quantitative calculation of the mixing of the configurations for these elements, the most reliable method of calculating Q is method III involving the fine structure splitting. In every case for which this calculation was carried out, the value of the quadrupole moment obtained was between the values obtained by methods I and II. This, coupled with the agreement between the value of the quadrupole moment of gallium by method III and the more exact method involving configuration interaction, seems to indicate that is method is fairly reliable.

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APPENDIX I.

By compounding the spins and the orbital angular momenta of the individual electrons, we find that

$$\begin{aligned}
&\Psi^0({}^2P_{\frac{3}{2}},\ m_J=\tfrac{3}{2})\\
&\quad=\{\psi_{4s}{}^0(1)\alpha(1)\psi_{4s}{}^0(2)\beta(2)\psi_{4p}{}^1(3)\alpha(3)\}\{\text{core}\}\\
&\Psi^1({}^2P_{\frac{3}{2}},\ m_J=\tfrac{3}{2})\\
&\quad=\{(\tfrac{1}{6})^{\frac{1}{2}}[\psi_{4s}{}^0(1)\beta(1)\psi_{5s}{}^0(2)\alpha(2)\psi_{4p}{}^1(3)\alpha(3)\\
&\qquad+\psi_{4s}{}^0(1)\alpha(1)\psi_{5s}{}^0(2)\beta(2)\psi_{4p}{}^1(3)\alpha(3)\\
&\qquad-(\tfrac{2}{3})^{\frac{1}{2}}\psi_{4s}{}^0(1)\alpha(1)\psi_{5s}{}^0(2)\alpha(2)\psi_{4p}{}^1(3)\beta(3)\}\{\text{core}\}\\
&\Psi^2({}^2P_{\frac{3}{2}},\ m_J=\tfrac{3}{2})\\
&\quad=\{(\tfrac{1}{2})^{\frac{1}{2}}[\psi_{4s}{}^0(1)\beta(1)\psi_{5s}{}^0(2)\alpha(2)\psi_{4p}{}^1(3)\alpha(3)\\
&\qquad-\psi_{4s}{}^0(1)\alpha(1)\psi_{5s}{}^0(2)\beta(2)\psi_{4p}{}^1(3)\alpha(3)]\}\{\text{core}\}\\
&\Psi^0({}^2P_{\frac{1}{2}},\ m_J=\tfrac{1}{2})\\
&\quad=\{(\tfrac{1}{3})^{\frac{1}{2}}\psi_{4s}{}^0(1)\alpha(1)\psi_{4s}{}^0(2)\beta(2)\psi_{4p}{}^0(3)\alpha(3)\\
&\qquad-(\tfrac{2}{3})^{\frac{1}{2}}\psi_{4s}{}^0(1)\alpha(1)\psi_{4s}{}^0(2)\beta(2)\psi_{4p}{}^1(3)\beta(3)\}\{\text{core}\}\\
&\Psi^1({}^2P_{\frac{1}{2}},\ m_J=\tfrac{1}{2})\\
&\quad=\{-\tfrac{2}{3}\psi_{4s}{}^0(1)\beta(1)\psi_{5s}{}^0(2)\beta(2)\psi_{4p}{}^1(3)\alpha(3)\\
&\qquad+\tfrac{1}{3}[\psi_{4s}{}^0(1)\beta(1)\psi_{5s}{}^0(2)\alpha(2)\psi_{4p}{}^1(3)\beta(3)\\
&\qquad+\psi_{4s}{}^0(1)\alpha(1)\psi_{5s}{}^0(2)\beta(2)\psi_{4p}{}^1(3)\beta(3)]\\
&\qquad+\tfrac{1}{3}(\tfrac{1}{2})^{\frac{1}{2}}[\psi_{4s}{}^0(1)\beta(1)\psi_{5s}{}^0(2)\alpha(2)\psi_{4p}{}^0(3)\alpha(3)\\
&\qquad+\psi_{4s}{}^0(1)\alpha(1)\psi_{5s}{}^0(2)\beta(2)\psi_{4p}{}^0(3)\alpha(3)]\\
&\qquad-\tfrac{1}{3}(2)^{\frac{1}{2}}\psi_{4s}{}^0(1)\alpha(1)\psi_{5s}{}^0(2)\alpha(2)\psi_{4p}{}^0(3)\beta(3)\}\{\text{core}\}\\
&\Psi^2({}^2P_{\frac{1}{2}},\ m_J=\tfrac{1}{2})\\
&\quad=\{(\tfrac{1}{6})^{\frac{1}{2}}[\psi_{4s}{}^0(1)\beta(1)\psi_{5s}{}^0(2)\alpha(2)\psi_{4p}{}^0(3)\alpha(3)\\
&\qquad-\psi_{4s}{}^0(1)\alpha(1)\psi_{5s}{}^0(2)\beta(2)\psi_{4p}{}^0(3)\alpha(3)]\\
&\qquad-(\tfrac{1}{3})^{\frac{1}{2}}[\psi_{4s}{}^0(1)\beta(1)\psi_{5s}{}^0(2)\alpha(2)\psi_{4p}{}^1(3)\beta(3)\\
&\qquad-\psi_{4s}{}^0(1)\alpha(1)\psi_{5s}{}^0(2)\beta(2)\psi_{4p}{}^1(3)\beta(3)\}\{\text{core}\}.
\end{aligned}\tag{26}$$

These wave functions must be antisymmetrized and multiplied by $(1/31!)^{\frac{1}{2}}$ in order to normalize. In Eq. (26) $\alpha(i)$ denotes the spin eigenfunction for the ith electron with the z component of spin $+\frac{1}{2}$ and $\beta(i)$ the spin eigenfunction with z component of spin $-\frac{1}{2}$. $\psi_{nl}{}^{m_l}(i)$ is the Hartree wave function of θ_i, φ_i, and r_i, with n the radial quantum number, l the orbital angular momentum quantum number, and m_l the z component of orbital angular momentum. By the symbol $\{\text{core}\}$, we mean the product of the Hartree wave functions with spin for all the core electrons up through the closed shell. $\psi_{nl}{}^{m_l}(i)$ are solutions of the equations

$$(-\nabla^2 - Z_p(nl, r)/r)\psi_n{}^{m_l} = -\epsilon_{nl}\psi_{nl}{}^{m_l} \tag{27}$$

and are written in the form

$$\psi_{nl}{}^{m_l} = [P_{nl}(r)/r]\Theta(l, m_l; \theta)\Phi_{m_l}(\varphi). \tag{28}$$

Θ and Φ_{m_l} are the usual spherical harmonics.[11] $Z_p(nl, r)/r$ is the potential arising from the nuclear charge at the origin and the charge distribution described by the spherical parts of the wave functions of all but the electron under consideration. Ψ^1 and Ψ^2 differ in that in Ψ^1 the spins of the $4s$ and $5s$ electrons are combined to form a system with angular momentum 1 which is then combined with the spin of the $4p$ electron to form a system of angular momentum $\frac{1}{2}$. In Ψ^2 the spins of the $4s$ and $5s$ electrons form a system of angular momentum 0 which forms, upon combination with the spin of the $4p$ electron, a system with angular momentum $\frac{1}{2}$.

We determine the α's by the condition that

$$\int \Phi^*({}^2P_{\frac{1}{2}})[H-E]\Phi({}^2P_{\frac{1}{2}})d\tau_1\cdots d\tau_{31} \qquad d\tau_i = r_i^2 \sin\theta_i d\theta_i d\varphi_i dr_i \tag{29}$$

should be a minimum subject to the normalization requirement

$$\alpha_0^2 + \alpha_1^2 + \alpha_2^2 = 1. \tag{30}$$

The integrations in Eq. (29) include a summation over the spin coordinates.

In order to calculate the integrals appearing in (29) use was made of the Hartree wave functions for gallium. The $5s$ radial wave function necessary for the calculation was calculated numerically by the methods used by Hartree.[5] The potential $Z_p(5s, r)/r$ which is necessary for this calculation was taken to be identical with $Z_p(4s, r)/r$. This is a good approximation since one would not expect that exciting a $4s$ electron to a $5s$ state would seriously alter the charge distribution of the remaining 30 electrons. This also has the advantage that now the $4s$ and $5s$ wave functions are orthogonal. Table III contains the values of $P_{5s}(r)$ along with the value of the normalization integral and the energy value ϵ_{5s}.

TABLE III. The $5s$ Hartree wave function for gallium (not normalized).

r	$P_{5s}(r)$	r	$P_{5s}(r)$	r	$P_{5s}(r)$
0.000	0.000	1.6	−5.90	26.0	0.07
0.005	0.427	1.8	−6.10	28.0	0.04
0.010	0.724	2.0	−5.84	30.0	0.02
0.015	0.914	2.2	−5.22	32.0	0.01
0.020	1.016	2.4	−4.34	34.0	0.00
0.025	1.046	2.6	−3.26		
0.030	1.017	2.8	−2.07		
0.035	0.943	3.0	−0.81		
0.040	0.832	3.2	0.47		
		3.4	1.74		
0.05	0.537	3.6	2.98		
0.06	0.187	3.8	4.16		
0.07	−0.180	4.0	5.27		
0.08	−0.535				
0.09	−0.861	4.5	7.67		
0.10	−1.15	5.0	9.52		
		5.5	10.82		
0.12	−1.57	6.0	11.62		
0.14	−1.78	6.5	12.00		
0.16	−1.81	7.0	12.03		
0.18	−1.67	7.5	11.80		
0.20	−1.41	8.0	11.35		
0.22	−1.07	8.5	10.76		
0.24	−0.66	9.0	10.07		
0.26	−0.22	9.5	9.33		
0.28	0.23	10.0	8.55		
0.30	0.67	10.5	7.78		
		11.0	7.03		
0.35	1.65	11.5	6.31		
0.40	2.38	12.0	5.63		
0.45	2.82	12.5	4.99		
0.50	2.99	13.0	4.41		
0.55	2.92				
0.60	2.67	14.0	3.40		
		15.0	2.58		
0.7	1.79	16.0	1.93		
0.8	0.64	17.0	1.43		
0.9	−0.58	18.0	1.05		
1.0	−1.76	19.0	0.77		
1.1	−2.84	20.0	0.56		
1.2	−3.77	21.0	0.40		
1.3	−4.54	22.0	0.29		
1.4	−5.15	24.0	0.14		

$\epsilon_{5s} = 0.201$

$\int_0^\infty P_{5s}{}^2(r)dr = 873$

By varying the α's to minimize (29) we are led to the set of linear homogeneous equations

$$\begin{aligned} (H_{00}-E)\alpha_0 + H_{01}\alpha_1 + H_{02}\alpha_2 &= 0 \\ H_{10}\alpha_0 + (H_{11}-E)\alpha_1 + H_{12}\alpha_2 &= 0 \\ H_{20}\alpha_0 + H_{21}\alpha_1 + (H_{22}-E)\alpha_2 &= 0. \end{aligned} \tag{31}$$

Here

$$H_{ij} = \int \Psi^{i*} H \Psi^j d\tau_1\cdots d\tau_{31} \quad i, j = 0, 1, 2. \tag{32}$$

In order that these equations have a nontrivial solution, the determinant of the coefficients of the α's must vanish. If we make the substitution $H_{00} - E = -E'$, and also simplify our matrix elements by use of the equations that $\psi_{nl}{}^{m_l}$ satisfy and the definition of $Z_p(nl, r)$, we find that this determinant can be written as

$$\begin{vmatrix} -E' & G_{01} & G_{02} \\ G_{10} & G_{11}-E' & G_{12} \\ G_{20} & G_{21} & G_{22}-E' \end{vmatrix} = 0. \tag{33}$$

TABLE IV. Values of $R^k(n^al^a, n^bl^b; n^cl^c, n^dl^d)$.

n^a	l^a	n^b	l^b	n^c	l^c	n^d	l^d	R^k
4	0	1	0	1	0	4	0	0.00419
4	0	2	0	2	0	4	0	0.00645
4	0	3	0	3	0	4	0	0.0185
4	0	5	0	5	0	4	0	0.00807
4	0	2	1	2	1	4	1	0.00800
4	0	3	1	3	1	4	1	0.0219
4	0	4	1	4	1	4	1	0.126
4	0	3	2	3	2	4	2	0.0408
4	0	1	0	1	0	5	0	0.00148
4	0	2	0	2	0	5	0	0.00227
4	0	3	0	3	0	5	0	0.00628
4	0	2	1	2	1	5	1	0.00283
4	0	3	1	3	1	5	1	0.00753
4	0	4	1	4	1	5	1	−0.0273
4	0	3	2	3	2	5	2	0.0129
5	0	1	0	1	0	5	0	0.000524
5	0	2	0	2	0	5	0	0.000800
5	0	3	0	3	0	5	0	0.00213
5	0	2	1	2	1	5	1	0.000997
5	0	3	1	3	1	5	1	0.00260
5	0	4	1	4	1	5	1	0.0383
5	0	3	2	3	2	5	2	0.00422

Here the G's are given by

$$\begin{aligned} G_{11} &= \epsilon_{4s} - \epsilon_{5s} - 2K_{4s,0}{}^{5s,0} + K_{5s,0}{}^{4p,1} + 3K_{4s,0}{}^{4p,1} \\ &\quad + 2\sum{}'[K_{4s,0}{}^{n'l',m'} - K_{5s,0}{}^{n'l',m_l'}] \\ G_{12} &= G_{21} = (3)^{\frac{1}{2}}[K_{4s,0}{}^{4p,1} - K_{4s,0}{}^{4p,1}] \\ G_{22} &= \epsilon_{4s} - \epsilon_{5s} + 2K_{4s,0}{}^{5s,0} + K_{4s,0}{}^{4p,1} - K_{5s,0}{}^{4p,1} \\ &\quad + 2\sum{}'[K_{4s,0}{}^{n'l',m_l'} - K_{5s,0}{}^{n'l',m_l'}] \\ G_{10} &= G_{01} = (6)^{\frac{1}{2}} N_{4p,1} \\ G_{20} &= G_{02} = (2)^{\frac{1}{2}}[N_{4p,1} + 2\sum{}' N_{n'l',m_l'}], \end{aligned} \tag{34}$$

where

$$\begin{aligned} K_{nl,m_l}{}^{n'l',m_l'} &= \int \psi_{nl}{}^{*m_l}(1)\psi_{n'l'}{}^{*m_l'}(2)[1/r_{12}] \\ &\qquad \times \psi_{nl}{}^{m_l}(2)\psi_{n'l'}{}^{m_l'}(1)d\tau_1 d\tau_2 \\ N_{nl,m_l} &= \int \psi_{5s}{}^{*0}(1)\psi_{nl}{}^{*m_l}(2)[1/r_{12}] \\ &\qquad \times \psi_{4s}{}^{0}(2)\psi_{nl}{}^{m_l}(1)d\tau_1 d\tau_2. \end{aligned} \tag{35}$$

In Eqs. (34) the primed summations extend over the core electrons through the closed d shell. The integrals in Eqs. (35) are all of the well-known type[11]

$$\begin{aligned} &\int \psi_{n^al^a}{}^{*m_{l^a}}(1)\psi_{n^bl^b}{}^{*m_{l^b}}(2)[1/r_{12}]\psi_{n^cl^c}{}^{m_{l^c}}(1) \\ &\qquad\qquad \times \psi_{n^dl^d}{}^{m_{l^d}}(2)d\tau_1 d\tau_2 \\ &= \delta(m_l{}^a + m_l{}^b, m_l{}^c + m_l{}^d) \sum_{k=0} c^k(l^a, m^a; l^c, m^c) \times \\ &\qquad c^k(l^d, m_l{}^d; l^b, m_l{}^b) R^k(n^a, l^a, n^b, l^b, n^c, l^c, n^d, l^d). \end{aligned} \tag{36}$$

This result is obtained by expanding $1/r_{12}$ in spherical harmonics. The c^k are the known result[11] of integration over angles and

$$\begin{aligned} &R^k(n^a, l^a, n^b, l^b, n^c, l^c, n^d, l^d) \\ &= \int_0^\infty \int_0^\infty (r_<{}^k/r_>{}^{k+1}) P_{n^al^a}(1) P_{n^bl^b}(2) P_{n^cl^c}(1) \\ &\qquad\qquad \times P_{n^dl^d}(2) dr_1 dr_2, \end{aligned} \tag{37}$$

where $r_<$ is the smaller and $r_>$ the greater of r_1 and r_2. Table IV contains a list of the values of those integrals which were necessary in the calculation. Numerical integration using Simpson's rule was used to obtain these values from our numerical wave function.

Solving the determinant for the lowest value of E' and our set of homogeneous equations for the α's, we find

$$\begin{gathered} -E' = 0.00894, \\ \alpha_0 = 0.995, \quad \alpha_1 = 0.0307, \quad \alpha_2 = -0.102. \end{gathered} \tag{38}$$

We can now see that the mixing of the configurations is small and that the energy of the ground state is only lowered slightly. The α's for the linear combination of Ψ's for the $J=\frac{1}{2}$ state are exactly the same as those we have calculated for the $J=\frac{3}{2}$ state.