Hyperfine Structure of Nine Levels in Two Configurations of V^{51}. II. Theoretical*

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The experimental data of the preceding paper on the hfs of nine low levels in two configurations of V^{51} are analyzed and compared with the theory. The effects of intermediate coupling, configuration interaction, and relativity are considered. Corrections for J mixing within each multiplet are made. The measured J dependence of the hyperfine-interaction constants and electronic g factors of the nine levels is in rather good agreement with the theory. The ground-state nuclear electric-quadrupole moment is evaluated independently in each of the two configurations. Since the two values are the same to within 3%, the differential Sternheimer effect is apparently small. Although the new value of the quadrupole moment is now in good agreement with the theoretical prediction, the absolute value of any Sternheimer shielding is still unknown.

I. INTRODUCTION

THE preceding paper[1] presented the experimental data on $\Delta F=0, \pm 1$ transitions observed in the nine lowest levels of V^{51}. The purpose of this paper is to investigate the consistency of all the observations, to extract the proper values of the hyperfine and atomic parameters for each state, and to evaluate the nuclear ground-state electric-quadrupole moment. Both the lack of consistency between $\Delta F=0$ and $\Delta F=1$ observations and the lack of self-consistency among the $\Delta F=0$ observations for several of the states indicate a clear need for detailed corrections for the mixing among members of each multiplet.

The magnetic-dipole hyperfine-interaction constants may include contributions from relativity and from configuration interaction. Though difficult to separate theoretically, these contributions are allowed for by the use of appropriate adjustable parameters. Relativistic contributions to the electric-quadrupole hyperfine interactions are expected to be $\ll 1\%$ and are ignored. The procedure will be to determine the intermediate-coupling wave functions and to make theoretical predictions for the magnetic-dipole and electric-quadrupole hyperfine-interaction constants A and B in terms of the appropriate hyperfine parameters. The experimental values of A, B, and C will then be corrected for the J mixing caused by the off-diagonal hyperfine interactions. The theoretical expression for A and B will be least-squares fitted to the corrected experimental values; and the resulting values for the hyperfine parameters will be used to extract the value of the quadrupole moment Q. Since observations in the two configurations $3d^34s^2$ and $3d^44s$ are completely independent, any difference between the Sternheimer shielding[2] in the two cases can be measured. Finally, the problem of extracting the proper value of g_J from the $\Delta F=0$ data will be considered.

II. INTERMEDIATE-COUPLING WAVE FUNCTIONS

Figure 1 shows schematically[3] the low even-parity configurations of V I. The small splitting of each multiplet shows immediately that the spin-orbit parameter ζ_{3d} is small in both the configurations of interest. Because of the small departure from the LS limit, it was not felt necessary to make a complete treatment of the spin-orbit mixing.

For the $3d^34s^2$ configuration, a computer program was used to vary the appropriate Slater parameters and the spin-orbit parameter to make a least-squares fit to the spectroscopic energies[3] of the 15 identified levels. Configuration interaction was ignored and its effects were thus absorbed to some extent in the best-fit

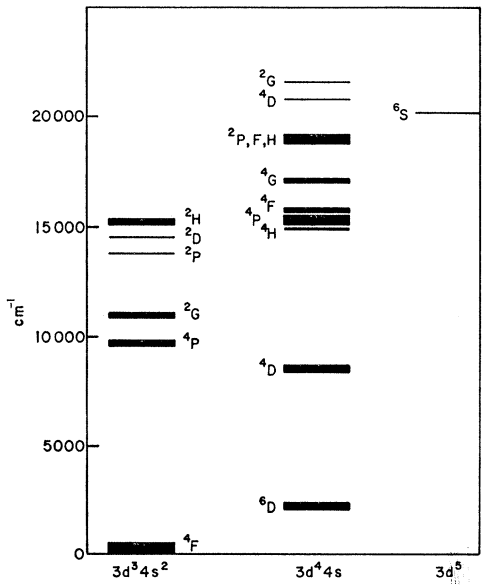

FIG. 1. The low even configurations of V I. Hfs measurements on the nine components of the two lowest multiplets are analyzed in the present paper.

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[1] W. J. Childs and L. S. Goodman, preceding paper, Phys. Rev. **156**, 64 (1967).

[2] R. M. Sternheimer, Phys. Rev. **146**, 140 (1966). References to earlier work are included.

[3] Taken from the data of *Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Printing and Publishing Office, Washington, D. C., 1949), Vol. I, p. 292.

values found for the parameters. This is probably the principal remaining source of inaccuracy in the intermediate-coupling wave functions calculated by the computer for the $3d^34s^2\,{}^4F$ states. The LS scheme was used for the calculation, and the departure from the LS limit was found to be very small for each state. As an example, the eigenvector found for the ${}^4F_{5/2}$ state is

$$|{}^4F_{5/2}'\rangle=0.999918|{}^4F_{5/2}\rangle +0.010444|{}_3{}^2D_{5/2}\rangle-0.006777|{}_1{}^2D_{5/2}\rangle +0.003073|{}^2F_{5/2}\rangle+0.000149|{}^4P_{5/2}\rangle, \quad (1)$$

in which the notation is standard except that the lower left-hand subscript on the ${}^2D$ states gives the seniority.

The $3d^44s$ configuration contains many more states than the $3d^34s^2$ configuration, and the effects of spin-orbit mixing were not investigated as completely. The computer program was used as described above to make a least-squares fit to the term energies[3] of the nine ${}^6D$ and ${}^4D$ levels of the $3d^4({}^5D)4s$ configuration. Terms of $3d^44s$ higher than ${}^4D$ (at 8500 cm^{-1}) were ignored, as was configuration interaction with terms of $3d^34s^2$. The nine levels were thus fitted to within 4 cm^{-1}. Although the coupling scheme most closely approached by the atom is again LS, the scheme used for computation in this case was (J_1,j), where the four d electrons couple to $\mathbf{J}_1$, which adds in turn to the $\mathbf{j}=\frac{1}{2}$ of the s electron to form $\mathbf{J}$. The eigenvectors are generated by the computer program. As an example, the eigenvector of the ${}^6D_{5/2}$ state in the (J_1,j) scheme was found to be

$$\psi({}^6D_{5/2})=0.897195\psi({}^5D_2,s;\tfrac{5}{2}) -0.441634\psi({}^5D_3,s;\tfrac{5}{2}), \quad (2)$$

which is extremely close to the composition in the LS limit ($\zeta_{3d}=0$).

III. HYPERFINE-INTERACTION CONSTANTS

The nonrelativistic magnetic-dipole hyperfine operator for configurations of the form nl^N is normally written[4]

$$\mathcal{H}_{\rm hfs}(M1)=a_{nl}\sum_{i=1}^{N}[\mathbf{l}_i-10^{1/2}(\mathbf{sC}^{(2)})_i{}^{(1)}]\cdot\mathbf{I}, \quad (3)$$

where

$$a_{nl}=2\beta\beta_N(\mu_I/I)\langle r^{-3}\rangle_{nl}. \quad (4)$$

Bauche and Judd[5] have pointed out that in calculating the magnetic hfs of states of the configuration l^N, one of the most important complications is the so-called core polarization. Since this may be regarded as configuration interaction with configurations containing unpaired s electrons, the hyperfine interaction will include a contribution $a(s)\mathbf{I}\cdot\mathbf{S}$ of the contact type, $a(s)$ being an adjustable parameter. Wybourne[6] has shown that all types of configuration interaction that can affect the magnetic-dipole hfs can be taken into account if the term $a(s)\mathbf{I}\cdot\mathbf{S}$ is added to Eq. (3) and, in addition, separate parameters are used to describe the radial dependence of the terms $\sum\mathbf{l}_i\cdot\mathbf{I}$ and $\sum(\mathbf{sC}^{(2)})_i{}^{(1)}\cdot\mathbf{I}$. For states of l^N, Sandars and Beck[7] have recently shown that relativistic effects on the magnetic-dipole hfs can be taken into account with a three-parameter Hamiltonian of exactly the same form. Thus, for states of an l^N configuration, the magnetic-dipole hfs Hamiltonian may be written[7]

$$\mathcal{H}_{\rm hfs}(M1) =\sum_{i=1}^{N}[a(l)\mathbf{l}_i-a(sC^2)10^{1/2}(\mathbf{sC}^{(2)})_i{}^{(1)}+a(s)\mathbf{s}_i]\cdot\mathbf{I}. \quad (5)$$

This Hamiltonian, which is a function of the three parameters $a(l)$, $a(sC^2)$, and $a(s)$, should be exactly consistent with the magnetic-dipole hfs of all the states of a term of l^N, regardless of the magnitude of relativistic contributions or the extent or type of configuration interaction. Sandars and Beck have emphasized that, because of the identity of the effective Hamiltonians for describing the effects of configuration interaction and relativity, it is difficult or impossible to distinguish between these effects. The extent to which the Hamiltonian of Eq. (5) is consistent with experiment will depend, however, on the accuracy with which the intermediate-coupling wave functions are known.

For configurations of the type $nl^Nn's$, the nonrelativistic magnetic-dipole hyperfine-interaction operator is given[8] by Eq. (3), but with the additional term $a_{n's}\mathbf{s}\cdot\mathbf{I}$ for the unbound s electron. The quantity $a_{n's}$, defined by Wybourne, is proportional to $g_I|\psi_s(0)|^2$. For states of such configurations, the Hamiltonian of Eq. (5) is not sufficiently general in that it fails to take adequate account of the unbound s electron. Equation (3), modified to apply to the $nl^Nn's$ configuration, thus contains the term $a_{n's}\mathbf{s}_{N+1}\cdot\mathbf{I}$ which does not behave like the operator $\sum_{i=1}^{N}\mathbf{s}_i\cdot\mathbf{I}$ of Eq. (5) in the presence of intermediate coupling. In principle, then, for l^Ns configurations a term $a_{n's}\mathbf{s}_{N+1}\cdot\mathbf{I}$ should be added to Eq. (5). The two contact terms, which have exactly the same J dependence in the LS limit, are difficult to distinguish in the ${}^6D$ states of V^{51} because of the extremely small extent of intermediate coupling. An attempt to include both terms led to nonphysical results, as will be discussed below. For this reason, the smaller of the two contact terms (that associated with the l^N core) was dropped. The Hamiltonian actually used for the $3d^44s$ configuration is

$$\mathcal{H}_{\rm hfs}(M1)=\sum_{i=1}^{N}[a(l)\mathbf{l}_i-a(sC^2)10^{1/2}(\mathbf{sC}^{(2)})_i{}^{(1)}]\cdot\mathbf{I} +a(s)\mathbf{s}_{N+1}\cdot\mathbf{I}. \quad (6)$$

[4] B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience Publishers, Inc., New York, 1965), pp. 112–113.
[5] J. Bauche and B. R. Judd, Proc. Phys. Soc. (London) **83**, 145 (1964).
[6] B. G. Wybourne, Ref. 4, pp. 148–150.
[7] P. G. H. Sandars and J. Beck, Proc. Roy. Soc. (London) **A289**, 97 (1965).
[8] B. G. Wybourne, Ref. 4, pp. 112, 113, 124, and 130.

TABLE I. Intermediate-coupling predictions for the magnetic-dipole and electric-quadrupole hyperfine-interaction constants A_J and B_J, and for the electronic g factors g_J.

Configuration	State	A_J	B_J	g_J
$3d^34s^2$	$^4F_{9/2}$	$0.666765a(l)+0.035527a(sC^2)+0.333235a(s)$	$-0.28549b_{3d}$	1.33398
	$^4F_{7/2}$	$0.761946a(l)-0.016447a(sC^2)+0.238055a(s)$	$-0.19041b_{3d}$	1.23860
	$^4F_{5/2}$	$0.971405a(l)-0.063763a(sC^2)+0.028596a(s)$	$-0.13476b_{3d}$	1.02867
	$^4F_{3/2}$	$1.599856a(l)-0.130084a(sC^2)-0.599857a(s)$	$-0.13723b_{3d}$	0.39873
$3d^4(^5D)4s$	$^6D_{9/2}$	$0.44444a(l)+0.06349a(sC^2)+0.11111a(s)$	$-0.57143b_{3d}$	1.55684
	$^6D_{7/2}$	$0.41271a(l)-0.05571a(sC^2)+0.11840a(s)$	$-0.09526b_{3d}$	1.58866
	$^6D_{5/2}$	$0.34287a(l)-0.13415a(sC^2)+0.13313a(s)$	$0.20407b_{3d}$	1.65865
	$^6D_{3/2}$	$0.13335a(l)-0.14091a(sC^2)+0.17567a(s)$	$0.28571b_{3d}$	1.86865
	$^6D_{1/2}$	$-1.33331a(l)+0.26708a(sC^2)+0.47002a(s)$	0	3.33872

The last term of this expression absorbs the large contact term of the unbound s electron and to some extent the smaller contact term by which Eq. (5) includes the contributions from relativity and configuration interaction. The quantity $a(s)$ is, of course, treated as a free parameter.

In calculating the expectation value of the magnetic-dipole hyperfine-interaction constants A_J, one uses the intermediate-coupling wave functions discussed above and the expressions for the matrix elements of the dipole operator between the basis states involved. Expressions for $\langle l^N\alpha SLJIFM|\mathcal{H}_{\rm hfs}(M1)|l^N\alpha'S'L'JIFM\rangle$ and $\langle l^N\alpha_1S_1L_1J_1,s;JIFM|\mathcal{H}_{\rm hfs}(M1)|l^N\alpha_1'S_1'L_1'J_1',s;JIFM\rangle$ are given by Eqs. (A7) and (A1), respectively, in the Appendix. The results are given in Table I. The calculated intermediate-coupling values of the electronic g factor are also given in the table. They follow from evaluating the matrix elements of the operator $\mathbf{L}+g_s\mathbf{S}$ (with $g_s=2.002319$) which, though diagonal in the LS scheme used for $3d^34s^2\,^4F$, is not diagonal in the J_1,j scheme used for $3d^4(^5D)4s\,^6D$.

It has been pointed out that the relativity and configuration-interaction contributions to the magnetic-dipole hfs cannot be distinguished because of the equivalence of the effective operators involved. The situation for the electric-quadrupole hyperfine interaction is quite different. The effect of configuration interaction is to multiply the interaction energy by a Sternheimer shielding factor[2], which in the nonrelativistic limit, is the same for every state of the configuration (i.e., independent of αSLJ). The effect of relativity[7] is to replace the single interaction by three terms, two of which vanish in the nonrelativistic limit. The three radial integrals involved, in addition to being different from each other, are not directly derivable from the observed magnetic-dipole hfs constants. For the $3d$ electrons in V^{51}, calculations of the Sandars-Beck type[7] using Casimir correction factors indicate that relativistic effects should be considerably smaller than 1%. The approach followed in the present treatment of the quadrupole interaction is nonrelativistic. The appropriate value of $\langle r^{-3}\rangle_{3d}$ to be used in estimating the nuclear electric-quadrupole moment will be discussed. Although the extent of configuration interaction is not known for either of the configurations studied, the relative importance of such shielding (or antishielding) is obtained.

The electric-quadrupole hyperfine operator for either configuration may be written[9]

$$\mathcal{H}_{\rm hfs}(E2)=-e^2(r_n^2/r_e^3)(\mathbf{C}_n^{(2)}\cdot\mathbf{C}_e^{(2)}), \qquad (7)$$

where n and e refer to the nucleus and the electrons, respectively. The electric-quadrupole moment Q is defined by the relation

$$Q=2\langle II|r_n^2\mathbf{C}_n^{(2)}|II\rangle. \qquad (8)$$

The quantity

$$b_{nl}=e^2Q\langle r^{-3}\rangle_{nl} \qquad (9)$$

is found to be a convenient parameter for the problem. Expressions for the quantities

$$\langle l^N\alpha SLJIFM|\mathcal{H}_{\rm hfs}(E2)|l^N\alpha'S'L'JIFM\rangle$$

and

$$\langle l^N\alpha_1S_1L_1J_1,s;JIFM|\mathcal{H}_{\rm hfs}(E2)|l^N\alpha_1'S_1'L_1'J_1',s;JIFM\rangle$$

are given by Eqs. (A9) and (A2), respectively, in the Appendix. With these and the intermediate-coupling wave functions, the expected J dependence of the electric-quadrupole hyperfine-interaction constants B_J was calculated for each multiplet. The results, which are functions only of the parameter b_{3d}, are also given in Table I. The value of b_{3d} need not be the same in the two configurations.

The J dependence of the magnetic-octupole hyperfine-interaction constants C_J was not calculated since no octupole interactions were observed. The expression for the F dependence of the octupole constants is given in Eq. (A5) of the Appendix.

It may be noted that the theory used in interpreting the magnetic-dipole and electric-quadrupole hfs and the electronic g factors of the $3d^4(^5D)4s\,^6D$ states also makes predictions, with no additional adjustable parameters, for the next higher multiplet $3d^4(^5D)4s\,^4D$. It is unfortunate that these levels were insufficiently populated for study in the present experiment.

[9] R. E. Trees, Phys. Rev. 92, 308 (1953); B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1963), p. 91.

IV. J MIXING WITHIN THE MULTIPLETS

Before the theoretical expressions for the hyperfine-interaction constants are compared with the experimental values, a comment concerning the signs of the interactions should be made. Since the sign (and value) of g_I is known[10] for V^{51}, the theoretical sign of a_{3d} and hence the signs of all the A factors are known. Experimentally, however, only the signs of B/A and C/A are determined. That the sign of A is positive for all the states measured is inferred from the high level of agreement between theory and experiment.

Theoretical expressions for the A and B factors of all the levels studied have now been developed in terms of a small number of adjustable parameters. The expressions for the dipole constants take account of intermediate coupling, configuration interaction, and relativistic effects. The expressions for the quadrupole constants, though nonrelativistic, take account of intermediate coupling and configuration interaction. The two configurations are considered independently; ratios between the configurations are of interest and will be dealt with below.

Before these expressions can be compared with the observed values of A_J and B_J for a particular state, however, it is necessary to take some account of the degree of admixture of states of different J. Since the admixture of a state $|SLJ'\rangle$ into $|SLJ\rangle$ depends on F, however, the most convenient approach leaves the theoretical prediction for the state of pure J untouched; instead, the observed values of A_J and B_J are corrected to those that would have been observed if all states of different J were infinitely far removed from the state under consideration. Theory and experiment can then be compared.

The complete hfs Hamiltonian for the problem is

$$\mathcal{H}=\mathcal{H}_{\rm hfs}+\mu_0\mathbf{H}\cdot[\alpha_{JJ'}(\mathbf{L}+g_s\mathbf{S})+g_I\mathbf{I}], \qquad (10)$$

where

$$\mathcal{H}_{\rm hfs}=\mathcal{H}_{\rm hfs}(M1)+\mathcal{H}_{\rm hfs}(E2)+\mathcal{H}_{\rm hfs}(M3)+\cdots. \qquad (11)$$

Within the limits of the simple theory, $\alpha_{JJ'}=1$. Because of complex configuration interactions, spin-orbit mixing in each of the configurations involved, relativistic and diamagnetic corrections, and other effects, however, it is found in practice that a J-dependent adjustable parameter must be kept for fitting the field dependence of transition frequencies. The simplest way to do this is to choose $\alpha_{JJ'}$ to reproduce the diagonal matrix elements that result from the Hamiltonian employed in the preceding paper (in which J is considered a good quantum number) and to give the theoretical values for the off-diagonal elements. For this, $\alpha_{JJ'}$ is defined by

$$\begin{aligned}\langle JIFM|\alpha_{JJ'}|J'IF'M\rangle&=1 \quad \text{for} \quad J'\neq J,\\ &=g_J/g_J{}^{LS} \quad \text{for} \quad J'=J,\end{aligned} \qquad (12)$$

regardless of F'. The quantity $g_J{}^{LS}$ is the LS limit obtained for the g factor when the Schwinger correction is included. The quantity g_J is an adjustable parameter and has the usual significance, and $g_s=2.002319$.

Zero or Very Low Field

Since the measured values of A_J, B_J, and C_J are derived from the transition frequencies of $\Delta F=1$ transitions at very low field (typically 1 G), the J mixing caused by the Zeeman operator can be ignored. (This will not be the case when values of g_J are to be extracted from high-field measurements.) For the field-independent part of the Hamiltonian (which is sufficient to describe the zero-field hyperfine-transition frequencies), perturbation theory with the lowest-order correction for J mixing yields the energy

$$\begin{aligned}E(\mathcal{SLJIFM})=E(\mathcal{SLJ})&+\langle JIFM|\mathcal{H}_{\rm hfs}(M1)+\mathcal{H}_{\rm hfs}(E2)+\mathcal{H}_{\rm hfs}(M3)|JIFM\rangle\\&+\sum_{J'\neq J}\frac{|\langle JIFM|\mathcal{H}_{\rm hfs}(M1)+\mathcal{H}_{\rm hfs}(E2)|J'IFM\rangle|^2}{E(\mathcal{SLJ})-E(\mathcal{SLJ}')},\end{aligned} \qquad (13)$$

where the quantum numbers represented by script letters are not entirely pure. The off-diagonal matrix elements of $\mathcal{H}_{\rm hfs}(M3)$ have been ignored in Eq. (13) as negligibly small. The first-order term in Eq. (13) (the second term on the right-hand side) is just

$$\langle FM|A_J\mathbf{I}\cdot\mathbf{J}+B_J\mathbf{Q}_{\rm op}+C_J\mathbf{\Omega}_{\rm op}|FM\rangle, \qquad (14)$$

in which the constituent matrix elements are as defined in Eqs. (A3), (A4), and (A5) of the Appendix. Hence, the final term of Eq. (13) is seen to be the lowest-order correction (for the effects of J mixing) to the zero-field theoretical energy. The next higher order should be negligibly small for V^{51} because the hyperfine interaction is extremely small compared with the fine-structure interaction for the multiplets considered. In Eq. (A12)–(A15) of the Appendix, the expressions for the required matrix elements are given in the LS basis; the energy denominators may be obtained from Table I of the preceding paper.[1]

The uncorrected values of the quantities A_J, B_J, and C_J given in the preceding paper[1] and again in Table II below were determined, in effect, by fitting the observed zero-field hyperfine intervals to the theoretical expressions involving A_J, B_J, C_J but not including the

[10] G. H. Fuller and V. W. Cohen, in *Nuclear Data Sheets*, compiled by K. Way *et al.* (Printing and Publishing Office, National Academy of Sciences—National Research Council, Washington 25, D. C., 1965), Appendix 1.

off-diagonal mixing term. The theoretical expressions for A_J and B_J (from Table I of the present paper) were then fitted to these uncorrected experimental values, and best-fit values of the parameters were obtained. These values were then used[11] to evaluate the off-diagonal matrix elements; and the theoretical expresions for the zero-field hyperfine intervals, including the off-diagonal contributions, were again fitted to the observed values by readjusting the values of A_J, B_J, and C_J. These new values are the final values, corrected for the off-diagonal effects of the hyperfine interactions with other members of the same multiplets.

Because of the large degree of mixing found within each multiplet, even at zero field, it becomes important to estimate the extent to which levels of other multiplets may be mixed in by the off-diagonal hyperfine interactions. The nearest other levels to both the $3d^34s^2\ ^4F$ and $3d^44s\ ^6D$ levels are about 50 times as far removed as the neighbors considered. In view of this, the additional perturbation to the values of A_J, B_J, and C_J caused by hyperfine mixing with more distant levels of the same configuration is probably somewhat smaller than the uncertainties found (from the computer fit) for the uncorrected values. However, interactions of the type

$$\langle 3d^34s^2\ ^4F; JIFM|\mathcal{H}_{\rm hfs}|3d^44s\ ^6D; J'IFM\rangle, \quad (15)$$

where J' need not equal J, might conceivably be larger because of the relatively closer spacing of the two multiplets. To estimate the additional uncertainty caused by such interconfiguration hyperfine interactions, the corrections already calculated for mixing within the multiplets can be scaled down in the ratios of the appropriate energy separations. The uncertainties calculated in this way (and combined with the experimental errors) are probably overestimates because the dipole orbital and contact operators, which contribute most of the corrections within each configuration, vanish between configurations.

The uncertainties in the corrected values of the hyperfine-interaction constants in Table II have been assigned on this basis. The uncertainties which the computer program deduces directly from the fitting of the experimental data are listed with the uncorrected values of the hfs constants. The off-diagonal correction is listed as a separate column in the table. It was, of course, not calculated directly, but rather was obtained by subtracting the uncorrected value of each constant from the corresponding corrected value. The corrections to the A factors are found to be extremely small ($\leqslant 0.01\%$), but corrections to the B factors range up to 17%. The magnetic-octupole hyperfine-interaction constants C_J, which were found to be zero within experimental error, were virtually unchanged by the corrections.

[11] The off-diagonal corrections were made with the simplification that $a(sC^2)$ has the value found for $a(l)$. The estimated resulting error is included in the uncertainties given for A_J, B_J, and C_J in Table II.

TABLE II. Values of A_J, B_J, and C_J for the nine lowest levels of V^{51}. Corrections for the effects of off-diagonal hyperfine mixing have been applied to the values in the right-hand column.

State		Quantity	Measured value (Mc/sec)	Off-diagonal correction (Mc/sec)	Corrected value (Mc/sec)
$3d^34s^2$	$^4F_{9/2}$	A	227.1324(6)	0.0035	227.136(1)
		B	7.822(15)	0.437	8.259(60)
		C	0.002(2)	0.000	0.002(2)
	$^4F_{7/2}$	A	249.7398(7)	0.0122	249.752(2)
		B	5.081(20)	0.514	5.595(60)
		C	−0.001(2)	0.000	−0.001(2)
	$^4F_{5/2}$	A	321.2265(12)	0.0239	321.251(3)
		B	3.384(25)	0.580	3.964(55)
		C	0.000(2)	0.000	0.000(2)
	$^4F_{3/2}$	A	560.0482(6)	0.0204	560.069(2)
		B	4.264(8)	−0.282	3.982(24)
		C	(Assumed to be 0; only two hyperfine intervals measured)		
$3d^44s$	$^6D_{9/2}$	A	406.8513(16)	0.0002	406.852(2)
		B	14.324(65)	0.020	14.344(65)
		C	0.006(9)	0.000	0.006(9)
	$^6D_{7/2}$	A	382.3670(10)	0.0022	382.369(1)
		B	2.268(29)	0.174	2.442(30)
		C	0.001(3)	0.000	0.001(3)
	$^6D_{5/2}$	A	373.5180(10)	0.0118	373.529(1)
		B	−5.459(25)	0.517	−4.942(35)
		C	0.000(2)	0.000	0.000(2)
	$^6D_{3/2}$	A	405.6038(12)	0.0443	405.648(2)
		B	−8.107(12)	1.191	−6.916(50)
		C	(Assumed to be 0; only two hyperfine intervals measured)		
	$^6D_{1/2}$	A	751.4778(28)	0.0668	751.545(3)
		B[a]	0	0	0
		C[a]	0	0	0

[a] The quantities B and C were assumed to be 0 for the $^6D_{1/2}$ state since $J=\frac{1}{2}$. The quadrupole and octupole interactions do contribute, however, to the single zero-field hyperfine interval $F=4 \leftrightarrow F=3$ because of the admixture of states with $J>\frac{1}{2}$. These contributions to the A factor, along with the off-diagonal dipole contribution, constitute the correction listed.

Nonzero Field

The considerable effect of J mixing on the resonance frequencies of the $\Delta F=0$ transitions has been pointed out above. When the $\Delta F=0$ transition frequencies are calculated with the uncorrected values of A_J, B_J, and C_J and with the assumption that J is a good quantum number, the values of χ^2 and of the residuals (presented in Tables V and II, respectively, of the preceding paper[1]) are very large in several cases. Very little improvement is obtained if one repeats the calculation using the corrected values of A_J, B_J, C_J and again treats g_J as an adjustable parameter. The point is that at finite field the Zeeman operator acts as an additional mixing agent to mix both F and J. It cannot, however, be treated separately since there are large interference effects between the hyperfine (both dipole and quadrupole) and Zeeman mixing mechanisms.

In considering J mixing at nonzero fields, it will be assumed that the resulting corrections to the resonance frequencies can be calculated in the limit of LS coupling. This assumption, which is inherent in the form of Eq. (10) for the Hamiltonian, should be excellent for V I.

In the case of the $3d^34s^2\,{}^4F$ and $3d^44s\,{}^6D$ multiplets in V^{51}, the matrix of $\mathcal{H}$ is of order $\geqslant 20$ for four different values of $|M|$, and in an optimization program for g_J many such matrices must be diagonalized repeatedly. Since the ratio of matrix elements off-diagonal in J to the difference of diagonal elements (for different J) is typically 3×10^{-5}, the use of perturbation theory would appear to be a simpler approach. If the zero-order energy of the level $|JI\mathfrak{F}M\rangle$ at field H is taken to be the value calculated on the assumption that J is a good quantum number, then the shift caused by J mixing may be expressed as

$$\delta E\approx\sum_{J'\neq J}\sum_{\mathfrak{F}'}\frac{|\langle JI\mathfrak{F}M|\mathcal{H}_{\rm hfs}(M1)+\mathcal{H}_{\rm hfs}(E2)+\mu_0\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})|J'I\mathfrak{F}'M\rangle|^2}{E(J)-E(J')}, \tag{16}$$

where the script $\mathfrak{F}$ indicates that the zero-order wave functions have the mixture of F's calculated for the field H with J considered a good quantum number. This may alternatively be written

$$\delta E\approx(\mu_0H)^2\sum_{J'\neq J}\sum_{F'\neq F}\frac{|\langle JI\mathfrak{F}M|\mathbf{L}+2\mathbf{S}|J'IF'M\rangle|^2}{E(J)-E(J')}+\sum_{J'\neq J}\frac{|\langle JI\mathfrak{F}M|\mathcal{H}_{\rm hfs}(M1)+\mathcal{H}_{\rm hfs}(E2)+\mu_0\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})|J'IFM\rangle|^2}{E(J)-E(J')}, \tag{17}$$

in which the pure Paschen-Back term is written separately. The matrix elements of the Zeeman operator are given by Eq. (A16) in the Appendix.

A computer program to make these corrections and then to vary g_J to obtain the best least-squares fit to the $\Delta F=0$ data is being written. The corrections to the various $\Delta F=0$ transition frequencies measured have been calculated by hand, however, under the assumption that $\mathfrak{F}$ is identical to F even at the strongest fields used (600 G). This is very nearly true, and the calculation for the ${}^6D_{1/2}$ state made possible the observation of the $\Delta F=1$ transition. In addition, the calculations for the other states reconcile the $\Delta F=0$ and $\Delta F=1$ observations.

TABLE III. The g_J values both before and after correction for J mixing within the multiplets. More precise evaluation of the corrections as discussed in the text will eventually permit reduction of the uncertainties assigned to the corrected values. The departure of these corrected values from the calculated intermediate-coupling values is also given. The discrepancies, which are remarkably independent of the state, are probably due primarily to relativistic and diamagnetic effects which were not taken into account in the calculation.

Configuration	State	Uncorrected g_J	Correction	Corrected g_J	g_J(exp) $-g_J$(calc)
$3d^34s^2$	${}^4F_{9/2}$	1.33362	−0.00002	1.33360(5)	−0.00038
	${}^4F_{7/2}$	1.23820	+0.00001	1.23821(4)	−0.00039
	${}^4F_{5/2}$	1.02839	0.00000	1.02839(4)	−0.00028
	${}^4F_{3/2}$	0.39899	−0.00051	0.39848(15)	−0.00025
$3d^44s$	${}^6D_{9/2}$	1.55649	−0.00002	1.55647(4)	−0.00037
	${}^6D_{7/2}$	1.58838	−0.00005	1.58833(5)	−0.00033
	${}^6D_{5/2}$	1.65846	−0.00015	1.65831(6)	−0.00034
	${}^6D_{3/2}$	1.86851	−0.00022	1.86829(10)	−0.00036
	${}^6D_{1/2}$	3.33683	+0.00164	3.33847(50)	−0.00025

When the $\Delta F=0$ resonance frequencies calculated by the fitting program are corrected in this approximate way, a high-quality least-squares fit is obtained for each state when the corrected values of A_J, B_J, and C_J are used and g_J is allowed to vary freely. The resulting values of g_J, referred to as the "corrected experimental values," are given in Table III, along with the uncorrected values described in the preceding paper. It is seen that the corrections, which are dominated by the interference term rather than the Paschen-Back term in nearly every case considered, are substantial for several levels. The departure of the corrected experimental values from those calculated in intermediate coupling is also given for each case. It is presumably due primarily to neglect of the relativistic and diamagnetic corrections,[12] and possibly also to the presence of configuration interaction.

The uncertainties assigned to the corrected values of g_J are larger than the experimental uncertainties; they reflect the additional uncertainty due to the approximation that $\mathfrak{F}$ is identical to F in the calculation of the corrections. The detailed results of the computer fitting calculations (in which the mixture $\mathfrak{F}$ is taken into account) and the resulting values of g_J will be published separately when complete. It is anticipated that uncertainties of 2 to 5 in the fifth decimal place will be found. These computed values will make possible a meaningful test of Judd's equation[12] giving the theoretical J dependence of g_J factors within a multiplet.

[12] B. R. Judd and I. Lindgren, Phys. Rev. 122, 1802 (1961); I. Lindgren, University of California, Lawrence Radiation Laboratory Report No. UCRL-9184 (unpublished).

TABLE IV. Best fits to the corrected experimental values of A_J and B_J in V^{51}.

Configuration	State	A factor Calc. (Mc/sec)	A factor Obs. (Mc/sec)	A factor Diff. (%)	B factor Calc. (Mc/sec)	B factor Obs. (Mc/sec)	B factor Diff. (%)
$3d^34s^2$	$^4F_{9/2}$	227.133	227.136	+0.001	8.332	8.259	−1.0
	$^4F_{7/2}$	249.769	249.752	−0.007	5.557	5.595	0.6
	$^4F_{5/2}$	321.233	321.251	+0.006	3.933	3.964	0.8
	$^4F_{3/2}$	560.073	560.069	−0.001	4.005	3.982	−0.5
$3d^4(^5D)4s$	$^6D_{9/2}$	407.168	406.852	−0.08	14.166	14.344	1.2
	$^6D_{7/2}$	381.879	382.369	0.13	2.361	2.442	3.3
	$^6D_{5/2}$	373.326	373.529	0.05	−5.059	−4.942	2.4
	$^6D_{3/2}$	406.078	405.648	−0.11	−7.083	−6.916	2.4
	$^6D_{1/2}$	751.491	751.545	0.01	0	0	0

V. COMPARISON OF HFS THEORY WITH EXPERIMENT

Now that the experimental values of the hyperfine-interaction constants A_J, B_J, and C_J have been corrected for the effects of J mixing, they may be compared with the theoretical expressions developed above. Least-squares fits to the observed values were made independently for the two configurations. The fit to the magnetic-dipole constants used three parameters; that to the electric-quadrupole constants used one parameter.

Table IV lists the results of the fits. The differences between the calculated and the corrected experimental values of the magnetic-dipole hyperfine-interaction constants A_J are not greater than 18 kc/sec (0.007%) for the ^4F states, and 0.13% for the ^6D levels. The agreement between theory and experiment appears remarkably good, although the differences are larger than experimental error for both multiplets. For the ^4F states, the differences are presumed to be due to extremely slight inaccuracies in the intermediate-coupling wave functions used. The sensitivity of the fit to the small departure from the LS limit is illustrated by the fact that the χ^2 for the fit found in intermediate coupling is only 1/147 of that for a similar fit in the LS limit.

For the ^6D states, the fit found in intermediate coupling is not appreciably better than that found in the LS limit. The remaining 0.1% difference between theory and experiment is probably due, in addition to inaccuracies in the intermediate-coupling wave functions, to failure of the contact term in Eq. (6) to simulate the effect of the other contact term (that associated with the d^4 core) as discussed above. To investigate this further, a 4-parameter fit, which included both contact terms properly, was made with the same intermediate-coupling wave functions. Although it was found possible to fit all five of the A factors of the ^6D term to within 8 kc/sec (0.002%), the values found for the four parameters were entirely unrealistic; $a(l)=+252.598$ Mc/sec, $a(sC^2)=-67.265$ Mc/sec, $a_d(s)=+9419.920$ Mc/sec, and $a_s(s)=-34\,989.953$ Mc/sec, where the subscripts on the contact terms identify their origin. In spite of the extremely high quality of this fit, no physical significance is assigned to it. The parameters have evidently assumed unreasonable values to compensate for deficiencies in the intermediate-coupling wave functions. Meaningful improvement of the agreement between theory and experiment will probably come for the ^6D states only when the basis states used in the calculation for the spin-orbit mixing are expanded to include all levels of the configuration, and both contact terms are included.

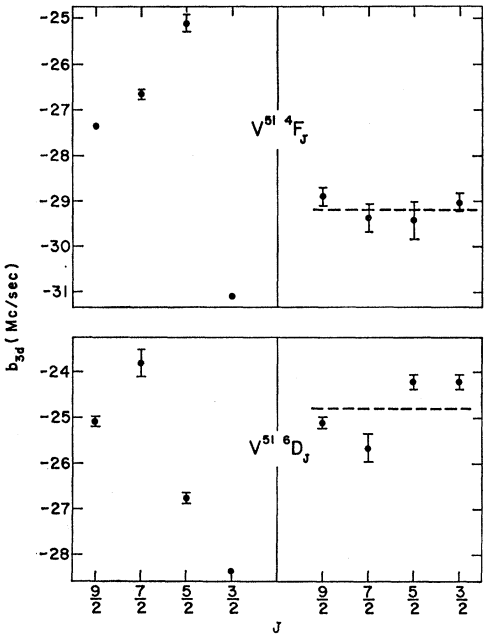

FIG. 2. Plot of the values of $b_{3d}=e^2Q\langle r^{-3}\rangle_{3d}$ both before and after correction for off-diagonal hfs in two multiplets of V^{51}. The data for $3d^34s^2$ $^4F_{9/2,7/2,5/2,3/2}$ are given at the top, and for $3d^4(^5D)4s$ $^6D_{9/2,7/2,5/2,3/2}$ at the bottom of the figure. The values obtained from the raw data are shown at the left and the values determined after correction for off-diagonal hyperfine interactions at the right. For each multiplet, applying the correction gives a dramatic improvement in the consistency of the results. The results are consistent within experimental error for the ^4F term, but not quite consistent for the ^6D levels. The slight remaining discrepancy is discussed in the text.

TABLE V. Values of parameters used for the fits of Table IV.

Quantity	$3d^34s^2(^4F)$	$3d^4(^5D)4s(^6D)$	$^4F/^6D$
$a(l)$ (Mc/sec)	353.662	302.013	1.172
$a(sC^2)$ (Mc/sec)	322.866	272.333	1.185
$a(l)/a(sC^2)$	1.095	1.109	0.987
$\bar{a}_{3d}$ (Mc/sec)	338.3	287.2	1.178
$a(s)$ (Mc/sec)	−60.456	2300.847	...
b_{3d} (Mc/sec)	−29.2±0.3	−24.8±0.7	1.177
$Q(V^{51})$ (b)	−0.0515	−0.0515	1.00±0.03

Thus the theory of the magnetic-dipole hyperfine interaction is felt to be entirely consistent with the experimental results. This agreement has been demonstrated to 0.13%, and this slight remaining discrepancy is thought to be understood.

The fits to the corrected observed electric-quadrupole hyperfine-interaction constants B_J are not as good as for the dipole interaction. The four constants are fitted within 1.0% for the $3d^34s^2$ configuration, and within 3.3% for the $3d^44s$ configuration. The fit is within experimental error in the case of the $3d^34s^2\ ^4F$ term, but outside it for the $3d^44s\ ^6D$ term. Figure 2 illustrates this graphically. For the ^4F term, shown in the upper half of the figure, the values of b_{3d} found from the uncorrected values of B_J are shown at the left; the large scatter is evident. The values of b_{3d} found after correction of the observed B_J values for off-diagonal hyperfine interactions are shown at the right. The dashed line gives the average value found for b_{3d} in this configuration. The corresponding plots for the $3d^44s\ ^6D$ term are given in the lower half of the figure. While the off-diagonal corrections clearly effect a dramatic improvement in consistency, the correction still does not bring complete agreement between the values of b_{3d} found from the four different levels. The origin of the discrepancy is not fully understood. While the quadrupole calculation did not take account of relativistic effects, it has been mentioned above that these effects are estimated to be too small to account for the discrepancy. Although inaccuracies in the intermediate-coupling wave functions could account for it, the wave functions used were far more satisfactory in accounting for the dipole effects. Configuration interaction, at least in first approximation, should scale the values of b_{3d} by the same factor for each of the four states. It is perhaps possible that the uncertainties assigned to the off-diagonal hfs corrections are underestimated, and that for this reason the uncertainties assigned to the corrected values of $B(^6D_J)$ should be increased. Because the discrepancy is not understood, the uncertainty given for b_{3d} in the $3d^44s$ configuration has been made large enough to include the spread of the points in Fig. 2.

Table V lists the values of the parameters used in calculating the results presented in Table IV. Calculations of the Sandars-Beck type,[7] using Casimir correction factors in place of relativistic radial wave functions, indicate that relativistic effects for the magnetic-dipole hfs of the $3d$ electrons in V^{51} should be much less than 1%. They also show that if the difference between $a(l)$ and $a(sC^2)$ were due to relativistic effects, then it would follow that $a(sC^2) \geqslant a(l)$ and that any difference should not exceed 1%. The fact that $a(sC^2)$ is found to be about 10% smaller than $a(l)$ (in both configurations) indicates strongly that the effect is due to configuration interaction rather than relativity. It is likely that interaction between the configurations $3d^34s^2$ and $3d^44s$ is involved.

While a_{3d} varies as r^{-3}, ζ_{3d} departs from an r^{-3} dependence to the extent that the nucleus is shielded. When the shielding is taken into account in the standard way (by the use of an effective charge), the observed values of a_{3d} are consistent with the observed values of ζ_{3d} and the previously known values[10] of μ_I and $I(=\frac{7}{2})$ for V^{51}.

The values of $a(s)$ found in the two configurations are not directly comparable since, as seen in Eqs. (5) and (6), they are not defined in the same way. The value expected for a_{4s} is calculated[13] to be +3500 Mc/sec while the observed value of $a(s)$ for the $3d^44s$ configuration is +2300 Mc/sec. The difference between these numbers is far too large to be due to relativistic effects, according to Sandars-Beck type calculations, and must be attributed to core polarization (i.e., to configuration interaction with configurations containing unpaired s electrons). The same conclusion can be drawn for the large negative value of $a(s)$ observed in the $3d^34s^2$ configuration. It would be interesting to compare these numbers with *ab initio* calculations.

The values obtained for b_{3d} in each configuration were discussed above and are illustrated in Fig. 2. The uncertainty assigned includes all four measured values. The electric-quadrupole moment of the nuclear ground state of V^{51} can be extracted from Eq. (9) once a value for $\langle r^{-3}\rangle_{3d}$ is chosen. The normal way of doing this is to calculate $\langle r^{-3}\rangle_{3d}$ from Eq. (4). Although the value obtained in this way clearly depends on whether one extracts it from $a(l)$ or $a(sC^2)$, the uncertainty is overshadowed by the still larger uncertainties associated with Sternheimer shielding.[2] For the virtually nonrelativistic $3d$ electrons of the V^{51} atom, each of these two sources of uncertainty is associated primarily with configuration interaction. The values of Q given in Table V are calculated by use of the values of $\langle r^{-3}\rangle_{3d}$ obtained from $\bar{a}_{3d}=\frac{1}{2}[a(l)+a(sC^2)]$. If one arbitrarily assigns an uncertainty of 20% to allow for these effects, the value[14]

$$Q(V^{51}) = -0.052 \pm 0.010 \text{ b} \qquad (18)$$

is obtained. The agreement between this value and the value −0.03 b predicted theoretically by Horie and

[13] The procedure is outlined, for example, on p. 131 of Ref. 4.
[14] K. Murakawa, J. Phys. Soc. Japan **21**, 1466 (1966).

Arima[15] is felt to be rather good for such a small moment.

The size of the Sternheimer shielding (or antishielding) cannot be measured in the present experiment because it is expected to be the same for every state of a configuration. It is possible, however, to determine the differential Sternheimer effect between the two configurations. This is just

$$\frac{b_{3d}(d^3s^2)/b_{3d}(d^4s)}{a_{3d}(d^3s^2)/a_{3d}(d^4s)}=1.00\pm0.03. \quad (19)$$

This ratio is nearly independent of the procedure used for evaluating $\langle r^{-3}\rangle_{3d}$ so long as the same procedure is used for each configuration. Thus, regardless of the size of the Sternheimer shielding in either configuration, it is clear that it is very nearly the same for the two cases.

VI. CONCLUSIONS

In general, it is felt that the extent of agreement between theory and experiment is excellent. The magnetic-dipole hyperfine-interaction constants are accounted for to within 0.13% for the nine states studied, and this small remaining difference is thought to be understood. The electric-quadrupole hyperfine-interaction constants are accounted for to within the 1% experimental error for one configuration, and to within about three probable errors for the other. Although the origin of this slight remaining discrepancy is not known, several possible sources are discussed. The differences between the (corrected) experimental electronic g factors and the calculated values are very small, and their signs and approximate magnitudes are as expected for the usual relativistic and diamagnetic effects. Computation of these corrections is extremely tedious and has not been carried out.

The value obtained for the ground-state nuclear electric-quadrupole moment of V^{51} is in good agreement with the expectation[15] from present nuclear theory. However, a theoretical calculation of the Sternheimer shielding factor for the two configurations would be of great interest for two reasons: (1) The value of $Q(V^{51})$, which has been the subject of some controversy in recent years, would be known very well if this last remaining uncertainty could be resolved, and (2) the ratio of the calculated shielding factors for the two configurations could be checked against the relatively accurate experimental value.

While the "effective operator" technique[7] used to take account of the magnetic-dipole hfs is in good agreement with experiment, it is not without its limitations. The parameters involved absorb many complex effects by being allowed to vary freely and are therefore difficult to interpret quantitatively. One cannot, for example, expect them to be in good agreement with any but the most sophisticated *ab initio* calculations. One approach to this problem for V^{51} might be to expand the set of LS basis states to include all levels of the three low even configurations ($3d^34s^2$, $3d^44s$, and $3d^5$) simultaneously. The configuration interaction between these could then be examined separately and compared with the results of the effective-operator treatment. Such a treatment might well help in the interpretation of the ratio $a(l)/a(sC^2)$ and shed more light on the quadrupole interaction.

[15] H. Horie and A. Arima, Phys. Rev. **99**, 778 (1955).

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APPENDIX

In writing this paper, an effort has been made to avoid detailed expressions for the matrix elements. For the convenience of other experimentalists engaged in similar calculations, however, the required matrix elements not tabulated elsewhere are listed below.

In setting up the matrices for the electrostatic and spin-orbit interactions for the states of the $l^N(S_1L_1J_1)s$ configuration, the matrix elements in the J_1j scheme may be computed from expressions on pp. 53 and 54 of Ref. 4. The matrix elements for l^Ns in the LS scheme are given in Ref. 4 on pp. 32, 33, and 39 (note that in Eq. (2–110) on p. 39, the quantity l in the third 6-j symbol should be l'); and the spin-orbit elements for l^N are given on p. 38. The values of $\langle l^N\alpha SL\|V^{(11)}\|l^N\alpha'S'L'\rangle$ and of the electrostatic elements for l^N may be found in the compilation of Nielson and Koster.[16]

In listing expressions for the matrix elements of the hyperfine operators, a considerable degree of generality has been retained to increase the usefulness of the expressions. Elements may be evaluated between any states of any configuration of the types nl^N and $nl^Nn's$. For the dipole elements, the three terms in the expressions for the matrix elements bear a one-to-one correspondence to, and are in the same order as, the three terms in the appropriate Hamiltonian [Eq. (5) for l^N and Eq. (6) for l^Ns].

For the l^Ns configuration, the J_1,j matrix elements of $\mathcal{H}_{\rm hfs}(M1)$ and $\mathcal{H}_{\rm hfs}(E2)$ that are off-diagonal in J_1 but

[16] C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations* (The MIT Press, Cambridge, Massachusetts, 1963).

diagonal in J are given by

$$\langle l^N\alpha_1 S_1 L_1 J_1, s; JIFM|\mathcal{H}_{\rm hfs}(M1)|l^N\alpha_1' S_1' L_1' J_1', s; JIFM\rangle = \langle FM|\mathbf{I}\cdot\mathbf{J}|FM\rangle$$

$$\times\Bigg((-1)^{J_1+J-\frac{1}{2}}\left[\frac{2J+1}{J(J+1)}\right]^{1/2}\begin{Bmatrix} J & J & 1\\ J_1' & J_1 & \frac{1}{2}\end{Bmatrix}[(2J_1+1)(2J_1'+1)]^{1/2}$$

$$\times\Bigg\{\delta(\alpha_1,\alpha_1')\delta(S_1,S_1')\delta(L_1,L_1')(-1)^{S_1+L_1+J_1+1}[L_1(L_1+1)(2L_1+1)]^{1/2}\begin{Bmatrix} J_1 & J_1' & 1\\ L_1 & L_1 & S_1\end{Bmatrix}a(l)$$

$$-(30)^{1/2}\begin{Bmatrix} S_1 & S_1' & 1\\ L_1 & L_1' & 2\\ J_1 & J_1' & 1\end{Bmatrix}\langle l\|C^{(2)}\|l\rangle\langle l^N\alpha_1 S_1 L_1\|V^{(12)}\|l^N\alpha_1' S_1' L_1'\rangle a(sC^2)\Bigg\}$$

$$+a(s)\delta(\alpha_1,\alpha_1')\delta(S_1,S_1')\delta(L_1,L_1')\delta(J_1,J_1')\left[\frac{J(J+1)+\frac{3}{4}-J_1(J_1+1)}{2J(J+1)}\right]\Bigg) \quad \text{(A1)}$$

and

$$\langle l^N\alpha_1 S_1 L_1 J_1, s; JIFM|\mathcal{H}_{\rm hfs}(E2)|l^N\alpha_1' S_1' L_1' J_1', s; JIFM\rangle = \langle FM|Q_{\rm op}|FM\rangle$$

$$\times\left[\frac{4J(2J-1)(2J+1)}{(J+1)(2J+3)}\right]^{1/2}\delta(S_1,S_1')b_{nl}(-1)^{2J_1+J+S_1+L_1'-\frac{1}{2}}[(2J_1+1)(2J_1'+1)]^{1/2}\begin{Bmatrix} J & J & 2\\ J_1' & J_1 & \frac{1}{2}\end{Bmatrix}$$

$$\times\begin{Bmatrix} J_1 & J_1' & 2\\ L_1' & L_1 & S_1\end{Bmatrix}\langle l^N\alpha_1 S_1 L_1\|U^{(2)}\|l^N\alpha_1' S_1' L_1'\rangle\langle l\|C^{(2)}\|l\rangle, \quad \text{(A2)}$$

where, as is shown by Ramsey,[17] for example,

$$\langle FM|\mathbf{I}\cdot\mathbf{J}|FM\rangle = \tfrac{1}{2}[F(F+1)-I(I+1)-J(J+1)] \equiv \tfrac{1}{2}K \quad \text{(A3)}$$

and

$$\langle FM|Q_{\rm op}|FM\rangle = \frac{\frac{3}{4}K(K+1)-I(I+1)J(J+1)}{2I(2I-1)J(2J-1)}. \quad \text{(A4)}$$

For completeness, the corresponding equation for the magnetic-octupole interaction is

$$\langle FM|\Omega_{\rm op}|FM\rangle = \frac{5}{4[I(I-1)(2I-1)J(J-1)(2J-1)]}$$

$$\times\{K^3+4K^2+\tfrac{4}{5}K[-3I(I+1)J(J+1)+I(I+1)+J(J+1)+3]-4I(I+1)J(J+1)\}. \quad \text{(A5)}$$

The reduced matrix elements of the tensor operator $\mathbf{U}^{(2)}$ are given for p^N, d^N, and f^N by Nielson and Koster,[16] and those for $\mathbf{V}^{(12)}$ are given by Racah[18] for p^N and d^N configurations. For f^N, they may be calculated from Eq. (2–101) of Ref. 4. The required coefficients of fractional parentage are listed by Nielson and Koster. The quantity $\langle l\|C^{(2)}\|l\rangle$ is defined by the expression

$$\langle l\|C^{(2)}\|l\rangle = -\left[\frac{l(l+1)(2l+1)}{(2l-1)(2l+3)}\right]^{1/2}. \quad \text{(A6)}$$

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[17] N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956), pp. 272, 277.
[18] Giulio Racah, Phys. Rev. **63**, 367 (1943).

In the LS scheme, the matrix elements of the magnetic-dipole hyperfine operator for the l^N configuration is

$$\langle l^N\alpha SLJIFM|\mathcal{H}_{\rm hfs}(M1)|l^N\alpha'S'L'JIFM\rangle=\langle FM|\mathbf{I}\cdot\mathbf{J}|FM\rangle$$
$$\times\Bigg\{(2-g_J{}^*)\delta(\alpha,\alpha')\delta(S,S')\delta(L,L')a(l)-\left(\frac{30(2J+1)}{J(J+1)}\right)^{1/2}\langle l\|C^{(2)}\|l\rangle\langle l^N\alpha SL\|V^{(12)}\|l^N\alpha'S'L'\rangle$$
$$\times\begin{Bmatrix}S & S' & 1\\ L & L' & 2\\ J & J & 1\end{Bmatrix}a(sC^2)+(g_J{}^*-1)\delta(\alpha,\alpha')\delta(S,S')\delta(L,L')a(s)\Bigg\}, \quad \text{(A7)}$$

in which $g_J{}^*$ is the electronic g factor computed without the Schwinger correction, i.e.,

$$g_J{}^*=1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}. \quad \text{(A8)}$$

The corresponding expression for the electric-quadrupole matrix element is

$$\langle l^N\alpha SLJIFM|\mathcal{H}_{\rm hfs}(E2)|l^N\alpha'S'L'JIFM\rangle=\langle FM|Q_{\rm op}|FM\rangle$$
$$\times\left[\frac{4J(2J-1)(2J+1)}{(J+1)(2J+3)}\right]^{1/2}b_{nl}(-1)^{S+L'+J+1}\begin{Bmatrix}J & J & 2\\ L' & L & S\end{Bmatrix}\delta(S,S')\langle l^N\alpha SL\|U^{(2)}\|l^N\alpha'S'L'\rangle\langle l\|C^{(2)}\|l\rangle. \quad \text{(A9)}$$

The expressions for the l^Ns configuration are

$$\langle l^N\alpha_1S_1L_1,s;SLJIFM|\mathcal{H}_{\rm hfs}(M1)|l^N\alpha_1'S_1'L_1',s;S'L'JIFM\rangle=\langle FM|\mathbf{I}\cdot\mathbf{J}|FM\rangle$$
$$\times\Bigg\{(2-g_J{}^*)\delta(\alpha_1,\alpha_1')\delta(S_1,S_1')\delta(L_1,L_1')\delta(S,S')a(l)-\left[\frac{30(2J+1)}{J(J+1)}\right]^{1/2}\begin{Bmatrix}S & S' & 1\\ L & L' & 2\\ J & J & 1\end{Bmatrix}(-1)^{S_1+S'-\frac{1}{2}}$$
$$\times[(2S+1)(2S'+1)]^{1/2}\begin{Bmatrix}S & S' & 1\\ S_1' & S_1 & \frac{1}{2}\end{Bmatrix}\langle l\|C^{(2)}\|l\rangle\langle l^N\alpha_1S_1L_1\|V^{(12)}\|l^N\alpha_1'S_1'L_1'\rangle a(sC^2)+\left[\frac{(2J+1)}{J(J+1)}\right]^{1/2}$$
$$\times(-1)^{L+2S+J+\frac{1}{2}+S_1}\delta(\alpha_1,\alpha_1')\delta(S_1,S_1')\delta(L,L')[\tfrac{3}{2}(2S+1)(2S'+1)]^{1/2}\begin{Bmatrix}J & J & 1\\ S' & S & L\end{Bmatrix}\begin{Bmatrix}S & S' & 1\\ \frac{1}{2} & \frac{1}{2} & S_1\end{Bmatrix}a(s)\Bigg\}, \quad \text{(A10)}$$

and

$$\langle l^N\alpha_1S_1L_1,s;SLJIFM|\mathcal{H}_{\rm hfs}(E2)|l^N\alpha_1'S_1'L_1',s;S'L'JIFM\rangle=\langle FM|Q_{\rm op}|FM\rangle b_{nl}\left[\frac{4J(2J-1)(2J+1)}{(J+1)(2J+3)}\right]^{1/2}$$
$$\times(-1)^{S+L'+J+1}\delta(S,S')\delta(S_1,S_1')\begin{Bmatrix}J & J & 2\\ L' & L & S\end{Bmatrix}\langle l\|C^{(2)}\|l\rangle\langle l^N\alpha_1S_1L_1\|U^{(2)}\|l^N\alpha_1'S_1'L_1'\rangle. \quad \text{(A11)}$$

Note that for l^Ns configurations, $L_1=L$ and $L_1'=L'$. For l^N, the hyperfine matrix elements that are off-diagonal in J are

$$\langle l^N\alpha SLJIFM|\mathcal{H}_{\rm hfs}(M1)|l^N\alpha'S'L'J'IFM\rangle=(-1)^{J'+I+F}\begin{Bmatrix}J & J' & 1\\ I & I & F\end{Bmatrix}[I(I+1)(2I+1)(2J+1)(2J'+1)]^{1/2}$$
$$\times\Bigg\{\delta(\alpha,\alpha')\delta(S,S')\delta(L,L')(-1)^{S+L+J+1}[L(L+1)(2L+1)]^{1/2}\begin{Bmatrix}J & J' & 1\\ L & L & S\end{Bmatrix}a(l)$$
$$-(30)^{1/2}\begin{Bmatrix}S & S' & 1\\ L & L' & 2\\ J & J' & 1\end{Bmatrix}\langle l\|C^{(2)}\|l\rangle\langle l^N\alpha SL\|V^{(12)}\|l^N\alpha'S'L'\rangle a(sC^2)$$
$$+\delta(\alpha,\alpha')\delta(S,S')\delta(L,L')(-1)^{J'+S+L+1}[S(S+1)(2S+1)]^{1/2}\begin{Bmatrix}J & J' & 1\\ S & S & L\end{Bmatrix}a(s)\Bigg\} \quad \text{(A12)}$$

and

$$\langle l^N\alpha SLJIFM|\mathcal{H}_{\rm hfs}(E2)|l^N\alpha'S'L'J'IFM\rangle=b_{nl}(-1)^{J'+I+F+1+S+L'+J}\delta(S,S')$$
$$\times\left[\frac{(I+1)(2I+1)(2I+3)(2J+1)(2J'+1)}{4I(2I-1)}\right]^{1/2}\begin{Bmatrix}J & J' & 2\\ I & I & F\end{Bmatrix}\begin{Bmatrix}J & J' & 2\\ L' & L & S\end{Bmatrix}$$
$$\times\langle l\|C^{(2)}\|l\rangle\langle l^N\alpha SL\|U^{(2)}\|l^N\alpha'S'L'\rangle. \quad \text{(A13)}$$

Similarly, for l^Ns the hyperfine matrix elements that are off-diagonal in J are

$$\langle l^N\alpha_1S_1L_1,s;SLJIFM|\mathcal{H}_{\rm hfs}(M1)|l^N\alpha_1'S_1'L_1',s;S'L'J'IFM\rangle=(-1)^{J'+I+F}$$
$$\times\begin{Bmatrix}J & J' & 1\\ I & I & F\end{Bmatrix}[I(I+1)(2I+1)(2J+1)(2J'+1)]^{1/2}\Bigg\{\delta(\alpha_1,\alpha_1')\delta(S_1,S_1')\delta(S,S')\delta(L,L')(-1)^{S+L+J+1}$$
$$\times[L(L+1)(2L+1)]^{1/2}\begin{Bmatrix}J & J' & 1\\ L & L & S\end{Bmatrix}a(l)-[30(2S+1)(2S'+1)]^{1/2}(-1)^{S_1+S'-\frac{1}{2}}\begin{Bmatrix}S & S' & 1\\ L & L' & 2\\ J & J' & 1\end{Bmatrix}$$
$$\times\begin{Bmatrix}S & S' & 1\\ S_1' & S_1 & \frac{1}{2}\end{Bmatrix}\langle l\|C^{(2)}\|l\rangle\langle l^N\alpha_1S_1L_1\|V^{(12)}\|l^N\alpha_1'S_1'L_1'\rangle a(sC^2)$$
$$+a(s)(-1)^{L+2S+J'+S_1+\frac{1}{2}}\delta(\alpha_1,\alpha_1')\delta(S_1,S_1')\delta(L,L')[\tfrac{3}{2}(2S+1)(2S'+1)]^{1/2}\begin{Bmatrix}J & J' & 1\\ S' & S & L\end{Bmatrix}\begin{Bmatrix}S & S' & 1\\ \frac{1}{2} & \frac{1}{2} & S_1\end{Bmatrix}\Bigg\} \quad \text{(A14)}$$

and

$$\langle l^N\alpha_1S_1L_1,s;SLJIFM|\mathcal{H}_{\rm hfs}(E2)|l^N\alpha_1'S_1'L_1',s;S'L'J'IFM\rangle=b_{nl}(-1)^{J'+I+F+1+S+L'+J}$$
$$\times\left[\frac{(I+1)(2I+1)(2I+3)(2J+1)(2J'+1)}{4I(2I-1)}\right]^{1/2}\begin{Bmatrix}J & J' & 2\\ I & I & F\end{Bmatrix}\begin{Bmatrix}J & J' & 2\\ L' & L & S\end{Bmatrix}$$
$$\times\delta(S,S')\delta(S_1,S_1')\langle l\|C^{(2)}\|l\rangle\langle l^N\alpha_1S_1L_1\|U^{(2)}\|l^N\alpha_1'S_1'L_1'\rangle. \quad \text{(A15)}$$

The (electronic) Zeeman operator may have nonzero matrix elements off-diagonal in F as well as in J. For either configuration, the general expression is

$$\langle\alpha SLJIFM|\mu_0\mathbf{H}\cdot(\mathbf{L}+g_s\mathbf{S})|\alpha'S'L'J'IF'M\rangle=\mu_0H\delta(\alpha,\alpha')\delta(S,S')\delta(L,L')(-1)^{F-M+J+I+F'+S+L}$$
$$\times\begin{pmatrix}F' & F & 1\\ M & -M & 0\end{pmatrix}\begin{Bmatrix}F' & F & 1\\ J & J' & I\end{Bmatrix}[(2F+1)(2F'+1)(2J+1)(2J'+1)]^{1/2}$$
$$\times\left[(-1)^J\begin{Bmatrix}J & J' & 1\\ L & L & S\end{Bmatrix}[L(L+1)(2L+1)]^{1/2}+g_s(-1)^{J'}\begin{Bmatrix}J & J' & 1\\ S & S & L\end{Bmatrix}[S(S+1)(2S+1)]^{1/2}\right]. \quad \text{(A16)}$$

For the l^Ns configuration, the element is also diagonal in S_1.

Note that all the expressions given for off-diagonal elements may be used to compute diagonal elements as well.