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Theoretical Investigation of Some Magnetic and Spectroscopic Properties of Rare-Earth Ions

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Investigations of some magnetic and spectroscopic properties of rare-earth ions based on approximate Hartree-Fock calculations are reported. First, a set of conventional, nonrelativistic Hartree-Fock wave functions were obtained for Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{2+}, Gd^{3+}, Dy^{3+}, Er^{3+}, and Yb^{3+}; second, calculations for Ce^{3+} were carried out in which spin-orbit coupling was directly included in the conventional Hartree-Fock equations in order to obtain some estimate of wave-function dependence on J and the resulting effects on experimental quantities. These results are then used to discuss spin-orbit splittings, hyperfine interactions, and the determination of nuclear magnetic moments, the Slater $F^k(4f,4f)$ integrals, and the crystal-field parameters, $V_n^m=A_n^m\langle r^n\rangle$, all of which depend fairly critically on the precise form of the $4f$ wave functions. Comparisons are made with experiment and with the result of previous theoretical investigations which relied on either Hartree or modified hydrogenic wave functions or on semiempirical parametrizations. The usual spin-orbit formula, $\langle r^{-1}dV/dr\rangle$, is found not to give agreement with experiment; the reasons for this are discussed, and some evidence is described which indicates the importance of including spin-orbit exchange terms between the $4f$ electrons and the core. The implications of this result for efforts to relate $\langle r^{-3}\rangle$ integrals to experimentally observed spin-orbit coupling parameters are discussed, as is the relation (and use) of $\langle r^{-3}\rangle$ integrals to the determination of nuclear magnetic moments. Our $\langle r^{-3}\rangle$ values agree very closely (i.e., to within 5%) with Bleaney's parametrized values, and, hence, so do our estimates for the hyperfine interactions. A sampling of estimated rare-earth nuclear magnetic moments, based on the conventional Hartree-Fock $\langle r^{-3}\rangle$ data, is given; comparison with previous estimates are made; and several causes of the uncertainty in these and all other estimates are discussed. The spectroscopic properties of these ions in a crystalline field are interpreted on the basis of the simple crystal-field theory. The $\langle r^n\rangle$ integrals are found to be in good agreement for $n=2$, 4, and 6 with the Elliott and Stevens parametrization formula, but the assumption of the constancy with Z of the A_n^m is not valid, as is shown by analysis of the available trichloride and ethyl-sulfate data. Systematic discrepancies between experimental and theoretical $F^k(4f,4f)$ have been found which are similar to but greater than what has been previously observed for smaller ions. Finally, the role of spin polarization and aspherical distortions (of the closed shells *and* the $4f$ electrons) is indicated, particularly from the "unrestricted" Hartree-Fock point of view, and an estimate of the field due to polarization of the core electrons is given for all the ions. Results for smaller ions and their implications for the interpretation of observed rare-earth magnetic and spectroscopic properties are sketched.

I. INTRODUCTION

THE rare-earth ions exhibit a wide variety of interesting properties. They are unusual in that they have an unfilled magnetic shell of electrons (the $4f$ shell) imbedded in the interior of the ion. Theoretical studies of many of the properties of these ions have, however, been hampered by the lack of precise $4f$ wave functions. For this reason, hydrogenic or modified hydrogenic behavior has been assumed, with the orbital exponent left as a semiempirical parameter determined so as to give a best fit to some experimental data. While this procedure has in many ways been quite successful, it is of theoretical interest to compare the predictions of *ab initio* calculations with experiment and, in this way, to extend our theoretical understanding of rare-earth properties. As a step in this direction, we will report a set of conventional approximate Hartree-Fock (H-F) calculations for nine ions of the group: Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{2+}, Gd^{3+}, Dy^{3+}, Er^{3+}, and Yb^{3+}; particular emphasis will be given to investigating certain of the resulting magnetic and spectroscopic properties of these ions.

Since the $4f$ electrons are deeply imbedded in the interior of the ion, it is expected, and indeed observed, that they are relatively unaffected by the ion's external environment. In metals the three free-atom valence electrons form the conduction and, while in the salts, these valence electrons are transferred to other ions; in both, it often appears to be a reasonable approximation to consider the constituent rare earths as behaving like trivalent ions. This suggests that the present calculations will not only be pertinent to the free-ion case, but to that of solids as well. This tendency to behave like free ions has greatly simplified theoretical interpretations in the past, but we are entering a period where experiments will "see" the effects of environment. In Sec. VII, we will discuss a reason why we believe the theoretical treatment of the interaction of a rare-earth ion with its environment to be more complicated than that for a d-shell ion.

In this paper we will utilize the wave functions in the investigation of several matters, namely, (1) the related problems of spin-orbit coupling, hyperfine effects, and the determination of nuclear magnetic moments and (2) optical spectra and crystal-field splittings. All of these are strongly dependent on the precise form of the $4f$ orbital behavior and are currently of interest because of the role they play in Mössbauer, nuclear magnetic resonance, paramagnetic resonance and optical absorption experiments.[1]

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[1] The magnetic scattering of neutrons by rare-earth ions is

Direct measurements of nuclear magnetic moments (nmm) have, to date, been limited to the special case of[2] Eu. For this reason, hyperfine-interaction measurements have been relied on in estimates of nmm's and, more often than not, these in turn rely on knowledge of the $4f$ expectation value of r^{-3} (i.e., $\langle r^{-3}\rangle$) which represents the (dominant) orbital contribution to the hyperfine field. Lack of wave functions has led to the utilization of observed spin-orbit coupling parameters ζ_{4f}, in estimates of $\langle r^{-3}\rangle$ and, in turn, of the nmm's. Because of this assumed relation and usage, ζ_{4f}'s, $\langle r^{-3}\rangle$'s, and the methods of estimating nmm's will be discussed together, with some emphasis on the nature of the approximations involved in such a procedure.

The Hartree-Fock (H-F) calculations used in the investigations which follow are of two types. First, there is a set of conventional H-F results for the ions already listed. Secondly, calculations in which spin-orbit coupling was directly included in the conventional H-F equations will be reported for Ce^{3+} ($4f^1$) in its two J states. These have been done in order to give some estimate of wave-function variation with J and of the repercussions of such variations on experimental quantities.

The H-F calculations are discussed in Sec. II, and the $4f$ orbitals resulting from the conventional H-F calculations are listed. These results have their own inherent interest, as this is the first time H-F calculations have been done for atoms of this high an atomic number. The results of the calculations in which spin-orbit coupling has been included are discussed in Sec. IV following the section on spin-orbit coupling, hyperfine fields, and the determination of nuclear magnetic moments (Sec. III). The subsequent sections are concerned with the rare-earth multiplet spectra (Sec. V) and crystal-field splitting parameters (Sec. VI). In Sec. VII, we discuss the problem of the distortion of an ion's closed shells by the aspherical $4f$ charge and spin distribution and the interaction between the $4f$ shell and an external environment. Finally, Sec. VIII presents some conclusions.

II. FREE-ION HARTREE-FOCK CALCULATIONS

Until very recently neither Hartree nor Hartree-Fock wave functions have been available for atoms or ions of the rare-earth series. For this reason, considerable use has been made of the screened hydrogenic functions, in a semiempirical manner, to describe a number of properties which involve $4f$ orbital behavior. Like many semiempirical treatments, this procedure has been quite successful. Ridley's[3] Hartree wave functions for Pr^{3+} and Tm^{3+} provided for the first time an important basis for carrying out, *a priori*, theoretical investigations of some of the properties of these ions and, in turn, for comparison with experiment. Much useful work has resulted from this, particularly on matters related to the determination of nuclear magnetic moments, fine structure, and hyperfine structure effects. However, it is well known that including exchange, as is done in the H-F scheme, produces significant changes in the wave functions as compared with Hartree functions which are, of course, determined without exchange. We are reporting results of approximate H-F calculations which are, in principle, a superior representation of the free-ion wave functions and the best available to date. In this section we discuss these calculations and some of their shortcomings. The second part of this work lies in the inclusion of a spin-orbit potential energy term in the H-F equations and this is discussed as well. In later sections, we apply these results in a study of some of the magnetic and spectroscopic properties of the rare-earth ions and compare these predictions with experiment.

Both the conventional H-F calculations and the spin-orbit calculations for Ce^{3+}, for which we are reporting results, were done using analytic techniques which have been described at length elsewhere.[4,5] Briefly, the radial functions are chosen to be linear combinations of a basis set which are in the form of powers of r times exponentials ($r^n e^{-Zr}$) with coefficients which are determined by solving the Hartree-Fock integro-differential equations. In this scheme this is done by straightforward matrix diagonalization and manipulation and avoids the problems of numerical accuracy inherent in the integrations of the numerical Hartree-Fock method. The finite nature of the basis set provides the limitations in the analytic approach. For a given choice of the *size* of the basis set, there is the problem of choosing the parameters n and Z which describe the basis, because there is, in principle, no unique choice for the basis set. In practice, we have used a *series* of Hartree-Fock calculations, in which Z was varied, to obtain a "best choice" for the basis set.

Two shortcomings of these calculations for the rare earths should be emphasized from the start. First, aside from the inclusion of LS coupling, these are nonrelativistic calculations, whereas it is well known that for ions of this size the inclusion of relativistic effects appreciably perturbs electron behavior in the immediate vicinity of the nucleus. Repercussions of these effects on the $4f$ orbitals are, however, small. Direct comparisons cannot yet be made for a rare-earth ion, but comparisons of relativistic[6] and nonrelativ-

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reported by M. Blume, A. J. Freeman, and R. E. Watson, J. Chem. Phys. **37**, 1245 (1962).

[2] F. M. Pichanick, P. G. H. Sandars, and G. K. Woodgate, Proc. Roy. Soc. (London) **A257**, 277 (1960) have obtained nmm's of several Eu isotopes. More recently, workers at the Clarendon Laboratory (unpublished) have observed these moments by use of double resonance techniques.

[3] E. C. Ridley, Proc. Cambridge Phil. Soc. **56**, 41 (1960).

[4] R. E. Watson, Phys. Rev. **118**, 1036 (1960).

[5] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955) and Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Quarterly Progress Reports No. 15, January, 1955, p. 10; No. 16, April, 1955, p. 38 and p. 41; No. 18, October, 1955, p. 4 (unpublished).

[6] D. F. Mayers, Proc. Roy. Soc. (London) **A241**, 93 (1957).

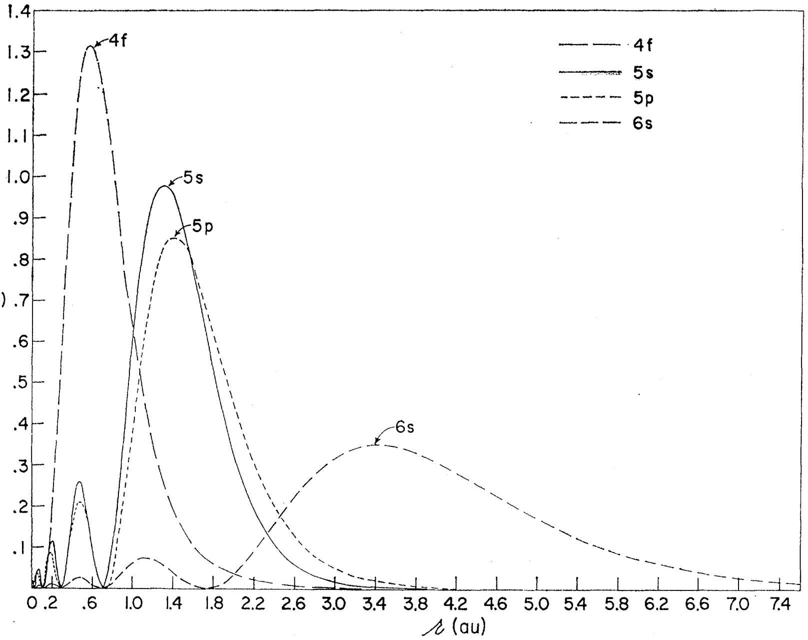

FIG. 1. $P^2(r)$ for the $4f$, $5s$, $5p$, and $6s$ electrons of Gd^+.

istic[7] Hartree functions which have been obtained for Hg show this to be so. While the charge densities for the inner shells differ strongly,[8] the $4f$ behavior is almost unchanged. If we assume that similar statements can be made for the rare-earth ions at hand, one concludes that the inclusion of relativistic effects would leave the F^k, $\langle r^{-3}\rangle$'s and ζ_{4f}'s substantially as they are reported in this paper. Actually, one would expect small increases in these integrals (since the relativistic Hg $4f$ orbitals are slightly contracted)—increases which would very likely affect the digits we are reporting.

A second shortcoming of the calculations arises from computational considerations which have limited the accuracy of the Hartree-Fock results. These limitations lead to limited accuracy[9] in the construction of $1s$, $2s$ and $2p$ orbitals and of the inner loops of the other s and p orbitals (i.e., just where relativistic effects are important). Given the other orbitals, the $4f$, $3d$, and $4d$ orbitals (as well as the outer loops of the others) have been obtained accurately, since greater variational freedom was allowed for these cases. We expect that improved computational accuracy would not greatly affect the $4f$ orbitals although it would profoundly affect such quantities as the ion's total energy, e.g., because of the large energies involved, a small improvement in a $1s$ orbital could have a sizeable effect on its one-electron energy and, in turn, on the total energy. In the results to be reported, the LS coupling energy is smaller than inaccuracies in the computed Hartree-Fock total energies. However, the inaccuracies are not random, and we believe that meaningful conclusions can be drawn by comparing results of common accuracy; such comparisons will in fact be made (in Sec. IV) between the three sets of Ce^{3+} results.

TABLE I. Eigenfunctions (C_i) and exponential parameters (Z_i) which define the $4f$ wave functions [see Eq. (1)].

	$Ce^{3+}(4f^1,{}^2F)$		$Pr^{3+}(4f^2,{}^3H)$		$Nd^{3+}(4f^3,{}^4I)$	
i	Z_i	C_i	Z_i	C_i	Z_i	C_i
1	9.815	752.34143	10.271	902.18300	10.727	1068.8902
2	5.585	103.11436	5.828	129.67688	6.071	159.82204
3	3.723	16.907927	3.885	20.006113	4.047	23.576709
4	2.034	0.44329929	2.125	0.52792993	2.216	0.64579716
	$Sm^{3+}(4f^5,{}^6H)$		$Eu^{2+}(4f^7,{}^8S)$		$Gd^{3+}(4f^7,{}^8S)$	
i	Z_i	C_i	Z_i	C_i	Z_i	C_i
1	11.639	1453.8583	11.764	1562.4702	12.554	1923.8151
2	6.557	233.10473	6.603	238.62615	7.046	329.66724
3	4.371	32.135274	4.402	30.621703	4.697	43.274827
4	2.398	1.0119994	2.416	1.3164826	2.578	1.5047469
	$Dy^{3+}(4f^9,{}^6H)$		$Er^{3+}(4f^{11},{}^4I)$		$Yb^{3+}(4f^{13},{}^2F)$	
i	Z_i	C_i	Z_i	C_i	Z_i	C_i
1	13.463	2480.4013	14.375	3141.6112	15.287	3914.4363
2	7.529	448.83699	8.015	601.33500	8.501	790.99957
3	5.019	55.967002	5.343	71.845565	5.667	90.998364
4	2.762	2.3524738	2.944	3.4191078	3.126	4.8064115

Conventional Hartree-Fock Results

In view of the poor behavior close to the nucleus, and in order to conserve space, the radial functions for shells other than the $4f$ will not be given here. The parameters defining the Hartree-Fock $4f$ orbitals (for the calcu-

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[7] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A149**, 210 (1935).

[8] See Table V of reference 6.

[9] The limit on $1s$, $2s$, and $2p$ (and inner loop) orbital accuracy is due to the size of the s and p basis sets used. These were too small to allow sufficient variational freedom. Computer capacity allowed the use of larger basis sets, but, unfortunately, the inclusion of added orbitals precipitated severe errors during matrix diagonalization, i.e., "useful additional basis" orbitals were not sufficiently linearly independent (from those already present) to allow reasonable computational accuracy.

lations without LS coupling) are given in Table I. The radial orbitals are of the form

$$P_{4f}(r)\equiv \sum_{i=1}^{4} C_i r^4 e^{-Z_i r}, \tag{1}$$

where the normalization condition is

$$\int_0^\infty P_{4f}^2(r)dr=1. \tag{2}$$

The advantages of the analytic form of the orbitals, i.e., the ease, accuracy, and convenience with which matrix elements can be obtained, have been exploited when quantities such as $\langle r^{-3}\rangle$ were determined. Thus, given the $P(r)$, these quantities have been obtained to high numerical accuracy.

A plot of the radial charge densities for the $4f$, $5s$, $5p$, and $6s$ electrons for Gd^+ is given in Fig. 1 in order to display visually the fact that the $4f$ shell really is deeply imbedded inside the $5s$ and $5p$ shells. These shells are almost totally unaffected by the presence of the $6s$ electrons, which have been plotted here (although this paper is concerned only with the properties of the trivalent ions) because of the interest in the behavior of these electrons. Figure 1 also supports some of the statements made in Sec. I regarding the behavior of the trivalent ions in solids.

Hartree-Fock Calculations for Ce^{3+} with Spin-Orbit Coupling

In the second set of calculations we have deviated from the usual Hartree-Fock treatment by inserting spin-orbit coupling into the Hartree-Fock self-consistent procedure. This has been done in order to observe how the wave functions vary with J and, in turn, how these variations affect the predictions of experimental quantities.

The spin-orbit interaction[10] may be represented by

$$H'=\sum_i \xi_i(r)\mathbf{l}_i\cdot \mathbf{s}_i, \tag{3}$$

where the summation is over all electrons with orbital and spin momenta $\mathbf{l}_i$ and $\mathbf{s}_i$, respectively. Sums over closed shells, for conventional H-F functions, yield nothing so the sum need be over only open shells. Normally, ξ_i is assumed to be given by

$$\xi_i=(1/2m^2c^2)[(1/r)(dv/dr)]_i. \tag{4}$$

For ions with only a single unfilled shell this leads to a single parameter,

$$\zeta_i=\hbar^2\int_0^\infty P_i^2(r)\xi_i(r)dr=\frac{\hbar^2}{2m^2c^2}\int_0^\infty P_i^2(r)\left(\frac{1}{r}\frac{dV}{dr}\right)_i dr, \tag{5}$$

to represent the spin-orbit splitting energy. This form for the spin-orbit interaction follows directly from the rigorous spin-orbit Hamiltonian if the potential, $[V(r)]_i$, seen by the ith electron is a spherical central field potential, such as a spherical *Hartree* potential, and if spin-other-orbit terms within the unfilled shell(s) and higher-order effects are neglected. If one further assumes that V is Coulombic, i.e., of the form $-e^2Z_{\text{eff}}/r$ with Z_{eff} an effective nuclear charge, then

$$\zeta_i=(\hbar^2e^2/2m^2c^2)Z_{\text{eff}}\langle r^{-3}\rangle_i, \tag{6}$$

where the $\langle r^{-3}\rangle$ integral has been evaluated for orbital i.

Ideally, we would like to include the H' of Eq. (3) in our Hamiltonian, set up the Hartree-Fock equations (which would then include these spin-orbit terms) and solve them self-consistently. Since we intend to conform to the conventional Hartree-Fock formalism with its single $P_i(r)$ per shell, the spin-orbit terms would cancel (actually average) out of the closed shell H-F equations, leaving only the $4f$ equation with a spin-orbit term in it. At this point we could approximate ζ_{4f} by using Eq. (5) with a Hartree potential V. We know of no way in which the Hartree-Fock electrostatic exchange terms can legitimately be inserted into the V of Eq. (5). We will return to this matter in the next section. A far simpler procedure would be to make use of the ζ_{4f} of Eq. (6). We have, in fact, used this because in our opinion Eq. (5) does not provide a sufficiently accurate representation of a rare earth ζ_{4f} to warrant the complications attending its use. A $Z_{\text{eff}}r^{-3}$ term is easily and conveniently handled in the analytic scheme we are using, but there remains the choice of Z_{eff}. This has been done by taking the Hartree-Fock $\langle r^{-3}\rangle$ for the ion without LS coupling and adjusting Z_{eff} so that Eq. (6) yields the experimentally observed ζ_{4f}. One then forms an operator Z_{eff} times an appropriate constant (determined by the ion's J value) times $1/r^3$ and adds this to the $4f$ Hartree-Fock operator. In the course of the computation Z_{eff} is held fixed.

Ce^{3+}, with its single $4f$ electron, is the simplest case for the insertion of this LS coupling operator into the Hartree-Fock formalism. Calculations will be reported for the two Ce^{3+} J (in this case also j) states, which are $J=5/2$, the ground state, and $J=7/2$. We believe that these calculations satisfactorily indicate the order of magnitude of the effects associated with changes in wave functions with changing J, but in view of the approximations discussed above we have not done and will not report additional calculations of this type.

III. SPIN-ORBIT COUPLING, HYPERFINE PARAMETERS, AND THEIR ROLE IN THE DETERMINATION OF NUCLEAR MAGNETIC MOMENTS

The magnetic hyperfine interaction can be expressed as an additional term in the Hamiltonian of the form

$$\mathcal{H}=-\boldsymbol{\mu}_I\cdot\mathbf{H}_{\text{eff}}, \tag{7}$$

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[10] See, for example, E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), p. 193.

where $\boldsymbol{\mu}_I$ is the magnetic moment associated with the nuclear spin I and $\mathbf{H}_{\text{eff}}$ is an effective magnetic field at the nucleus which arises from the spin and angular momenta of the electronic distribution. Equation (7) follows in a trivial way from the basic Hamiltonian for the interaction between a single electron and the nuclear magnetic moment first derived by Fermi,[11]

$$\mathcal{H}=-gg_I\mu_0\mu_N[(8\pi/3)\delta(r)\mathbf{I}\cdot\mathbf{S}+r^{-3}\mathbf{I}\cdot(\mathbf{L}-\mathbf{S})+3r^{-5}(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})]. \quad (8)$$

Here g and g_I are the electronic and nuclear spectroscopic splitting factors; μ_0 and μ_N are the Bohr and nuclear magnetons; and **L** and **S** represent electron-orbital and electron-spin angular momentum operators, respectively. The delta function term[12] (called the Fermi contact term) is nonzero only for s electrons, for which case the last two terms, which are dipolar interaction terms, are zero.

If the nucleus possesses a quadrupole moment, Q, then there is an additional term[13] in the interaction (per electron) of the form

$$\frac{e^2Q}{2I(2I-1)}\left(\frac{I(I+1)}{r^3}-\frac{3(\mathbf{r}\cdot\mathbf{I})^2}{r^5}\right). \quad (9)$$

In this paper we will emphasize the magnetic interaction but it should be borne in mind that the results are applicable to the electric quadrupole interaction as well. The relation between magnetic and electric $\langle r^{-3}\rangle$ integrals is discussed in Sec. VII.

Since measurements of the magnetic hyperfine interaction, Eq. (7), give the product of the nuclear magnetic moment, μ_I, and an effective magnetic field, H_{eff}, one needs an accurate value of either of these quantities if Eq. (7) is to be used to obtain the other. For many elements, accurate μ_I's are known and this has allowed highly accurate measurements of H_{eff}, as has recently been emphasized particularly by NMR and Mössbauer methods.[14] No such fortunate situation exists, however, for the rare earths, because, with the exception of the nuclear magnetic moment for[2] Eu, precise nmm's are not yet known. For this reason it has been a common practice to rely on theoretical estimates of H_{eff} to determine nuclear magnetic moments from experiment. Uncertainties in these estimates have been the main cause of uncertainties in the resultant nmm's.

Nuclear magnetic moments have been obtained in the following ways: (1) nuclear magnetic resonance (NMR), (2) atomic beam magnetic resonance, (3) optical spectroscopy, (4) electron-paramagnetic resonance (EPR), and (5) nuclear alignment measurements. To date, direct determinations of nmm's for rare-earth nuclei by means of (1) or (2) have proven experimentally very difficult and only the moment for Eu^{151} has been measured with atomic beams by Pichanick, Sandars, and Woodgate,[2] who used three radio-frequency loops in a row. The remaining measurements have involved indirect determinations based on hyperfine interactions with some unfilled electron shells. Of these, the major source of moment values involves systems with an unfilled $4f$ shell (such as we shall consider in detail in this paper). Optical hyperfine data[15–18] has also been obtained for ions with unfilled $5d$ or $6p$ electrons, and estimates of nmm's based on theoretical estimates of H_{eff} for these systems are subject to the same uncertainties as apply to the case of unfilled $4f$ shells. Finally, optical hyperfine data[15–17,19–22] for an ion with an unpaired $6s$ electron had been combined with the semiempirical Fermi-Segrè-Goudsmit[23] formula to relate an observed hyperfine parameter, a_{6s}, to the nuclear moment.

As already noted, in the absence of precise $4f$ electronic wave functions, theoretical estimates of the hyperfine interaction have, of necessity, been somewhat crude. Assuming separability of the one-electron wave functions, the angular factors have been worked out in a rather elegant way[24] for free atoms and ions and for ions in crystalline environments. For the radial part of the one-electron wave functions, it has been very common to assume a hydrogenic form (r^ne^{-ar}) and to relate somehow the hyperfine field arising from the $4f$ electrons [which from Eq. (8) is taken to be proportional to $\langle r^{-3}\rangle$] to the spin-orbit coupling parameter, ζ, obtained from experiment.[24–26]

Spin-Orbit Coupling Parameters

As we have seen in Sec. II, the spin-orbit coupling parameter, ζ, is related to $\langle r^{-3}\rangle$ when the potential $V(r)$ is taken to be Coulombic. This relation has in part been used to justify the use of observed values to obtain information about $\langle r^{-3}\rangle$. Analytic expression for $\langle r^{-3}\rangle$, based on optical spin-orbit measurements and a modified hydrogenic relationship for the quantities $\langle r^{-3}\rangle$ and ζ,

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

[12] The delta function form for the contact term was apparently first used by Abragam and Pryce [A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951)].

[13] See H. Casimir, Arch. musée Teyler **8**, 201 (1936); H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958); and reference 12.

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[17] K. Krebs and H. Nelkowski, Z. Physik **141**, 254 (1955).

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[20] P. F. A. Klinkenberg and F. S. Tomkins, Physica **26**, 103 (1960).

[21] V. B. Belyanin, Optika i Spektroskopiya **5**, 340 (1958).

[22] K. H. Lindenberger, Z. Physik **141**, 476 (1955).

[23] See H. Kopfermann, reference 13.

[24] By R. J. Elliott and K. W. H. Stevens [Proc. Roy. Soc. (London) **A219**, 387 (1953)] among others.

[25] B. Bleaney, Proc. Phys. Soc. (London) **68A**, 937 (1955).

[26] C. K. Jørgensen, J. Inorg. Nuclear Chem. **1**, 301 (1955).

have been worked out by Elliott and Stevens[24,27] and by Bleaney[25] and others, and a good deal of useful work and valuable information has resulted from these early efforts. More recently, Judd and Lindgren[28] and Lindgren[29] have used a modified hydrogenic function having the form[30]

$$R(r)=Nr^4e^{-ar}\cosh[\kappa(ar-4)] \tag{10}$$

(which is identical to a sum of two exponentials), where N is a normalizing constant and κ and a are two adjustable parameters. By choosing a and κ so as to match Ridley's Hartree $4f$ functions[3] and experimental spin-orbit coupling measurements, these authors have determined $\langle r^{-3}\rangle$ values and, hence, nuclear magnetic moments (nmm's). Lindgren[29] has refined and extended this procedure to yield a set of predicted nmm's for the entire rare-earth series.

Before proceeding further, we should point out that in all the work cited so far, there are a number of assumptions which are generally made for relating observed fine structure data to $\langle r^{-3}\rangle$ values. Let us consider three of these. First, some sort of analytic relationships must be assumed[24–29] for the ζ_{4f}'s, for the $\langle r^{-3}\rangle$'s and (most importantly) between them. Second, it must be assumed that the LS coupling does not perturb the orbitals in such a way as to create $4f$ orbitals for different J states which differ appreciably from one another, as this in turn affects the observed energy separation between J states. It has been seen[31] that the relaxation of such an assumption of common orbital behavior does in fact appreciably perturb observations made concerning the multiplet and ionization spectra of iron-series ions. A similar situation may very likely occur for the rare earths, but the present investigation will be limited to the case of a set of common L and S and differing J's. In addition to the J dependence of average $4f$ orbital behavior, there is also the one-electron j dependence of the orbitals. These matters will be investigated by inspection of the LS Hartree-Fock solutions which will be reported in Sec. IV. Third, it is assumed that, quite aside from the above, an experimental ζ_{4f} is the familiar theoretical quantity given by Eq. (5) and that other effects, such as spin-spin interactions, do not contribute appreciably to the observed splitting between J states. These assumptions play an important role in any discussion of ζ and are of interest in themselves, quite aside from any repercussions they may have on an estimated $\langle r^{-3}\rangle$. More will be said about this shortly.

TABLE II. Theoretical and experimental $4f$ spin-orbit coupling parameters ζ_{4f} for some rare-earth trivalent ions (in cm^{-1}).

	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Dy^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}
Hartree-Fock	830	980	1130	1480	2310	2830		3400
Hartree[b]		785					2740	
Experimental[a]	640	750	900	1180	1920	2470	2750	2950

[a] See references 26, 33, 34, and 35.
[b] See reference 3.

We have calculated ζ_{4f}'s for the nonspherical rare-earth ions for which we have obtained conventional Hartree-Fock wave functions. For this, Eq. (5) was used with a potential, $V(r)$, which included Coulomb but *no* exchange interactions between electrons. These results are listed in Table II along with experimental values and ζ_{4f}'s obtained by Ridley (also with Eq. 5) for her Pr^{3+} and Tm^{3+} Hartree functions. It should be noted that with the exception of the Ce^{3+} data, we are dealing with values obtained for the trivalent ions in salts or solutions. It is generally thought that parameters such as ζ_{4f} (or F^k) are but slightly affected[32] by the ion's environment. The fact that the discrepancy for Ce^{3+} is as great as for the other ions supports this. Despite the small magnitude of the effect, the fact that we are generally not dealing with free-ion data should be borne in mind. The experimental values are those tabulated by Jørgensen,[26] Runciman,[33] Wybourne,[34] and McClure[35] with compromises where necessary (and with uncertainties of at least 50 cm^{-1}). Inspection of Table II shows the Hartree ζ_{4f} to be in excellent numerical agreement with experiment, whereas the Hartree-Fock values are appreciably larger. More accurate relativistic or nonrelativistic H-F solutions should not substantially reduce these discrepancies. They will, in fact, very likely increase the discrepancies.

Before discussing the discrepancies between the Hartree-Fock results and experiment, let us review what is known for other ions. Powell,[36] using Eq. (5), has computed ζ for iron-series Hartree-Fock functions[31] and has observed them to lie 10–20% above experiment. Hartree-Fock ζ's for $2p$-shell ions lie similarly high.[37] It should be noted that in all these cases (i.e., $4f$, $3d$, and $2p$ shells) the radial functions do not have nodes. For unfilled shell ions whose $P(r)$'s have nodes, there appears to be a tendency[37,38] for the Hartree-Fock ζ to lie below experiment. It should also be noted that the ζ discrepancies are as great when there is but a single electron in the unclosed shell as they are when there is more than one electron there. This observation suggests

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[27] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

[28] B. R. Judd and I. Lindgren, Phys. Rev. **122**, 1802 (1961).

[29] I. Lindgren, Nuclear Phys. **32**, 151 (1962).

[30] A. Y. Cabezas and I. Lindgren, Phys. Rev. **120**, 920 (1960).

[31] See reference 4 and R. E. Watson, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Technical Report No. 12, 1959 (unpublished).

[32] C. K. Jørgensen, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **29**, No. 11 (1955); see also **30**, No. 22 (1956) for the effect of environment on the spectra.

[33] W. A. Runciman, *Reports on Progress in Physics* (The Physical Society, London, 1958), Vol. XXI, p. 30.

[34] W. A. Runciman and B. G. Wybourne, J. Chem. Phys. **31**, 1149 (1959); and B. G. Wybourne, *ibid.* **32**, 639 (1960).

[35] D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 9, p. 399.

[36] M. J. D. Powell (unpublished results).

[37] M. Blume and R. E. Watson (to be published).

[38] L. Liu (to be published).

TABLE III. Hartree-Fock, Hartree, Thomas-Fermi, and parameterized $\langle r^{-3}\rangle$ integrals for rare-earth ions (in units of a_0^{-3}).

	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{2+}	Gd^{3+}	Dy^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}
Hartree-Fock	4.72	5.37	6.03	7.36	7.53	8.84	10.34	12.01		13.83
Hartree[a]		4.33							11.42	
Thomas-Fermi[b]					6.95					
Parametrized $\langle r^{-3}\rangle$'s										
Elliott and Stevens	4+1	5+1.2	6+1.5	7.5+2		9.2+2.3	10.5+2.6	12+3	13+3.2	13.5+3.5
Bleaney[c]	4.8	5.5	6.2	7.5		9.2	10.9	12.7	13.6	14.5
Lindgren[d]	3.66	4.26	4.86	6.07		7.35	8.74	10.32	11.20	12.18

[a] See reference 3.
[b] See reference 45.
[c] See reference 25.
[d] See reference 29.

that spin-spin and spin-other-orbit effects within an unclosed shell are not important contributors to the discrepancies. This is borne out by Horie's[39] investigation into these effects.

The good agreement with experiment for the Hartree ζ_{4f} is, we believe, due to a cancellation of errors. The Hartree $P_{4f}(r)$ is radially expanded relative to the H-F $4f$ function and, hence, has a smaller ζ_{4f}. One expects the "true" many-electron eigenfunction to have a charge density which is, if anything, more contracted than that of the H-F; thus, the source of the smaller magnitude of the Hartree ζ_{4f} is apparently not the key to the discrepancies of the H-F values.

It has been noted that inclusion of relativistic effects leads to a radical contraction of the innermost charge density of an ion as large as the rare earths. Thus, while one might suspect that the change in $V(r)$ might have substantial repercussions on a rare earth ζ_{4f}, such effects would not be expected for $2p$ or $3d$ ions and a reversal could not be expected for, say, a $4p$ ion. Crude calculations show that such is not even the case for the rare earths, because the electrons primarily involved in the contraction are already so far inside the $4f$ shell that their contraction has little effect on a computed ζ_{4f}. This is a manifestation of the $4f$ orbital insensitivity already discussed in Sec. II. It appears that the relativistic effects most important to $4f$ orbitals are those which directly involve the $4f$ orbitals.

There is one obvious shortcoming of Eq. (5). It does not account for the fact that our wave function is antisymmetric, i.e., "exchange" effects have been neglected. While it may be possible to relate an "effective" exchange potential to spin-orbit effects, it appears that the naive insertion of such a term into the $V(r)$ of Eq. (5) is incorrect. Doing this would deepen the potential (note that exchange causes orbitals to contract) and, hence, *increase* a computed ζ_{4f}, increasing the disagreement with experiment. If, on the other hand, one takes the spin-orbit and spin-other-orbit Hamiltonian,[40]

$$\mathcal{H}=-(e^2/2m^2c^2)(1/r_{12}^3)[(\mathbf{r}_1-\mathbf{r}_2)\times(\mathbf{p}_1-2\mathbf{p}_2)\cdot\mathbf{s}_1 +(\mathbf{r}_2-\mathbf{r}_1)\times(\mathbf{p}_2-2\mathbf{p}_1)\cdot\mathbf{s}_2], \quad (11)$$

and evaluates it for an antisymmetric function, one obtains "exchange" terms between closed shells and the unclosed shell in addition to terms contributing to Eq. (5). For $2p$- and $3d$-shell ions, these terms cause a reduction[37] in ζ, i.e., the reverse of what is predicted by the (incorrect) use of an "effective exchange" potential. The first investigation into this appears to have been done by David[41] for the $1s^22p$ state of *Li*. Using analytic functions which crudely approximated the Hartree-Fock solutions, David calculated spin-orbit splitting contributions of $+1.55$ cm^{-1} from the nuclear Z/r^3 term, -0.84 cm^{-1} from the $1s$-shell contribution [via $V(r)$] to Eq. (5) and -0.45 cm^{-1} from exchange. This gave a total of $+0.26$ cm^{-1}, compared with the experimental value of 0.34 cm^{-1}. In other words, core exchange made a substantial ***negative*** contribution and greatly reduced the difference between the Eq. (5) value and experiment. Investigations[37] of the role of this for larger ions are under way and will eventually be extended to the case of the rare-earths.

There are, of course, other potential contributors to the ζ_{4f} discrepancies. Systematic variation of $P_{4f}(r)$ with the J state of the ion could contribute to the energy difference between J states and thus affect an observed ζ_{4f}. This will be touched on in Sec. IV. A partial breakdown of Russell-Saunders coupling is known to occur for the rare-earths, and this is generally accounted for when the experimental data is fitted. The investigations[42,43,28] of Judd and others in related topics suggest that any such repercussions on ζ_{4f} would be small. In any case, a lengthy discussion of these matters should perhaps wait until the exact role of the core open-shell exchange terms is better understood.

We have been discussing the ζ_{4f} discrepancies at some length because of the general belief that Eq. (5) provides at least an adequate description of electron core contributions to ζ_{4f}. This belief does not appear to be justified if one is interested in accurate quantitative effects. In turn, this has rather important implications to any effort which attempts to relate

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[39] H. Horie, Progr. Theoret. Phys. (Kyoto) **10**, 296 (1953).

[40] Breit's equation [G. Breit, Phys. Rev. **34**, 553 (1929)] forms the starting point for discussions of electron-electron interactions.

[41] E. David, Z. Physik **91**, 289 (1934).

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

[43] B. R. Judd, Proc. Phys. Soc. (London) **69A**, 157 (1956); for spin-spin effects also see G. Araki, Progr. Theoret. Phys. (Kyoto) **3**, 152 and 262 (1953).

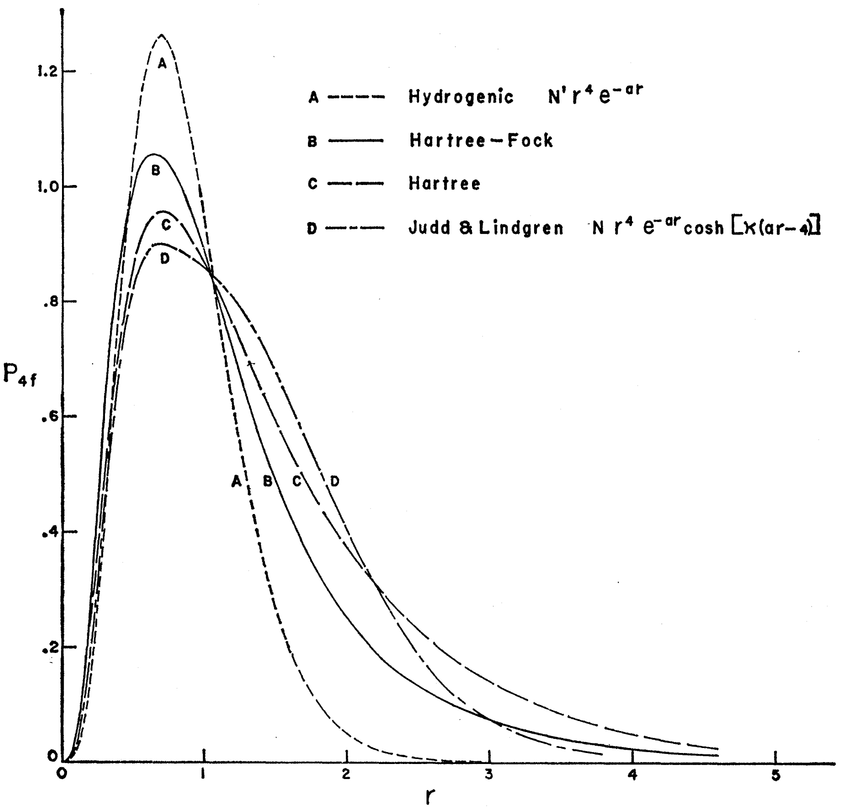

FIG. 2. The radial $4f$ wave function for Pr^{3+} from several sources. Curve A is a simple hydrogenic function, $N'r^4e^{-ar}$ (with a taken as in curve D), curve B is the Hartree-Fock result, curve C is the Hartree function, and curve D is the modified hydrogenic function of Judd and Lindgren, $Nr^4e^{-ar}\cosh[\kappa(ar-4)]$.

$\langle r^{-3}\rangle$ integrals to experimentally observed ζ's. Let us now turn to the matter of the $\langle r^{-3}\rangle$'s and their relation to the determination of nuclear magnetic moments.

Hyperfine Fields and Nuclear Magnetic Moments

If accurate values of the nuclear magnetic moments of the rare-earth ions were known, we would be in a position to compare the predicted hyperfine fields as determined from our calculated wave functions with experiment. In this way, it would be possible to correlate a number of NMR, Mössbauer, and specific heat measurements which have been made of the hyperfine fields in magnetic materials and obtain some information about electron distributions in the rare earths [as has already been done for (say) the iron-group transition elements]. Lacking this information about the nmm's, we shall instead see what theoretical predictions one may make for these values on the basis of our approximate H-F calculations. To do this, we need first to calculate the matrix elements $\langle r^{-3}\rangle$ for the ions for which $L\neq 0$; the ions Gd^{3+} and Eu^{2+} are in ^8S ground states and will not be discussed here, as the predominant source of the hyperfine field for these ions is the contact interaction arising from the exchange polarization of the core electrons by the spin of the $4f$ electrons.[44] Core polarization effects for all the rare-earth ions will be estimated in Sec. VII.

Our calculated values of $\langle r^{-3}\rangle$ are listed in Table III, where for comparison we have also tabulated those based on Ridley's Hartree results, Sternheimer's[45] (neutral atom) Thomas-Fermi calculation, Judd and Lindgren's[28] modified hydrogenic function, and the Elliott and Stevens[24,27] and Bleaney[25] parametrization schemes. It is seen that the Hartree-Fock $\langle r^{-3}\rangle$'s are similar in behavior to either those of Elliott and Stevens or of Bleaney; differences between Bleaney's and our values are less than 5%, whereas both Ridley's and Lindgren's values are approximately 20% smaller. The close agreement between Ridley's and Lindgren's $\langle r^{-3}\rangle$'s is not surprising since, as described earlier, the latter

TABLE IV. The magnitudes of the nuclear magnetic moments μ's of a few rare-earth isotopes as estimated by Bleaney and Lindgren, from optical (other than $4f$ shell) hyperfine parameters and by using the current Hartree-Fock $\langle r^{-3}\rangle$'s.

	Pr^{141}	Nd^{143}	Sm^{147}	Ho^{165}	Er^{167}	Yb^{173}
μ as estimated by Bleaney	3.9	1.0	0.83	3.3	0.48	0.68
μ as estimated by Lindgren	5.0	1.23	1.03	4.1	0.58	0.72
Optical μ	4.0	1.1	0.76	3.7	...	0.67
μ obtained using Hartree-Fock $\langle r^{-3}\rangle$'s	4.0	0.99	0.85	3.5	0.50	0.63

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[44] The role of core polarization is discussed in greater detail in Sec. VII. See also Watson and Freeman, reference 14.

[45] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950).

author relied heavily on matching the Hartree functions obtained by the former. Furthermore, the good agreement between the experimental and the Hartree ζ_{4f}'s suggests that Judd's and Lindgren's $4f$ orbitals [defined in Eq. (10)] should be almost identical with the Hartree orbitals. Their close correspondence for Pr^{3+} is shown in Fig. 2, where we have also plotted our Hartree-Fock $4f$ function and a simple hydrogenic function (with a screening constant chosen to match the corresponding Judd and Lindgren parameter).

The implications of using the various $\langle r^{-3}\rangle$'s in estimates of the nuclear magnetic moments can be seen by inspecting Table IV where we list μ for some isotopes for which there have also been estimates by Bleaney[25] by Lindgren,[29] *and* from optical hyperfine parameters involving electrons other than the $4f$ electrons, i.e., unfilled $6s$, $6p$, and/or $5d$ shells. The μ values reflect what we have already seen in Table III, i.e., both the Bleaney and the Hartree-Fock μ's are quite similar, while those of Lindgren are consistently larger. This follows quite naturally from Eq. (8) if one assumes that the observed hyperfine parameter is of the form

$$a_{4f}\sim(|\mu|/I)\langle r^{-3}\rangle. \qquad (12)$$

The "optical" μ's generally lie between the other values and are closest to those of Bleaney. If we grant the assumption that only the $4f$ shell contributes to the hyperfine field and that an average $4f$ orbital $\langle r^{-3}\rangle$ suffices to describe the hyperfine interaction, then the Hartree-Fock μ's are, in principle, the best estimates appearing in Table IV. We do not believe that such assumptions are valid (see Secs. IV and VII); instead, one must define and use "*effective*" $\langle r^{-3}\rangle$ parameters which are not identical with the $\langle r^{-3}\rangle$ *integrals*. While the optical values are also subject to theoretical uncertainty, those obtained from a_{6s}'s (i.e., all but Nd^{143}) and the Fermi-Segrè-Goudsmit formula have at least been obtained by different means and so may give some indications of "effective" $\langle r^{-3}\rangle$ behavior. These data suggest smaller deviations than we would expect between "effective" $\langle r^{-3}\rangle$'s and $\langle r^{-3}\rangle$ integrals. We believe, however, that there are rather substantial uncertainties associated with the μ values given in any row of Table IV.[45a]

IV. THE DEPENDENCE OF 4f WAVE FUNCTIONS ON TOTAL ANGULAR MOMENTUM

Consider a Hamiltonian which contains spin-orbit interaction terms for an ion which has $4f$ electrons whose wave functions are to be determined as eigenfunctions of this Hamiltonian. The $4f$ orbitals can depend on angular momentum in several ways: First, the orbitals for states of different J will be different; second, orbitals for electrons of differing j will, if allowed, have different radial behavior. The second of these follows naturally from a relativistic Hartree-Fock description,[46] while the first can be associated with a conventional Hartree-Fock description which restricts the electrons to a single orbital per shell. As discussed in Sec. II, we are going to consider the relatively simple case of Ce^{3+} which, with its $4f$ electron, merges the two types of variation, since $J=j$. Effects of more electrons in a $4f$ shell will not be investigated, but it is expected that similar considerations apply for these more complicated cases as well.

Before discussing our Ce^{3+} results, let us briefly review a feature of Swirles'[46] relativistic Hartree-Fock formalism, for while we will be reporting results of nonrelativistic calculations, the relativistic description is more appropriate for rare-earth ions. This is particularly so if, as in Sec. VII, we are interested in inner-shell behavior. Swirles used a many-electron determinantal function constructed from one-electron Dirac wave functions, each one-electron function being a two-component function, with j a good quantum number. This means that any one determinant is constructed in a j-j coupling scheme and that the Russell-Saunders states (which we want[47] for the rare-earths) will be linear combinations of these. Each shell divides into two distinct subshells with $j=l+1/2$ and $l-1/2$. The complications associated with multi-determinantal functions have not been encountered in the existing (Hartree) relativistic calculations[48] because they were done for closed-shell ions. With such multi-determinantal functions, one ceases to be able to describe an open-shell electron (unless it is an s electron) as an orbital with specific one-electron quantum numbers.

As noted earlier (Sec. II), the present calculations for Ce^{3+} have incorporated LS coupling by including a term of the form of Eq. (6) in the $4f$-electron Hartree-Fock equation with Z_{eff} chosen so that, together with the $\langle r^{-3}\rangle$ from the restricted calculation, the experimental ζ_{4f} would be reproduced. Hartree-Fock results for the ion with $J(=j)=5/2$ and $7/2$ as well as results for the

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[45a] *Note added in proof.* Since this writing we have learned that several nuclear moments have been determined but have not yet been reported: G. Ritter has measured the moment of Tm^{169} (-0.229 ± 0.003 nuclear magnetons); V. Jaccarino, A. Gossard, and J. P. Remeika, that of Yb^{171} ($+0.4930\pm0.0004$); and D. W. Halford and C. A. Hutchinson, that of Nd^{143} (-1.079 ± 0.06) and Nd^{145} (-0.671 ± 0.04). Using Low's EPR measurements [W. Low, Phys. Rev. **118**, 1608 (1960)], Jacarino *et al.*, also deduced the moment of Yb^{173} (-0.6725 ± 0.0028). (We are grateful to these authors for communicating their measurements and for allowing us to quote their results prior to publication.)

Comparison of these measurements with the estimates referred to above shows one striking feature: Bleaney's estimates and those based on optical data are in close agreement with experiment. By contrast, the agreement of the theoretical estimates with experiment is not good. The estimates by Lindgren and by ourselves fall on either side of the experimental data (for Nd and Yb our values lie closer, whereas for Tm, Lindgren's estimate is closer). In view of the above discussion of aspherical distortions we feel that these results are not surprising.

[46] B. Swirles, Proc. Roy. Soc. (London) **A152**, 625 (1935); and I. P. Grant, *ibid.* **A262**, 555 (1961).

[47] While the rare earths are known for the partial breakdown of the Russell-Saunders coupling scheme, this scheme is far superior to the j-j coupling scheme as a first-order description and is the more appropriate basis for going on to treat the breakdown.

[48] See reference 6 and A. O. Williams, Phys. Rev. **58**, 723 (1940); S. Cohen, *ibid.* **118**, 489 (1960).

TABLE V. One-electron kinetic plus nuclear potential energies K_i, $\langle r^n\rangle$, $\langle r^{-3}\rangle$, J state splittings and total energies with and without LS coupling for Ce^{3+} obtained with Hartree-Fock calculations with and without LS coupling (see text for details). All quantities are in atomic units.

	Ce^{3+} (no LS)	Ce^{3+} ($J=5/2$)	Ce^{3+} ($J=7/2$)
K_{1s}	1681.81	1681.81	1681.81
K_{2s}	417.683	417.683	417.683
K_{3s}	177.915	177.915	177.915
K_{4s}	87.659	87.658	87.660
K_{5s}	40.154	40.153	40.156
K_{2p}	417.271	417.271	417.271
K_{3p}	175.982	175.982	175.982
K_{4p}	84.638	84.637	84.639
K_{5p}	36.838	36.836	36.839
K_{3d}	173.336	173.336	173.336
K_{4d}	77.511	77.509	77.513
K_{4f}	61.083	61.204	60.993
$\langle r^2\rangle$	1.200	1.193	1.205
$\langle r^4\rangle$	3.454	3.418	3.487
$\langle r^6\rangle$	21.226	20.836	21.519
$\langle r^{-3}\rangle$	4.720	4.751	4.697
Total E[a]	−8564.9892	−8564.9955	−8564.9849
LS coupling energy	−0.00592[b]	−0.00596	+0.00442
Total E (without LS energy)		−8564.989	−8564.989

[a] Note that these cannot be taken seriously to the last digit quoted.
[b] Adjusted so that const $\times\langle r^{-3}\rangle$ equals this value in au.

ion without LS coupling are listed in Table V. Included are the one-electron kinetic plus nuclear potential integrals K_i which are sensitive indicators[49] of orbital variation, since they exclude the two-electron contributions which appear in the more familiar one-electron energies. Total energies with and without LS coupling, $\langle r^{-3}\rangle$'s and J-state splittings (computed with the $\langle r^{-3}\rangle$'s) are also listed in Table V. Inspection of the K_i shows that the variation in K_{4f} between the 5/2 and 7/2 states is almost twenty times larger than the observed LS splitting of 0.0104 au (atomic units), indicating that energetically significant orbital variations occur. As one would expect, the $4f$ orbital is more contracted, i.e., K_{4f} is more negative for the ground ($J=5/2$) state. Further inspection of Table V shows that the orbitals representing the outer closed-shell electrons have shifted in the reverse direction, i.e., their K_i are smaller in magnitude. (This trend would also be seen in the $3s$, $3p$, and $3d$ shells if it were reasonable to quote the K_i to another digit.) These energy shifts have, however, almost exactly canceled the effect of the $4f$ energy shift on the total energy when computed without LS coupling, and this, in turn, implies that the $4f$ orbital variation will have little effect on the observed J-state splitting. Inspection of the $\langle r^{-3}\rangle$'s, or the J-state splittings computed with them, shows only a 1% variation of these quantities. These are far less than other uncertainties associated with either ζ_{4f}'s or effective $\langle r^{-3}\rangle$'s, but they cannot be neglected in any treatment which requires high accuracy.

The closed-shell variations point up a fact which, while fairly obvious, has yet to be sufficiently emphasized. There are serious implications introduced by the presence of these closed shells when one tries to deal with a perturbation of the $4f$ shell, e.g., the interaction with a crystalline field or an exchange interaction with a neighboring unclosed shell.[50] In the case of a crystalline field, there is not only the shielding (or antishielding) due to the distortion of these spherical shells, but there can be a radial shift, such as we have seen here, which compensates for any net shift in the $4f$ shell. While rare-earth ion crystal-field effects are small, it is, or at least will be, desirable to investigate them. Such an investigation will be more complicated than one into the larger, and currently incompletely resolved,[51] crystal-field effects for iron-series ions for which the $3d$ electrons are in the outermost shell.

The present calculations have shown the J or j variations to be small and, for our present purposes, unimportant. However, while small, these effects can still be relatively important for certain properties.[52]

V. THE RARE-EARTH MULTIPLET SPECTRA

In or near the Russell-Saunders limit, the spin-orbit interaction is very much smaller than the electrostatic interaction between electrons. Assuming separability of wave functions, and a single radial function, $P_i(r)$, to describe the ith shell, the energy of a term in a multiplet, characterized by the spin and orbital quantum numbers S and L, is usually expressed as a definite function of the Slater F^k radial integrals defined by

$$F^k(i,j)=\int_0^\infty\int_0^\infty \frac{{r_<}^k}{{r_>}^{k+1}}[P_i(r_1)P_i(r_2)]^2dr_1dr_2$$

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[49] For an example of how misleading one-electron energies (vs the K_i) can be when used as a test of wave-function variation, see R. E. Watson and A. J. Freeman, Phys. Rev. **124**, 1117 (1961).

[50] One aspect (spin polarization) of this has been discussed for Gd^{3+} in R. E. Watson and A. J. Freeman, Phys. Rev. Letters **6**, 277 (1961).

[51] See A. J. Freeman and R. E. Watson, Phys. Rev. **120**, 1254 (1960), and, for a recent advance in crystal-field theory for iron-series ions, see S. Sugano and R. G. Shulman, Phys. Rev. Letters **7**, 157 (1961).

[52] P. G. H. Sandars (to be published) has considered j variations in relating the hyperfine parameter A (appearing in the $A\mathbf{S}\cdot\mathbf{I}$ term of the spin Hamiltonian) for neutral Eu with that for Eu^{2+} in salts. A for the divalent ion is larger in magnitude than A for the neutral atom and appears to be almost entirely due to spin polarization (see reference 44) of the s shells. (The spin-polarized $6s$ shell of the neutral atom makes a contribution to A which is opposite in sign and largely cancels that from the other s shells, similar to the cancellation which occurs (see reference 14) due to the $4s$ shell in neutral iron-series atoms.) The total s-shell spin-polarization contribution to the neutral Eu A is not only small but is appreciably smaller than the observed A. Sanders has shown the existence of a term of the form $A'\mathbf{S}\cdot\mathbf{I}$ arising from the difference in $4f$ orbital behavior with j, where A' is an integral in which the difference between orbitals appears explicitly. This term was obtained for the ion in the appropriate Russell-Saunders coupling scheme. A' was calculated with Thomas-Fermi orbitals, and while its value was small, it appears to be the primary term contributing to A. It must be emphasized again that this is a small effect, although in this case it is relatively important.

for $4f$ electrons, $k=2$, 4, and 6. These integrals appear as parameters in the Slater-Racah parametrization scheme for fitting observed multiplet spectra. While this method has been highly successful, empirically determined F^k, for iron-series ions,[4] have been in systematic disagreement with theoretical F^k determined from Hartree-Fock functions. The discrepancies are attributed to correlation effects[53] which are well outside the Hartree-Fock formalism which was the original basis for the parametrization procedure.[54] Similar disagreements are therefore expected for the rare-earths; hence, we will compare computed F^k integrals with experiment. Furthermore, for many purposes, such as the fitting of experimental $4f^n$ multiplet spectra, it has been common to assume, in the absence of Hartree-Fock data, that the ratios of the integrals F^6, F^4, and F^2 to each other are the same as for hydrogenic orbitals.[55] The use of hydrogenic ratios has again proven quite successful and most surprising in view of the crude description hydrogenic functions give of $4f$ wave functions (e.g., see Fig. 1).

Before comparing our computed $F^k(4f,4f)$ with ones obtained by fitting rare-earth multiplet spectra, let us consider the simpler and more thoroughly studied case of the iron-series $3d^n$ spectra for which two parameters, $F^2(3d,3d)$ and $F^4(3d,3d)$, appear in the theory. Here, we can rely on data[56] which show all, or nearly all, the multiplet levels for the majority of the free ions. Fits for experimental $F^2(3d,3d)$'s and $F^4(3d,3d)$'s have been done with this data by a number of workers over the years. Since the theory does not fit the experimental data exactly (it sometimes predicts the energy levels in the wrong order), the experimental F^k values tend to vary with the fitter. Whereas one worker will use a least-squares fit, another will use a weighted least-squares fit, and yet another will use one of these methods but will omit an "obviously" questionable level from the fit. It is therefore not surprising that rather different values will be obtained for $F^2(3d,3d)$ and even more widely variable values for the less important (hence more susceptible to variation) $F^4(3d,3d)$'s. As a result of all these data, a somewhat coherent picture can be obtained[57] of $F^2(3d,3d)$ behavior as a function of nuclear charge and degree of ionization for the iron series, whereas, for F^4/F^2 ratios [which are usually considered in preference to the $F^4(3d,3d)$'s alone] little more can be said than that they seem to center about a value of 0.67. Computed[4] divalent iron-series ion $F^2(3d,3d)$'s are larger than the experimental parameters by approximately 25%; the discrepancies are largest for ions of low ionization and least for those of high ionization. The computed F^4/F^2 ratios, which are roughly independent of Z for divalent and trivalent ions, lie below the hydrogenic orbital ratio of 0.65, which in turn is less than the observed ratio of 0.67. The observed ratio implies a one-electron function which is more narrowly peaked than a hydrogenic function, whereas the partial screening due to the presence of other electrons has, of course, the reverse effect. In addition, there are widespread data for the ions in salts and solutions, and these show substantial decreases in the magnitude of observed $F^k(3d3d)$ from their free-ion values—decreases which have been associated with a $3d$-shell expansion[58] (due to charge overlap and covalency effects) in such environments. Similar but relatively smaller (a few percent) effects occur[32] for rare-earth ions.

Since LS coupling is important for the rare earths, the parametrization of the spectra must include ζ_{4f} as a parameter as well as the $F^k(4f,4f)$. (Henceforth the $4f$, $4f$ index will be omitted.) While Russell-Saunders coupling is a good first approximation to the ions' behavior, the breakdown of this coupling does affect the spectra. Elliott, Judd, and Runciman[42] have shown how to include this in obtaining fits to the data, and Wybourne and Runciman[34] have produced such fits for the $4f^2$, $4f^3$, $4f^{11}$, and $4f^{12}$ ions (i.e., those ions for which the Slater-Racah, Condon, and Shortley formalism had been fully worked out). Due to the complexity of and limitations in the data, assumptions concerning the F^k (e.g., that the F^k ratios were those of hydrogenic orbitals) are required in order to reduce the number of variational parameters. It should be remembered that none of the fits which were obtained are for the free ions.

Hartree-Fock F^2's, F^4's, F^6's and F^4/F^2 ratios are listed in Table VI along with Hartree F^2's and F^4/F^2's, experimental F^2's of Jørgensen[32] and Judd and Lindgren,[28] and F^2's and F^4/F^2's found by Wybourne and Runciman.[34] No F^6/F^2 ratios have been included, because their behavior parallels that of the F^4/F^2's. We see that the three sets of experimental data are in substantial agreement. The variation between sets is due to variation in fitting schemes (note that the Judd and Lindgren values were obtained with Judd's[43]

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[53] By correlation effects we mean discrepancies occuring due to the differences between the Hartree-Fock and the "true" eigenfunctions of our Hamiltonian. When considering parameters such as ζ_{4f}, these effects can enter in two ways. First, while $P(r)$ and $V(r)$ [see Eq. (5)] cannot be exactly defined for the "true" eigenfunction, one can at least crudely estimate the effect on a "$V(r)$" or "$P(r)$" (and in turn on ζ_{4f}) when going to the "true" eigenfunction. Secondly, there are effects that cannot be so sorted, such as the possibility that correlation effects are different for states of differing J. To the extent that this type of correlation effect is important, the ζ_{4f} of Eq. (5) has no meaning.

[54] For some recent investigations concerned with improving the parametrization see G. Racah and Y. Shadmi, Phys. Rev. **119**, 156 (1960); C. K. Jørgensen, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13 (to be published).

[55] See, for example, reference 42, where the energies of all the terms of the f^n configurations possessing the highest and next-to-highest multiplicities have been calculated under this assumption.

[56] *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vols. I–III.

[57] See, for example, Fig. 1 of reference 4.

[58] For example see C. K. Jørgensen, Discussions Faraday Soc. **26**, 110 (1958); and L. Orgel, J. Chem. Phys. **23**, 1824 (1955).

TABLE VI. Theoretical and experimental $F^k(4f,4f)$ parameters and their ratios for rare-earth ions. All energies are in atomic units (1 au $=2ry$).

	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{2+}	Gd^{3+}	Dy^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}
Hartree-Fock F^2	0.453	0.477	0.498	0.532	0.516	0.565	0.589	0.616	···	0.642
Hartree[a] F^2	···	0.406	···	···	···	···	···	···	0.573	···
Experimentally Fitted F^2										
Jørgensen[b]	···	0.314	0.327	0.327	···	0.346	0.355	···	0.447	···
Judd and Lindgren[c]	0.306	0.318	0.330	0.356	···	0.381	0.407	0.433	0.445	0.457
Wybourne and Runciman[d]	···	0.314	0.340	···	···	···	···	0.445	0.459	···
Hartree-Fock F^4/F^2	0.629	0.629	0.630	0.630	0.627	0.630	0.630	0.629	···	0.629
Hartree[a] F^4/F^2	···	0.623	···	···	···	···	···	···	0.624	···
Experimentally fitted[d] F^4/F^2	···	0.813	0.716	···	···	···	···	0.753	0.665	···
Hydrogenic $F^4/F^2=0.668$										
Hartree-Fock F^4	0.284	0.300	0.314	0.335	0.324	0.356	0.371	0.387	···	0.404
Hartree-Fock F^6	0.205	0.216	0.226	0.242	0.233	0.257	0.267	0.279	···	0.291

[a] See reference 3.
[b] See reference 32.
[c] See reference 28: Note that these are not experimental fits as such but utilize Eq. (5) of reference 43.
[d] See reference 34.

semiempirical formula for F^2) rather than to any variations in environment.

The next feature to note in Table VI is that not only are the Hartree-Fock F^2's larger than the experimental values, but the disagreement is appreciably larger than what has been seen[4] for divalent or trivalent iron-series ions. The Hartree $4f$ orbitals, which are more extended than the Hartree-Fock functions, yield F^2's which are still appreciably larger than the corresponding experimental parameters. Inspection of the experimental F^4/F^2 ratios shows them to center above the hydrogenic orbital value of 0.668, thereby reflecting an improbable orbital shape, whereas both the Hartree and Hartree-Fock ratios lie below this value and are quite independent of Z. The deviations between experimental and hydrogenic ratios are more pronounced than has been observed for the iron series, but this may be due to the limited sampling of experimental results.

It is perhaps of interest to note that while the Hartree functions yielded ζ_{4f}'s which were in good numerical agreement with experiment, the Hartree F^k's are almost as inadequate as the Hartree-Fock ones in reproducing the multiplet spectra. Of greater interest is the fact that the Hartree-Fock F^k *integrals* are less able to reproduce observed rare-earth multiplet spectra, i.e., the observed F^k *parameters*, than they were in the case of the iron-series ions.

The observation that the experimental F^k's are smaller than the corresponding Hartree-Fock values may be understood on the basis of a simple, if overly naive, physical argument. The parametrization scheme which is used to obtain the F^k's from experiment is based on a Hartree-Fock description of the multiplet states. As is well known, the Hartree-Fock formalism includes exchange, i.e., interelectronic correlation, between electrons of common spin. This implies that a state with maximum spin will have the maximum of such correlation built into it and in turn that it will have the smallest (remaining) correlation energy.[53] Now states of maximum multiplicity lie lowest in energy, and, by having smaller (remaining) correlation energies, they lie comparatively low within a Hartree-Fock scheme of the multiplet levels. Thus, the predicted multiplet levels are more expanded and the F^k's larger than the observed values. This naive argument is also consistent with the observation[59] that it is generally the states of lowest multiplicity which are most appreciably out of their predicted positions.

VI. CRYSTALLINE-FIELD INTERACTIONS

So far, we have been considering the rare-earth ions as being free, although, as previously noted, most of the data referred to were for ions in crystalline environments. A theory for the behavior of these ions in crystals has been given by Stevens,[60] Elliott and Stevens,[24,27] and others,[61] based on a static crystalline field whose effect is smaller than the spin-orbit splitting. (For the iron-group ions, the spin-orbit coupling is smaller than the crystalline-field splitting.) In this theory, the energy due to the crystalline field acts as a perturbation on the $4f$ electrons, with the potential energy, $V(r)$, taken as the superposition of point charge (or point dipole) terms representing the electric field set up by the surrounding ions. If one assumes no overlap between the $4f$ electrons and the surrounding ionic charge distributions (which, incidentally, is a better approximation than a similar one made for iron-series ions), then V can be represented quite simply as

$$V=\sum_{n,m} A_n{}^m r^n Y_n{}^m(\theta,\phi),$$

where the $A_n{}^m$ are lattice sums and represent the effects from the static charges of the lattice of neighboring ions and the $Y_n{}^m(\theta,\phi)$ are the usual spherical

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[59] For example see Table IV of Watson (see reference 4).

[60] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

[61] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932); G. J. Kynch, Trans. Faraday Soc. **33**, 1402 (1937); W. G. Penney and G. J. Kynch, Proc. Roy. Soc. (London) **A170**, 112 (1939); and B. R. Judd, *ibid.* **A227**, 552 (1955).

harmonics. With V as a perturbation, the problem is, therefore, one of calculating matrix elements with respect to the $4f$ wave functions; this requires knowledge of the quantities $\langle r^n\rangle$, where the brackets denote integration with respect to the $4f$ radial function.

For systems of high symmetry, simple expressions are easily obtained for V. For example, in the ethylsulfates and trichlorides, the rare-earth sites have C_{3h} symmetry (which is a rather high symmetry for rare-earth salts), and the effect of V is completely represented by the terms $A_2^0\langle r^2\rangle$, $A_4^0\langle r^4\rangle$, $A_6^0\langle r^6\rangle$, and $A_6^6\langle r^6\rangle$, while for a crystal field corresponding to a point symmetry of the type C_{3v}, the only nonzero parameters are $A_2^0\langle r^2\rangle$, $A_4^0\langle r^4\rangle$, $A_4^3\langle r^4\rangle$, $A_6^0\langle r^6\rangle$, $A_6^3\langle r^6\rangle$, and $A_6^6\langle r^6\rangle$. By contrast, in the case of an iron-group ion in a cubic field, the static crystalline field can be represented (for most purposes) by a single parameter called $10Dq$. The greater complexity in the case of the rare earths arises from the higher orbital angular momentum of the $4f$ electrons as well as from the lower crystal-field symmetry which exists for rare-earth ions in salts.

In applications of the crystal-field theory, the quantities $V_n^m=A_n^m\langle r^n\rangle$ are used as parameters to fit the observed level splittings, but in only a few cases has there been enough data to fit these parameters unambiguously. In the absence of precise values for $\langle r^n\rangle$ it has been common to follow, at least as a starting point in the analysis of spectra, the pioneering work of Elliott and Stevens and assume that $\langle r^n\rangle$, and, hence, also V_n^m (provided the A_n^m are constant), vary as $(Z-55)^{-n/4}$ where Z is the atomic number. (This variation was obtained from observed spin-orbit coupling variation with Z and the use of hydrogenic $4f$ radial functions.) Recently, with the determination of new and more accurate data, the validity of this procedure has been questioned.[62,63] For the trichlorides, Judd[62] has found that screening effects were indicated to be important. Powell and Orbach[63] have further suggested, on the basis of parameterizations for Dy^{3+}, Pr^{3+}, and Eu^{3+} in the ethyl sulfate, that a different empirical representation for V_n^m was required. Assuming that a relation of the form $V_n^m\propto(Z-55)^p$ was demanded, values of $p=+0.8$, -1.4 and -0.33 were offered by these authors for $n=2$, 4, and 6 in place of $p=-0.5$, -1.0, and -1.5 as suggested by Elliott and Stevens. In view of these results, Powell and Orbach concluded that the hydrogenic approximation may be in serious error.

We now know[51] that the static crystal-field model is an inadequate description for iron-group ions and that factors such as covalency play a dominant role. It is naive to assume that the situation is very much better, i.e., simpler, for the rare-earth ions (although direct ligand overlaps are indeed smaller). Despite this, and especially in view of the interest in the results, we will report values of $\langle r^n\rangle$ integrals and make comparisons with experiment. Afterwards we will return to a brief discussion of the adequacy of the model and the applicability of the results.

TABLE VII. Calculated values of $\langle r^2\rangle$ in a_0^{-2} units, $\langle r^4\rangle$ in a_0^{-4} units, and $\langle r^6\rangle$ in a_0^{-6} units, using the $4f$ wave functions defined in Table I.

	$\langle r^2\rangle$	$\langle r^4\rangle$	$\langle r^6\rangle$
Ce^{3+}	1.200	3.455	21.226
Pr^{3+}	1.086	2.822	15.726
Nd^{3+}	1.001	2.401	12.396
Sm^{3+}	0.883	1.897	8.775
Eu^{2+}	0.938	2.273	11.670
Gd^{3+}	0.785	1.515	6.281
Dy^{3+}	0.726	1.322	5.102
Er^{3+}	0.666	1.126	3.978
Yb^{3+}	0.613	0.960	3.104

The Hartree-Fock $\langle r^2\rangle$, $\langle r^4\rangle$, and $\langle r^6\rangle$ integrals are tabulated in Table VII. The $\langle r^6\rangle$ integrals are more sensitive to errors in the functions than any other integral reported in this paper, and an uncertainty of several percent should be attached to them. Close inspection of Table VII shows the variation of any one $\langle r^n\rangle$ with Z to be approximately, but by no means exactly, smooth. (The same situation occurs for the quantities reported in Tables II, III, and VI.) This is due to our having solved the Hartree-Fock equations for ground multiplet states. As one goes from one to another of these states the "amount" of $4f$ exchange (and aspherical effects) per $4f$ electron does not vary smoothly. As an example, consider Gd^{3+}, which has seven $4f$ electrons of parallel spin. This is the case of "maximum" exchange effects and, as a result, the $4f$ orbitals are relatively contracted. In turn, the Gd^{3+} integrals for positive n lie slightly below a smooth curve, as can be seen by close inspection of the table. Hartree-Fock calculations for the averages of configurations[64] would yield smooth behavior.

Shown in Fig. 3, as a function of Z, are plots of the $\langle r^2\rangle$, $\langle r^4\rangle$, and $\langle r^6\rangle$ values taken from Table VII, Elliott and Stevens' formula $\langle r^n\rangle\propto(Z-55)^{-n/4}$, and Powell and Orbach's $V_n^m\propto(Z-55)^p$ parametrization, assuming, as they did *not*, that the A_n^m are constant. For convenience all three curves were matched at $Z=62$ (Sm^{3+}). The fairly close agreement between the Hartree-Fock data and the formula of Elliott and Stevens is surprising and all the more remarkable in view of the procedure used to obtain the formula. At first sight, the very poor agreement between the

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[62] B. R. Judd, Proc. Roy. Soc. (London) **A251**, 134 (1959).

[63] M. J. D. Powell and R. Orbach, Proc. Phys. Soc. (London) **78**, 753 (1961).

[64] G. H. Shortley, Phys. Rev. **50**, 1072, (1936); J. C. Slater, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Quarterly Progress Report No. 27, January, 1958 (unpublished), p. 3; and for examples of average of configuration Hartree-Fock calculations see R. E. Watson, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Technical Report No. 12, 1959 (unpublished but available on request) and reference 4.

TABLE VIII. A_n^m determined for some rare-earth ions in the ethyl sulfate using the $\langle r^n \rangle$ listed in Table VII (in cm^{-1} per a_0^{-n} units).

Ion	Reference	A_2^0	$-A_4^0$	$-A_6^0$	A_6^6
Pr^{3+}	65	47	35	3.0	42.0
Sm^{3+}	66	87	25.6	4.47	63.8
[a]Eu^{3+}	67	96	36	5.3	68
Dy^{3+}	63	171	20.0	6.08	96.5
Er^{3+}	68	188	28	20.4	97.3
[a]Tm^{3+}	69	202	65	7.9	120

[a] Interpolated values for $\langle r^n \rangle$ were used.

Hartree-Fock data and the Powell and Orbach parametrization (note the disagreement in slopes) is also surprising. However, as already stated, the Powell and Orbach parametrization is for the measured V_n^m and so plotting these in Fig. 3 assumes a constancy of the A_n^m. Figure 3 shows that this assumption is *not* correct; we have, in fact, presented such a plot in order to display this.

If one believes that the relations for the parameters $V_n^m = A_n^m \langle r^n \rangle$ are valid, one can invert the procedure, i.e., divide the observed V_n^m by our $\langle r^n \rangle$ integrals and so obtain information about the A_n^m. The A_n^m calculated in this way for some ions[63,65–69] in the ethyl sulfate are listed in Table VIII. Aside from the A_2^0, which show the marked variation observed by other workers, the other A_n^m also show a strong dependence on Z. Similar variations are also seen in Table IX for A_n^m calculated for some trichloride data.[62,70–72] In view of the various approximations involved in both the model (which we feel to be an inadequate one) and the variety of the fitting schemes which are used to derive the "observed" crystalline-field parameters, we shall not dwell upon these data any longer.

Recently Burns[73] has calculated some A_n^m coefficients by performing the proper lattice sums for the various lattices. Assuming shielding (and other) effects to be negligible, he did the calculations for the $\mathrm{LaCl_3}$ and ethyl sulfate lattices but observed difficulties because A_2^0 is sensitive to the x-ray coordinates, and A_6^0 and A_6^6 to the nearest-neighbor distances. Burns finds values of (469, −14.4, −0.352, +3.94) and (570, −11.9, −0.240, +3.25) for A_2^0, A_4^0, A_6^0, and A_6^6 in erbium and praseodymium ethyl sulfate, respectively. These agree in sign but have different magnitudes, as well as much smaller variations with Z, than the corresponding A_n^m listed in Table VIII. Note that the calculated ratios of A_6^6 to A_6^0 for the two cases agree (as is required by the point-charge model).

TABLE IX. A_n^m determined for some rare-earth ions in the trichlorides or in $\mathrm{LaCl_3}$ using the $\langle r^n \rangle$ listed in Table VII (in cm^{-1} per a_0^{-n} units).

Ion	Reference	A_2^0	$-A_4^0$	$-A_6^0$	A_6^6
Pr^{3+} in $\mathrm{PrCl_3}$	70	45.6	14.1	2.49	25.2
Nd^{3+} in $\mathrm{NdCl_3}$	62	103.6	15.0	3.59	34.4
Dy^{3+} in $\mathrm{DyCl_3}$	[a]	124	30.3	4.57	49.6
Pr^{3+} in $\mathrm{LaCl_3}$	72	56.6	16.3	2.23	22.6
Sm^{3+} in $\mathrm{LaCl_3}$	71	91.5	12.0	5.06	48.5
Dy^{3+} in $\mathrm{LaCl_3}$	71	126	29.5	4.54	50.5

[a] H. M. Crosswhite and G. H. Dieke, J. Chem. Phys. **35**, 1535 (1961).

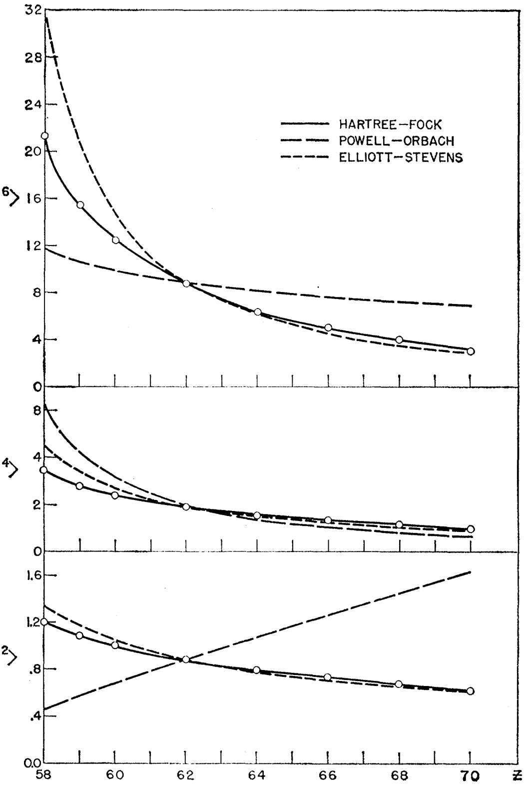

FIG. 3. Values of $\langle r^2 \rangle$, $\langle r^4 \rangle$, and $\langle r^6 \rangle$ based on the H-F results, compared with the Elliott and Stevens formula and the Powell and Orbach parametrization of the V_n^m. For convenience all the curves were matched at Sm^{3+} ($Z=62$).

Before leaving the discussion of crystal-field effects, we should note that, quite aside from the complications indicated above, the rare earths suffer from a feature which is not met, or at least is unimportant, for the iron-series ions. This is associated with the fact that the 5s and 5p shells lie well outside of the 4f shell (cf. Fig. 1), and any distortion of these shells, after the manner discussed in the following section, can play an important role in "crystal field" effects. Since these lie pretty well outside of the 4f shell, yet inside the "external" potential, any distortion or other effect associated with them is likely to be relatively important for just the same reason that quadrupole antishielding

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[65] J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156 (1958).

[66] H. Lämmerman, Z. Physik **150**, 551 (1958).

[67] B. R. Judd, Molecular Phys. **2**, 407 (1959).

[68] E. H. Erath, J. Chem. Phys. **34**, 1985 (1961).

[69] E. Y. Wong and I. Richman, J. Chem. Phys. **34**, 1182 (1961).

[70] B. R. Judd, Proc. Roy. Soc. (London) **A241**, 414 (1957).

[71] J. Axe, Bull. Am. Phys. Soc. **7**, 196 (1962).

[72] C. A. Hutchinson and E. Y. Wong, J. Chem. Phys. **29**, 754 (1958).

[73] G. Burns (to be published).

factors, γ_∞, are large (~ -100) when computed[74,75] for an external potential. This promises to complicate greatly any theoretical investigation of rare-earth crystal-field interactions, for it will not be a matter of just dealing with the interaction of unclosed shell with an external environment, but there will also have to be a careful accounting of "small" effects associated with additional closed shells.

VII. EFFECTS OF ASPHERICAL DISTORTIONS AND EXCHANGE (SPIN) POLARIZATION

The parametrizations of the preceding sections utilizing ζ_{4f}'s, $\langle r^{-3}\rangle$'s and F^k's assume that the ions can be described by the "conventional" Hartree-Fock formalism. The "conventional" or "restricted" nonrelativistic atomic Hartree-Fock formalism and its relation to more general forms has been discussed elsewhere,[76,77] and so we will not go into details here. Its prominent features are that the one-electron Hartree-Fock functions are assumed to be separable into products of radial functions $P(r)$, spherical harmonics, and spin functions *and* that there be but one $P(r)$ per shell, i.e., that the $P(r)$ are independent of both m_l and m_s. In the "conventional" relativistic Hartree-Fock formalism the two-component radial wave functions are assumed to be independent of m_j. These assumptions are rigorously justified if and only if (1) the Hartree-Fock potential is spherical (in which case wave-function separability and $P(r)$ independent of m_l follow), and (2) the system has no net spin [in which case electrons differing only in m_s undergo the same exchange effects and in turn have the same $P(r)$]. For most atoms and ions, these two conditions are not fulfilled. Nevertheless, there are both physical and practical reasons which compel one to apply these restraints to the one-electron wave functions. Without these restraints one abandons the traditional and very successful shell structure description of atoms. The closed shells of a "conventional" determinantal function are no longer "closed" in the "unrestricted" description, i.e., closed in the sense that they make a ^1S contribution to the function's symmetry. As a result, functions which were proper eigenfunctions of $\mathbf{L}^2$ and $\mathbf{S}^2$ when "restricted" are no longer so when the restraints are relaxed. Properly symmetrized "unrestricted" many-electron functions, however, present formidable computational problems which cannot be discussed here. While we are not prepared in this paper to drop the assumption of separability of the one-electron wave functions, the simultaneous relaxation of the m_l and m_s restrictions (with or without separable one-electron wave functions) leads to physical consequences which have not been widely investigated.

It should be noted that an alternate approach is available, namely configuration interaction,[78–80] but its application[78,79] to hyperfine effects has so far been restricted to s electron spin polarization. A direct relation exists[80] between "single substitution" configuration interaction and the correctly symmetrized, unrestricted Hartree-Fock method. By its nature, a configuration-interaction treatment is correctly symmetrized; and an advantage *and* a disadvantage associated with it is the fact that correlation[52] effects can be included in it. The disadvantage arises because it is, at best, a slowly convergent method for correlation effects. "Full" calculations utilizing either the configuration-interaction approach or the correctly symmetrized, unrestricted Hartree-Fock method present almost insurmountable difficulties for ions having high atomic number.

We are concerned with the way in which an unfilled $4f$ shell distorts the closed shells and how its aspherical charge and unbalanced spin distributions cause the $4f$ orbitals themselves to differ radially (i.e., how the $4f$ shell distorts itself), and, in turn, in the contributions these distortions make to the electric and magnetic interactions between electrons and the nucleus. The "unrestricted" Hartree-Fock formalism gives the following picture for the rare-earth ions. First, spin polarization of s-shell electrons yields a contact term which is relatively small (as can be seen by comparing observed hyperfine parameters for the half-closed shell ^8S-state ions[81,82] with the parameters for aspherical ions).[83] Secondly, the aspherical charge distribution (for any but an S-state ion) causes charge

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[74] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **95**, 736 (1954). It should be noted that in the matter at hand, combined exchange and nonspherical Coulomb polarization effects must be considered.

[75] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956); and Wikner and T. P. Das, *ibid.* **109**, 360 (1958).

[76] Among recent discussions, for example see R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960); P. O. Löwdin, Revs. Modern Phys. **32**, 328 (1960); R. K. Nesbet, *ibid.* **33**, 28 (1961); D. A. Goodings, Phys. Rev. **123**, 1706 (1961).

[77] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961); A. J. Freeman and R. E. Watson, Phys. Rev. Letters **5**, 498 (1960).

[78] Investigations discussing or computing s-electron spin polarization through the use of configuration interaction, for either a single outer shell (usually of necessity) or all shells, include: E. Fermi and E. Segrè, Rend. R. Acad. d'Italia **4**, 18 (1933); E. Fermi and E. Segrè, Z. Physik **82**, 729 (1933); A. Abragam, Phys. Rev. **79**, 534 (1950); A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951); **A206**, 164 (1951); **A206**, 173 (1951); G. F. Koster, Phys. Rev. **86**, 148 (1952); and R. K. Nesbet, *ibid.* **118**, 681 (1960).

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

[80] For some pertinent discussions see R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, **312** (1955); W. Marshall, Proc. Phys. Soc. (London) **78**, **113** (1961); and N. Bessis, H. Lefebvre-Brion and C. M. Moser, Phys. Rev. **124**, 1124 (1961).

[81] See W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), Tables XXVI through XXVIII for a summary of S-state ion hyperfine data. For Eu^{2+} also see J. M. Baker, B. Bleaney and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958); and M. Abraham, R. Kedzie and C. D. Jeffries, Phys. Rev. **108**, 58 (1957). See also K. Krebs and R. Winkler, Z. Physik **160**, 320 (1960).

[82] W. E. Blumberg and J. Eisinger, Bull. Am. Phys. Soc. **6**, 141 (1961).

[83] For example, compare with J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A247**, 156 (1958).

distortions which give a contribution to the quadrupole interaction with the nucleus in addition to the average $4f$ shell $\langle r^{-3}\rangle$ term. Finally, combined spin polarization and aspherical distortions will lead to an aspherical magnetic-dipole interaction term. We believe that this, rather than spin polarization of s shells, is the primary cause of discrepancies between "effective" $\langle r^{-3}\rangle$'s and $\langle r^{-3}\rangle$ integrals.

A "proper," correctly symmetrized, sufficiently "unrestricted" Hartree-Fock calculation for the above effects is beyond current computational abilities, as is the case also for ions far smaller than the rare earths. In such a procedure, it is also necessary to ignore the important role played by correlation effects—a role found to be important for low-Z ions. Unfortunately, a not quite "proper" calculation (which we would consider not too ludicrously "improper") is also a major undertaking and beyond the scope of the present paper. The reason for this will be more apparent after we inspect what can be learned from hyperfine experiments on rare-earth ions and from calculations for smaller ions.

Spin Polarization of the Core Electrons

For systems with a net spin, electrons in a given n_l shell which have different m_s quantum numbers (i.e., differing spin) experience different exchange interactions and so have different radial wave functions and a spin density at the nucleus (for "closed" s shells) which is now nonvanishing. This effect, called exchange (or spin) polarization, has recently played a prominent role in the interpretation of observed hyperfine fields,[76,77] particularly for the $3d$-transition series.

A spin-polarized Hartree-Fock calculation has been done[50] for Gd^{3+}, but, quite aside from deficiencies in the formalism, it is an inadequate source of information concerning the ion's contact term interaction, because the calculation is nonrelativistic and poorly describes electron behavior at the nucleus. (Quite surprisingly, and clearly by accident, the calculated hyperfine field from core polarization agrees in sign and magnitude with the observed value.) However, an estimate of spin polarization effects can be made by inspection of experimental hyperfine data for S-state ions (like Eu^{2+} and Gd^{3+}). Blumberg and Eisinger[82] have reported an ENDOR measurement of the hyperfine interaction for Eu^{2+} in CaF_2 which (together with the accurately known moment of^2 Eu) gives a hyperfine field of -335 kG or $-95\ S$ kG (where S is the spin of the ion and equal to 7/2 for Eu^{2+}). Estimates of the hyperfine field for the other ions can be made in the following way. First, following observations for iron-group ^6S-state ions[77] (i.e., Mn^{2+} and Fe^{3+}), one would expect the field at the Gd^{3+} nucleus to be somewhat smaller; second, the hyperfine field should depend on covalency, the more covalent the environment of the rare-earth ion, the smaller the field. If one assumes that the hyperfine field for Gd^{3+} is about the same as that observed for Eu^{2+} and that covalency effects are small in CaF_2 (a reasonable approximation for iron-group ions in the fluorides and a better one here), then one can use the observation of Abragam, Horowitz, and Pryce[79] to extend this result to the other ions. These authors found that, for the divalent iron-series ions, the core polarization contribution was roughly proportional to S, the spin of the ion. Such a proportionality has since been found to be valid for these elements in a variety of environments, and so it seems reasonable to expect it to hold, at least qualitatively, for the rare earths as well. For the rare earths, however, we must replace the proportionality to S (actually S_z) by the projection of S along J. Hence, we suggest that the core polarization contribution for the other trivalent ions should be taken as approximately $(-90\ \text{kG})\times(g_J-1)J$. Further, since $(g_J-1)J$ is a maximum for Gd^{3+} (and Eu^{2+}) and smaller for ions of both lower and higher atomic number, the core polarization contribution is indeed a very small contribution to the $L\neq 0$ ions (whose hyperfine fields are measured in millions of gauss). While small, it represents yet another factor which must be considered in any attempt at accuracy when either estimating a nuclear magnetic moment, μ, or, if μ is known, relating hyperfine data for ions in different environments.

Aspherical Distortions and Hyperfine Interactions

In ions with an unfilled shell of electrons having a net orbital angular momentum $(L\neq 0)$, aspherical distortions of the electronic shells are produced by the aspherical orbital distribution of the unfilled shell electrons, because the interactions between these electrons depend on the m_l quantum numbers of the one-electron wave functions. As mentioned earlier, this effect follows naturally from relaxing the m_l restriction in the "unrestricted" Hartree-Fock description, i.e., electrons in the same nl shell but differing in m_l are allowed different *radial* wave functions and so the shell appears distorted (non-spherically symmetric), and makes contributions to Eq. (9) and to the $\mathbf{L}\cdot\mathbf{I}$ term of Eq. (8) (if the ion's $M_L\neq 0$). Simultaneous relaxation of the m_l and m_s restrictions leads to contributions to the spin dipolar terms of Eq. (8) as well, unless, of course, the ion is a spin singlet. The additional relaxation of the requirement for separable radial and angular parts of one-electron functions leads to Sternheimer "angular" distortions and in turn to additional contributions to Eqs. (8) and (9). While these are not negligible, for the case at hand the m_l and m_s uhf contributions are the more important.

One might be tempted to try to obtain a theoretical estimate of these aspherical effects by applying Sternheimer's[84] or Dalgarno's[85] perturbation methods to our

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[84] R. M. Sternheimer, Phys. Rev. **84**, 244 (1951); **86**, 316 (1953); and **105**, 158 (1957).

[85] A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 282 (1959).

conventional Hartree-Fock functions. Unfortunately, these functions poorly describe electron behavior in the immediate vicinity of the nucleus, as compared with a "best" conventional relativistic Hartree-Fock description, and so provide a poor starting point for such a calculation. In addition there are serious problems introduced by the failure of the state function to remain an eigenfunction of $\mathbf{L}^2$ and $\mathbf{S}^2$. A few calculations have been done to estimate distortions in an ion due to an aspherical shell, but all these also suffer from the L and S symmetry inadequacy. These include the pioneering perturbation investigations by Sternheimer[84] for many ions, Ingalls'[86] quadrupole polarizability calculation for Fe^{2+} (using the analytic perturbation method of Das and Bersohn[75]), and an unpublished m_l and m_s unrestricted calculation for Cl which we have done. In each case, the source of the aspherical distortions is a single outer electron or a single hole in an outer shell.

We can make use of these results in estimating the effect of the distorted charge distributions on the hyperfine interactions (magnetic dipole or electric quadrupole). We here ignore the contribution from spin polarization discussed above. If one uses Eqs. (8) and (9) and the aspherical charge distributions determined by these calculations, one finds:

(1) That an "effective" $\langle r^{-3}\rangle$ computed for the magnetic hyperfine interaction will be similar to (but not identical with) an "effective" $\langle r^{-3}\rangle$ calculated for the electric quadrupole interaction.

(2) Increases *or* decreases of as much as 30% occur in "effective" $\langle r^{-3}\rangle$ integrals.

(3) That the unfilled shells, which are responsible for the distortions produced in the closed shells, are themselves distorted and, hence, yield a different contribution to the hyperfine interactions than would be predicted with the "conventional" Hartree-Fock functions. Distortions of this type are important sources of differences between $\langle r^{-3}\rangle$ integrals and parameters.

As already noted (it is worth repeating), there are serious deficiencies in such calculations.[87] There is also the question as to whether results of a rather different magnitude would be obtained for a rare-earth ion (whose unfilled shell is imbedded inside the ion). In any case, if it were not for some of the "optical" data, such as that given in Table IV, it would appear to be overly optimistic to ascribe an uncertainty as small as 20% to μ's estimated by using conventional $\langle r^{-3}\rangle$'s.

An analysis of experimental data to yield information about these aspherical effects is not possible until direct determinations are made of nuclear magnetic moments for nuclei other than Gd or Eu. We believe that such direct measurements of μ will be reported prior to a "correct" calculation of the effects discussed in this section. Such measurements, in conjunction with magnetic hyperfine data, will define "effective" $\langle r^{-3}\rangle$'s which include all effects, e.g., correlation, and which may shed some light on the above-mentioned symmetry problems. These "effective" $\langle r^{-3}\rangle$'s will allow estimates to be made of the nuclear quadrupole moments, as has been done by Sternheimer.[84] The precise relation between "effective" $\langle r^{-3}\rangle$'s for magnetic dipole and electric quadrupole interactions requires further investigation. In particular, the reader may have been surprised at the observation [(1) above] that the "effective" $\langle r^{-3}\rangle$'s are similar. The source of this is not without interest, but, since all "observed" nuclear, quadrupole moments are based on such an observation knowledge of the extent to which this holds is far more important. Investigations (mostly for smaller ions) into this and other matters cited in this section are now under way.

VIII. CONCLUSION

We have reported two sets of approximate, nonrelativistic Hartree-Fock calculations for rare-earth ions and have discussed their relevance to a number of the physical properties of these ions.

The problem of spin-orbit splittings was discussed at great length because of its own inherent interest (as an important quantity for rare-earth ions) and because of the important role it has played in almost all previous estimates of nuclear magnetic-moments, μ, for these ions. It was seen that the usual expression for ζ_{4f}, when evaluated using the H-F wave functions, was in appreciable disagreement with experiment. Such discrepancies have been observed previously for smaller ions, and we have reviewed evidence which suggest that the discrepancies are in part due to the omission of exchange terms (with the core electrons) from the definition of ζ. These results thus have some rather important implications for those efforts which estimate $\langle r^{-3}\rangle$ integrals from experimental ζ_{4f}'s and then in turn use these to estimate μ values.

Hyperfine fields were discussed in two parts. In Sec. III, we used our $\langle r^{-3}\rangle$ results to estimate μ for a sampling of rare-earth isotopes according to the conventional scheme using the Fermi hyperfine Hamiltonian. These were found to agree closely with earlier parametrized estimates by Bleaney, but to differ with those of Lindgren. We suggested that it is necessary to use "effective" $\langle r^{-3}\rangle$ values instead of $\langle r^{-3}\rangle$ integrals and that uncertainties are associated with any of the μ estimates given in Table IV. In Sec. VII, we discussed these matters in greater detail, particularly from the "unrestricted" Hartree-Fock point of view, and sketched the role played by spin polarization and aspherical distortions in discussions of rare-earth

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[86] R. Ingalls (to be published); this calculation was discussed by G. Lang at the second Annual Conference on the Mössbauer Effect, Saclay, France, 1961.

[87] It is to be noted that there are no such L and S symmetry problems when dealing with the distortion of a closed shell by an external field.

properties, notably magnetic dipole and electric quadrupole interactions. We utilized the observed hyperfine effects for spherical ions, such as Eu^{2+} and Gd^{3+}, to give an estimate of the field due to the spin polarization of the core s electrons for all the trivalent ions; and while the resulting hyperfine interaction is small, we believe this estimate will prove useful for any detailed analysis of experimental rare-earth hyperfine data. Also discussed was the way in which the unfilled $4f$ shell distorts the closed shells and how its aspherical charge distribution causes the $4f$ orbitals themselves to differ radially. The order of magnitude of the effect of these distortions on hyperfine interactions was estimated from calculations on other smaller ions and the effect appears to be substantial. The need to consider these effects in any estimate of μ from $\langle r^{-3}\rangle$ was indicated, as was the need to investigate more thoroughly the precise relation between "effective" $\langle r^{-3}\rangle$'s and $\langle r^{-3}\rangle$ integrals. With the future appearance of other direct measurements of μ, interest will be particularly centered about the difference between effective $\langle r^{-3}\rangle$'s for magnetic and electric quadrupole interactions, because experimental values for the "magnetic" $\langle r^{-3}\rangle$ will likely be equated to the "electric" $\langle r^{-3}\rangle$ in estimates of the nuclear quadrupole moments. As was pointed out, current evidence suggests that these parameters are similar but by no means identical.

The Slater $F^k(4f,4f)$ integrals, which appear in parametrization schemes for fitting observed multiplet spectra, were calculated and compared with other theoretical estimates and experiment. The calculated F^k integrals for the rare-earth ions were found to be in poor agreement with experiment—the disagreement being in fact larger than similar disagreements observed previously for $3d$ ions. Both the Hartree-Fock and Hartree F^4/F^2 ratios were seen to be below the hydrogenic value and to be independent of Z, whereas the experimental ratios centered above the hydrogenic value. A simple physical argument based on correlation effects was then given in order to explain the large observed differences between theory and experiment.

The effects of the crystalline environment on spectra were discussed within the framework of the simple static crystal-field model. Results were given for the $\langle r^n\rangle$ integrals for $n=2$, 4, and 6, and these were found to be in (surprisingly) good agreement with the Elliott and Stevens parametrization formula. The assumption of the constancy of the A_n^m parameters with Z was shown not to be valid for the available crystal-field data on the ethyl sulfates and trichlorides. Finally, it was stressed that the rare earths suffer from the additional complication, not met in the case of $3d$ ions, of having several complete shells of electrons which lie outside the $4f$ shell and which can appreciably affect the behavior of these ions in any interactions with an external environment.

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