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Relativistic extension of the spin-polarized local-density-functional theory: Study of the electronic and magnetic properties of the rare-earth ions

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We have extended the von Barth—Hedin local-spin-density theory to treat the relativistic spin-polarized case as proposed by Doniach and Sommers. This extension permits us to do actual numerical calculations on atomic and solid-state systems. A technique for integrating the resulting coupled Dirac equations is presented. As a test the theory is applied to the study of the magnetic and electronic properties of some rare-earth ions. We analyze the relativistic and spin-polarization effects on the $4f$ spin densities and evaluate the polarization effect on the core electrons. Tables of form factors for the first seven rare-earth ions are also presented.

INTRODUCTION

The importance of including relativistic effects in interpreting the magnetic properties of Gd was first shown by Moon *et al.*[1] The precise measurements of the magnetic form factors of metallic Gd by polarized neutron scattering enabled the determination of the localized magnetic-moment distribution. It was shown that the width of this distribution was larger than the nonrelativistic Hartree-Fock $4f$ charge density calculated by Freeman and Watson.[2] Moon *et al.* suggested that this was due to the larger nuclear screening in the relativistic case, which was later confirmed in a relativistic-Hartree-Fock calculation by Freeman and Desclaux.[3] The latter were able to obtain good agreement with experiment in spite of the fact that their calculations were nonmagnetic. Further theoretical and experimental works on the rare-earth metals and compounds gave similar results.[4,5] Spin polarization was not included in these calculations because of the difficulty in introducing this effect in the Dirac Hamiltonian where spin is not a good quantum number.

Our primary interest is in the calculation of the magnetic and electronic properties of solids where the Hartree-Fock scheme is impracticable. Thus, we use a local-spin-density formalism for treating exchange and correlation of a many-electron system.[6–9] This formalism gives us a set of one-electron equations which are relatively simple to treat numerically. We consider the extension of this formalism to the relativistic case. A relativistic spin-polarized density-functional theory was first proposed by Rajagopal and Callaway.[9] This was followed by the work of MacDonald and Vosko,[10] who actually wrote down the one-electron equations. Two years later Doniach and Sommers,[11] guided by the nonrelativistic approach of von Barth and Hedin,[8] rederived the relativistic spin-density theory. This latter work produced a practical theory for atomic or solid-state calculations. In this paper, we revise their theory and use it to do actual calculations on the rare-earth ions. This required some new numerical techniques to solve two-coupled Dirac equations. The actual use of these equations in a band-structure calculation will be considered at a later time.

In our calculations we make use of the results of the theory of the homogeneous electron gas. This theory was extended to the relativistic case by several authors. We refer to Ramana and Rajagopal[12] for a general review of this subject. In particular, for the spin-polarized case, a calculation of the exchange energy was first done by Ramana and Rajagopal[13,14] but their papers contained some errors. This was pointed out by MacDonald,[15] who (using another theoretical approach) obtained a different expression for the exchange energy. Recently, Xu *et al.*[16] revised the Ramana and Rajagopal calculations and their result agrees with MacDonald to first order in $(1/c^2)$. We have used the resulting expressions for the exchange energy and potential $[O(1/c^2)]$ in our calculations. We assume that the higher-order terms are not really important in applications to atomic or solid-state systems. Finally, to our knowledge, no expressions exist for the correlation energy of a relativistic spin-polarized homogeneous gas as a function of the density and magnetization. In order to compare with Dirac-Fock results, we include only the exchange terms in our calculations and not the nonrelativistic spin-polarized counterpart for the correlation energy.

We wish to mention the fact that there does exist a semirelativistic theory due to Koelling and Harmon[17] including spin-polarization effects but neglecting spin-orbit coupling. In our theory there is no such approximation.

One important consequence of this is that a unique Fermi surface is generated by our equations.

RELATIVISTIC SPIN-POLARIZED DENSITY-FUNCTIONAL THEORY

In what follows we describe the fundamental lines of the extension of the von Barth—Hedin[8] nonrelativistic spin-polarized theory to the relativistic case.

We consider N electrons in an external potential $W_{\mu\nu}(\mathbf{r})$. Using the 16 Dirac covariant matrices, this can be expressed as

$$W_{\mu\nu}(\mathbf{r})=\sum_{M=1}^{16} w^M(\mathbf{r})\Gamma^M_{\mu\nu}\,. \tag{1}$$

We introduce the density matrix

$$\rho_{\mu\nu}(\mathbf{r})=\langle\Psi\,|\,\psi^\dagger_\mu(\mathbf{r})\psi_\nu(\mathbf{r})\,|\,\Psi\rangle=\sum_{M=1}^{16}\rho^M(\mathbf{r})\Gamma^M_{\mu\nu}\,, \tag{2}$$

where

$$\rho^M(\mathbf{r})=\pm\tfrac{1}{4}\mathrm{Tr}(\Gamma^M\rho)=\pm\tfrac{1}{4}\sum_{\mu,\nu}\Gamma^M_{\mu\nu}\rho_{\mu\nu} \tag{3}$$

with the plus or minus corresponding to $(\Gamma^M)^2=\pm1$.

Let H_0 be the Hamiltonian describing the kinetic and interaction energy of the electronic system. The mean energy can be written as

$$E=\langle\Psi\,|\,H_0\,|\,\Psi\rangle+\sum_{\mu,\nu}\int d^3r\,W_{\mu\nu}(\mathbf{r})\rho_{\mu\nu}(\mathbf{r})\,. \tag{4}$$

The two Hohenberg-Kohn theorems are still valid in the von Barth-Hedin form: (1) The ground-state wave function is a unique functional of the density matrix $\rho_{\mu\nu}(\mathbf{r})$. (2) The ground-state energy is a functional of $\rho_{\mu\nu}(\mathbf{r})$ (depending upon $W_{\mu\nu}(\mathbf{r})$; this functional has an absolute minimum when $\rho_{\mu\nu}(\mathbf{r})$ is the ground-state density matrix of the system. The variation of $\rho_{\mu\nu}(\mathbf{r})$ must satisfy the constraint

$$\sum_{\mu}\int d^3r\,\rho_{\mu\mu}(\mathbf{r})=N \tag{5}$$

and states of negative energy are not to be included in the variation.

Varying the energy of Eq. (4) under the constraint of Eq. (5), we obtain a one-electron Dirac equation of the form (in atomic units)

$$\sum_{\nu}[c\alpha_{\mu\nu}\cdot\mathbf{p}+\beta_{\mu\nu}c^2+W_{\mu\nu}(\mathbf{r})+V^{ee}(\mathbf{r})\delta_{\mu\nu}+V^{\mathrm{xc}}_{\mu\nu}(\mathbf{r})]\Phi^{(i)}_\nu(\mathbf{r})=E^{(i)}\Phi^{(i)}_\mu(\mathbf{r})\,, \tag{6}$$

where $V^{ee}(\mathbf{r})$ is the classical term describing the Coulombic electron-electron interaction and where $V^{\mathrm{xc}}_{\mu\nu}(\mathbf{r})$ is the exchange and correlation potential

$$V^{ee}(\mathbf{r})=\int d^3r'\,\frac{\sum_\mu\rho_{\mu\mu}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}=\int d^3r'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,, \tag{7}$$

$$V^{\mathrm{xc}}_{\mu\nu}(\mathbf{r})=\frac{\delta E_{\mathrm{xc}}}{\delta\rho_{\mu\nu}}\,. \tag{8}$$

One can express the density matrix in terms of the solutions of Eq. (6) as follows:

$$\rho_{\mu\nu}(\mathbf{r})=\sum[\Phi^{(i)}_\mu(\mathbf{r})]^*\Phi^{(i)}_\nu(\mathbf{r})\,, \tag{9}$$

where the sum is on all the occupied states.

With the help of the chain rule for derivatives and the use of Eq. (3), we obtain an expression for $V^{\mathrm{xc}}_{\mu\nu}(\mathbf{r})$ in the form

$$V^{\mathrm{xc}}_{\mu\nu}(\mathbf{r})=\sum_M\frac{\delta E_{\mathrm{xc}}}{\delta[\mathrm{Tr}(\Gamma^M\rho)]}\Gamma^M_{\mu\nu}\,. \tag{10}$$

We assume an external potential of the type

$$W_{\mu\nu}(\mathbf{r})=V^{en}(\mathbf{r})\delta_{\mu\nu}+\frac{1}{2c}h(\mathbf{r})\sigma^z_{\mu\nu}\,, \tag{11}$$

where the first term is the familiar electron-nucleus electrostatic interaction and the second term is the paramagnetic interaction with an external magnetic field directed along the z axis. We have not included the diamagnetic term because in a spin-polarized theory the field is produced internally only by exchange which has no direct l dependence.

As for the exchange-correlation potential, one obtains

$$\frac{\delta E_{\mathrm{xc}}}{\delta\rho_{\mu\nu}}=\frac{\delta E_{\mathrm{xc}}}{\delta n}\delta_{\mu\nu}+\frac{\delta E_{\mathrm{xc}}}{\delta m_z}\sigma^z_{\mu\nu}\,, \tag{12}$$

where

$$n(\mathbf{r})=\mathrm{Tr}(\rho)=\sum_\mu\sum_{\substack{i\\ \text{occupied}}}[\Phi^{(i)}_\mu(\mathbf{r})]^*\Phi^{(i)}_\mu(\mathbf{r})\,, \tag{13}$$

$$m_z(\mathbf{r})=\mathrm{Tr}(\sigma^z\rho)=\sum_{\mu,\nu}\sum_{\substack{i\\ \text{occupied}}}\sigma^z_{\nu\mu}[\Phi^{(i)}_\mu(\mathbf{r})]^*\Phi^{(i)}_\nu(\mathbf{r})\,. \tag{14}$$

We now make use of the local approximation. An expression for the exchange energy of the homogeneous gas as a function of density and magnetization was given by MacDonald[15] and Xu *et al.*[16]

Let

$$\xi=\frac{|\mathbf{m}|}{n} \tag{15}$$

and define a parameter z by the three expressions

$$x=(1+z)^{1/3},\quad y=(1-z)^{1/3}\,, \tag{16}$$

$$\xi=\frac{1}{2\beta^3}\{[\tfrac{1}{3}\beta^3x^3+\beta x(1+\beta^2x^2)^{1/2}-\sinh^{-1}(\beta x)]-[x\rightarrow y]\}\,, \tag{17}$$

where

$$\beta=\frac{\hbar k_F}{mc}=\frac{1}{c}(3\pi^2n)^{1/3}\ \text{a.u.}$$

At the first order in $(1/c^2)$, the total exchange energy $E_x=E_x^{(c)}+E_x^{(\mathrm{tr})}$, where $E_x^{(c)}$ and $E_x^{(\mathrm{tr})}$ are the Coulombic and transverse contributions then take the form

$$E_x^{(c)}=-\frac{3}{4\pi}nE_F\frac{\alpha}{\beta}\left[x^4+y^4-\frac{1}{9}\beta^2(x^6+y^6)\right]\,, \tag{18}$$

$$E_x^{(\mathrm{Tr})}=\frac{3}{4\pi}nE_F\frac{\alpha}{\beta}\frac{10}{9}\beta^2[(1+\tfrac{7}{60}(x^3-y^3)^2] , \tag{19}$$

where

$$\alpha=\frac{e^2}{\hbar c}=1/c \text{ a.u.}$$

SOLUTION IN AN EXTERNAL CENTRAL FIELD

In the case of a central external potential and a uniform magnetic field, one must solve the following equation:

$$\sum_{\nu}[c\boldsymbol{\alpha}_{\mu\nu}\cdot\mathbf{p}+\beta_{\mu\nu}c^2+V(r)\delta_{\mu\nu}+b(r)\sigma^z_{\mu\nu}]\Phi_\nu^{(i)}(\mathbf{r}) = E^{(i)}\Phi_\mu^{(i)}(\mathbf{r}) , \tag{20}$$

where

$$V(r)=V^{en}(r)+V^{ee}(r)+\frac{\delta E_{\mathrm{xc}}}{\delta n} , \tag{21}$$

$$b(r)=\frac{1}{2c}h+\frac{\delta E_{\mathrm{xc}}}{\delta m_z} . \tag{22}$$

Without the symmetry-breaking term σ^z, the eigenfunctions reduce to the ordinary solutions of the Dirac equation[18]

$$\psi_{nkm}=\frac{1}{r}\begin{bmatrix} P_{nk}(r)\ \chi_{km}(\theta,\varphi) \\ iQ_{nk}(r)\ \chi_{-km}(\theta,\varphi)\end{bmatrix} . \tag{23}$$

In order to proceed we must calculate the matrix elements $\langle \chi_{km} \,|\, \sigma_P^z \,|\, \chi_{k'm'}\rangle$, where σ_p^z is a 2×2 Pauli matrix. One can easily verify that the matrix elements vanish except when $l=l'$ and $m=m'$.

We define the coefficient $C_{kk'}^{lm}$ as

$$C_{kk'}^{lm}=\langle \chi_{km} \,|\, \sigma_P^z \,|\, \chi_{k'm}\rangle \tag{24}$$

and obtain the result

$$C_{kk}^{lm}=\begin{cases} m/J \ \text{ if } k<0 \\ -m/(J+1) \ \text{ if } k>0 \end{cases} \tag{25}$$

$$C_{kk'}^{lm}=\frac{(l+\frac{1}{2}-m)^{1/2}(l+\frac{1}{2}+m)^{1/2}}{l+\frac{1}{2}} \quad \text{if } k\neq k' . \tag{26}$$

In order to investigate the form of the solutions of Eq. (20), one can ask how the wave function ψ_{nk_1m} is modified by the magnetic term.

A series expansion for the wave function gives

$$\Phi^{(i)}=\frac{1}{N}\left[\psi_{nk_1m}+\sum_{n',k'}{}' C_{n'k'm}\psi_{n'k'm}\right] . \tag{27}$$

Perturbative theory shows that only the terms with $n=n'$ are important. By neglecting terms of order $(1/c)^2$, the series reduces to the term nk_2m such that $k_2\neq k_1$ but the orbital angular momentum l_1 of the large component of the nk_1m term is equal to the corresponding value l_2 of the nk_2m term

$$\Phi^{(i)}=\frac{1}{N}(\psi_{nk_1m}+C_{nk_2m}\psi_{nk_2m}) . \tag{28}$$

So we are led to write the solutions of Eq. (20) as follows:

$$\begin{aligned}\Phi^{(i)}&=\varphi_{nk_1m}+\varphi_{nk_2m}\\ &=\frac{1}{r}\begin{bmatrix} P_{nk_1m}\chi_{k_1m}+P_{nk_2m}\chi_{k_2m} \\ iQ_{nk_1m}\chi_{-k_1m}+iQ_{nk_2m}\chi_{-k_2m}\end{bmatrix} ,\end{aligned} \tag{29}$$

where the φ_{nkm} are ψ_{nkm} like but not necessarily a solution of the nonmagnetic equation. Furthermore the radial part can be m dependent.

Using Eqs. (20) and (29), one obtains for the radial solutions a set of two coupled Dirac equations (denoting P_{nk_1m} as P_1, etc.)

$$\begin{aligned}
&\left[\frac{\partial}{\partial r}+\frac{k_1}{r}\right]P_1-\left[2c+\frac{E-V(r)}{c}\right]Q_1+\frac{1}{c}b(r)C^{lm}_{-k_1-k_1}Q_1=0 ,\\
&\left[\frac{\partial}{\partial r}-\frac{k_1}{r}\right]Q_1+\frac{E-V(r)}{c}P_1-\frac{1}{c}b(r)C^{lm}_{k_1k_1}P_1-\frac{1}{c}b(r)C^{lm}_{k_1k_2}P_2=0 ,\\
&\left[\frac{\partial}{\partial r}+\frac{k_2}{r}\right]P_2-\left[2c+\frac{E-V(r)}{c}\right]Q_2+\frac{1}{c}b(r)C^{lm}_{-k_2-k_2}Q_2=0 ,\\
&\left[\frac{\partial}{\partial r}-\frac{k_2}{r}\right]Q_2+\frac{E-V(r)}{c}P_2-\frac{1}{c}b(r)C^{lm}_{k_2k_2}P_2-\frac{1}{c}b(r)C^{lm}_{k_2k_1}P_1=0 .
\end{aligned} \tag{30}$$

These equations must be solved simultaneously, with the constraints

$$\begin{aligned}
&\int_0^\infty (P_1^2+P_2^2+Q_1^2+Q_2^2)dr=1 ,\\
&P_1(0)=P_2(0)=Q_1(0)=Q_2(0)=0 ,\\
&P_1(\infty)=P_2(\infty)=Q_1(\infty)=Q_2(\infty)=0 .
\end{aligned} \tag{31}$$

They have two solutions which are the two energies and wave functions corresponding to the quantum numbers n,k_1,m and n,k_2,m in the nonspin-polarized limit.

NUMERICAL SOLUTION

In this paper we are interested in the case pertaining to $H(r)\rightarrow0$. A finite field $H(r)$ is used in the first iteration (as in the nonrelativistic case) only to break the degeneracy. Thereafter its value is taken to be zero and the system itself generates an internal magnetic field proportional to $\delta E_x/\delta m_z$.

In order to start the numerical integration of Eqs. (30) we must specify the values of P and Q on a fixed mesh for several points at the origin and at infinity. At these points the internal magnetic field vanishes and Eqs. (30) decouple into two independent sets of equations which we can treat by the standard methods.[18]

Thus the wave function at the origin is expressed as a series

$$\begin{aligned} P_i(r)&=r^{\gamma_i}(p_i^{(0)}+p_i^{(1)}r+p_i^{(2)}r^2+\cdots), \quad i=1,2 \\ Q_i(r)&=r^{\gamma_i}(q_i^{(0)}+q_i^{(1)}r+q_i^{(2)}r^2+\cdots), \quad i=1,2 \end{aligned} \tag{32}$$

where $\gamma_i=(k_i^2-Z^2/c^2)$ and where all the coefficients are linear functions of $p_i^{(0)}$.

For the last points of the mesh we use the asymptotic form

$$\begin{aligned} P_i(r)&=A_i\exp(-\mu r)\,, \\ Q_i(r)&=B_i\exp(-\mu r)\,, \end{aligned} \tag{33}$$

where

$$\mu=\left[-2E-\frac{E^2}{c^2}\right]^{1/2}$$

and

$$\mu A_i=-(2c+E/c)B_i\,.$$

Specifying trial values for the four parameters $p_1^{(0)}$, $p_2^{(0)}$, A_1, A_2, one can integrate Eqs. (30) from the origin to some fixed matching point r_m and likewise from infinity, obtaining a solution $(P_i^{\mathrm{in}},Q_i^{\mathrm{in}})$ and $(P_i^{\mathrm{out}},Q_i^{\mathrm{out}})$ respectively, in the internal and the external region.

In order that the function be continuous at r_m we must satisfy the following conditions:

$$\begin{aligned} P_i^{\mathrm{in}}(r_m,p_1^{(0)},p_2^{(0)},E)&=P_i^{\mathrm{out}}(r_m,A_1,A_2,E)\,, \\ Q_i^{\mathrm{in}}(r_m,p_1^{(0)},p_2^{(0)},E)&=Q_i^{\mathrm{out}}(r_m,A_1,A_2,E)\,. \end{aligned} \tag{34}$$

These conditions, plus the normalization of the wave function, can only be satisfied for the correct energies and choice of parameters.

Since Eqs. (30) are linear, the inner and the outer solutions are defined to within a multiplicative constant. Thus one can take a fixed value for $p_2^{(0)}$ and multiply P_i^{in} and Q_i^{in} by a constant. The same can be repeated with A_2 and the external solution.

However only the ratio D of these two multiplicative constants need be varied in order to obtain a matching condition at r_m. The two constants are determined by the normalization condition. Equation (34) now becomes

$$\begin{aligned} DP_i^{\mathrm{in}}(r_m,p_1^{(0)},E)&=P_i^{\mathrm{out}}(r_m,A_1,E)\,, \\ DQ_i^{\mathrm{in}}(r_m,p_1^{(0)},E)&=Q_i^{\mathrm{out}}(r_m,A_1,E)\,. \end{aligned} \tag{35}$$

The determination of the parameters is done in the following manner. First we require that $P_1^{\mathrm{in}}/P_1^{\mathrm{out}}=P_2^{\mathrm{in}}/P_2^{\mathrm{out}}$ at $r=r_m$ by varying $p_1^{(0)}$. If it were not for the coupling term we could exactly obtain this condition using the value of $p_1^{(0)}$:

$$p_{1\,\mathrm{new}}^{(0)}=\frac{P_2^{\mathrm{in}}(r_m)}{P_2^{\mathrm{out}}(r_m)}\,\frac{P_1^{\mathrm{out}}(r_m)}{P_1^{\mathrm{in}}(r_m)}p_{1\,\mathrm{old}}^{(0)}\,. \tag{36}$$

Even though this is not true in our case, we use Eq. (36) to determine a new value of $p_1^{(0)}$. Since the coupling terms are small, this process converges rather rapidly.

The first and second conditions of Eqs. (35) are now satisfied with the value of D:

$$D=P_1^{\mathrm{out}}(r_m)/P_1^{\mathrm{in}}(r_m)\,. \tag{37}$$

In order to satisfy the third and fourth condition we must vary A_1 and E.

For a given A_1 we can find two energies ϵ_1 and ϵ_2 such that condition three and four are satisfied independently. This can be obtained by developing $Q_i^{\mathrm{in}}(r_m,E)-Q_i^{\mathrm{out}}(r_m,E)=\Delta Q_i(E)$ in a series expansion. In order that $\Delta Q_i=0$, we use the first three terms of the series to predict a new value of E. Only for the correct value of A_1 will $\epsilon_1=\epsilon_2$.

If we knew the dependence of ϵ_i on A_1 we could find A_1 by resolving the equation

$$\epsilon_1(A_1)=\epsilon_2(A_1)\,. \tag{38}$$

A_1 is nearly a multiplicative constant for P_1 and Q_1. It has the effect of rigidly displacing the values of (P_1,Q_1) in relation to (P_2,Q_2). Its value measures the relative contribution of the two components of the wave function (29).

This property of A_1 enables us to guess the dependence of ϵ_i on A_1 following

$$\begin{aligned} \epsilon_1&=\frac{\alpha_1}{A_1}+\alpha_2\,, \\ \epsilon_2&=\alpha_3A_1+\alpha_4\,. \end{aligned} \tag{39}$$

For two arbitrary values of A_1 we determine the four values of α. We then set

$$\frac{\alpha_1}{A_1}+\alpha_2=\alpha_3A_1+\alpha_4 \tag{40}$$

in order to predict a new value of A_1. This process is repeated until the value of A_1 is found such that $\epsilon_1=\epsilon_2$.

The remaining problems are how to choose the value of A_1 from Eq. (40) and how to find the two solutions of Eqs. (30). The two problems are interelated. In fact the two solutions of Eqs. (30) correspond to a symmetric or antisymmetric combination of Eq. (29). The relative sign of the two functions in Eq. (29) can be included in the parameter A_1. Thus we can find the two solutions of Eqs. (30) by choosing systematically a positive or negative value of A_1.

RESULTS AND DISCUSSION

We calculated the electronic properties of the first seven positive trivalent ions of the rare-earth elements

TABLE I. (a) $4f$ eigenvalues, in hartrees, from nonspin-polarized-nonrelativistic (LD) calculations. (b) $4f$ eigenvalues, in hartrees, from nonspin-polarized-relativistic (RLD) calculations. (c) $4f$ eigenvalues, in hartrees, from spin-polarized-relativistic (RLSD) calculations.

				(a)			
	${}_{58}\mathrm{Ce}^{3+}$	${}_{59}\mathrm{Pr}^{3+}$	${}_{60}\mathrm{Nd}^{3+}$	${}_{61}\mathrm{Pm}^{3+}$	${}_{62}\mathrm{Sm}^{3+}$	${}_{63}\mathrm{Eu}^{3+}$	${}_{64}\mathrm{Gd}^{3+}$
	1.1257	1.1706	1.2106	1.2466	1.2792	1.3088	1.3357
				(b)			
J	${}_{58}\mathrm{Ce}^{3+}$	${}_{59}\mathrm{Pr}^{3+}$	${}_{60}\mathrm{Nd}^{3+}$	${}_{61}\mathrm{Pm}^{3+}$	${}_{62}\mathrm{Sm}^{3+}$	${}_{63}\mathrm{Eu}^{3+}$	${}_{64}\mathrm{Gd}^{3+}$
2.5	1.0124	1.0543	1.0906	1.1225	1.1506	1.1754	1.1996
3.5	1.0000	1.0395	1.0736	1.1031	1.1285	1.1505	1.1716
				(c)			
J_z	${}_{58}\mathrm{Ce}^{3+}$	${}_{59}\mathrm{Pr}^{3+}$	${}_{60}\mathrm{Nd}^{3+}$	${}_{61}\mathrm{Pm}^{3+}$	${}_{62}\mathrm{Sm}^{3+}$	${}_{63}\mathrm{Eu}^{3+}$	${}_{64}\mathrm{Gd}^{3+}$
2.5	1.0239	1.0777	1.1257	1.1689	1.2081	1.2441	1.2772
1.5	1.0225	1.0759	1.1235	1.1664	1.2052	1.2408	1.2735
0.5	1.0210	1.0740	1.1212	1.1637	1.2022	1.2373	1.2696
−0.5	1.0194	1.0720	1.1188	1.1609	1.1990	1.2338	1.2656
−1.5	1.0175	1.0698	1.1163	1.1580	1.1957	1.2300	1.2614
−2.5	1.0153	1.0673	1.1136	1.1550	1.1923	1.2261	1.2570
−3.5	1.0125	1.0646	1.1106	1.1517	1.1886	1.2220	1.2535
−2.5	0.9954	1.0213	1.0399	1.0529	1.0613	1.0658	1.0668
−1.5	0.9932	1.0189	1.0372	1.0499	1.0580	1.0620	1.0626
−0.5	0.9914	1.0167	1.0347	1.0471	1.0548	1.0584	1.0586
0.5	0.9898	1.0147	1.0324	1.0444	1.0517	1.0550	1.0548
1.5	0.9883	1.0128	1.0302	1.0419	1.0488	1.0517	1.0511
2.5	0.9869	1.0110	1.0280	1.0394	1.0460	1.0485	1.0476
3.5	0.9857	1.0093	1.0260	1.0370	1.0433	1.0455	1.0441

TABLE II. Total energies, in hartrees, from spin-polarized-relativistic (RLSD), nonspin-polarized-relativistic (RLD), and nonspin-polarized-nonrelativistic (LD) calculations.

	${}_{58}\mathrm{Ce}^{3+}$	${}_{59}\mathrm{Pr}^{3+}$	${}_{60}\mathrm{Nd}^{3+}$	${}_{61}\mathrm{Pm}^{3+}$	${}_{62}\mathrm{Sm}^{3+}$	${}_{63}\mathrm{Eu}^{3+}$	${}_{64}\mathrm{Gd}^{3+}$
RLSD	−8834.02	−9209.94	−9595.66	−9991.31	−10 397.04	−10 812.97	−11 239.25
RLD	−8834.01	−9209.92	−9595.61	−9991.22	−10 396.90	−10 812.77	−11 238.96
LD	−8556.52	−8910.55	−9273.03	−9644.04	−10 023.66	−10 411.96	−10 809.01

TABLE III. Exchange energies, in hartrees, from spin-polarized-relativistic (RLSD), nonspin-polarized-relativistic (RLD), and nonspin-polarized-nonrelativistic (LD) calculations.

	${}_{58}\mathrm{Ce}^{3+}$	${}_{59}\mathrm{Pr}^{3+}$	${}_{60}\mathrm{Nd}^{3+}$	${}_{61}\mathrm{Pm}^{3+}$	${}_{62}\mathrm{Sm}^{3+}$	${}_{63}\mathrm{Eu}^{3+}$	${}_{64}\mathrm{Gd}^{3+}$
RLSD	−179.17	−184.01	−188.93	−193.92	−198.98	−204.10	−209.29
RLD	−179.16	−183.98	−188.86	−193.79	−198.78	−203.81	−208.89
LD	−190.13	−195.72	−201.42	−207.23	−213.14	−219.15	−225.27

TABLE IV. Mean values of various powers of r from relativistic calculations by the Hartree-Fock (RHF), spin-polarized-local-density (RLSD), and nonspin-polarized-local-density (RLD) approximations.

		$\langle r^{-3}\rangle$			$\langle r^{2}\rangle$			$\langle r^{4}\rangle$			$\langle r^{6}\rangle$	
	RHF	RLSD	RLD	RHF	RLSD	RLD	RHF	RLSD	RLD	RHF	RLSD	RLD
${}_{58}\mathrm{Ce}^{3+}$	4.462	4.445	4.440	1.309	1.427	1.437	3.964	5.013	5.113	23.31	35.19	36.44
${}_{59}\mathrm{Pr}^{3+}$		5.033	5.025		1.296	1.313		4.142	4.294		26.69	28.45
${}_{60}\mathrm{Nd}^{3+}$	5.627	5.638	5.630	1.114	1.190	1.211	2.910	3.505	3.682	15.03	20.99	22.92
${}_{61}\mathrm{Pm}^{3+}$		6.264	6.260		1.103	1.126		3.020	3.207		16.97	18.91
${}_{62}\mathrm{Sm}^{3+}$	6.886	6.913	6.915	0.9743	1.028	1.053	2.260	2.641	2.829	10.55	14.03	15.90
${}_{63}\mathrm{Eu}^{3+}$	7.555	7.585	7.599	0.9175	0.9641	0.9891	2.020	2.336	2.521	9.039	11.80	13.58
${}_{64}\mathrm{Gd}^{3+}$	8.254	8.281	8.280	0.8671	0.9081	0.9352	1.820	2.079	2.276	7.831	10.08	11.84

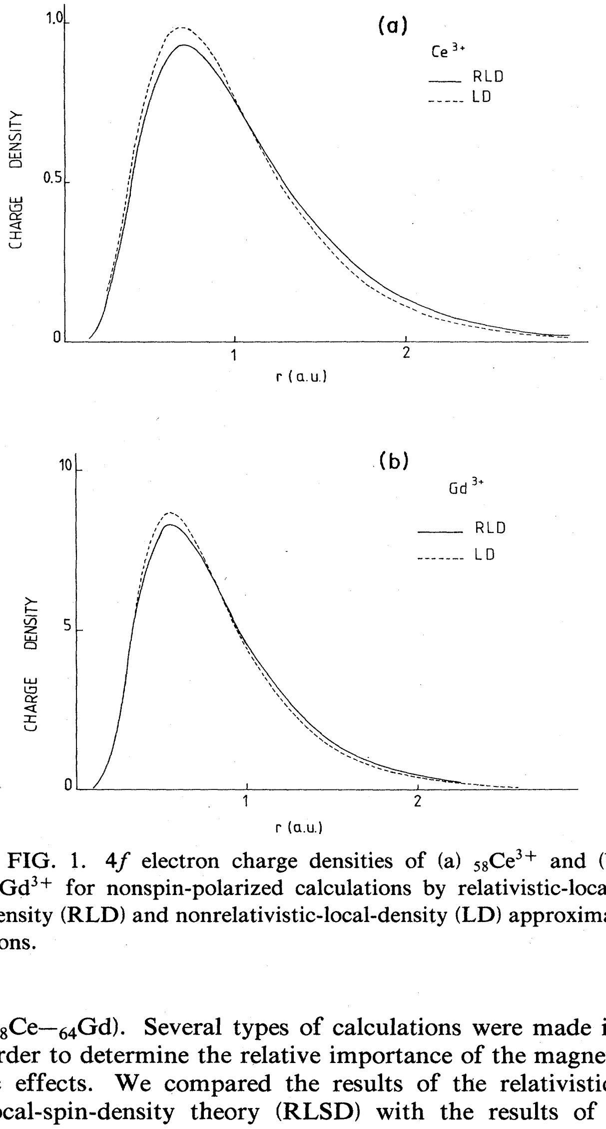

FIG. 1. $4f$ electron charge densities of (a) ${}_{58}\mathrm{Ce}^{3+}$ and (b) ${}_{64}\mathrm{Gd}^{3+}$ for nonspin-polarized calculations by relativistic-local-density (RLD) and nonrelativistic-local-density (LD) approximations.

(${}_{58}$Ce—${}_{64}$Gd). Several types of calculations were made in order to determine the relative importance of the magnetic effects. We compared the results of the relativistic-local-spin-density theory (RLSD) with the results of a nonspin-polarized relativistic-local density calculation (RLD) and with a nonrelativistic nonspin-polarized local density calculation (LD). We also compared our calculations with the nonspin-polarized relativistic-Hartree-Fock results (RHF) of Freeman and Desclaux.[19]

Let us first examine the value of the z component of the total spin, defined as the sum of the mean values of σ_z in the occupied states. We obtain values between 0.97 for ${}_{58}$Ce and 6.96 for ${}_{64}$Gd which is in agreement with Hund's first rule for filling up the orbitals according to a parallel spin alignment. Thus, the number of bohr magnetons is essentially determined by the number of $4f$ electrons. This is an important test for our theory, in particular with regard to the approximate from of Eq. (29) for the wave function. Consider, for example, the case of Ce. If we had used only the first term of Eq. (29), we would obtain a mean value of about 0.7 for σ_z. Thus Eq. (29) is an extremely good approximation to the exact infinite series. Alternately this shows that the spin polarization is much more important than the spin-orbit coupling. A more quantitative verification of this is given in Table I. In this table we show the one-electron energies obtained from LD (a), RLD (b), and RLSD (c) calculations. In the RLSD theory the degeneracy of the orbitals is completely broken. Thus there are fourteen $4f$ orbitals that must be progressively filled up in order of increasing energy. The remaining empty orbitals for each element were also included in the calculation. The RLD calculations [Table I(b)] give the spin-orbit splitting which can be seen to vary regularly between 0.012 a.u. for ${}_{58}$Ce to 0.028 a.u. for ${}_{64}$Gd. In Table I(c) one can see the spin-polarized splitting. The eigenvalues are clearly divided into two groups corresponding to a symmetrical or antisymmetrical linear combination of Eq. (29). Thus the two eigenvalues, belonging to different groups and corresponding to equal and opposite eigenvalues of J_z differ only because of the spin polarization. One sees that these differences do not depend on the absolute value of J_z and vary regularly between 0.03 a.u. for ${}_{58}$Ce to 0.21 a.u. for ${}_{64}$Gd. One can also verify that for each ion the spread in energy of the two groups is about the same and nearly corresponds to the spin-orbit coupling.

The effect of spin polarization on the total and exchange energies can be estimated from Tables II and III.

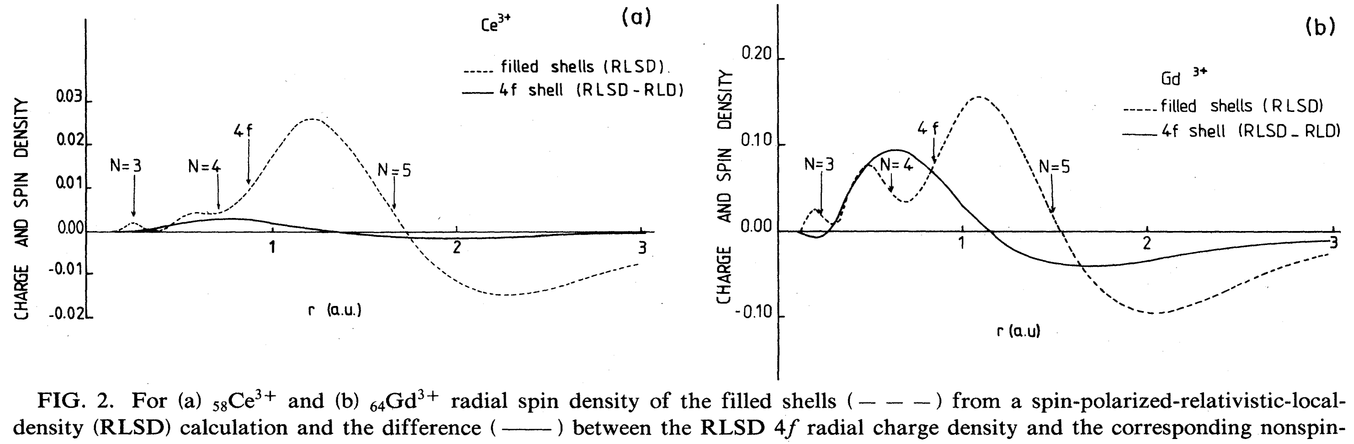

FIG. 2. For (a) ${}_{58}\mathrm{Ce}^{3+}$ and (b) ${}_{64}\mathrm{Gd}^{3+}$ radial spin density of the filled shells (— — —) from a spin-polarized-relativistic-local-density (RLSD) calculation and the difference (——) between the RLSD $4f$ radial charge density and the corresponding nonspin-polarized-relativistic-local-density (RLD) distribution. The mean values of r (RLSD) for the $n=3,4(s,p,d),5$, and $4f$ shells are also shown.

TABLE V. Bessel integrals $\bar{j}_n=\int_0^\infty j_n(kr)m_{4f}(r)dr$ of the magnetic spin moment densities of the 4f electrons divided by the number of electrons as a function of $(\sin\theta)/\lambda$ (Å^{-1}).

$(\sin\theta)/\lambda$	$\bar{j}_0$	$\bar{j}_2$	$\bar{j}_4$	$\bar{j}_6$	$(\sin\theta)/\lambda$	$\bar{j}_0$	$\bar{j}_2$	$\bar{j}_4$	$\bar{j}_6$
		$_{58}$Ce^{3+}					$_{59}$Pr^{3+}		
0.05	0.9454	0.0099	0.0001	0.0000	0.05	0.9591	0.0092	0.0001	0.0000
0.10	0.8756	0.0367	0.0009	0.0000	0.10	0.8945	0.0341	0.0007	0.0000
0.15	0.7749	0.0728	0.0038	0.0002	0.15	0.8000	0.0683	0.0032	0.0001
0.20	0.6595	0.1099	0.0097	0.0007	0.20	0.6900	0.1044	0.0085	0.0006
0.25	0.5434	0.1418	0.0186	0.0021	0.25	0.5771	0.1367	0.0165	0.0017
0.30	0.4356	0.1654	0.0295	0.0045	0.30	0.4702	0.1618	0.0266	0.0037
0.35	0.3409	0.1799	0.0412	0.0079	0.35	0.3745	0.1786	0.0377	0.0067
0.40	0.2609	0.1864	0.0526	0.0123	0.40	0.2920	0.1875	0.0489	0.0106
0.45	0.1952	0.1861	0.0628	0.0172	0.45	0.2229	0.1898	0.0593	0.0152
0.50	0.1423	0.1809	0.0714	0.0224	0.50	0.1663	0.1868	0.0684	0.0201
0.60	0.0679	0.1611	0.0831	0.0324	0.60	0.0846	0.1702	0.0817	0.0300
0.70	0.0242	0.1359	0.0880	0.0409	0.70	0.0347	0.1466	0.0885	0.0388
0.80	0.0003	0.1104	0.0875	0.0472	0.80	0.0061	0.1214	0.0898	0.0457
0.90	−0.0115	0.0873	0.0834	0.0511	0.90	−0.0090	0.0977	0.0870	0.0505
1.00	−0.0162	0.0676	0.0771	0.0529	1.00	−0.0157	0.0769	0.0816	0.0532
1.10	−0.0170	0.0514	0.0696	0.0530	1.10	−0.0177	0.0595	0.0747	0.0541
1.20	−0.0157	0.0384	0.0617	0.0518	1.20	−0.0171	0.0452	0.0672	0.0535
		$_{60}$Nd^{3+}					$_{61}$Pm^{3+}		
0.05	0.9651	0.0085	0.0000	0.0000	0.05	0.9689	0.0079	0.0000	0.0000
0.10	0.9051	0.0317	0.0006	0.0000	0.10	0.9129	0.0296	0.0006	0.0000
0.15	0.8165	0.0640	0.0028	0.0001	0.15	0.8295	0.0602	0.0025	0.0001
0.20	0.7119	0.0989	0.0074	0.0005	0.20	0.7300	0.0939	0.0066	0.0004
0.25	0.6030	0.1310	0.0146	0.0014	0.25	0.6251	0.1256	0.0131	0.0012
0.30	0.4982	0.1570	0.0239	0.0032	0.30	0.5226	0.1520	0.0217	0.0027
0.35	0.4027	0.1754	0.0345	0.0058	0.35	0.4280	0.1717	0.0317	0.0050
0.40	0.3191	0.1864	0.0454	0.0093	0.40	0.3439	0.1843	0.0421	0.0081
0.45	0.2479	0.1908	0.0557	0.0134	0.45	0.2712	0.1906	0.0523	0.0119
0.50	0.1886	0.1898	0.0651	0.0180	0.50	0.2099	0.1914	0.0617	0.0162
0.60	0.1010	0.1766	0.0794	0.0276	0.60	0.1174	0.1813	0.0769	0.0254
0.70	0.0457	0.1549	0.0877	0.0365	0.70	0.0572	0.1618	0.0864	0.0343
0.80	0.0127	0.1305	0.0905	0.0439	0.80	0.0201	0.1385	0.0905	0.0419
0.90	−0.0055	0.1068	0.0891	0.0492	0.90	−0.0013	0.1151	0.0904	0.0478
1.00	−0.0145	0.0854	0.0848	0.0526	1.00	−0.0126	0.0934	0.0872	0.0518
1.10	−0.0179	0.0671	0.0787	0.0543	1.10	−0.0175	0.0744	0.0818	0.0540
1.20	−0.0181	0.0518	0.0715	0.0544	1.20	−0.0187	0.0583	0.0752	0.0548
		$_{62}$Sm^{3+}					$_{63}$Eu^{3+}		
0.05	0.9719	0.0074	0.0000	0.0000	0.05	0.9745	0.0069	0.0000	0.0000
0.10	0.9193	0.0278	0.0005	0.0000	0.10	0.9249	0.0262	0.0004	0.0000
0.15	0.8405	0.0569	0.0022	0.0001	0.15	0.8503	0.0539	0.0020	0.0001
0.20	0.7457	0.0893	0.0059	0.0003	0.20	0.7596	0.0852	0.0053	0.0003
0.25	0.6445	0.1205	0.0118	0.0010	0.25	0.6619	0.1158	0.0108	0.0009
0.30	0.5445	0.1472	0.0198	0.0023	0.30	0.5645	0.1426	0.0182	0.0021
0.35	0.4511	0.1677	0.0292	0.0044	0.35	0.4723	0.1638	0.0270	0.0039
0.40	0.3669	0.1817	0.0392	0.0072	0.40	0.3885	0.1789	0.0366	0.0065
0.45	0.2933	0.1896	0.0492	0.0107	0.45	0.3143	0.1881	0.0463	0.0097
0.50	0.2303	0.1921	0.0586	0.0147	0.50	0.2501	0.1921	0.0556	0.0134
0.60	0.1336	0.1850	0.0742	0.0235	0.60	0.1498	0.1878	0.0716	0.0217
0.70	0.0691	0.1676	0.0847	0.0322	0.70	0.0813	0.1726	0.0829	0.0303
0.80	0.0281	0.1457	0.0901	0.0400	0.80	0.0366	0.1520	0.0893	0.0381
0.90	0.0036	0.1227	0.0911	0.0462	0.90	0.0090	0.1298	0.0914	0.0445
1.00	−0.0100	0.1010	0.0889	0.0507	1.00	−0.0070	0.1081	0.0902	0.0494
1.10	−0.0166	0.0815	0.0844	0.0535	1.10	−0.0153	0.0884	0.0865	0.0527
1.20	−0.0189	0.0647	0.0784	0.0548	1.20	−0.0187	0.0710	0.0811	0.0546

TABLE V. (*Continued*).

$(\sin\theta)/\lambda$	$\bar{j}_0$	$\bar{j}_2$	$\bar{j}_4$	$\bar{j}_6$	$(\sin\theta)/\lambda$	$\bar{j}_0$	$\bar{j}_2$	$\bar{j}_4$	$\bar{j}_6$
		$_{64}$Gd^{3+}							
0.05	0.9771	0.0065	0.0000	0.0000					
0.10	0.9302	0.0248	0.0004	0.0000					
0.15	0.8591	0.0513	0.0018	0.0001					
0.20	0.7723	0.0815	0.0048	0.0003					
0.25	0.6779	0.1115	0.0098	0.0008					
0.30	0.5829	0.1382	0.0168	0.0018					
0.35	0.4922	0.1599	0.0251	0.0035					
0.40	0.4088	0.1760	0.0343	0.0058					
0.45	0.3343	0.1864	0.0437	0.0088					
0.50	0.2691	0.1916	0.0529	0.0122					
0.60	0.1658	0.1899	0.0690	0.0202					
0.70	0.0937	0.1769	0.0809	0.0285					
0.80	0.0456	0.1577	0.0882	0.0363					
0.90	0.0150	0.1363	0.0913	0.0429					
1.00	−0.0034	0.1149	0.0910	0.0481					
1.10	−0.0135	0.0950	0.0881	0.0518					
1.20	−0.0182	0.0773	0.0835	0.0541					

This effect is seen to vary between 0.01 a.u. for $_{58}$Ce to 0.29 a.u. for $_{64}$Gd.

In Figs. 1 and 2, we compare the different effects on the radial spin and charge distribution for Ce and Gd. In Figs. 1(a) and 1(b), we compare the charge distributions of the 4*f* electrons obtained by LD and RLD calculations. The relativistic expansion of the 4*f* shell is evident and corresponds to the results of RHF calculations by Freeman and Desclaux. In Fig. 2(a), we show the radial spin density [Eq. (14)] of the filled shells of Ce. In the same figure we also show the difference between the 4*f* electron charge densities obtained by the RLSD and RLD calculations. The same is shown for Gd in Fig. 2(b). We note that the 4*f* radial densities, calculated by Eq. (13), and the corresponding spin distributions, calculated by Eq. (14), are very similar. This result is not evident in relativistic theory and is a strong indication of the accuracy of our approximation [see Eq. (29)]. Summing the two curves, in Figs. 2(a) and 2(b), gives the total change in the spin density of the ions due to spin polarization. We note that the spin-polarization effect on the 4*f* charge distribution is much smaller than the polarization of the filled shells. The two effects reduce the magnitude of the total spin density in the outer region of the ions and increases it in the internal region. This competes with the broadening of the spin distribution due to the nonspin-polarized Dirac equation. The position of the peaks in the spin density of the filled shells corresponds to the localization of the charge density of the filled shells. We have indicated in Fig. 2 the position of the mean value of *r* for the $n=3,4(s,p,d)$, $4(f)$,5 shells. In order to compare our results with the RHF calculations of Freeman and Desclaux

TABLE VI. Fourier transforms, as a function of $(\sin\theta)/\lambda$ ($\text{\AA}^{-1}$), of the 4*f* electron charge densities by the relativistic-Hartree-Fock calculations of Freeman and Desclaux.[19]

$(\sin\theta)/\lambda$	$_{58}$Ce^{3+}	$_{60}$Nd^{3+}	$_{62}$Sm^{3+}	$_{63}$Eu^{3+}	$_{64}$Gd^{3+}
0.05	0.9763	0.9798	0.9823	0.9833	0.9842
0.10	0.9096	0.9224	0.9317	0.9355	0.9389
0.15	0.8116	0.8366	0.8552	0.8629	0.8698
0.20	0.6968	0.7338	0.7620	0.7739	0.7846
0.25	0.5785	0.6249	0.6612	0.6768	0.6909
0.30	0.4663	0.5184	0.5605	0.5788	0.5957
0.35	0.3660	0.4200	0.4652	0.4853	0.5039
0.40	0.2800	0.3329	0.3787	0.3994	0.4189
0.45	0.2087	0.2581	0.3024	0.3229	0.3424
0.50	0.1510	0.1955	0.2369	0.2564	0.2753
0.60	0.0698	0.1029	0.1359	0.1523	0.1684
0.70	0.0227	0.0446	0.0686	0.0811	0.0938
0.80	−0.0025	0.0104	0.0263	0.0350	0.0442
0.90	−0.0144	−0.0080	0.0013	0.0069	0.0130
1.00	−0.0186	−0.0167	−0.0122	−0.0090	−0.0053
1.10	−0.0187	−0.0196	−0.0184	−0.0170	−0.0152
1.20	−0.0169	−0.0193	−0.0202	−0.0200	−0.0195

TABLE VII. Fourier transforms of the core electron-spin magnetic-moment densities as a function of $(\sin\theta)/\lambda$ (Å^{-1}).

$(\sin\theta)/\lambda$	$_{58}$Ce^{3+}	$_{59}$Pr^{3+}	$_{60}$Nd^{3+}	$_{61}$Pm^{3+}	$_{62}$Sm^{3+}	$_{63}$Eu^{3+}	$_{64}$Gd^{3+}
0.05	0.0017	0.0033	0.0047	0.0059	0.0069	0.0079	0.0087
0.10	0.0056	0.0108	0.0154	0.0195	0.0232	0.0264	0.0293
0.15	0.0095	0.0185	0.0267	0.0341	0.0408	0.0469	0.0524
0.20	0.0113	0.0224	0.0330	0.0428	0.0519	0.0603	0.0681
0.25	0.0104	0.0213	0.0321	0.0426	0.0527	0.0623	0.0715
0.30	0.0075	0.0162	0.0254	0.0349	0.0444	0.0538	0.0630
0.35	0.0038	0.0094	0.0159	0.0232	0.0310	0.0390	0.0471
0.40	0.0007	0.0031	0.0068	0.0115	0.0170	0.0229	0.0293
0.45	−0.0015	−0.0014	0.0000	0.0023	0.0055	0.0094	0.0138
0.50	−0.0025	−0.0038	−0.0040	−0.0033	−0.0019	0.0001	0.0027
0.60	−0.0021	−0.0038	−0.0049	−0.0057	−0.0061	−0.0061	−0.0057
0.70	−0.0007	−0.0014	−0.0019	−0.0023	−0.0026	−0.0029	−0.0030
0.80	0.0002	0.0004	0.0007	0.0010	0.0013	0.0016	0.0019
0.90	0.0004	0.0010	0.0016	0.0023	0.0031	0.0038	0.0046
1.00	0.0003	0.0007	0.0013	0.0019	0.0027	0.0036	0.0045
1.10	0.0001	0.0002	0.0005	0.0009	0.0014	0.0021	0.0029
1.20	−0.0001	−0.0002	−0.0002	−0.0001	0.0001	0.0004	0.0009

as well as to provide some useful quantities for phenomenological theories of the crystalline field and hyperfine interaction, we have calculated the mean values of various powers of r for the $4f$ states (see Table IV).

We have also calculated (Table V) certain integrals of the radial spin magnetic moment $[\int_0^\infty j_n(kr)m_{4f}(r)dr;\ n=0,2,4,6]$, where j_n are spherical Bessel functions. These integrals are of use by the experimentalists for calculating magnetic form factors as well as to analyze neutron diffraction results. For comparison we include the results ($n=0$ only) of Freeman and Desclaux (Table VI). The agreement is generally good, especially for the heavier ions ($_{62}$Sm, $_{63}$Eu, $_{64}$Gd). Larger differences are found in $_{58}$Ce. One can see the effect of local exchange by comparing the results of RHF with RLD in Table IV: the RLD $4f$ distributions are broader than the corresponding RHF distributions. The spin-polarization effect competes with the latter. In general the RLSD $4f$ charge densities are between those of RHF and RLD and tend to approach the RHF results as the number of $4f$ electrons is increased. The same general trend is found in the results of the integrals of the spherical Bessel functions. It should be noted that the RLSD integrals were calculated using the correct spin distribution $m_{4f}(r)$ and not the charge densities $n_{4f}(r)$ as in the RHF or RLD theories. Lastly we present in Table VII the Fourier transforms of the spin densities of the core electrons.

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