

Relativistic  $\Xi$  method for atoms

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Approximate relativistic corrections to the atomic radial wave functions of the recently reported  $\Xi$  method are presented based on the approach of Cowan and Griffin. The major relativistic effects are shown to be incorporated into the wave function while retaining the nonrelativistic format. The one-electron eigenvalues, total energies, expectation values of  $r^n$  for  $n = -1, 1, 2$  and spin-orbit parameter values are reported. The results are comparable with the fully relativistic Dirac-Hartree-Fock values.

## I. INTRODUCTION

Photoelectron spectroscopy<sup>1</sup> has now developed into a powerful tool for providing accurate electron binding energies. The electron binding energies provide a useful check for the accuracy of the wave functions. The Hartree-Fock (HF) scheme provides such accurate wave functions. But computations using the HF method are fairly complicated due to the presence of a nonlocal exchange potential. Slater<sup>2</sup> introduced the local density approximation to the HF exchange potential and the method is commonly known as the Hartree-Fock-Slater (HFS) method. Gopinathan<sup>3</sup> proposed an improved local approximation by evaluating the self-interaction term explicitly and treating the remaining exchange as in the HFS method. This method is now called the  $\Xi$  method. The  $\Xi$  method has been further improved by Tseng and Whitehead<sup>4</sup> and more recently by Vaidehi and Gopinathan.<sup>5</sup> The  $\Xi$  method<sup>5</sup> has been shown to give orbital eigenvalues and total energies of nearly HF accuracy. The purpose of this paper is to extend the  $\Xi$  method to the relativistic case.

There is abundant evidence<sup>6</sup> in the literature indicating the importance of taking into account the relativistic effects in atomic structure calculations. The most rigorous way of doing this is the Dirac-Hartree-Fock (DHF) method which was formulated by Grant.<sup>7</sup> The DHF computer code and DHF results<sup>8</sup> for atoms ( $Z = 1-120$ ) are available. In the many-electron Hamiltonian of this method, the one-electron operators are the hydrogenic Dirac Hamiltonians and the two-electron operators are the same as in the nonrelativistic Hamiltonian. In solving the DHF problem exactly, one computes two radial wave functions for each set of central-field quantum numbers  $n, l$ , and  $j$ , commonly known as large and small components. As in the nonrelativistic case, the DHF nonlocal exchange potential can be approximated by Slater's exchange potential. This method, called the Dirac-Hartree-Fock-Slater (DHFS) method,<sup>9</sup> is somewhat simpler than the DHF method. But in both the DHF and DHFS methods, one has to compute nearly 4 times as many wave functions as in the nonrelativistic method. So it is desirable to have a simpler relativistic method, within the format of the nonrelativistic model, but incorporating major relativistic ef-

fects. Cowan and Griffin's<sup>10</sup> approach provides one such scheme. Wood and Boring<sup>11</sup> have applied this approach to the DHFS method. In the present work, the approach of Cowan and Griffin is applied to the  $\Xi$  method.

## II. THE METHOD

First, we briefly describe the relevant features of the nonrelativistic  $\Xi$  method.<sup>5</sup> The total energy of the atom or ion can be written exactly as

$$\begin{aligned} \langle E \rangle = & \sum_i n_i u_i^*(r) f_1 u_i(r) dr \\ & + \frac{1}{2} \int \rho(r) \rho(r') g_{rr'} dr dr' \\ & - \frac{1}{2} \int \rho_{\uparrow}(r) U_{\uparrow}^{\text{exc}}(r) dr - \frac{1}{2} \int \rho_{\downarrow}(r) U_{\downarrow}^{\text{exc}}(r) dr, \end{aligned} \quad (1)$$

where  $u_i$ 's are the spin orbitals with occupancy  $n_i$ ;

$$f_1 = -\nabla^2 - \frac{2Z}{r}, \quad g_{rr'} = \frac{2}{|r-r'|},$$

$$\rho_{\uparrow}(r) = \sum_{i_{\uparrow}} n_i u_i^*(r) u_i(r), \quad \rho(r) = \rho_{\uparrow}(r) + \rho_{\downarrow}(r),$$

$\rho(r)$  is the total charge density,  $U_{\uparrow}^{\text{exc}}(r)$  is the exchange correlation potential at point  $r$  for up-spin electrons, and similarly for  $U_{\downarrow}^{\text{exc}}(r)$ . In the  $\Xi$  method, the exchange correlation potential is separated into a self-interaction part<sup>3</sup> and a pure exchange part as

$$U_{\uparrow}^{\text{exc}}(r) = U_{\uparrow}^s(r) + U_{\uparrow}^{\text{ex}}(r).$$

The self-interaction part, which is evaluated exactly, is given by

$$U_{\uparrow}^s(r) = \sum_{i_{\uparrow}} \left[ n_i u_i^*(r) u_i(r) \int n_i u_i^*(r') u_i(r') g_{rr'} dr' \right] / \rho_{\uparrow}(r). \quad (2)$$

The exchange potential  $U_{\uparrow}^{\text{ex}}(r)$  is given by the weighted average over all occupied up-spin orbitals:<sup>5</sup>

$$\begin{aligned} U_{\uparrow}^{\text{ex}}(r) = & 4\pi^{1/3} (2^{1/3} - 1) (1/n_{\uparrow} + \frac{1}{3})^{-2/3} \\ & \times \sum_{i_{\uparrow}} \rho_{i_{\uparrow}}(r) \rho_{\uparrow}^{-2/3}(r) n_i u_i^*(r) u_i(r) / \rho_{\uparrow}(r), \end{aligned} \quad (3)$$

where  $n_{\uparrow}$  equals the total number of up-spin electrons,  $\rho_{i_{\uparrow}}(r)$  is the density of electrons of up spin at point  $r$ , excluding the density of the electron in spin orbital  $u_{i_{\uparrow}}(r)$ ,

$$\rho_{i_{\uparrow}}(r) = \sum_{j (\neq i)} n_j u_j^*(r) u_j(r).$$

Substitution of Eqs. (2) and (3) into Eq. (1) and the application of the variational principle to  $\langle E \rangle$  leads to the set of one-electron Schrödinger equations:

$$[f_1 + V^C(r) + V_{i_{\uparrow}}^s(r) + V_{i_{\uparrow}}^{\text{ex}}(r)] u_{i_{\uparrow}}(r) = \epsilon_i u_{i_{\uparrow}}(r). \quad (4)$$

$$V_{i_{\uparrow}}^{\text{ex}}(r) = -4\pi^{1/3} (2^{1/3} - 1) (1/n_{\uparrow} + \frac{1}{3})^{-2/3} \left[ 2\rho_{i_{\uparrow}}(r) \rho_{i_{\uparrow}}^{-2/3}(r) - \frac{2}{3} \rho_{i_{\uparrow}}^{-5/3}(r) \sum_{i_{\uparrow}} n_i u_i^*(r) u_i(r) \rho_{i_{\uparrow}}(r) \right]. \quad (7)$$

The  $\Xi$  wave functions  $u_i$ 's and the eigenvalues  $\epsilon_i$ 's are obtained as usual by the iterative solution of Eq. (4).

The equations for the Dirac-Hartree-Fock central-field problem<sup>12</sup> written in Rydberg units are

$$\frac{dP_{nk}(r)}{dr} + \frac{k}{r} P_{nk}(r) - \left[ \frac{2}{\alpha} + \frac{\alpha}{2} [V(r) - \epsilon_{nk}] \right] Q_{nk}(r) = 0, \quad (8a)$$

$$\frac{dQ_{nk}(r)}{dr} - \frac{k}{r} Q_{nk}(r) + \left[ \frac{\alpha}{2} [V(r) - \epsilon_{nk}] \right] P_{nk}(r) = 0, \quad (8b)$$

where  $V(r)$  is the central-field potential,  $\epsilon_{nk}$  is the eigenvalue (less the rest energy of the electron),  $k$  is the relativistic quantum number

$$k = -(j + \frac{1}{2})a \text{ and } l = j - \frac{1}{2}a, \quad a = \pm 1$$

and  $\alpha$ , the fine-structure constant, is equal to  $1/137.036$ .  $P_{nk}(r)$  is the large component and it approaches the nonrelativistic central-field radial wave function  $P_{nl}$  for small atomic numbers. The standard treatment for this coupled set of equations is to solve the Eq. (8a) for  $Q$  and substitute it into Eq. (8b) to get

$$\frac{d^2 P_{nk}(r)}{dr^2} = (g + f) P_{nk}(r) \quad (9)$$

with

$$g = -\epsilon_{nk} + \frac{l(l+1)}{r^2} + V(r)$$

$$-\frac{d^2}{dr^2} + \frac{l_i(l_i+1)}{r^2} + V_i(r) - \frac{\alpha^2}{4} [\epsilon_i - V_i(r)]^2 - \delta_{li,0} \frac{\alpha^2}{4} \left[ 1 + \frac{\alpha^2}{4} [\epsilon_i - V(r)] \right]^{-1} \frac{dV_i(r)}{dr} \left[ \frac{dP_i/dr}{P_i} - \frac{1}{r} \right] P_i(r) = \epsilon_i P_i(r). \quad (11)$$

Cowan and Griffin have made use of the appropriate nonlocal HF potential for the third term in Eq. (11). For the relativistic terms, they have used the Hartree-exchange (HX) potential function of the HX method,<sup>13</sup> evaluated from HF radial wave functions. Gopinathan<sup>3</sup> has pointed out that the Hartree-exchange potential function of the HX method is not variationally derived.

$V^C(r)$  is the Coulomb potential given by

$$V^C(r) = \sum_j n_j \int u_j^*(r') u_j(r') g_{rr'} dr' \quad (5)$$

and  $V_{i_{\uparrow}}^s(r)$  is the self-interaction potential of the electron in  $u_i$

$$V_{i_{\uparrow}}^s(r) = -n_i \int u_i^*(r') u_i(r') g_{rr'} dr'. \quad (6)$$

$V_{i_{\uparrow}}^{\text{ex}}(r)$  is the variationally determined pure exchange potential of the  $\Xi$  method and is given by

and

$$f = -K [\epsilon - V(r)]^2 - KB \frac{dV(r)}{dr} \left[ \frac{d}{dr} - \frac{1}{r} \right] - KB \left[ \frac{k+1}{r} \right] \frac{dV(r)}{dr} = H_m(r) + H_D(r) + H_{s.o.}(r),$$

where

$$K = \alpha^2/4, \quad B = \left[ 1 + \frac{\alpha^2}{4} [\epsilon - V(r)] \right]^{-1}.$$

The operator  $f$  is the sum of the mass velocity  $H_m(r)$ , Darwin  $H_D(r)$ , and spin-orbit coupling  $H_{s.o.}(r)$  terms. The spin-orbit term only depends on the value of the relativistic quantum number  $k$ . For the present we neglect the spin-orbit term in the potential and choose to evaluate spin-orbit coupling parameters by perturbative theory. Thus from Eq. (9) we get the following second-order differential equation:

$$\left[ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) + H_m(r) + H_D(r) \right] P_{nl}(r) = \epsilon_{nl} P_{nl}(r). \quad (10)$$

If we approximate  $V(r) = -2Z/r$ , then the Darwin correction is positive for all orbitals with  $l=0$ , and it is zero for all orbitals with  $l \neq 0$ , we get the equation used by Cowan and Griffin,<sup>10</sup>

We have used the local density potentials  $V_{\Xi}(r)$  of the  $\Xi$  method for the central-field potential and in the relativistic terms in Eq. (11):

$$V_{\Xi}(r) = -\frac{2Z}{r} + V^C(r) + V_{i_{\uparrow}}^s(r) + V_{i_{\uparrow}}^{\text{ex}}(r), \quad (12)$$

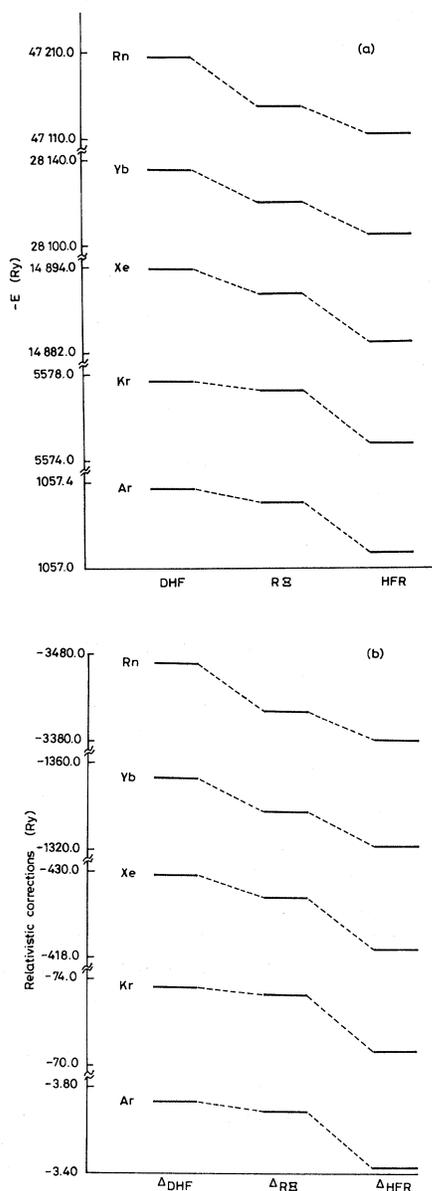


FIG. 1. (a) Relativistic total energies of atoms by the DHF, R $\Xi$ , and HFR methods. (b) Relativistic corrections to the total energies by the DHF, R $\Xi$ , and HFR methods.  $\Delta_{\text{DHF}}$  is given by  $(E_{\text{DHF}} - E_{\text{HF}})$ ;  $\Delta_{\text{R}\Xi}$  is given by  $(E_{\text{R}\Xi} - E_{\Xi})$  and  $\Delta_{\text{HFR}}$  is given by  $(E_{\text{HFR}} - E_{\text{HF}})$ .

where  $V^C(r)$ ,  $V_i^s(r)$ , and  $V_i^{\text{ex}}(r)$  are given by Eqs. (5), (6), and (7), respectively. It is already pointed out that the potential  $V_{\Xi}(r)$  is variationally derived. We shall designate the present method as the relativistic  $\Xi$  method (R $\Xi$ ).

We have solved Eq. (11) numerically by means of standard self-consistent-field (SCF) procedures. Two initial values, needed to start the outward integration via the Numerov method, are obtained by means of a small  $r$  series solution as described in the Appendix of Ref. 10. The relativistic operators are treated as part of the potential function. For the first SCF iteration, the relativistic terms are completely neglected; for the  $n$ th iteration, the

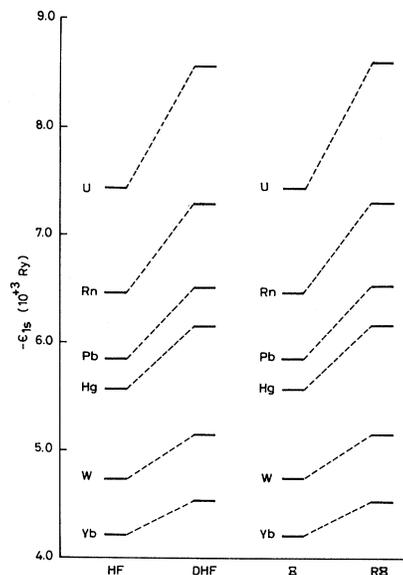


FIG. 2.  $1s$  orbital eigenvalues of various atoms by the HF, DHF,  $\Xi$ , and R $\Xi$  methods.

values of  $P_i(r)$  and  $\epsilon_i$  determined in the  $(n-1)$ th iteration are used. The radial mesh used is the Herman-Skillman<sup>14</sup> mesh in which the first mesh point  $r_1$  is given by  $r_1 = c \times 0.0025$  with  $c = \frac{1}{2}(3\pi/4)^{2/3}Z^{-1/3}$ .

### III. RESULTS

Table I gives a comparison of the total energies for various atoms as determined by the present R $\Xi$  method with those found by the DHF method and the Hartree-Fock relativistic (HFR) method.  $E_{\text{R}\Xi}$  refers to the total energy of Eq. (1) calculated using R $\Xi$  wave functions and the HF Hamiltonian. Gopinathan and Rao<sup>15</sup> have pointed out that it is appropriate only to compare the total energy of

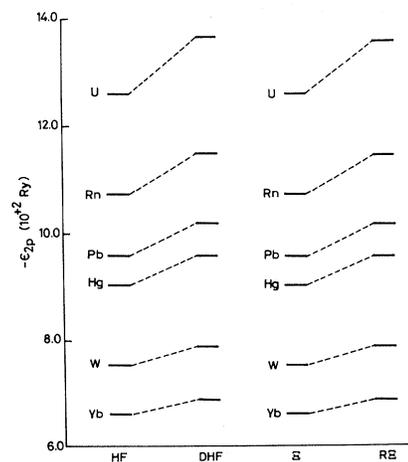


FIG. 3.  $2p$  orbital eigenvalues of various atoms by the HF, DHF,  $\Xi$ , and R $\Xi$  methods.

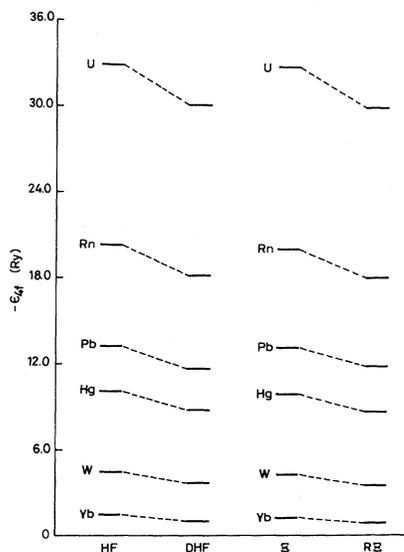


FIG. 4.  $4f$  orbital eigenvalues of various atoms by the HF, DHF,  $\Xi$ , and  $R\Xi$  methods.

the system calculated using an approximate wave function with the exact minimum energy of the *same* Hamiltonian. Table I demonstrates that, in the nonrelativistic case, the  $E_{\Xi}$  values compare well with the HF total energies, and in the relativistic case, the  $E_{R\Xi}$  values compare well with DHF total energies. Table I and Fig. (1a) also show that the  $E_{R\Xi}$  values are in better agreement with the DHF values than the values of the HFR method of Cowan and

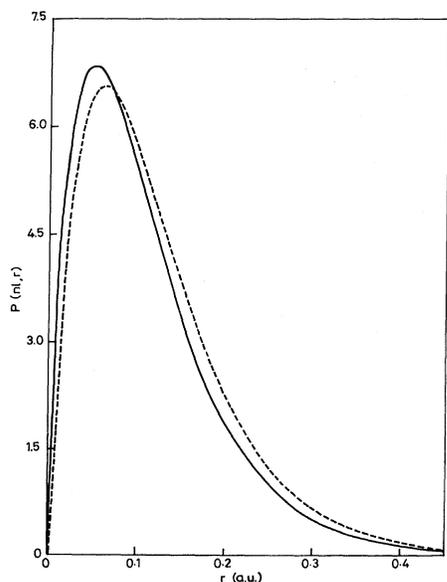


FIG. 5. Radial plot for the  $1s$  orbital of mercury. Solid line represents the relativistic wave function of the  $R\Xi$  method and the dashed line indicates the nonrelativistic wave function of the  $\Xi$  method.

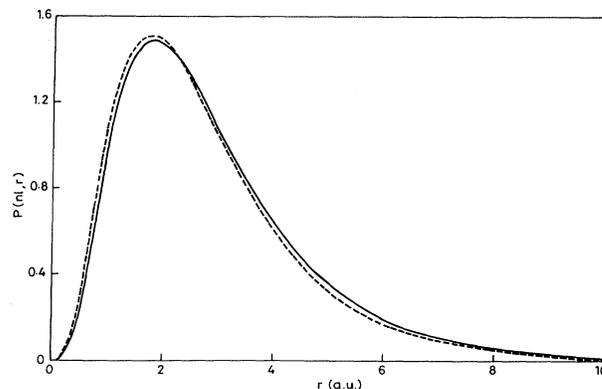


FIG. 6. Radial plot for the  $4f$  orbital of mercury. Solid line represents the relativistic wave function of the  $R\Xi$  method and the dashed line indicates the nonrelativistic wave function of the  $\Xi$  method.

Griffin. The fact that the nonrelativistic HF and  $\Xi$  total energies are nearly the same whereas the relativistic HFR total energy is poorer than that of the  $R\Xi$  values shows clearly that the present relativistic treatment is more accurate than that of Ref. 10. This is obvious from Fig. (1b), where the relativistic corrections by the various methods are compared.

Table II gives a comparison of the one-electron eigenvalues for the various atoms by the present  $R\Xi$  method, the DHF method, and the nonrelativistic HF and  $\Xi$  methods with experimental binding energies obtained by electron spectroscopy for chemical analysis (ESCA) measurements.<sup>1</sup> The one-electron eigenvalues for uranium, obtained by the HFR method, also appear in Table III. In Tables II and III the  $R\Xi$  eigenvalues refer to the HF one-electron eigenvalues calculated using  $R\Xi$  wave functions. Tables II and III indicate, generally for all orbitals, that  $R\Xi$  values are in satisfactory agreement with those obtained by the DHF method. The agreement is particularly satisfactory for the valence orbitals. For instance, our calculated valence orbital energy for the mercury  $6s$  orbital is  $-0.645$  Ry and the corresponding DHF value is  $-0.656$  Ry. Tables II and III also show small but systematic discrepancies for the inner-shell energies of heavy atoms. The calculated  $R\Xi$  value for mercury  $1s$  orbital energy is  $-6164.1$  Ry whereas the corresponding DHF value is  $-6148.5$  Ry. Part of this discrepancy may be due to the finite size of the nucleus<sup>8</sup> employed in the DHF method; we have employed the point-nucleus model in our calculations. Another discrepancy occurs for the inner shells  $1s$ ,  $2s$ , and  $2p$  in uranium (Table III), for which the present  $R\Xi$  values are inferior to the HFR values. The reason for this is not clear at present.

In Figs. 2, 3, and 4 we show the comparison of the one-electron eigenvalues by the HF, DHF,  $\Xi$ , and  $R\Xi$  methods for various atoms for various orbitals. These figures clearly show that the relativistic corrections by the present method and the DHF method are comparable.

Table IV gives the expectation values of  $r^n$  (for  $n = -1, 1, \text{ and } 2$ ) for xenon, mercury, and uranium by the rela-

TABLE I. Total energies (in Ry) for various atoms by the relativistic DHF,  $R\Xi$ , and HFR methods and the nonrelativistic HF and  $\Xi$  methods.

Atom	Relativistic		Nonrelativistic		
	$-E_{\text{DHF}}^{\text{a}}$	$-E_{R\Xi}^{\text{b}}$	$-E_{\text{HFR}}^{\text{c}}$	$-E_{\text{HF}}^{\text{d}}$	$-E_{\Xi}^{\text{b}}$
Ne( $2p^6$ )	257.3831	257.3504	257.3990	257.0948	257.0660
Ar( $3p^6$ )	1 057.3669	1 057.3046	1 057.0660	1 053.6370	1 053.6198
Zn( $3d^{10}$ )	3 589.2363	3 588.9257	3 589.8131	3 555.6940	3 555.5380
Kr( $4p^6$ )	5 577.7163	5 577.2506	5 574.7880	5 504.1140	5 503.9609
Xe( $5p^6$ )	14 893.8013	14 890.2080	14 883.5300	14 464.3000	14 463.8610
Yb( $4f^{14}$ )	28 315.4392	28 120.1210	28 104.8400	26 782.8600	26 782.2730
Hg( $6s^2$ )	39 297.7060	39 261.8790	39 259.0086	36 817.9400	36 817.0790
Rn( $6p^6$ )	47 203.9558	47 147.7620	47 115.8300	43 733.5800	43 732.3900
U( $5f^36d$ )	56 105.0414	56 019.4180		51 328.4354	51 327.2360

<sup>a</sup>DHF values from Ref. 8.

<sup>b</sup>See the text for the explanation of symbols.

<sup>c</sup>Hartree-Fock-relativistic (HFR) values of Cowan and Griffin from Ref. 10. For the atoms Zn and Hg the HFR values are taken from Ref. 16.

<sup>d</sup>Hartree-Fock average energy values from Ref. 17. Values for U taken from Ref. 18.

TABLE II. Comparison of orbital eigenvalues  $-\epsilon_i$  (in Ry) for various atoms by HF,  $\Xi$ , DHF, and  $R\Xi$  methods with experimental binding energies.

Atom	Orbital	Nonrelativistic		Relativistic		Expt. <sup>d</sup>
		HF <sup>a</sup>	$\Xi^{\text{b}}$	DHF <sup>c</sup>	$R\Xi^{\text{b}}$	
Ne	1s	65.5451	65.2391	65.6349	65.3293	63.9618
	2s	3.8608	3.7669	3.8617	3.7779	3.5590
	2p	1.7008	1.6216	1.6996	1.6207	1.5869
Ar	1s	237.2216	236.6493	238.2352	237.6992	235.6413
	2s	24.6443	24.4085	24.8232	24.5893	23.9838
	2p	19.1429	18.8998	19.1507	18.9150	18.3134
	3s	2.5547	2.5177	2.5732	2.5363	2.1536
	3p	1.1820	1.1530	1.1807	1.1519	1.1621
Kr	1s	1040.3320	1039.1797	1059.3710	1058.6990	1053.0687
	2s	139.8067	139.1402	144.1596	143.6116	141.4627
	2p	126.0194	125.3102	127.0887	126.5055	124.6527
	3s	21.6990	21.4613	22.4489	22.2197	21.5215
	3p	16.6630	16.4274	16.8303	16.6060	15.9500
	3d	7.6504	7.4144	7.4943	7.2684	6.9298
	4s	2.3059	2.2680	2.3755	2.3373	2.0140
	4p	1.0484	1.0179	1.0468	1.0162	1.0450
Xe	1s	2448.8070	2447.1850	2554.5180	2555.4979	2540.6101
	2s	378.6815	377.7408	404.9300	404.6909	400.8232
	2p	355.5651	354.5529	363.3923	362.8151	359.7158
	3s	80.3517	79.9218	86.0209	85.7181	84.4322
	3p	70.4435	69.9993	72.2069	71.8266	70.6431
	3d	52.2378	51.7644	51.4632	51.1056	50.0875
	4s	15.7127	15.5538	16.8599	16.7179	15.6707
	4p	12.0167	11.8613	12.2787	12.1269	10.9764
	4d	5.5567	5.4139	5.3296	5.2006	5.0202
	5s	1.8889	1.8502	2.0203	1.9820	1.7126
	5p	0.9146	0.8816	0.9148	0.8810	0.9234
Yb	1s	4209.1960	4207.3076	4535.3120	4542.3610	4508.2690
	2s	692.0199	690.8602	777.7854	778.9684	771.0400
	2p	660.3944	659.1516	688.6859	687.3961	682.9107
	3s	158.3792	157.8126	179.4192	179.3423	176.4792
	3p	143.8618	143.2676	151.7399	151.1508	149.2098

TABLE II. (Continued).

Atom	Orbital	Nonrelativistic		Relativistic		Expt. <sup>d</sup>
		HF <sup>a</sup>	$\Xi^b$	DHF <sup>c</sup>	$R\Xi^b$	
	3d	117.1693	116.5152	116.2222	115.9673	113.9728
	4s	32.1902	31.9965	37.3450	37.2363	36.0162
	4p	26.1673	25.9730	28.0149	27.7838	26.8778
	4d	15.3226	15.1320	15.1289	14.9847	14.2595
	4f	1.4647	1.3083	1.0107	0.8620	0.5460
	5s	4.1977	4.1284	4.8790	4.8136	4.2631
	5p	2.4117	2.3407	2.5232	2.4364	2.4256
	6s	0.3649	0.3497	0.3930	0.3749	0.4593
Hg	1s	5557.3690	5555.3859	6148.4700	6164.0942	6108.6365
	2s	941.4719	940.1737	1100.5024	1103.8112	1091.1430
	2p	904.3595	902.9795	958.1104	954.8370	950.3859
	3s	226.2741	225.6121	266.2262	266.6287	262.1830
	3p	208.6814	207.9823	223.8189	222.7984	220.1887
	3d	176.2901	175.5155	174.7734	174.7568	171.7016
	4s	51.1474	50.8962	61.2967	61.2721	54.2429
	4p	43.3981	43.1474	47.0008	46.6248	45.1060
	4d	29.2193	28.9685	28.7004	28.5708	27.1060
	4f	10.0247	9.7952	8.7615	8.5824	7.6968
	5s	8.3643	8.2997	10.2061	10.1825	9.1878
	5p	5.7019	5.6308	6.1479	6.0490	5.4147
	5d	1.4284	1.3611	1.2096	1.1601	0.9408
	6s	0.5221	0.5029	0.6561	0.6451	0.7644
Rn	1s	6460.6530	6458.3467	7282.3020	7307.2580	7232.9291
	2s	1113.8300	1112.4455	1337.6060	1343.1836	1327.0856
	2p	1073.3550	1071.8791	1149.6882	1143.8094	1140.8551
	3s	276.8453	276.0867	333.6624	334.5580	329.5112
	3p	257.3436	256.5552	278.9040	277.3017	271.1258
	3d	221.4026	220.5221	219.3645	219.5518	216.2146
	4s	67.8421	67.5158	82.6266	82.6865	80.5586
	4p	58.9825	58.6568	64.1741	63.5811	62.4035
	4d	42.6624	42.3312	41.7652	41.6194	40.3969
	4f	20.2148	19.8934	18.6843	17.8531	17.4936
	5s	13.8119	13.6880	16.8180	16.7728	15.5825
	5p	10.4505	10.3288	11.1740	10.9900	10.6579
	5d	4.6525	4.5429	4.1718	4.0956	3.8589
	6s	1.7480	1.7106	2.1429	2.1144	1.7641
	6p	0.8560	0.8231	0.8723	0.8276	0.8673

<sup>a</sup>Hartree-Fock values from Ref. 17.

<sup>b</sup>See the text for the explanation of symbols.

<sup>c</sup>Dirac-Hartree-Fock values from Ref. 8. Values quoted are for the centers of gravity of  $j$  doublets.

<sup>d</sup>Experimental binding energies by ESCA (electron spectroscopy for chemical analysis) measurements from Ref. 1.

tivistic DHF and  $R\Xi$  methods as well as by the nonrelativistic HF and  $\Xi$  methods. From Tables II, III, and IV it is quite clear that the present approach approximates the major relativistic effects remarkably well. These tables also support the following observations made earlier by Mayers,<sup>19</sup> Boyd *et al.*,<sup>20</sup> Desclaux and Kim,<sup>21</sup> and Rose *et al.*<sup>22</sup>

(i) In the inner core of an atom, the motion of an electron is primarily affected by the nuclear potential and the direct relativistic effect dominates. This effect causes the contraction of the orbital. Therefore, the relativistic  $s$  and

$p$  electrons are more tightly bound than the nonrelativistic ones, as is evident from the  $\langle r \rangle$  values. For example, see Fig. 5 where the relativistic contraction of the  $1s$  orbital of mercury is shown.

(ii) Because of the increased screening by the contracted relativistic core, the nonpenetrating valence electrons do expand. This is an indirect relativistic effect and because of this the relativistic  $d$  and  $f$  electrons are more loosely bound than the nonrelativistic ones. In Fig. 6 the relativistic expansion of the  $4f$  orbital of mercury is shown.

(iii) However, the valence  $6s$  orbital of mercury and  $7s$

TABLE III. Comparison of orbital eigenvalues  $-\epsilon_i$  (in Ry) for various calculations on  $U(5f^36d^17s^2)$  with experimental binding energies.

Orbital	Nonrelativistic		DHF <sup>c</sup>	Relativistic		Expt. <sup>e</sup>
	HF <sup>a</sup>	$\Xi^b$		R $\Xi^b$	HFR <sup>d</sup>	
1s	7433.4780	7431.3617	8558.4660	8598.4962	8591	8497
2s	1301.9399	1300.4437	1612.3184	1621.4147	1619	1599
2p	1258.0847	1256.4983	1365.0096	1354.5310	1357	1374
3s	333.3312	332.5270	413.2196	415.0074	415	407.8
3p	311.8888	311.0510	342.4964	339.9068	340.8	337.9
3d	272.3442	271.4213	270.1173	270.5888	271.6	266.3
4s	87.0378	86.6612	108.6484	108.9070	109.0	106.0
4p	77.0320	76.6537	84.8512	83.9495	84.3	82.4
4d	58.5181	58.1392	57.5436	57.4187	57.8	55.5
4f	32.8164	32.4342	29.9379	29.6932	30.1	28.4
5s	20.1194	19.9604	25.1926	25.1652	25.3	23.8
5p	16.0654	15.9078	17.5423	17.2401	17.4	15.9
5d	8.8843	8.7360	8.3311	8.2224	8.37	7.3
5f	1.2689	1.1511	0.6627	0.5611	0.663	
6s	3.3647	3.2880	4.2759	4.2123	4.28	5.2
6p	2.0715	1.9947	2.2083	2.0940	2.17	2.67
6d	0.5331	0.4707	0.3741	0.3290	0.376	
7s	0.3334	0.3143	0.4047	0.3830	0.4030	

<sup>a</sup>Hartree-Fock values taken from Ref. 18.

<sup>b</sup>See the text for explanation.

<sup>c</sup>Dirac-Hartree-Fock values from Ref. 8. Values quoted are for the centers of gravity of  $j$  doublets.

<sup>d</sup>Hartree-Fock-relativistic values of Cowan and Griffin from Ref. 10.

<sup>e</sup>Experimental values by ESCA measurements from Ref. 1.

TABLE IV. Expectation values of  $r^n$  ( $n = -1, 1, 2$ ) for Xe, Hg, and U (in atomic units). The numbers in parentheses indicate the powers of 10 by which the associated numbers are to be multiplied, e.g.,  $0.5811(+2) = 0.5811 \times 10^2$ .

Atom, orbital, and $\langle r^n \rangle$		DHF <sup>a</sup>	HF <sup>b</sup>	R $\Xi^c$	$\Xi^c$	
Xe	1s	$\langle r^{-1} \rangle$	0.5811(+2)	0.5347(+2)	0.5806(+2)	0.5345(+2)
		$\langle r \rangle$	0.2665(-1)	0.2814(-1)	0.2666(-1)	0.2814(-1)
		$\langle r^2 \rangle$	0.9634(-3)	0.1059(-2)	0.9635(-3)	0.1059(-2)
	2s	$\langle r^{-1} \rangle$	0.1361(+2)	0.1231(+2)	0.1333(+2)	0.1232(+2)
		$\langle r \rangle$	0.1140	0.1209	0.1143	0.1207
		$\langle r^2 \rangle$	0.1540(-1)	0.1716(-1)	0.1541(-1)	0.1711(-1)
	2p	$\langle r^{-1} \rangle$	0.1283(+2)	0.1229(+2)	0.1272(+2)	0.1235(+2)
		$\langle r \rangle$	0.1001	0.1031	0.1001	0.1026
		$\langle r^2 \rangle$	0.1227(-1)	0.1292(-1)	0.1221(-1)	0.1278(-1)
	3s	$\langle r^{-1} \rangle$	0.4884(+1)	0.4527(+1)	0.4798(+1)	0.4502(+1)
		$\langle r \rangle$	0.3046	0.3187	0.3061	0.3201
		$\langle r^2 \rangle$	0.1062	0.1159	0.1070	0.1169
	3p	$\langle r^{-1} \rangle$	0.4607(+1)	0.4445(+1)	0.4538(+1)	0.4436(+1)
		$\langle r \rangle$	0.3030	0.3094	0.3040	0.3101
		$\langle r^2 \rangle$	0.1064	0.1108	0.1071	0.1112
	3d	$\langle r^{-1} \rangle$	0.4321(+1)	0.4304(+1)	0.4327(+1)	0.4316(+1)
		$\langle r \rangle$	0.2897	0.2803	0.2795	0.2798
		$\langle r^2 \rangle$	0.9258(-1)	0.9263(-1)	0.9222(-1)	0.9228(-1)
	4s	$\langle r^{-1} \rangle$	0.1950(+1)	0.1843(+1)	0.1959(+1)	0.1857(+1)
		$\langle r \rangle$	0.7172	0.7453	0.7159	0.7462
		$\langle r^2 \rangle$	0.5800	0.6256	0.5790	0.6286
	4p	$\langle r^{-1} \rangle$	0.1787(+1)	0.1741(+1)	0.1792(+1)	0.1759(+1)
		$\langle r \rangle$	0.7645	0.7770	0.7640	0.7770
		$\langle r^2 \rangle$	0.6646	0.6855	0.6646	0.6872

TABLE IV. (Continued).

Atom, orbital, and $\langle r^n \rangle$		DHF <sup>a</sup>	HF <sup>b</sup>	RE <sup>c</sup>	$\Xi^c$		
	4d	$\langle r^{-1} \rangle$	0.1504(+1)	0.1509(+1)	0.1519(+1)	0.1528(+1)	
		$\langle r \rangle$	0.8763	0.8705	0.8740	0.8680	
		$\langle r^2 \rangle$	0.8944	0.8809	0.8908	0.8778	
	5s	$\langle r^{-1} \rangle$	0.6812	0.6479	0.7069	0.6732	
		$\langle r \rangle$	0.1905(+1)	0.1981(+1)	0.1861(+1)	0.1942(+1)	
		$\langle r^2 \rangle$	0.4111(+1)	0.4440(+1)	0.3924(+1)	0.4274(+1)	
	5p	$\langle r^{-1} \rangle$	0.5560	0.5472	0.5671	0.5619	
		$\langle r \rangle$	0.2315(+1)	0.2338(+1)	0.2296(+1)	0.2314(+1)	
		$\langle r^2 \rangle$	0.6167(+1)	0.6277(+1)	0.6068(+1)	0.6161(+1)	
	Hg	1s	$\langle r^{-1} \rangle$	0.9750(+2)	0.7945(+2)	0.9750(+2)	0.7943(+2)
			$\langle r \rangle$	0.1691(-1)	0.1892(-1)	0.1658(-1)	0.1892(-1)
			$\langle r^2 \rangle$	0.3809(-3)	0.4780(-3)	0.3803(-3)	0.4783(-3)
2s		$\langle r^{-1} \rangle$	0.2403(+2)	0.1873(+2)	0.2294(+2)	0.1874(+2)	
		$\langle r \rangle$	0.6923(-1)	0.7962(-1)	0.6975(-1)	0.7952(-1)	
		$\langle r^2 \rangle$	0.5735(-2)	0.7429(-2)	0.5766(-2)	0.7408(-2)	
2p		$\langle r^{-1} \rangle$	0.2091(+2)	0.1874(+2)	0.2016(+2)	0.1880(+2)	
		$\langle r \rangle$	0.6276(-1)	0.6734(-1)	0.6335(-1)	0.6710(-1)	
		$\langle r^2 \rangle$	0.4853(-2)	0.5491(-2)	0.4895(-2)	0.5449(-2)	
3s		$\langle r^{-1} \rangle$	0.8830(+1)	0.7284(+1)	0.8500(+1)	0.7268(+1)	
		$\langle r \rangle$	0.1798	0.20004	0.1803	0.2006	
		$\langle r^2 \rangle$	0.3712(-1)	0.4577(-1)	0.3720(-1)	0.4581(-1)	
3p		$\langle r^{-1} \rangle$	0.7943(+1)	0.7226(+1)	0.7640(+1)	0.7230(+1)	
		$\langle r \rangle$	0.1809	0.1911	0.1820	0.1909	
		$\langle r^2 \rangle$	0.3813(-1)	0.4222(-1)	0.3831(-1)	0.4209(-1)	
3d		$\langle r^{-1} \rangle$	0.7269(+1)	0.7144(+1)	0.7266(+1)	0.7170(+1)	
		$\langle r \rangle$	0.1651	0.1670	0.1646	0.1663	
		$\langle r^2 \rangle$	0.3195(-1)	0.3256(-1)	0.3168(-1)	0.3225(-1)	
4s		$\langle r^{-1} \rangle$	0.3720(+1)	0.3193(+1)	0.3649(+1)	0.3182(+1)	
		$\langle r \rangle$	0.3990	0.4393	0.3989	0.4414	
		$\langle r^2 \rangle$	0.1798	0.2172	0.1796	0.2193	
4p		$\langle r^{-1} \rangle$	0.3349(+1)	0.3103(+1)	0.3261(+1)	0.3097(+1)	
		$\langle r \rangle$	0.4232	0.4433	0.4249	0.4449	
		$\langle r^2 \rangle$	0.2039	0.2228	0.2050	0.2245	
4d		$\langle r^{-1} \rangle$	0.2958(+1)	0.2920(+1)	0.2942(+1)	0.2919(+1)	
		$\langle r \rangle$	0.4481	0.4503	0.4489	0.4512	
		$\langle r^2 \rangle$	0.2336	0.2336	0.2325	0.2347	
4f		$\langle r^{-1} \rangle$	0.2537(+1)	0.2584(+1)	0.2548(+1)	0.2595(+1)	
		$\langle r \rangle$	0.4804	0.4692	0.4781	0.4672	
		$\langle r^2 \rangle$	0.2775	0.2634	0.2746	0.2610	
5s		$\langle r^{-1} \rangle$	0.1488(+1)	0.1303(+1)	0.1510(+1)	0.1338(+1)	
		$\langle r \rangle$	0.9152	0.1010(+1)	0.9009	0.1000(+1)	
		$\langle r^2 \rangle$	0.9396	0.1143(+1)	0.9105(+1)	0.1122(+1)	
5p		$\langle r^{-1} \rangle$	0.1270(+1)	0.1193(+1)	0.1279(+1)	0.1220(+1)	
		$\langle r \rangle$	0.1048(+1)	0.1095(+1)	0.1037(+1)	0.1084(+1)	
		$\langle r^2 \rangle$	0.1216(+1)	0.1355(+1)	0.1216(+1)	0.1329(+1)	
5d	$\langle r^{-1} \rangle$	0.8943	0.9103	0.8864	0.9079		
	$\langle r \rangle$	0.1472(+1)	0.1433(+1)	0.1493(+1)	0.1454(+1)		
	$\langle r^2 \rangle$	0.2566(+1)	0.2410(+1)	0.2646(+1)	0.2494(+1)		
6s	$\langle r^{-1} \rangle$	0.4506	0.3761	0.4818	0.4149		
	$\langle r \rangle$	0.2843(+1)	0.3328(+1)	0.2655(+1)	0.3058(+1)		
	$\langle r^2 \rangle$	0.9353(+1)	0.1280(+2)	0.8102(+1)	0.1078(+2)		
U	1s	$\langle r^{-1} \rangle$	0.1224(+3)	0.9144(+2)	0.1227(+3)	0.9142(+2)	
		$\langle r \rangle$	0.1366(-1)	0.1644(-1)	0.1363(-1)	0.1644(-1)	
		$\langle r^2 \rangle$	0.2620(-3)	0.3610(-3)	0.2609(-3)	0.3610(-3)	
	2s	$\langle r^{-1} \rangle$	0.3096(+2)	0.2170(+2)	0.2898(+2)	0.2172(+2)	
		$\langle r \rangle$	0.5653(-1)	0.6877(-1)	0.5714(-1)	0.6869(-1)	
		$\langle r^2 \rangle$	0.3858(-2)	0.5539(-2)	0.3887(-2)	0.5525(-2)	

TABLE IV. (Continued).

Atom, orbital, and $\langle r^n \rangle$	DHF <sup>a</sup>	HF <sup>b</sup>	RE <sup>c</sup>	$\Xi^c$	
2p	$\langle r^{-1} \rangle$	0.2548(+2)	0.2172(+2)	0.2395(+2)	0.2178(+2)
	$\langle r \rangle$	0.5263(-1)	0.5804(-1)	0.5350(-1)	0.5786(-1)
	$\langle r^2 \rangle$	0.3439(-2)	0.4075(-2)	0.3497(-2)	0.4047(-2)
3s	$\langle r^{-1} \rangle$	0.1128(+2)	0.8558(+1)	0.1068(+2)	0.8546(+1)
	$\langle r \rangle$	0.1470	0.1711	0.1475	0.1711
	$\langle r^2 \rangle$	0.2491(-1)	0.3333(-1)	0.2492(-1)	0.3332(-1)
3p	$\langle r^{-1} \rangle$	0.9753(+1)	0.8509(+1)	0.9183(+1)	0.8517(+1)
	$\langle r \rangle$	0.1505	0.1624	0.1519	0.1622
	$\langle r^2 \rangle$	0.2648(-1)	0.3048(-1)	0.2670(-1)	0.3037(-1)
3d	$\langle r^{-1} \rangle$	0.8666(+1)	0.8444(+1)	0.8643(+1)	0.8473(+1)
	$\langle r \rangle$	0.1385	0.1409	0.1382	0.1403
	$\langle r^2 \rangle$	0.2244(-1)	0.2311(-1)	0.2228(-1)	0.2291(-1)
4s	$\langle r^{-1} \rangle$	0.4820(+1)	0.3884(+1)	0.4660(+1)	0.3862(+1)
	$\langle r \rangle$	0.3198	0.3640	0.3198	0.3658
	$\langle r^2 \rangle$	0.1156	0.1490	0.1154	0.1504
4p	$\langle r^{-1} \rangle$	0.4237(+1)	0.3804(+1)	0.4049(+1)	0.3788(+1)
	$\langle r \rangle$	0.3418	0.3637	0.3442	0.3652
	$\langle r^2 \rangle$	0.1331	0.1498	0.1342	0.1510
4d	$\langle r^{-1} \rangle$	0.3723(+1)	0.3648(+1)	0.3686(+1)	0.3640(+1)
	$\langle r \rangle$	0.3570	0.3603	0.3581	0.3612
	$\langle r^2 \rangle$	0.1467	0.1489	0.1473	0.1498
4f	$\langle r^{-1} \rangle$	0.3351(+1)	0.3397(+1)	0.3363(+1)	0.3409(+1)
	$\langle r \rangle$	0.3544	0.3481	0.3529	0.3470
	$\langle r^2 \rangle$	0.1469	0.1412	0.1456	0.1403
5s	$\langle r^{-1} \rangle$	0.2111(+1)	0.1776(+1)	0.2103(+1)	0.1793(+1)
	$\langle r \rangle$	0.6720	0.7567	0.6662	0.7563
	$\langle r^2 \rangle$	0.5043	0.6377	0.4961	0.6386
5p	$\langle r^{-1} \rangle$	0.1804(+1)	0.1686(+1)	0.1805(+1)	0.1703(+1)
	$\langle r \rangle$	0.7497	0.7900	0.7487	0.7892
	$\langle r^2 \rangle$	0.6317	0.6981	0.6287	0.6981
5d	$\langle r^{-1} \rangle$	0.1488(+1)	0.1485(+1)	0.1496(+1)	0.1501(+1)
	$\langle r \rangle$	0.8868	0.8813	0.8836	0.8793
	$\langle r^2 \rangle$	0.8930	0.8794	0.8861	0.8764
5f	$\langle r^{-1} \rangle$	0.9224	0.1025(+1)	0.9193	0.1022(+1)
	$\langle r \rangle$	0.1445(+1)	0.1274(+1)	0.1456(+1)	0.1286(+1)
	$\langle r^2 \rangle$	0.2583(+1)	0.1944(+1)	0.2617(+1)	0.1983(+1)
6s	$\langle r^{-1} \rangle$	0.8848	0.7469	0.8969	0.7659
	$\langle r \rangle$	0.1497(+1)	0.1708(+1)	0.1472(+1)	0.1690(+1)
	$\langle r^2 \rangle$	0.2505(+1)	0.3248(+1)	0.2421(+1)	0.3189(+1)
6p	$\langle r^{-1} \rangle$	0.7152	0.6636	0.7101	0.6759
	$\langle r \rangle$	0.1820(+1)	0.1914(+1)	0.1818(+1)	0.1904(+1)
	$\langle r^2 \rangle$	0.3746(+1)	0.4114(+1)	0.3724(+1)	0.4080(+1)
6d	$\langle r^{-1} \rangle$	0.3986	0.4419	0.3988	0.4371
	$\langle r \rangle$	0.3236(+1)	0.2875(+1)	0.3254(+1)	0.2964(+1)
	$\langle r^2 \rangle$	0.1246(+2)	0.9629(+1)	0.1260(+2)	0.1036(+2)
7s	$\langle r^{-1} \rangle$	0.2879	0.2418	0.3128	0.2700
	$\langle r \rangle$	0.4341(+1)	0.5050(+1)	0.4047(+1)	0.4659(+1)
	$\langle r^2 \rangle$	0.2141(+2)	0.2884(+2)	0.1861(+2)	0.2467(+2)

<sup>a</sup>Weighted average of the Dirac-Hartree-Fock values from Ref. 8.

<sup>b</sup>Hartree-Fock values from Ref. 18.

<sup>c</sup>Present work.

orbital of uranium contract. This has been attributed to the expansion of 5d in the case of mercury and 6d in the case of uranium causing a decrease in the shielding of the valence s electrons by the d electrons. Hence a contraction of the valence orbital occurs.

(iv) For the valence orbitals, the relativistic values are

closer to the experimental binding energies than the nonrelativistic values.

Experimental and calculated spin-orbit parameter values for uranium appear in Table V. We have used first-order perturbation theory to compute the spin-orbit parameter. The usual Pauli form of the spin-orbit opera-

TABLE V. Spin-orbit parameters (in Ry) for uranium ( $5f^36d^17s^2$ ).

Orbital	HF <sup>a</sup>	$\Xi^b$	DHF <sup>c</sup>	$R\Xi^d$	HFR <sup>e</sup>	Expt. <sup>f</sup>
2p	132.8	134.492	187.8	192.670	199.1	185.3
3p	30.1	30.306	43.72	43.989	46.2	43.0
3d	4.93	4.996	5.29	5.364	5.33	5.17
4p	7.80	7.778	11.54	11.355	11.98	11.2
4d	1.166	1.165	1.288	1.253	1.264	1.23
4f	0.231	0.237	0.250	0.227	0.221	0.23
5p	1.761	1.857	2.763	2.687	2.701	3.2
5d	0.216	0.229	0.334	0.239	0.230	0.26
5f	0.021	0.022		0.017	0.017	0.016
6p	0.267	0.299	0.539	0.431	0.427	0.49
6d	0.021	0.017		0.014	0.014	0.019

<sup>a</sup>Hartree-Fock values taken from Ref. 10.

<sup>b</sup>Nonrelativistic  $\Xi$  values calculated using the operator  $\xi(r)=2Kr^{-1}dV(r)/dr$ .

<sup>c</sup>Dirac-Hartree-Fock values calculated using Eq. (16) in the text.

<sup>d</sup>Present work.

<sup>e</sup>Taken from Ref. 10.

<sup>f</sup>Experimental values quoted in Ref. 10.

tor<sup>12</sup> for a central-field problem is given by

$$H_{s.o.}^P(r) = -K \left[ \frac{-l}{l+1} \right] \frac{1}{r} \frac{dV}{dr}, \quad (13)$$

where  $-l$  refers to  $j = 1 + \frac{1}{2}$  and  $(l+1)$  to  $j = l - \frac{1}{2}$ . The more correct form of the spin-orbit operator,<sup>10,11</sup> obtained from Eq. (9), is given by

$$H_{s.o.}(r) = BH_{s.o.}^P(r). \quad (14)$$

We have used the following operator in the perturbation theory to compute spin-orbit parameter values:

$$\xi(r) = 2KB \frac{1}{r} \frac{dV(r)}{dr}, \quad (15)$$

where

$$K = \alpha^2/4, \quad B = \left[ 1 + \frac{\alpha^2}{4} [\epsilon - V(r)] \right]^{-1},$$

and  $V(r)$  is the  $\Xi$  potential given by Eq. (12). The spin-orbit parameter values quoted in Table V for the DHF method are calculated using the equation

$$\xi_{nl} = \frac{2}{(2l+1)} (\epsilon_{nlj_+} - \epsilon_{nlj_-}), \quad (16)$$

where the  $\epsilon$ 's are the central-field eigenvalues, taken from Ref. 8. Except for the 2p spin-orbit parameter values, all the other values by the present method are comparable to the DHF and experimental values. The higher value for

the 2p orbital may be due to the fact that the expectation value of  $r^{-1}dV(r)/dr$  is very sensitive to the nature of the wave function near the nucleus; furthermore, we have not considered the finite size of the nucleus in the present calculations.

#### IV. CONCLUSIONS

The results given above show that the  $R\Xi$  method presented in this paper is able to approximate the major relativistic effects of contraction and dilation of the orbitals. The present method is somewhat simpler than the HFR method of Cowan and Griffin in the sense that the fairly tedious nonlocal exchange computations are absent, and may save considerable computer time when this potential is used in molecular calculations. Total energies of atoms calculated by the  $R\Xi$  method are closer to the DHF results than the previously reported HFR results. The relativistic effects on the spin-orbit coupling parameter are also well described by our formalism as is evident from the results for  $U$ . Note that this method does not distinguish between the spin-orbit levels for electrons with  $l \neq 0$ .

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