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Improved Pauli Hamiltonian for local-potential problems

J. H. Wood and A. Michael Boring
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

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A recently published scheme for obtaining an approximate solution of the Dirac-Hartree-Fock equations for an atom is adapted and applied to the related Dirac-Slater problem. For a given nl, one solves explicitly only for one large component orbital instead of the four determined in the Dirac-Slater calculations. The equation for this single component is closely akin to the Pauli equation. [We find that the Pauli mass-velocity and Darwin operators are accurate to only zeroth (instead of first) order in $(E-V)/c^2$. We present forms which are accurate to first order for cases in which the expansion in $(E-V)/c^2$ is valid.] Atomic calculations for uranium and plutonium demonstrate that this approximate method yields eigenvalues, eigenfunctions, spin-orbit parameters, and excitation energies in close agreement with the Dirac-Slater results. The method can be incorporated into existing nonrelativistic molecular and energy-band computer programs (such as those for the molecular scattered-wave method and the KKR and APW energy-band methods). This would then permit nearly relativistic solutions of the related problems without the complications introduced by the four-component-type solutions. We discuss implementation of the method for the scattered wave and APW methods.

INTRODUCTION

Cowan and Griffin[1] have described an approximate method of solution of the Dirac-Hartree-Fock equations for an atom. Here we apply their methods to the Dirac-Slater atomic problem.[2] In solving this latter problem exactly, one computes two radial wave functions G_{nlj} and F_{nlj} for each set of the one-electron central-field quantum numbers n, l, and j. (Pictures of these functions appropriate to the central-field Coulomb potential may be found in Rose's book.[3]) The so-called large component G_{nlj} approaches the nonrelativistic central-field radial function P_{nl} for small atomic numbers. The radial electronic charge density $R(r)$ is given by the sum over occupied orbitals

$$R(r)=\sum (2j+1)[G^2_{nlj}(r)+F^2_{nlj}(r)]\,. \tag{1}$$

Taking the Dirac-Slater solutions for the uranium atom as an example and integrating this equation from $r=0$ to $r=\infty$, we find that the integral over the large components yields 91.25 charge units and that over the small components gives 0.75 charge units. That is, only about 1% of the total charge is described by the small components–this strongly suggests that some sort of approximation scheme is feasible. We find that the Cowan-Griffin method, in which only the large components G are explicitly treated, provides such a scheme.

APPROXIMATION SCHEMES

The equations for the Dirac central-field problem[4] written in rydberg atomic units[5] are

$$F_k=\frac{\alpha}{2}\frac{1}{1+\frac{1}{4}\alpha^2(\epsilon-V)}\left(\frac{d}{dr}+\frac{k}{r}\right)G_k\,,$$
$$G_k=\frac{-2}{\alpha(\epsilon-V)}\left(\frac{d}{dr}-\frac{k}{r}\right)F_k \tag{2}$$

where V is the central-field potential, ϵ is the eigenvalue (less the rest energy of the electron) and where the quantum number k is related to the more familiar l and j according to $k=l$ for $j=l-\frac{1}{2}$ and $k=-(l+1)$ for $j=l+\frac{1}{2}$. The second-order equation used by Cowan and Griffin (and also derived in the work of Choo and Pratt[6]) is obtained by substituting F from the first of these equations into the second:

$$\frac{d^2G}{dr^2}=(g+f)G\,,$$

with

$$g=-\epsilon+l(l+1)/r^2+V\,,$$

and with

$$f=-K(\epsilon-V)^2-KB\frac{dV}{dr}\left(\frac{d}{dr}-\frac{1}{r}\right)-KB\left(\frac{k+1}{r}\right)\frac{dV}{dr}$$
$$=H_m(r)+H_D(r)+H_{so}(r)\,, \tag{3}$$

where

$$K=\alpha^2/4 \quad\text{and}\quad B=[1+\tfrac{1}{4}\alpha^2(\epsilon-V)]^{-1}\,. \tag{4}$$

The operator f is the sum of the mass-velocity, Darwin, and spin-orbit coupling terms. Equation (3) of Cowan and Griffin,[7]

$$\left(-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}+V+H_m(r)+H_d(r)\right)G_{nl}=\epsilon_{nl}G_{nl}\,, \tag{5}$$

follows by dropping the spin-orbit term; following those authors, we propose to handle spin-orbit effects by first-order perturbation theory.

The difference between these results and what is usually called the Pauli theory[4] is the presence of the factor B in the Darwin and spin-orbit operators. The Pauli expressions arise from expanding B according to

$$B=[1+\tfrac{1}{4}\alpha^2(\epsilon-V)]^{-1}=1-\tfrac{1}{4}\alpha^2(\epsilon-V)+\tfrac{1}{16}\alpha^4(\epsilon-V)^2\cdots \tag{6}$$

and although it is generally claimed[4] that the first two terms of the expansions are retained in the Pauli expressions, we see that only the first term is retained—that is, B is set to 1; this matter is pursued in Appendix A. As Cowan and Griffin have shown, use of the expansion is unnecessary. Its employment leads to fairly serious errors for high Z atoms. The expansion is valid only for $K(\epsilon-V)<1$ and if for small r we approximate V as $-2Z/r$ and neglect ϵ, the requirement is $r>2.7\times10^{-5}Z$ which for uranium yields $r>2.4\times10^{-3}$ a.u. [If the standard Herman-Skillman radial mesh (see Appendix B) is used, this value of r corresponds to the sixth mesh point.]

We could get an approximate (because of the neglect of the spin-orbit terms) solution of the Dirac-Slater (DS) problem by a self-consistent treatment of the second-order equations (5) for the large components G and the first-order equations (2) for F. However, following Cowan and Griffin,[1] we go further and ignore the contributions of the F to the self-consistent field V (which here is that of the $X\alpha$ method[8]) and solve only the equations for the G self-consistently. In so doing, we require the various G^2 to have unit norm; in the true DS calculations G^2+F^2 is required to have unit norm. As a check, at the end of this procedure, which we call the relativistic $X\alpha$(R-$X\alpha$) method, we used the self-consistent G and the first-order equations (2) to generate a set of F_{nlj}; as we shall show, these approximate small-component functions turn out to be surprisingly close to those of the exact DS method.

Koelling and Harmon[9] have also discussed approximating the solution of the DS problem and have given particular attention to spin-orbit effects in a spin-polarized system. The major difference between their approach and the present treatment is in the method of solving for the large components. Instead of solving Eq. (5), Koelling and Harmon solve two coupled first-order equations from which the effects of the spin-orbit operator of Eq. (3) have been removed; these equations determine the large component G and an auxiliary function ϕ and the small component F is easily recovered (if desired) as a combination of G and ϕ. The main advantage of this procedure is that derivatives of the potential V are not required as they are in the present treatment (Appendix B). However, we have not encountered any problems in calculating or using these derivatives and, as we argue in the following section, we obtain accurate self-consistent fields without including the small components. The present method, being a Pauli-like scheme, also has a certain conceptual appeal as the relativistic effects appear in the form of operators added on to the conventional nonrelativistic operators. For practical calculations, the choice of the present scheme or that of Koelling and Harmon would seem to be largely a matter of taste and convenience.

NUMERICAL RESULTS FOR ATOMS

Table I contains a comparison of the eigenvalues for the uranium atom as determined by the DS method with those found by various approximate methods. These are the present R-$X\alpha$ method, the Pauli-Choo-Pratt method (PCP) of Ref. 6 which solves the conventional Pauli equation for the $X\alpha$ potential, the nonrelativistic $X\alpha$ method[8,10] corrected by first order perturbation theory (P-$X\alpha$) for mass-velocity and Darwin effects, and the uncorrected nonrelativistic $X\alpha$ method. In Table II we compare the R-$X\alpha$ results with Dirac-Hartree-Fock (DHF) one-electron energies.[11] It is known[8] that Hartree-Fock (HF) and $X\alpha$ eigenvalues have different meanings and should not be directly compared. In order to afford a comparison, we have used the orbitals from a R-$X\alpha$ calculation to compute DHF one-electron energies[12] (labeled R-$X\alpha$-DHF in the table); it should be noted that the R-$X\alpha$ calculation for this comparison did not include the Latter correction to the one-electron potential function. These one-electron energies may then be properly compared with the HF results; in Table II, these latter are the exact DHF results and the Cowan and Griffin approximation[1] [Hartree-Fock-relativistic (HF-R)] to the DHF method. (Roughly, the HF-R method bears the same relation to the DHF method as the R-$X\alpha$ method does to the DS method.)

Table I demonstrates that the R-$X\alpha$ method affords an excellent approximation to the Dirac-Slater method. The other approximations fail most severely in their description of the valence levels (Fig. 1). The solution of the Pauli equation (PCP approximation) is the best of these but it, too, fails to produce the proper ordering of the valence levels. This appears to be an indirect effect of the poor description of the 1s and 2s

TABLE I. Comparisons of eigenvalues for various calculations on U($f^3d^1s^2$). Exchange parameter $\alpha = \frac{2}{3}$ and Latter potential cutoff used in all calculations. Negatives of eigenvalues in rydbergs.

nl	DS[a]	R-$X\alpha$[b]	PCP[c]	P-$X\alpha$[d]	$X\alpha$
1s	8507.3	8505.9	7235.8	8202.3	7378.6
2s	1588.8	1590.2	1372.8	1523.9	1279.5
2p	1344.6	1324.4	1334.7	1354.8	1238.1
3s	401.0	401.5	349.7	388.6	322.2
3p	332.0	327.6	330.5	337.9	301.9
3d	261.7	262.7	264.6	275.0	263.9
4s	102.1	102.2	88.3	99.7	81.0
4p	79.2	78.0	79.0	81.8	71.7
4d	53.2	53.5	54.1	57.5	54.2
4f	27.3	27.4	27.9	40.0	30.0
5s	22.7	22.7	19.3	22.5	17.6
5p	15.5	15.2	15.2	16.5	14.0
5d	7.24	7.28	7.47	8.41	7.71
6s	3.52	3.53	2.89	3.58	2.64
6p	1.78	1.73	1.82	2.04	1.64
5f	0.253	0.266	0.366	0.816	0.716
6d	0.205	0.207	0.243	0.335	0.286
7s	0.356	0.358	0.314	0.368	0.297

DS total energy,	−56 118 Ry;
DS total kinetic energy,	68 868 Ry;
R-$X\alpha$ total energy,	−55 854 Ry;
R-$X\alpha$ total kinetic energy,	65 536 Ry.

[a] SCF calculation performed with the Liberman, Cromer, and Waber program, Ref. 2. Configuration $(5f_{5/2})^{1.3}(5f_{7/2})^{1.7}(6d_{3/2})^{0.4}(6d_{5/2})^{0.6}(7s_{1/2})^{2.0}$. Eigenvalues quoted are centers of gravity of j doublets.

[b] Radial mesh $x_1 = 0.001\,25$ (see Appendix B).

[c] In this calculation we have used the r^γ-type starting values (see Appendix B).

[d] $X\alpha$ eigenvalues from column 6 corrected for the mass-velocity and Darwin effects by first-order perturbation theory; in this calculation we have used the conventional Pauli form for the mass-velocity and Darwin operators.

TABLE II. Comparisons of relativistic Hartree-Fock one-electron energies for U($f^3d^1s^2$) with various approximations thereto. Negatives of energies in rydbergs.

nl	DHF[a]	HF-R[b]	R-$X\alpha$–DHF[c]	Experiment[d]
1s	8559	8591	8572	8497
2s	1612	1619	1616	1599
2p	1365	1357	1346	1374
3s	413.2	415.0	414.4	407.8
3p	342.5	340.8	338.4	337.9
3d	270.1	271.6	271.4	266.3
4s	108.6	109.0	109.0	106.0
4p	84.8	84.3	83.8	82.4
4d	57.5	57.8	57.9	55.5
4f	29.9	30.1	30.2	28.4
5s	25.2	25.3	25.3	23.8
5p	17.5	17.4	17.3	15.9
5d	8.29	8.37	8.42	7.3
6s	4.25	4.28	4.31	5.2
6p	2.24	2.17	2.16	2.67
5f	0.641	0.663	0.669	···
6d	0.373	0.376	0.362	···
7s	0.394	0.403	0.408	···

[a] These results of relativistic Hartree-Fock calculations supplied by J. B. Mann (private communication). Centers of gravity of j doublets are tabulated.

[b] Reference 1 and R. D. Cowan (private communication).

[c] These energies calculated from the R-$X\alpha$ orbitals using formula from Ref. 12. SCF calculation as in Table I except Latter cutoff was *not* used.

[d] K. Siegbahn *et al.*, *ESCA-Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy* (Almqvist and Wiksells, Uppsala, 1967).

levels and this, in turn, we believe to be due to improper use of the expansion of Eq. (6). The R-$X\alpha$ p levels are in worst disagreement with the DS levels; the 2%–3% difference is most likely traceable to the omission of the spin-orbit operator from the radial differential equations. Table II illustrates that the R-$X\alpha$–DHF description provides almost as good an approximation to the DHF results as does the approximate HF-R method of Cowan and Griffin.[1] We had not anticipated this aspect of the calculations and regard it as a bonus of the R-$X\alpha$ approximation.

Table III compares calculations for the plutonium atom. *Apropos* of our previous remarks, column 3 is to be compared with column 2 and column 5 with column 4. In the R-$X\alpha$ calculations, we employed the standard Herman-Skillman mesh[10] with $x_1 = 0.0025$ (see Appendix B). This accounts for the poorer agreement (especially noticeable for the inner core levels) as compared with the uranium calculations which used $x_1 = 0.00125$. Allowing for that, we believe this table reinforces the conclusions drawn from Tables I and II.

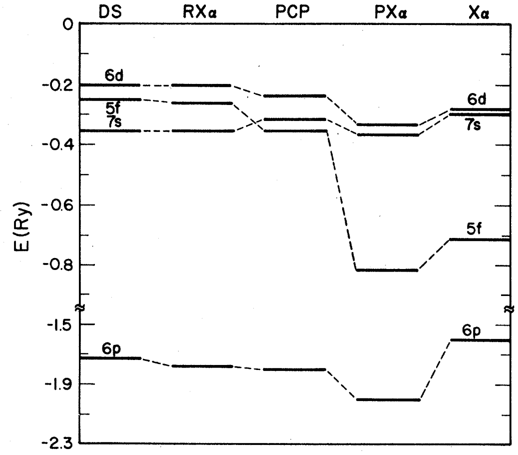

FIG. 1. Comparison of eigenvalues for upper levels of neutral uranium. Data and notation from Table I.

TABLE III. Comparisons of eigenvalues and one-electron energies for Pu(f^6s^2). Exchange parameter $\alpha=\frac{2}{3}$ and latter potential cutoff used for DS and R-$X\alpha$ calculations.

nl	DS[a]	R-$X\alpha$[b]	HF-R[c]	R-$X\alpha$–DHF[d]	Experiment[e]
1s	8967.7	8882.8	9055.2	8950.6	8957.2
2s	1688.4	1673.2	1720.0	1700.1	1698.7
2p	1420.4	1397.1	1431.1	1419.5	1430.9
3s	429.0	425.5	443.7	438.9	436.3
3p	353.7	348.6	362.3	359.9	359.6
3d	278.5	279.8	288.8	288.8	283.5
4s	110.5	109.5	117.7	116.7	114.6
4p	85.5	84.2	90.7	90.3	88.7
4d	57.8	58.1	62.5	62.8	60.3
4f	30.4	30.7	33.4	33.7	31.0
5s	24.7	24.4	27.4	27.3	25.9
5p	16.8	16.4	18.7	18.7	17.2
5d	8.06	8.13	8.98	9.19	8.04
6s	3.60	3.55	4.37	4.46	...
6p	1.73	1.66	2.10	2.20	...
5f	0.154	0.166	0.554	0.687	...
7s	0.340	0.337	0.376	0.398	...

DS total energy, −59 334 Ry; DS total kinetic energy, 73 729 Ry;
R-$X\alpha$ total energy, −58 813 Ry; R-$X\alpha$ total kinetic energy, 68 945 Ry.

[a] See footnote a, Table I. Configuration $(5f_{5/2})^{2.57}(5f_{7/2})^{3.43}(7s_{1/2})^2$.

[b] Radial mesh $x_1=0.0025$ (see Appendix B).

[c] R. D. Cowan (private communication).

[d] See footnote c, Table II.

[e] See footnote d, Table II.

Experimental and calculated spin-orbit parameters for neutral uranium and plutonium appear in Tables IV and V. The usual (Pauli) form of the spin-orbit operator for a central-field problem is given by[4]

$$H_{\mathrm{so}}^{P}(r)=-K\begin{pmatrix}-l\\ l+1\end{pmatrix}\frac{1}{r}\frac{dV}{dr}, \tag{7}$$

where $-l$ refers to $j=l+\frac{1}{2}$ and $l+1$ to $j=l-\frac{1}{2}$. The Cowan-Griffin approximation provides the expression

$$H_{\mathrm{so}}(r)=BH_{\mathrm{so}}^{P}(r) \tag{8}$$

and we regard this form as more nearly correct. [The Pauli form is a consequence of cutting off the expansion of Eq. (6).] For a central-field j

TABLE IV. Spin-orbit parameters (Ry) for uranium ($f^3d^1s^2$).

nl	DS[a]	R-$X\alpha$	DHF[b]	HF-R[b]	Experiment[c]	$X\alpha$[d]	PCP[d]
2p	187.5	185.2	187.8	199.1	185.3	134.8	257.6
3p	43.2	43.3	43.7	46.2	43.0	30.4	63.5
3d	5.26	5.43	5.29	5.33	5.17	5.09	5.7
4p	11.3	11.3	11.5	12.0	11.2	7.83	16.8
4d	1.24	1.28	1.29	1.26	1.23	1.20	1.4
4f	0.23	0.24	0.25	0.22	0.23	0.24	0.24
5p	2.68	2.68	2.76	2.70	3.2	1.86	4.0
5d	0.24	0.25	0.33	0.23	0.2	0.24	0.26
5f	0.017	0.018	...	0.017	0.016	0.023	0.019
6p	0.44	0.43	0.54	0.43	0.49	0.30	0.65
6d	0.012	0.012	...	0.014	0.011	0.016	0.016

[a] From Eq. (9). See footnote a, Table I.

[b] As quoted in Ref. 1.

[c] See footnote d, Table II.

[d] Operator defined in Eq. (10) used in these computations.

TABLE V. Spin-orbit parameters (Ry) for plutonium (f^6s^2).

nl	DS[a]	R-$X\alpha$	HF-R[b]	Experiment[c]
$2p$	208.08	205.4	222.3	206.3
$3p$	48.4	48.4	51.9	48.2
$3d$	5.82	6.02	5.9	5.74
$4p$	12.8	12.7	13.6	12.6
$4d$	1.40	1.44	1.43	1.41
$4f$	0.27	0.27	0.25	⋯
$5p$	3.12	3.10	3.15	3.28
$5d$	0.28	0.29	0.27	0.32
$5f$	0.021	0.022	0.02	⋯
$6p$	0.49	0.47	0.48	⋯

[a] See footnote a, Table IV.

[b] R. D. Cowan (private communication).

[c] See footnote d, Table II.

TABLE VI. $5f$ spin-orbit parameters (cm^{-1}) for assorted actinides.

Configuration	Label[a]	Experiment[b]	DS[c]	R-$X\alpha$	$X\alpha$
$\mathrm{Th}^{+}\, f^1d^1s^1$	A	1195	1290	1332	1858
$\mathrm{Th}^{+2}\, f^1s^1$	B	1240	1374	1396	1887
$\mathrm{Th}^{+2}\, f^2$	C	1035	⋯	1134	1650
$\mathrm{Th}^{+3}\, f^1$	D	1236	1426	1418	1904
$\mathrm{U}\, f^3d^1s^2$	E	1773	1856	1945	2481
$\mathrm{U}\, f^3d^2s^1$	F	1773	1832	1936	2470
$\mathrm{U}^{+}\, f^3s^2$	G	⋯	1905	1990	2508
$\mathrm{U}^{+}\, f^4s^1$	H	⋯	1682	1737	2280
$\mathrm{U}^{+2}\, f^4$	I	⋯	1725	1757	2286
$\mathrm{U}^{+3}\, f^3$	J	⋯	1977	2017	2525
$\mathrm{U}^{+4}\, f^2$	K	⋯	2212	2261	2758
$\mathrm{U}^{+5}\, f^1$	L	⋯	2442	2500	2988
$\mathrm{Pu}\, f^5d^1s^2$	M	⋯	⋯	2590	3159
$\mathrm{Pu}\, f^6s^2$	N	2150	2232	2372	2949
$\mathrm{Pu}^{+}\, f^6s^1$	O	⋯	2264	2380	2951
$\mathrm{Pu}^{+2}\, f^6$	P	⋯	2594	2394	2957
$\mathrm{Pu}^{+3}\, f^5$	Q	⋯	2550	2650	3200
$\mathrm{Pu}^{+4}\, f^4$	R	⋯	2808	2898	3438

[a] For purposes of identification in Fig. 2.

[b] See Ref. 14.

[c] See footnote a, Table I.

doublet, the spin-orbit parameter ζ_{nl} is

$$\zeta_{nl} = \frac{2}{2l+1}(\epsilon_{nlj+} - \epsilon_{nlj-}) \qquad (9)$$

where the ϵ's are the central-field eigenvalues. The appropriate operators to be used in perturbation theory applied to approximate levels which are j degenerate are

$$\zeta_P(r) = 2K\frac{1}{r}\frac{dV}{dr} \qquad (10)$$

and

$$\zeta(r) = B\zeta_P(r)\,. \qquad (11)$$

The spin-orbit parameters quoted for the DS and DHF methods were computed from Eq. (9). In the computation of the nonrelativistic $X\alpha$ values we used the operator $\zeta_P(r)$ while for the R-$X\alpha$ relativistic approximation we used the more accurate $\zeta(r)$. The values quoted for the HF-R method are due to Cowan and Griffin[1] and result from application of the many electron Hartree-Fock treatment of Blume and Watson.[13]

We see again that the R-$X\alpha$ results match the Dirac-Slater results (and, indeed, experiment) very well. The nonrelativistic $X\alpha$ results are in error because the core functions are too difuse and (as a consequence) the valence functions are too compact; had we used the operator $\zeta(r)$ instead of $\zeta_P(r)$ for these calculations, the comparison would be even worse. The PCP calculations, for which the operator $\zeta_P(r)$ was used, yield parameters that are no better than the $X\alpha$ values; when the $X\alpha$ parameter is too small the PCP parameter is too large by about the same amount, and vice versa. [Use of the operator $\zeta_P(r)$ instead of $\zeta(r)$ in the R-$X\alpha$ calculation of the spin-orbit parameters produces core spin-orbit parameters about 20% greater than those tabulated; it is important to use the proper $\zeta(r)$.] While outside the purview of this paper, it may be that the too large values of the HF-R $2p$ and $3p$ parameters arise because the Blume-Watson theory[13] is nonrelativistic—a relativistic generalization might include the analogue of B in Eq. (8).

To illustrate the performance of the R-$X\alpha$ method for excited and ionic configurations, we give in Table VI and Fig. 2 the $5f$ spin-orbit parameters for a number of configurations of thorium, uranium, and plutonium. The maximum disagreement between the R-$X\alpha$ and DS numbers is about 5%. Again, the nonrelativistic $X\alpha$ values are too large although, as Fig. 2 shows, their behavior with change in configuration closely follows that of the relativistic values. The deviation between the calculated relativistic values and experiment is largest for the f^1 configuration of Th^{3+}. There are some indications that there is appreciable configuration interaction[14] here (probably with $6p^56d^1$).

To check the usefulness of the R-$X\alpha$ total energies, we have calculated the excited-state spectrum of Th^{3+}, using ΔSCF methods (changes in

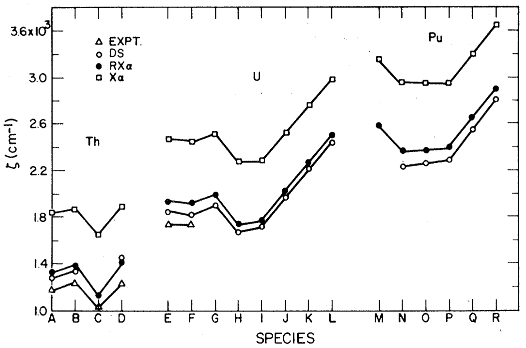

FIG. 2. Comparison of $5f$ spin-orbit parameters for a number of actinides. Data and labeling from Table VI.

self-consistent-field method in which the threshold energy is taken as the difference in total energies of two SCF calculations); these results are seen in Fig. 3. Both the R-$X\alpha$ and HF-R results[1] were obtained by determining the energy differences between the averages of configuration for the ground and excited states and then shifting by the spin-orbit energies. The R-$X\alpha$ results generally compare well with the DS results, although the $6d$ excitations are in error by about 5000 wave numbers. However, we here see a big difference between the predictions of the Hartree-Fock and $X\alpha$ methods. The former predicts the $6d-$ level to be below the $5f+$ level, in disagreement with experiment, while the latter yields the correct ordering. Presumably, correlation corrections (or, what is the same thing, configuration interaction) are necessary to correct the Hartree-Fock results. The nonrelativistic $X\alpha$ method is clearly unreliable here—errors of as much as 500% are found.

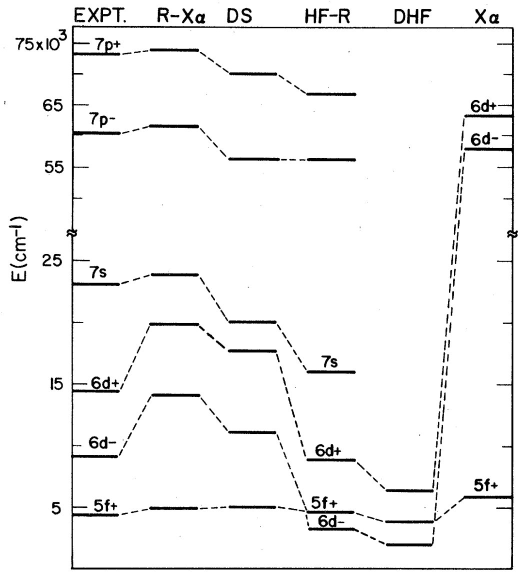

FIG. 3. Excitation energies of Th^{3+} as determined by experiment, the present R-$X\alpha$ method, the Dirac-Slater (DS) method, the Cowan-Griffin approximation (HF-R) to the Dirac-Hartree-Fock (DHF) method, the DHF method itself, and the nonrelativistic $X\alpha$ method.

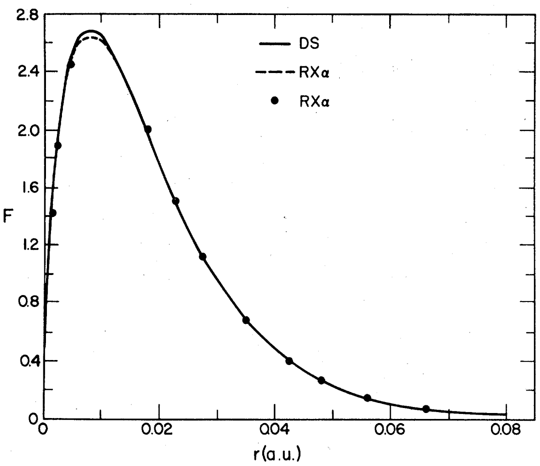

FIG. 4. Small component $F_{1s_{1/2}}(r)$ for uranium. Solid curve is Dirac-Slater function, dashes and dots represent "after the fact" R-$X\alpha$ function.

We now turn to a comparison of wave functions and radial charge densities. Although the R-$X\alpha$ calculations omit any direct computation of the small components F, a measure of the agreement between the large components G found by the R-$X\alpha$ method and those from the DS method can be determined by employing Eq. (2) and the self-consistent R-$X\alpha$ G_{nl} to obtain approximate F_{nlj}. We anticipate the greatest disagreement for the innermost functions and in Figs. 4 and 5 we present the calculations for the $1s$ and $2p$ shells of neutral uranium. The agreement is surprisingly good; the somewhat larger errors in the $2p$ functions are, no doubt, associated with effects of the spin-orbit potential, which is absent from the R-$X\alpha$

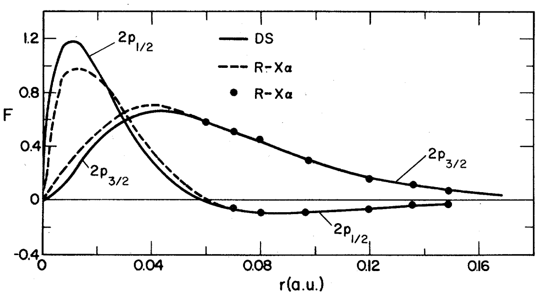

FIG. 5. Small components $F_{2p_{1/2}}(r)$ and $F_{2p_{3/2}}(r)$ uranium. Solid curves are Dirac-Slater functions, dashes and dots represent "after the fact" R-$X\alpha$ functions.

calculations. (In the DS calculations, the function F_{nlj} is determined from G_{nlj+} and F_{nlj-} from G_{nlj-}; in the R-$X\alpha$ calculations both F's are determined from the single G_{nl}.) This determination of the F's for the R-$X\alpha$ calculation involves a renormalization so that $\int_0^\infty (F^2+G^2)\,dr = 1$. Hence, as well as comparing plots of the functions we are able to compare the norms of the small components with those of the DS calculation. For uranium, the largest difference occurs for $F_{1s_{1/2}}$- the DS norm is 0.128 while the R-$X\alpha$ value is 0.125. With these approximate F_{nlj} and G_{nl}, we defined a total radial charge density $R_{R\text{-}X\alpha}(r)$ according to Eq. (1). We then computed the integral of the square of the deviation from the DS radial charge density,

$$\Delta = \int_0^\infty [R_{\mathrm{DS}}(r) - R_{R\text{-}X\alpha}(r)]^2\,dr\,. \tag{12}$$

For the uranium calculations, $\Delta = 0.6$. Using the R-$X\alpha$ SCF charge density from the function G alone yields a value of 2.0. Replacing $R_{\mathrm{R}\text{-}X\alpha}$ with the nonrelativistic charge density $R_{X\alpha}$ gives $\Delta = 45.1$!

APPLICATION TO MOLECULES AND SOLIDS

Pratt,[15] Hemstreet,[16] and Choo and Pratt[6] have published work in which the Pauli forms of the mass-velocity and Darwin operators have been incorporated into the molecular scattered wave method of Johnson.[17] We would only suggest that the corresponding operators for Eq. (3) should be used instead. This change is formally trivial and amounts to nothing more than multiplying the Pauli form of the Darwin operator by the factor B from Eq. (4). The necessary computational changes to existing nonrelativistic scattered wave computer programs can be handled by the methods of Appendix B. Our present experience with the free-atom calculations suggests that these changes will greatly improve the accuracy of such semirelativistic computations when compared against computations made by the fully relativistic scattered wave method of Yang and Rabii.[18] The general methodology for iterating to self-consistency is, of course, the same as in the nonrelativistic case. As with the free-atom calculations, the spin-orbit splittings should be accurately obtained by use of first-order perturbation theory.

The method of Yang and Rabii is fully relativistic in the same sense as the DS atomic method; it has the advantage that all the relativistic effects are included from the beginning with no necessity for carrying out a perturbation calculation for spin-orbit splittings at the end of the SCF process. The disadvantages are that the elements of the secular equation are somewhat more complicated and that the construction of the charge density needed for the SCF process is more difficult. These disadvantages are a consequence of the form of the basis functions employed in the method. The method assumes a muffin-tin potential for which the molecular orbitals within the muffin-tin spheres are expanded in partial wave sums over four component central-field wave functions whose radial parts are the F and G of Eq. (2); in the regions between the spheres where the potential is a constant (generally adjusted to zero), the molecular orbitals are expanded in solutions of the free-electron Dirac equation. Considering R-$X\alpha$ results for the free atoms, it may well be that one could develop a viable two-component version of the Yang and Rabii theory in which the central-field wave functions would be taken as Pauli central-field spinors whose radial parts would be solutions $G_j(r)$ of Eq. (3) (which *includes* the spin-orbit operator) while the exterior basis functions would be solutions of the free-electron Pauli equation. The absence of the small components F should lead to less complex matrix elements for the secular equation and should simplify the process of constructing the charge density.

We next consider application of the R-$X\alpha$ method to a relativistic-augmented-plane-wave (RAPW) energy-band calculation.[19] If we choose the periodic potential to be of the muffin-tin form, then the matrix elements of the energy-dependent RAPW secular equation include the effects of the locally spherically symmetric potential function V within the muffin-tin spheres via a certain combination of the functions F and G of Eq. (2). Using the notation of Mattheiss,[20] we write this combination as

$$\eta_k = (2/\alpha)F_k(R_s,E)/G_k(R_s,E) - (k+1)/R_s\,, \tag{13}$$

where F and G are evaluated at the radius R_s of the muffin tin sphere and for energy E (which replaces the eigenvalue ϵ in Eq. (2)). As Dimmock notes,[21] this expression is given more simply as

$$\eta_k = g_k'(R_s,E)/g_k(R_s,E)\,, \tag{14}$$

where $g_k(r,E) = G_k(r,E)/r$ and $g_K'(R_s,E) = dg_k(r,E)/dr\big|_{r=R_s}$. [This follows from substituting the first of Eq. (2) into Eq. (13).] We can, then, calculate the η_k directly from the exact second-order differential equation (3) and need not calculate the small components F_k. By changing notation from the quantum number k to the pair l and j, Mattheiss[20] shows that the η enter the RAPW matrix elements in the two combinations,

$$l\eta_l^- + (l+1)\eta_l^+ \quad\text{and}\quad \eta_l^+ - \eta_l^-\,, \tag{15}$$

where $\eta_l^\pm$ correspond to solutions g with $j = l \pm \frac{1}{2}$.

If we follow the approach used in the R-$X\alpha$ atomic calculations and omit the spin-orbit operator from the equation (3) for G, then the distinction between j values disappears and we have a single $\eta_l = g_l'(R_s, E)/g_l(R_s, E)$ which includes only the mass-velocity and Darwin effects. The first of the expressions (15) then becomes $(2l+1)\eta_l$ and the second vanishes identically. The structure of the RAPW secular equation collapses to that of the nonrelativistic APW method with the g_l'/g_l replacing their nonrelativistic analogs, which are generally called u_l'/u_l. The solution of this non-spin-orbit (NSO) secular equation will then yield Bloch functions and eigenvalues that include mass-velocity and Darwin effects; the spin-orbit splitting can then be obtained by the use of first-order perturbation theory or by solution of the exact RAPW secular equation.

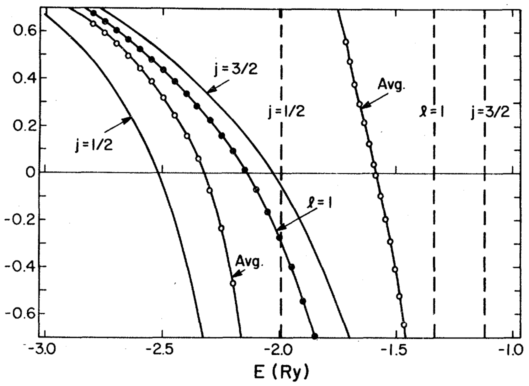

FIG. 6. $\eta_1^-(j=\frac{1}{2})$, $\eta_1^+(j=\frac{3}{2})$, weighted average (Avg.) and $\eta_1(l=1)$ computed for DS uranium atom potential. $R_s = 2.834$ bohrs.

This omission of the spin-orbit operator in a "first pass" at the band-structure determination is very close to a procedure outlined by Mattheiss, but it has some calculation advantages over his scheme. Mattheiss suggests that spin-orbit effects in the RAPW secular equation may be dropped by setting the various $\eta_l^+ - \eta_l^-$ null. If this is done, the structure of the RAPW secular equation again reverts to that of the nonrelativistic APW method[22] with the quantities $[l\eta_l^- + (l+1)\eta_l^+]/(2l+1)$ replacing the u_l'/u_l. [This can be only an *approximate* neglect of spin-orbit effects for, as we have seen, full neglect results in $\eta_l^+ = \eta_l^-$ while in Mattheiss' procedure η_l^+ and η_l^- are still to be evaluated from Eqs. (13) or (14).] To illustrate the differences between using $\eta_l = g_l'/g_l$ and $[l\eta_l^- + (l+1)\eta_l^+]/(2l+1)$ in the NSO problem, we have evaluated these quantities for $l=1$ using the potential function determined in the course of the DS atomic calculation reported in Table I and an arbitrarily chosen sphere radius R_s of 2.834 Bohrs (1.5 Å). (We might imagine that this is a starting potential for a SCF band calculation on metallic uranium.) The energy range chosen is that appropriate to the $6p$ bands; that is, the functions g have four nodes within the sphere. In Fig. 6 η_1 is represented by the dotted curve which has a zero at -2.13 Ry where $g_1'(R_s) = 0$ and an asymptote at -1.34 Ry where $g_1(R_s) = 0$. (On the right-hand side of the asymptote, g has five nodes within the sphere, so the asymptote delimits the $6p$ from the $7p$ region of energy.) The $j=\frac{1}{2}$ and $j=\frac{3}{2}$ curves in the figure represent η_1^- $(j=\frac{1}{2})$ and η_1^+ $(j=\frac{3}{2})$; their zeroes are at -2.52 and -2.03 Ry, respectively, and the asymptotes are at -1.99 and -1.12 Ry. The curve labeled Avg. represents the weighted average $(\eta_1^- + 2n_1^+)/3$. In the energy region below the $\frac{1}{2}$ asymptote, the difference between the curve for η_1 and that for the weighted average is not great (compared to the spin-orbit splitting of roughly 0.5 Ry); the latter curve is "pushed" below the former by the presence of the $\frac{1}{2}$ asymptote with the difference between the curves increasing as this asymptote is approached from below. One would get plausible $6p$ NSO energy bands in this region from the use of either curve although we would prefer using that for η_1. Our concern is not so much with this energy region as it is with the region between the $\frac{1}{2}$ and $\frac{3}{2}$ asymptotes (where the functions g are formally $7p_{1/2}$ and $6p_{3/2}$) where the curve for the weighted average has an extra branch. This branch results from combining very large negative values of η_1^+ and very large positive values of η_1^-. (The latter are off scale on Fig. 6.) This branch is physically meaningless but unless it is artifically removed from consideration there is the very real possibility that the solution of the corresponding NSO secular equation will yield (false) energy band eigenvalues in this interasymptote region. (These extra branches are present for all nonzero l. Our choice of $l=1$ for illustration was made because the large spin-orbit splitting makes the differences more visible on a plot.) We conclude that if we wish to carry out a RAPW NSO band calculation, the use of a single n_l for each l value is preferable (as well as simpler) to the use of the weighted average of n_l^+ and n_l^-. Koelling and Harmon[9] have tested this procedure in a sample band calculation for gadolinium and find good agreement with the fully relativistic RAPW results.

If we were to consider a self-consistent RAPW NSO band calculation, we believe it is reasonable to proceed, as in the atomic case, by neglecting any explicit computation of the small components. Also, while we have confined this discussion to use of a muffin-tin potential, we think it likely that the suggested procedures would also be applicable to the more elaborate self-consistent non-muffin-tin RAPW problem treated by Elyashar and Koelling.[23]

CONCLUSIONS

We have shown that application of the Cowan-Griffin approximation[1] to the Dirac-Slater method gives results very close to those of the DS method itself, even for atoms as heavy as the actinides. The approximation omits explicit determination of the small components of the central-field orbitals and treats spin-orbit effects by first-order perturbation theory. These attractive features make the approximation a candidate for inclusion in molecular or solid-state programs and the success with the atomic calculations augurs well for such applications. Suggestions for incorporation of the approximation into the molecular scattered wave method[17] and the augmented-plane-wave method[22] have been outlined. In the latter case, we believe the approximation leads to a more tractable secular equation than does the original prescription of Mattheiss.[19] We find that the Pauli approximation (PCP) and the completely nonrelativistic method plus first-order perturbation theory corrections (P-$X\alpha$) are poor approximations to the relativistic method when actinide atoms are considered.

From consideration of the second-order differential equation satisfied by the large components in Dirac central-field theory, we conclude that the mass-velocity and Darwin operators are not uniquely defined—only their sum is so defined. We find that the usual Pauli forms for the operators are such that this sum is correct only to zeroth order in the expansion parameter $K(\epsilon - V)$; in Appendix A we give expressions for the operators which are correct to first order, providing the conditions of the expansion are satisfied. The Pauli form of the spin-orbit operator [Eq. (7)] is inaccurate when used in actinide atom calculations. The spin-orbit parameters are obtained accurately only if the correct form of the operator given in Eq. (8) is used.

When used to calculate Hartree-Fock one-electron energies the R-$X\alpha$ orbitals give these energies nearly as accurately as does the HF-R method, which is to say quite close to the Dirac-Hartree-Fock values. This accords with previous experience with the respective nonrelativistic methods; while using dramatically different one-electron Hamiltonians, the Hartree-Fock and $X\alpha$ methods nevertheless yield very similar one-electron orbitals.

Applications of the Cowan-Griffin approximation[1] to the $X\alpha$ method is actually more straightforward than it is to the Hartree-Fock method for which it was originally devised; one can assess its shortcomings more easily in the $X\alpha$ context. For example, the neglect of the spin-orbit distortion of the p orbitals appears more serious than the neglect of explicit inclusion of the small components; this is not so obvious from the original calculations of Cowan and Griffin.[1] While the present work has considered relativistic $X\alpha$ problems, the methods suggested should be applicable to any relativistic one-electron problem employing a local exchange-correlation potential.

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APPENDIX A: PAULI APPROXIMATION

We have said that we believe the usual (Pauli) form of the mass velocity and Darwin operators[4] is accurate not to first order but only to zeroth order in $K(\epsilon - V)$. This is, we believe, obvious from Eq. (3), which is exact for the Dirac-Slater theory. To properly obtain the results to first order we use the expansion of Eq. (6) and the Darwin term

$$\begin{aligned} H_D(r) &= -KBV'\left(\frac{d}{dr} - \frac{1}{r}\right) \\ &= BH_D^P(r) , \end{aligned} \tag{A1}$$

where H_D^P is the Pauli form of the Darwin operator. The expansion to first order in $K(\epsilon - V)$ is

$$H_D(r) \approx H_D^P(r) - K(\epsilon - V)H_D^P(r), \tag{A2}$$

so that if we wish to call the Darwin operator the term H_D^P, then we must absorb the remaining term into the mass-velocity operator which is then (to first order)

$$H_m^P(r) \approx -K(\epsilon - V)[(\epsilon - V) + H_D^P(r)]. \tag{A3}$$

Now, H_D^P and the *new* H_m^P *are* correct to first order in $K(\epsilon - V)$.

The same result is obtained by a somewhat more roundabout approach which has, however, the advantage of displaying the error in the usual derivation. The second-order differential equation for G before simplification to the form of Eq. (3) is

$$\left[B\frac{p^2}{2m} + V - KB^2V'\left(\frac{d}{dr} - \frac{1}{r}\right)\right]G = \epsilon G , \tag{A4}$$

in which $p^2/2m$ is an abbreviation for $-d^2/dr^2 + l(l+1)/r^2$ and where we have omitted the spin-orbit operator. Equation (3) follows from multiplying the above by B^{-1} and simplifying. If instead we multiply (from the left) by B^{-2} than we obtain the operator equation

$$B^{-2}(\epsilon - V) = B^{-1}p^2/2m + H_D^P \tag{A5}$$

leading to

$$\begin{aligned}\epsilon = p^2/2m + V - (\epsilon - V)[2K(\epsilon - V) + K^2(\epsilon - V)^2] \\ + K(\epsilon - V)p^2/2m + H_D^P\,,\end{aligned} \tag{A6}$$

which means the new form of the mass-velocity operator H_m^N is

$$H_m^N = -2K(\epsilon - V)^2 - K^2(\epsilon - V)^3 + K(\epsilon - V)p^2/2m\,. \tag{A7}$$

We then substitute

$$p^2/2m = (\epsilon - V) - H_m^N - H_D^P \tag{A8}$$

into the above. The usual treatment as in, for example, Ref. 4 is to use $p^2/2m = \epsilon - V$; the omission of the other two terms is, we believe, the fly in the ointment. H_m^N can now be written

$$H_m^N = \frac{-K(\epsilon - V)[(\epsilon - V) + K(\epsilon - V)^2 + H_D^P]}{1 + K(\epsilon - V)} \tag{A9}$$

This "partitioning" of the operators into H_D^P and H_m^N is just as valid (if less convenient) than our previous choice of H_m and H_D as in Eq. (3). (If the spin-orbit operator is carried along in the previous discussion, then with H_m^N and H_D^P as written goes the spin-orbit operator $H_{so} = BH_{so}^P$—this is the same operator as in Eq. (3) as, of course, it must be.) Now the second and third terms in the square brackets of Eq. (A9) are recognized as the mass-velocity and Darwin operators as conventionally written; they are of the same order of magnitude and are of first order in $K(\epsilon - V)$ as compared with the first term $(\epsilon - V)$. We then see that to zeroth order in $K(\epsilon - V)$ we have

$$H_m^N \approx -K(\epsilon - V)^2\,, \tag{A10}$$

as we claimed. Using the expansion of Eq. (6) and retaining only the first two terms we then obtain to first order in $K(\epsilon - V)$

$$H_m^N \approx -K(\epsilon - V)[(\epsilon - V) + H_D^P]\,, \tag{A11}$$

in agreement with our previous results.

This proper first-order form of the operators will be more accurate than the zeroth order form, but we can expect trouble whenever the conditions of the expansion of Eq. (6) are violated. It is best to avoid use of the expansion altogether.

APPENDIX B: NUMERICAL METHODS

Because of the presence of the Darwin operator, Eq. (3) contains the first derivative of the wave function, and the usual Numerov method of solution cannot be directly applied. Cowan and Griffin treat this operator as part of the potential function; at SCF iteration n they use the G determined in iteration $n-1$ to evaluate $(1/G)dG/dr$. Choo and Pratt[6] write $G(r) = y(r)Q(r)$ and by proper choice of y obtain a differential equation (for Q) without the first derivative term. Following Choo and Pratt we define

$$g(r) = V(r) + \frac{l(l+1)}{r^2} - K\left((\epsilon - V)^2 - \frac{B}{r}V'\right) - \epsilon\,, \tag{B1}$$

with K and B given by Eq. (4). The radial equation then becomes

$$\left(\frac{d^2}{dr^2} + f\frac{d}{dr} - g\right)G = 0, \quad f(r) = KBV'\,. \tag{B2}$$

We set $G = yQ$ and obtain

$$\left(\frac{d^2}{dr^2} + \frac{2y' + fy}{y}\frac{d}{dr} + \frac{y'' + fy'}{y} - g\right)Q = 0\,. \tag{B3}$$

Choo and Pratt then eliminate the first derivative term by requiring

$$2y' + fy = 0\,, \tag{B4}$$

which yields in our case the multiplicative function y as

$$y = [1 + K(\epsilon - V)]^{1/2} = B^{-1/2}\,. \tag{B5}$$

(It is assumed that y does not vanish; this is indeed satisfied for our problem—the vanishing of y requires $\epsilon - V \approx -75\,000$ Ry.) With

$$(y'' + fy')/y = -\tfrac{1}{2}f' - \tfrac{1}{4}f^2 \tag{B6}$$

the equation for Q is

$$\begin{aligned}\Bigg[-\frac{d^2}{dr^2} + V(r) + \frac{l(l+1)}{r^2} - K(\epsilon - V)^2 \\ + \frac{KB}{2}\left(\frac{1}{r}\frac{d^2(rV)}{dr^2} + \frac{3KB}{2}(V')^2\right)\Bigg]Q = \epsilon Q\,.\end{aligned} \tag{B7}$$

This equation is then solved for ϵ and Q by the Numerov method and G is recovered as

$$G = [1 + \tfrac{1}{4}\alpha^2(\epsilon - V)]^{1/2}Q\,. \tag{B8}$$

Two initial values are needed to start the outward integration by the Numerov method; a good choice is important since relativistic effects are especially large at small r. In the R-$X\alpha$ and PCP calculations we have used virtually the same prescription as in the Dirac-Slater code.[2] There the wave function is taken to behave as r^γ, where

$$\gamma = (k^2 - \alpha^2 Z^2)^{1/2}, \tag{B9}$$

with Z being the atomic number. This exponent is j (or k) dependent; for our functions G_{nl} we used an arithmetic average $\gamma_l = \frac{1}{2}(\gamma_{l+1/2} + \gamma_{l-1/2})$. The starting values for Q are then determined by division by the function y.

The radial mesh used in the calculations is the telescoping Herman-Skilman mesh[10] in which the first point r_1 is given by $R_1 = (\frac{9}{2}\pi^2)^{1/3} x_1 / 4Z^{1/3}$ and where the standard value of $x_1 = 0.0025$. A finer mesh is obtained by reducing x_1 and we found a choice of 0.001 25 helpful in improving the values of some quantities (such as the 1s eigenvalue) which are sensitive to the values of the orbitals at small r.

The total energy for an atomic $X\alpha$ calculation is the sum of the total kinetic energy, the Coulomb energy of interaction among the electrons, the energy of attraction between the nucleus and the electrons, and the total $X\alpha$ exchange energy.[8] This holds for both the nonrelativistic and relativistic cases. The computer programs actually calculate the kinetic energy of an orbital eigenfunction from the orbital eigenvalue and the radial differential equation; this avoids the calculation of derivatives of the eigenfunction. The total energies and the total kinetic energies for the DS and R-$X\alpha$ computations are included in the tables.

An interesting and useful aspect of the DS kinetic energies turned up in the course of the present work; this is made clearest by an example. Suppose we consider the $1s_{1/2}$ shell for the DS calculation on the uranium atom (Table I). The norm of the square of the small component $F_{1s_{1/2}}$ is 0.127 551 and that of $G_{1s_{1/2}}$ is 0.872 449. The expectation values of the kinetic energy for functions of unit norm are 13 031.62 Ry (small) and 12 886.57 Ry (large), yielding

$$E_K(1s_{1/2}) = 0.127\,551(13\,031.62) + 0.872\,449(12\,886.57)$$
$$= 12\,905.1 \text{ Ry}.$$

This is a persistent pattern—orbital by orbital, the small component has the higher kinetic energy. Thus a necessary—although far from sufficient—condition on the total R-$X\alpha$ kinetic energy is that it be less than the total DS kinetic energy. This condition is indeed satisfied by the present calculations (Tables I and III).

For both nonrelativistic calculations and completely relativistic (DS) $X\alpha$ atomic calculations, the virial theorem provides another useful numerical check. In the nonrelativistic case, it tells us that the total energy is given by the negative of the total kinetic energy. We have determined that in the relativistic case it provides the relation

$$E_{\text{total}} = -2mc^2 \sum (2j+1)\langle F_{nlj} | F_{nlj}\rangle, \tag{B10}$$

where the sum is over the norms of the occupied small-component functions. Unfortunately, since the R-$X\alpha$ method omits consideration of the small components such a useful numerical check is not available unless, of course, one goes to the extra trouble of calculating small components after completion of the R-$X\alpha$ computation (see example in main text).

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