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Self-Consistent-Field Dirac-Slater Wave Functions for Atoms and Ions. I. Comparison with Previous Calculations*

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Self-consistent-field solutions have been obtained of the two first-order linear differential equations that result from the Dirac equation. These solutions for the major and minor components of the (nlj) eigenfunctions were obtained by the relativistic equivalent of the method Herman and Skillman used for atomic structure calculations in which exchange was handled by Slater's $\rho^{1/3}$ method. Detailed comparisons between the energy eigenvalues and electronic energy levels determined from x-ray spectroscopic data have been made for Cu^{+1}, Fe, W, and Pt, and particularly for Hg and U. The agreement was very good—better than that obtained in any previous self-consistent-field calculations available to the authors.

I. INTRODUCTION

When Knox[1] surveyed the status of self-consistent-field calculations in 1958, information for only 29 atoms and 103 ions of varying degrees of ionization was available. Of these, all but eleven had atomic numbers lower than 36 (krypton). Data for a few of these in the immediate vicinity of ^{80}Hg resulted from the pioneering calculation made by Hartree and Hartree[2] using a differential analyzer at Massachusetts Institute of Technology.

Since that survey such information has been burgeoning. For example Watson and Freeman[3] have completed Hartree-Fock calculations for the elements up to krypton and for the lanthanide ions from $^{58}Ce^{+3}$ to $^{71}Lu^{+3}$. Recently, Herman and Skillman[4] computed for all the elements what they call Hartree-Fock-Slater eigenfunctions; that is, they used Slater's approximate $\rho^{1/3}$ method[5] rather than Fock's method to incorporate exchange. Clementi[6] obtained analytic Hartree-Fock wave functions by using large basis sets for the elements with $Z<37$. Almost simultaneously, Boyd, Larson, and Waber[7] completed Hartree calculations for all the elements, a number of them in excited states, as well as for most of the chemically significant positive ions. A few calculations for anions with unit negative charge were also done.

In this rich field, there have been few relativistic calculations. The first significant one was published by Williams[8] for $^{29}Cu^{+1}$ in 1940. The next was by Mayers[9] for ^{80}Hg in 1957. Cohen[10] in 1960 published a set of careful calculations for ^{26}Fe, ^{74}W, ^{78}Pt, $^{80}Hg^{+2}$, ^{80}Hg, and ^{92}U. All of these were done without exchange. Mayers[11] has very recently completed a relativistic Hartree-Fock calculation for ^{80}Hg.

In the present work, two first-order Dirac equations have been solved for each (nlj) set of quantum numbers characterizing the electrons in an atom or ion. Slater's $\rho^{1/3}$ method was employed to calculate the exchange potential that a given electron experiences. Although a large number of calculations have been completed, the present paper is limited to comparing the energy eigenvalues obtained by previous authors for ^{26}Fe, $^{29}Cu^{+1}$, ^{74}W, ^{78}Pt, ^{80}Hg, and ^{92}U.

II. DESCRIPTION OF THE CALCULATION

For the model employed, it is assumed that the wave function of an atom can be represented by a determinant of one-electron wave functions. These are calculated with the approximation suggested by Slater, i.e., by replacing the exchange potential with an approximate one characteristic of a free-electron gas having the local density of a given point in the atom. The direct potential acting on an electron is that of the nucleus and of all the electrons (spherically averaged if there is an unfilled shell). The Dirac equation expressed in spherical coordinates was used. No account was taken of the Breit interaction term or higher-order relativistic corrections, and corrections for the finite size of the nucleus were omitted.

The Dirac equation is in the usual notation

$$[c\alpha\cdot p+\beta mc^2+V(r)-W]\psi(r)=0. \qquad (1)$$

We write the four-component Dirac wave function in the form

$$\psi(r)=\begin{pmatrix}(1/r)f(r)i^l\Omega_{jlm}\\(1/r)g(r)i^{l'}\Omega_{jl'm}\end{pmatrix}, \qquad (2)$$

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[1] R. S. Knox, *Solid State Physics* (Academic Press Inc., New York, 1957), Vol. 4, p. 413.

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

[3] R. E. Watson and A. J. Freeman, Phys. Rev. **118**, 1036 (1960); **119**, 1934 (1960); **120**, 1125, 1134 (1960); **123**, 521, 2027 (1961); **124**, 1117 (1961); **127**, 2058 (1962).

[4] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[5] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[6] E. Clementi, J. Chem. Phys. **38**, 996, 1001 (1963); E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

[7] R. G. Boyd, A. C. Larson, and J. T. Waber (to be published).

[8] A. O. Williams, Phys. Rev. **58**, 723 (1940).

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

[10] S. Cohen, Phys. Rev. **118**, 489 (1960).

[11] D. F. Mayers (private communications) .

where the Ω's are two-component normalized spinors with the indicated quantum numbers. The relationships between the various quantum numbers may be conveniently expressed as follows:

$$\begin{aligned} l' &= l+s\,, \\ j &= l+s/2 = l'-s/2\,, \\ \kappa &= -s(j+\tfrac{1}{2})\,, \\ s &= \pm 1\,. \end{aligned} \tag{3}$$

The differential equations for the radial functions $f(r)$ and $g(r)$ are

$$\frac{d}{dr}\begin{pmatrix} f \\ g \end{pmatrix} = \begin{pmatrix} -\kappa/r & (V-E_0-W)/cs \\ -(V+E_0-W)/cs & \kappa/r \end{pmatrix}\begin{pmatrix} f \\ g \end{pmatrix}, \tag{4}$$

where E_0 is the rest mass of the electron and $W=E+E_0$. In atomic units, $e=\hbar=m=1$ and $c=137.037$.

The pertinent potential energy terms in the Hartree-Fock equation for eigenfunction $\psi_i(r)$ are

$$\begin{aligned} \psi_i(r)V(r) = &-\frac{Z\psi_i(r)}{r} \\ &+\sum(j)\int \psi_j^*(r')\frac{1}{|r-r'|}\psi_i(r)\psi_j(r')d^3r' \\ &-\sum(j)\delta_{\sigma_i\sigma_j}\int \psi_j^*(r')\frac{1}{|r-r'|}\psi_j(r)\psi_i(r')d^3r'\,, \end{aligned} \tag{5}$$

where the charge density of electrons at r' is given by

$$\rho(r') = \sum(j)\psi_j^*(r')\psi_j(r') \tag{6}$$

$$= \sum(j)[f_j(r')^2+g_j(r')^2]/r'^2 \tag{6a}$$

and where the summation index j runs over the electrons in all occupied (nlj) subshells. After replacing the third or exchange term in (5) by Slater's average value which is based on a free-electron model, one may write

$$\begin{aligned} rV(r) = -Z + &\int_0^r 4\pi r'^2\rho(r')dr' \\ &+ r\int_r^\infty 4\pi r'\rho(r')dr' - Cr[\rho(r)]^{1/3}\,, \end{aligned} \tag{7}$$

where

$$C \equiv (81/8\pi)^{1/3}. \tag{8}$$

At large r, $rV(r)$ should approach N-Z-1, but because of the use of Slater's approximation[5] it will, if defined as in Eq. (7), go to N-Z. We adopt Latter's suggestion[12] and set $rV(r)$ equal to N-Z-1 for all values of the radius greater than the one where it first reaches that value. This modification has been discussed by Herman and Skillman.[4] The suggestion of Coulson and Sharma[13] is not applicable when the Slater exchange potential is used.

Details of the Calculation

Two first-order differential equations were integrated by a modification of Milne's method for each set of (nlj). For a heavy element such as ^{92}U, this constitutes a set of 58 coupled differential equations. The radial domain extended from 1.056×10^{-4} Bohr units, well within the average nucleus, to 60 Bohr units. To have a finer mesh of points for the numerical integration near the nucleus the new dependent variable $x=\ln r$ was introduced. This range was divided into 420 equally spaced intervals in x. Δx was set equal to $\frac{1}{32}$. To avoid calculations over long ranges where the wave functions are not significantly different from zero, such as would be the case with, for example, the $1s\,\frac{1}{2}$ electron at large radii, the practical infinity was determined by the condition

$$[V(r)-E]r^2 \approx 75\,. \tag{9}$$

The radial differential equations were integrated outward from the origin to the classical turning point, starting with a power series near the origin. The inward integration was started at the practical infinity or the outmost mesh point, whichever was smaller. The two solutions were joined at or near the classical turning point. After requiring that $f(r+)=f(r-)$, the attempt to match the minor components yielded a correction to the energy eigenvalue, namely

$$\Delta E = sc\left\{f[g(r+)-g(r-)]\Big/\int_0^\infty (f^2+g^2)dr\right\} \tag{10}$$

for each nlj.

Modification of E_{nlj} was discontinued on any iteration cycle when $|\Delta E/E|$ became less than 10^{-5}. The energy eigenvalues presented in the accompanying tables are equal to $-2E_{nlj}$, i.e., are in rydbergs.

With the eigenfunctions found by integrating the set of differential equations, a new charge density $\rho(r)$ was computed. To achieve more stability, the charge density used for the next step of iteration was

$$\rho_{\text{new}} = \phi\rho_{\text{calc}} + (1-\phi)\rho_{\text{old}}\,. \tag{11}$$

For the present calculations, the value of ϕ was 0.15. Iteration was continued until

$$\left|\frac{V_{\text{new}}(x_i)-V_{\text{old}}(x_i)}{V_{\text{old}}(x_i)+Z/r_i}\right| < 10^{-6} \tag{12}$$

for each x_i.

Results

The numerical results for the energy eigenvalues, which have been obtained by using various approximations, are compared below. The Boyd-Larson-Waber

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[12] R. Latter, Phys. Rev. **99**, 510 (1955).

[13] C. A. Coulson and C. S. Sharma, Proc. Phys. Soc. (London) **79**, 920 (1962).

TABLE I. Energy eigenvalues for cuprous ion $^{29}\mathrm{Cu}^{+1}$ ($3d^{10}$ configuration) in rydbergs. Abbreviations NR-H, R-DS, etc., are explained in the text.

Shell	j	NR-H BLW Ref. 7	NR-HF Hartree Ref. 14	NR-HFS HS Ref. 4	R-D Williams Ref. 8	R-DS LWC present	Exper. x-ray levels
1s	$\frac{1}{2}$	657.92	658.4	650.40	664.8	658.07	661.6
2s	$\frac{1}{2}$	78.477	82.30	78.87	79.52	80.558	81.00
2p	$\frac{1}{2}$	69.865	71.83	69.74	70.66	71.180	70.3
2p	$\frac{3}{2}$				69.14	69.625	68.9
3s	$\frac{1}{2}$	8.9909	10.651	9.355	8.998	9.6410	8.9
3p	$\frac{1}{2}$	6.0809	7.279	6.429	6.012	6.6447	5.7
3p	$\frac{3}{2}$				5.818	6.4470	
3d	$\frac{3}{2}$	1.1994	1.613	1.459	1.020	1.4622	0.4
3d	$\frac{5}{2}$				1.000	1.4395	

(BLW) results which are solutions of the simple nonrelativistic Hartree equations will be designated (NR-H). The Herman-Skillman (HS) results are also nonrelativistic, but Slater's method was employed to estimate the exchange contribution to the potential. They will be designated (NR-HFS) as these authors describe their method as Hartree-Fock-Slater. The proper Hartree-Fock (NR-HF) solutions for the Cu^{+1} ion were obtained by Hartree and Hartree.[14] The subsequent NR-HF values obtained by Watson[15] differ only slightly from the latter. The solutions of the Dirac equations obtained without exchange by Williams,[8] Mayers,[9] and Cohen[10] will be designated (R-D); the more recent results of Mayers,[11] with exchange, by (R-DF). Finally, the present results (LWC) will be designated (R-DS). In the tables following, the experimental values used were deduced from x-ray spectra and tabulated by Sandström.[16]

The results for the $^{29}\mathrm{Cu}^{+1}$ ion are presented in Table I. The several relativistic corrections to the eigenvalues that Herman and Skillman developed by a perturbation treatment will not be included in the values presented here but the detailed values for comparison are available on pp. 3–12 of their book.[4] It is perhaps surprising that there is so little difference between the NR-H, NR-HF, and R-DS values for the 1s eigenvalue. Considering all of the eigenvalues, the Williams R-D and the Herman-Skillman NR-HFS values appear to be poorer when compared with the experimental value.

The three nonrelativistic results are presented in Table I to permit some estimation of the reliability and usefulness of Slater's approximate method of dealing with exchange. It is seen that the NR-HFS eigenvalues are of smaller magnitude than the more rigorous NR-HF values. A large number of further comparisons of this type could be made but these would take us away from from the major purpose of this paper.

Energy eigenvalues for $^{26}\mathrm{Fe}$ are presented in Table II. The x-ray values tabulated by Sandström[16] were determined on solids; Slater's[17] has applied appropriate corrections such as the Fermi energy to construct a table of ionization energies for free atoms up to Nb. The NR-HF energies in Table II obtained by Watson[18] are larger in magnitude than the NR-HFS values. As would

TABLE II. Energy eigenvalues for iron $^{26}\mathrm{Fe}$ ($3d^6 4s^2$ configuration) in rydbergs.

Shell	j	NR-H BLW Ref. 7	NR-HFS HS Ref. 4	NR-HF Watson Ref. 18	R-D Cohen Ref. 10	R-DS LWC Present	X-ray levels Ref. 16	Slater values Ref. 17
1s	$\frac{1}{2}$	522.32	515.81	522.709	527.18	520.628	523.77	524.3
2s	$\frac{1}{2}$	60.33	60.957	63.836	61.30	61.954	61.94	63.0
2p	$\frac{1}{2}$	52.90	53.084	54.792	53.72	53.912	53.06	52.8
2p	$\frac{3}{2}$				52.78	52.961	52.11	
3s	$\frac{1}{2}$	6.931	7.269	8.308	7.09	7.423	6.87	7.3
3p	$\frac{1}{2}$	4.569	4.891	5.450	4.68	4.9998	3.93	4.4
3p	$\frac{3}{2}$				4.56	4.8801		
3d	$\frac{3}{2}$	0.764	0.9625	1.2718	0.751	0.94513	0.14	0.64
3d	$\frac{5}{2}$				0.736	0.93203		
4s	$\frac{1}{2}$	0.4827	0.5451	0.5100	0.459	0.55352	···	0.53

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[14] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

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

[16] A. E. Sandström, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 30, p. 78.

[17] J. C. Slater, Phys. Rev. **98**, 1039 (1955).

[18] R. E. Watson, Phys. Rev. **119**, 1934 (1960).

TABLE III. Energy eigenvalues for ^{80}Hg. ($5d^{10}6s^2$ configuration) in rydbergs.

Shell	j	NR-H BLW Ref. 7	NR-H with rel. corr.	NR-HFS with rel. corr.	R-D Cohen Ref. 10	R-DS LWC present	R-DF Mayers Ref. 11	Exper. x-ray levels
1*s*	$\frac{1}{2}$	5551.78	6088.94	6154.7	6145.7	6130.18	6152.35	6121.7
2*s*	$\frac{1}{2}$	924.40	1062.10	1085.6	1081.8	1090.31	1101.12	1093.6
2*p*	$\frac{1}{2}$	892.11	1029.81	1038.9	1041.7	1047.75	1053.77	1046.9
	$\frac{3}{2}$		919.65	924.7	897.9	903.03	910.34	904.93
3*s*	$\frac{1}{2}$	216.99	251.68	260.6	255.7	260.14	266.40	262.5
3*p*	$\frac{1}{2}$	200.49	235.10	240.4	236.1	240.68	245.32	241.9
	$\frac{3}{2}$		212.03	215.4	204.7	208.50	213.15	210.3
3*d*	$\frac{3}{2}$	170.47	176.86	183.3	173.2	176.01	179.91	176.4
	$\frac{5}{2}$		172.60	176.5	166.4	169.07	172.08	169.3
4*s*	$\frac{1}{2}$	46.06	55.76	58.48	55.86	57.94	61.53	59.3
4*p*	$\frac{1}{2}$	38.88	48.58	49.84	47.42	49.51	52.26	50.6
	$\frac{3}{2}$		42.61	43.86	39.81	41.68	44.43	43.1
4*d*	$\frac{3}{2}$	25.78	27.68	29.87	26.19	27.80	29.59	28.3
	$\frac{5}{2}$		26.67	28.44	24.78	26.32	28.11	26.8
4*f*	$\frac{5}{2}$	8.365	8.569	9.962	7.44	8.324	8.943	···
	$\frac{7}{2}$		8.452	9.614	7.13	7.999	8.588	···
5*s*	$\frac{1}{2}$	6.936	···	9.536	8.806	9.251	10.215	9.2
5*p*	$\frac{1}{2}$	4.589	···	6.645	5.997	6.421	7.077	6.8
	$\frac{3}{2}$		···	5.586	4.626	5.013	5.692	5.2
5*d*	$\frac{3}{2}$	0.9174	···	1.544	0.858	1.167	1.291	1.0
	$\frac{5}{2}$		···	1.389	0.712	1.016	1.153	···
6*s*	$\frac{1}{2}$	0.4682	···	0.748	0.5665	0.6974	0.6569	0.7682

be expected, the simple NR-H values are relatively close to the experimental values cited by Cohen[10] for this low atomic number element. When the relativistic corrections from perturbation analysis are applied to the NR-HFS as in the book of Herman and Skillman,[4] the agreement becomes quite close. However, if one were to calculate other expectation values with the HS eigenfunctions, the results would be anticipated to be less accurate than indicated by this agreement. Aside from the value for the 1*s* electrons,[19] Cohen's R-D eigenvalues are smaller than the present values, which indicates the effect of including the exchange correction.

In contrast, the energy eigenvalues for ^{80}Hg are compared in Table III. The NR-H values of Boyd, Larson, and Waber are substantially in error for the inner electrons. When the Sommerfeld correction

$$\text{Rel. corr.} = \frac{\alpha^2 z^4}{n^3}\left(\frac{3}{4n} - \frac{1}{j+\frac{1}{2}}\right) \tag{13}$$

is applied, the agreement with the experimental x-ray values is improved. In (15), α is the fine-structure constant, n is the principal quantum number, and z is the effective (screened) nuclear charge experienced by a given electron. These approximate corrections were not applied for the outer electron shells. When the Herman-Skillman values of the mass-velocity, Darwin and spin-orbit corrections are applied to their NR-HFS eigenvalues, the agreement is improved. Cohen's R-D values are not in closer agreement with the experimental values than are these more approximate values. The present results are in excellent agreement. The unpublished "provisional" R-DF calculations of Mayers[11] made with the most rigorous method used to date, namely made with a proper treatment of the Dirac equations with exchange as is done in the Hartree-Fock method, are presented in the penultimate column of Table III. It is surprising that in almost every case the experimental values agree better with the R-DS values, i.e., obtained with Slater's approximation to exchange, than with Mayers' R-DF values. As discussed below, this situation may be the result of experimental difficulties and not reflect on the accuracy of Mayers' results. M. Cohen[20] recently suggested that Slater's method may overcorrect for exchange and may include a part of the correlation effects.

Cohen's R-D values are presented for tungsten ^{74}W and platinum ^{78}Pt in Table IV. The present values agree well with the experimental values.

The energy eigenvalues for uranium ^{92}U are compared for two configurations in Table V. Of the relativistically corrected NR-H and NR-HFS values, the latter are superior. As observed before, Cohen's R-D values are in no better agreement with the experimental values than are the Herman-Skillman estimates.

The effect of configuration is larger than might have been anticipated for the inner electrons. The difference

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[19] One feature of employing Slater's average exchange potential is that the 1*s* electron is bound less tightly than in either the Hartree or Hartree-Fock solutions. This can be seen in both the NR and R sets of energies in Tables I, II, and III. The effect is much smaller for other electrons.

[20] M. Cohen (private communication).

TABLE IV. Energy eigenvalues for ^{74}W and ^{78}Pt in rydbergs.

		W ($5d^46s^2$ configuration)			Pt ($5d^96s^1$ configuration)		
Shell	j	R-D Cohen Ref. 10	R-DS LWC present	Exper. x-ray levels	R-D Cohen Ref. 10	R-DS LWC present	Exper. x-ray levels
1s	½	5139.0	5124.1	5120.4	5796.7	5781.2	5773.5
2s	½	880.90	887.93	890.8	1011.44	1019.3	1022.7
2p	½	845.74	850.63	849.93	973.04	978.60	977.06
2p	3/2	745.82	750.05	751.38	845.37	850.10	851.18
3s	½	202.21	205.61	207.4	236.76	240.73	242.3
3p	½	185.21	188.75	189.3	218.05	222.17	222.3
3p	3/2	163.93	166.89	167.6	190.38	193.80	194.3
3d	3/2	136.10	138.21	137.5	160.11	162.60	161.7
3d	5/2	131.44	133.43	132.9	154.11	156.45	155.7
4s	½	41.47	42.976	43.4	50.59	52.399	52.7
4p	½	34.39	35.896	36.0	42.63	44.433	44.4
	3/2	29.40	30.803	31.0	36.01	37.633	37.7
4d	3/2	17.91	19.074	18.7	23.11	24.480	23.8
	5/2	17.00	18.126	17.7	21.89	23.203	22.7
4f	5/2	2.701	3.301	2.3	5.57	6.266	5.0
4f	7/2	2.529	3.124	2.1	5.32	5.995	4.6
5s	½	5.889	6.230	5.4	7.666	7.9784	6.9
5p	½	3.785	4.087	3.2	5.102	5.392	4.3
5p	3/2	3.058	3.323	2.5	3.980	4.239	3.3
5d	3/2	0.411	0.5851	...	0.5992	0.8057	0
5d	5/2	...	...	...	0.486	0.6943	0
6s		0.4927	0.5588	...	0.502	0.5929	...

TABLE V. Energy eigenvalues for two configurations of ^{92}U in rydbergs.

		$5f^36d^17s^2$				$5f^47s^2$		
Shell	j	NR-H with rel. corr.	NR-HFS with rel. corr.	R-D Cohen Ref. 10	R-DS LWC present	NR-H with rel. corr.	R-DS LWC present	Exper. x-ray level
1s	½	8367.41	8486.2	8562.76	8546.83	8367.01	8546.53	8514.7
2s	½	1528.96	1564.22	1589.79	1602.17	1528.38	1601.85	1602.6
2p	½	1490.36	1503.37	1537.77	1546.87	1490.01	1546.56	1542.2
2p	3/2	1292.13	1299.24	1255.32	1262.27	1292.11	1262.35	1264.2
3s	½	384.14	400.276	399.48	406.33	386.35	405.99	408.5
3p	½	363.92	373.879	373.79	380.88	366.12	380.54	381.4
3p	3/2	321.99	327.633	309.50	315.17	322.51	314.83	316.6
3d	3/2	276.58	287.859	270.05	274.54	276.27	274.20	273.9
3d	5/2	268.30	274.916	256.95	261.15	267.98	260.82	261.5
4s	½	91.705	103.941	101.02	104.48	91.206	104.135	105.5
4p	½	82.336	92.171	89.40	92.895	81.842	92.562	92.3
4p	3/2	75.247	80.188	72.71	75.655	74.862	75.324	76.6
4d	3/2	55.528	61.5795	54.45	57.111	55.210	56.779	57.3
4d	5/2	54.446	58.5191	51.40	53.918	54.129	53.587	54.1
4f	5/2	30.219	33.4507	27.69	29.442	29.898	29.108	28.4
4f	7/2	29.912	32.5550	26.89	28.598	29.693	28.264	27.9
5s	½	18.034	23.9109	22.62	25.544		23.220	23.6
5p	½	14.415	19.3209	18.11	19.005	13.723	18.684	18.6
5p	3/2	14.118	16.4455	14.11	14.873	13.648	14.560	14.5
5d	3/2	7.6694	9.5357	7.58	8.1820	7.362	7.884	7.2
5d	5/2	7.6560	8.9260	7.00	7.5632	7.349	7.267	
5f	5/2	0.6949	1.35020	0.274	0.57877	0.41764	0.37545	...
6s	½	2.0938	4.03646	3.598	3.7992	2.5219	3.6060	5.32
6p	½	1.6788	2.67315	2.287	2.4624	1.5348	2.2941	2.2
6p	3/2	1.6765	2.19036	1.625	1.7642	1.5178	1.6265	
6d	3/2	0.3027	0.54915	0.225	0.32306	...	...	0.27
7s	½	0.3108	0.46349	0.379	0.41218	0.29159	0.38264	...

TABLE VI. Comparison of the calculated x-ray spectra of mercury with experimental data.

		Calculated values			Experimental values		
Line	Transition	Cohen	LCW	Mayers	Sandström	Beckman[a]	Cauchois[b]
			K Spectrum				
$K\alpha_2$	K_{I}–L_{II}	5104.0	5082.43	5098.58	5074.8	5064.51	
$K\alpha_1$	K_{I}–L_{III}	5247.8	5227.15	5242.01	5216.77	5205.78	
$K\beta_1$	K_{I}–M_{II}	5909.6	5889.50	5907.03	5889.8	5902.06	
$K\beta_{2\mathrm{II}}$	K_{I}–N_{II}	6097.27	6080.67	6100.09	6071.1	6062.59	
$K\beta_{2\mathrm{I}}$	K_{I}–N_{III}	6105.89	6088.50	6107.92	6078.6	6071.04	
0_{II}-0_{III}	K_{I}–$0_{\mathrm{II,III}}$	6139.7	6123.7	6145.27	6114.9	6107.35	
			L Spectrum				
$L\alpha_1$	L_{III}–M_{V}	731.5	733.96	738.96	735.63		735.706
$L\alpha_2$	L_{III}–M_{IV}	726.7	727.02	731.33	728.53		728.96
Lβ_1	L_{II}–M_{IV}	868.5	871.74	873.86	870.50		870.759
Lβ_2	L_{III}–N_{V}	873.12	876.71	882.23	878.13		878.161
$L\beta_3$	L_{I}–M_{III}	877.1	881.81	887.97	883.3		883.44
$L\gamma_1$	L_{II}–N_{IV}	1015.51	1019.95	1024.18	1018.6		1018.8
$L\gamma_2$	L_{I}–N_{II}	1034.37	1040.81	1048.86	1043.6		1043.1

[a] Reference 21.
[b] Reference 22.

in energy between the two NR-H sets of data is quite close to the difference between the two present R-DS values.

DISCUSSION

Sandström[16] points out that the x-ray energy levels are based for the most part on the L_{III} absorption edge. But because of ". . .the ladder-shaped structure due to unresolved details, it is very difficult to decide what is the true inflexion point of such edges." While this does not matter very much in establishing the energy-level system on a relative basis, it does reduce the value of such data in making a comparison with our calculations. Sandström's values are adjusted to give reasonable agreement with a range of x-ray data, not all of the data having uniform precision or having been based on the same values of the calibration points. There is attendant loss in accuracy of any energy level.

For this reason, some of the transition energies are compared in Table VI for mercury. Both the energies obtained from Sandström's energy levels and from the precise measurements of Beckman[21] on the *K* spectrum and Cauchois[22] on the *L* spectrum are included as experimental data. Her data were corrected by Sandström using more recent values of the physical constants to convert from x units. Sandström's values and those of Beckman differ by less than 0.2%. This is comparable to the difference between Sandström's values and the present LWC values. Here again, the LWC values agree with experiment better than Mayers' provisional values do. Undoubtedly, if this anomaly is due to computational difficulties, such as insufficient convergence, it will be eliminated in the near future.

The values of the *K* spectrum are strongly dependent on the eigenvalue of the 1*s* electron which will be significantly affected by the Breit and higher interactions and by the finite size of the nucleus. Since the three states $2s\,\frac{1}{2}$, $2p\,\frac{1}{2}$, and $2p\frac{3}{2}$ are involved in the *L* spectrum presented above, and radiative corrections are much smaller than in the case of the 1*s* electron, the agreement between LWC and experimental energy is less likely to result fortuitously from neglecting higher order interactions.

Several *L* x-ray lines of uranium are compared with experimental values of Claëson,[23] Shacklett and DuMond,[24] and Merrill and DuMond[25] in Table VII.

TABLE VII. Comparison of calculated *L* x-ray spectra of uranium with experimental values.

	Calculated values				Experimental values		
Term	Present $5f^47s^2$	Present $5f^36d7s^2$	Cohen Ref. 10	Sandström	Ref. 23	Ref. 24	Ref. 25
α_1	1001.53	1001.12	998.37	1002.7	1000.80	· · ·	1000.69
α_2	988.15	987.73	985.27	990.3	987.89	987.767	987.767
β_1	1272.36	1272.33	1267.72	1268.3	1265.64	1265.701	1265.694
β_2	1208.76	1208.35	1203.92	1210.1	1207.50	· · ·	1207.50
β_3	1287.02	1287.00	1280.29	1285.8	1283.01	· · ·	1282.97

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[21] O. Beckman, Phys. Rev. **109**, 1590 (1958).
[22] Y. Cauchois, Compt. Rend. **200**, 1194, 1314 (1935).
[23] H. Claëson, Z. Physik **101**, 499 (1936).
[24] R. R. Shacklett and J. W. M. DuMond, Phys. Rev. **106**, 501 (1957).
[25] J. J. Merrill and J. W. M. DuMond, Phys. Rev. **110**, 79 (1958).

Both uranium configurations are included. It will be seen that the terms for the $5f^3 6d 7s^2$ configuration agree well with the experimental results.

The effect of exchange on the transitions between inner electron levels is seen to be rather small. That is, Cohen's (R-D) values in Tables VI and VII are not substantially different from the present (R-DS) values.

An indirect relativistic effect was noted[26] by comparing Cohen's R-D eigenvalues for the outer electrons of uranium with Boyd, Larson, and Waber's NR-H value. Because of the relativistic effect of concentrating the electron with low angular momentum near the nucleus and thus screening the nuclear charge more effectively, the electrons with $l=2$ or 3 would be more loosely bound. The observed ratios of R-D/NR-H presented in Table VIII varied from about 0.4 for $5f$ to 1.34 for $6s$ electrons. In contrast, the effect of exchange is to bind more tightly the electrons having large angular momenta. The ratios of uncorrected NR-HFS to the uncorrected NR-H values were 1.71 for $5f$ and 1.48 for $6d$ and all the values of NR-HFS/NR-H exceeded unity. Thus one would anticipate that the indirect relativistic effect would be largely offset for electrons with large l values. The results agree with expectation. Although the values are nearer unity, a regular decrease occurs in the R-DS/NR-H as a function of l for the $n=5$ and $n=6$ shells. The substantial effect on the $7s$ level is undoubtedly due to increased screening of the nuclear charge from both these effects.

As a test of Koopman's theorem, the R-DS total energy was calculated by the method outlined by Snow, Canfield, and Waber[27] for the neutral mercury atom and for one in which one $1s$ electron was removed. A self-consistent solution was readily found for this ion. The $1s$ eigenvalue for the neutral ^{80}Hg is 6130.1 and for ^{80}Hg^{+1} was 6216.1 Ry. The difference in total energies between the atom and ion is 6144.2, which is to be compared with the experimental value of 6121.7 Ry. Slater[28] has previously pointed out that the difference between two total energies does not lead to the precise ionization energy for an outer electron of elements near oxygen. Thatcher[29] made in 1936 the first calculation for K^+; the first for any ion in which an inner electron was removed. Apparently, no other results prior to the present study are available. Slater's prescription[28] for obtaining a better estimate of the ionization energy has not been tried.

TABLE VIII. Effect of including exchange on the indirect relativistic effect for ^{92}U.

	NR-HFS	R-DS	R-D	R-DS
Ratio	NR-H	R-D	NR-H	NR-H
$5s$	1.055	1.129	1.290	1.346
$5p$	1.066	1.052[a]	1.110[a]	1.156[a]
$5d$	1.104	1.086[a]	0.942[a]	1.017[a]
$5f$	1.710	2.113[b]	0.396[b]	0.781[b]
$6s$	1.102	1.056	1.338	1.396
$6p$	1.145	1.081[a]	1.102[a]	1.168[a]
$6d$	1.482	1.436[b]	0.742[b]	0.942[b]
$7s$	1.136	1.088	1.219	0.891

[a] Based on barycenter value.
[b] If both j states were occupied, ratio would be smaller.

TABLE IX. Comparison of expectation values calculated for $5f$ electrons in uranium atom $(5f^3 6d^1 7s^2)$.

			R-DS
Quantity	NR-H	R-DS	NR-H
$\langle r^{-3} \rangle$	5.2722	6.6915	1.269
$\langle r^{2} \rangle$	2.6364	2.2234	0.843
$\langle r^{4} \rangle$	15.2220	10.8734	0.714
$\langle r^{6} \rangle$	180.190	115.398	0.640

The effect of the exchange potential concentrating the $5f$ electrons nearer the nucleus in spite of the indirect relativistic effect can be assessed in another way. In Table IX, the values $\langle r^\nu \rangle$ obtained by using the NR-H and R-DS wave functions are compared for the free ^{92}U atom. The ratio R-DS/NR-H decreases regularly with ν, indicating a substantial reduction in charge density in the outer radial portion of the atom.

The effect of using the Slater exchange contribution to the potential without the Latter correction for self-interaction has been assessed. In Table X the energy eigenvalues obtained with and without this correction are compared for Fe, Hg, and U. As is seen, the modification of the potential to remove the self-interaction of each electron increases the binding energy of each electron, the change being largest for the outer portion of the atom. In percentage the increase in eigenvalue is the largest for the outer electron shells, as would be expected. The experimental values have been given for comparison in Tables II, III, and V.

CONCLUSIONS

The energy eigenvalues obtained as solutions of the relativistic Dirac-Slater eigenvalue problem for a central field potential have been compared with those obtained by using various other approximations. Specifically, it was found that for ^{29}Cu^{+1} ion and ^{26}Fe, the relativistic energies were not much different from those obtained by the simple Hartree method, but the Herman-Skillman values for the Hartree-Fock-Slater method were poorer.

However, for heavy elements such as ^{80}Hg and ^{92}U, there was a large disparity between the relativistic and

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[26] R. G. Boyd, A. C. Larson, and J. T. Waber, Phys. Rev. **129**, 1629 (1963).

[27] E. C. Snow, J. Canfield, and J. T. Waber, Phys. Rev. **135**, A969 (1964).

[28] J. C. Slater *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. 1, 364.

[29] W. A. Thatcher, Proc. Roy. Soc. (London) **A172**, 242 (1939).

TABLE X. Comparison of energy eigenvalues obtained without and with Latter correction for self interaction (rydbergs).

		Iron ($3d^6 4s^2$)		Mercury $5d^{10}6s^2$		Uranium $5f^3 6d^1 7s^2$	
Shell	j	without	with	without	with	without	with
1*s*	$\frac{1}{2}$	520.56	520.628	6130.1	6130.18	8546.78	8546.83
2*s*	$\frac{1}{2}$	61.893	61.954	1090.3	1090.31	1602.12	1602.17
2*p*	$\frac{1}{2}$	53.850	53.912	1047.7	1047.75	1546.84	1546.87
2*p*	$\frac{3}{2}$	52.899	52.961	903.0	903.03	1262.64	1262.27
3*s*	$\frac{1}{2}$	7.3612	7.4230	260.1	260.14	406.30	406.33
3*p*	$\frac{1}{2}$	4.9382	4.9998	240.6	240.68	380.84	380.88
3*p*	$\frac{3}{2}$	4.8188	4.8801	208.4	208.50	315.14	315.17
3*d*	$\frac{3}{2}$	0.8862	0.94513	176.0	176.01	274.50	274.54
3*d*	$\frac{5}{2}$	0.8730	0.93203	169.0	160.07	261.12	261.15
4*s*	$\frac{1}{2}$	0.4854	0.55352	57.89	57.94	104.42	104.48
4*p*	$\frac{1}{2}$	···	···	49.46	49.51	92.86	92.895
4*p*	$\frac{3}{2}$	···	···	41.63	41.68	75.62	75.655
4*d*	$\frac{3}{2}$	···	···	27.75	27.80	57.08	57.111
4*d*	$\frac{5}{2}$	···	···	26.28	26.32	53.88	53.918
4*f*	$\frac{5}{2}$	···	···	8.28	8.324	29.40	29.442
4*f*	$\frac{7}{2}$	···	···	7.95	7.999	28.56	28.598
5*s*	$\frac{1}{2}$	···	···	9.21	9.251	23.50	23.544
5*p*	$\frac{1}{2}$	···	···	6.38	6.421	18.964	19.005
5*p*	$\frac{3}{2}$	···	···	4.97	5.013	14.832	14.873
5*d*	$\frac{3}{2}$	···	···	1.126	1.167	8.142	8.1820
5*d*	$\frac{5}{2}$	···	···	0.975	1.016	7.522	7.5632
5*f*	$\frac{5}{2}$	···	···	···	···	0.5402	0.57877
5*f*	$\frac{7}{2}$	···	···	···	···	···	···
6*s*	$\frac{1}{2}$	···	···	0.6436	0.6974	3.756	3.7992
6*p*	$\frac{1}{2}$	···	···	···	···	2.420	2.4624
6*p*	$\frac{3}{2}$	···	···	···	···	1.725	1.7642
6*d*	$\frac{3}{2}$	···	···	···	···	0.2854	0.32306
7*s*	$\frac{1}{2}$	···	···	···	···	0.2770	0.41218

nonrelativistic results. Applying the Sommerfeld correction to the NR-H or the Herman-Skillman relativistic corrections to the NR-HFS eigenvalues, one could obtain reasonable agreement with experimental x-ray levels. The present results gave the best agreement for the elements considered.

The effect of exchange was shown to largely offset the indirect relativistic effect discussed previously for electrons with large angular momentum; a slower decrease of the R-DS/NR-H ratio with l was observed. The effect of using the more compact R-DS wave functions on $\langle r^\nu \rangle$ was also discussed. The inclusion of the Latter correction for self-interaction in the potential with Slater's exchange term increases the binding of all electrons, but the relative effect is larger for the outer electrons.