Relativistic Self-Consistent Fields with Exchange*†

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A relativistic Hartree-Fock calculation of atomic wave functions and energy levels is carried out. The relativistic Hamiltonian is the sum of the Dirac Hamiltonian of the electrons and the retarded Breit interaction. Expressions for the matrix elements of the Hamiltonian are given for closed-shell configurations of electrons, and the relativistic Hartree-Fock equations are derived. A numerical program to compute the Dirac radial functions and energy eigenvalues for an arbitrary closed-shell atom is described. Results obtained for the energies of the ground states of He and Be are found to be in precise agreement with previous nonrelativistic calculations. Results for Ne, Ar, and Cu^+ are also presented and compared with previous self-consistent-field calculations.

I. INTRODUCTION

ALTHOUGH the Hartree and Hartree-Fock methods have been widely used to calculate atomic structures, comparatively few relativistic calculations have been carried out. At present, all of the relativistic self-consistent-field calculations in the literature either neglect exchange or use approximations to the exchange forces.

The best agreement to date with the experimental energy levels of the inner electrons of heavy atoms has been obtained from the relativistic Hartree-Fock-Slater calculation of Liberman, Waber, and Cromer.[1] For the K-shell of a heavy element, the difference between these eigenvalues and the experimental energy levels is of the order of $\alpha(\alpha Z)^4\ mc^2$, which agrees in sign and order of magnitude with the Lamb shift for a hydrogenlike atom.[2] In subsequent calculations of higher-order corrections it would be desirable to have a calculation of the wave functions including exchange exactly as a starting point and basis for comparison. Grant[3] has derived relativistic Hartree-Fock equations using an unretarded relativistic electron-electron interaction. Racah's algebra of spherical tensor operators is used to simplify the formula for the expectation value of the Hamiltonian. Although a numerical calculation is mentioned in Grant's work, no description of the calculation has been published. In addition, we have found some of Grant's tabulated coefficients to be in error.

More recently a relativistic generalization of the Hartree-Fock-Roothaan equations has been formulated and solved by Kim,[4] who gives numerical results for He, Be, and Ne.

The object of this work is to present a relativistic Hartree-Fock calculation for closed-shell configurations of atoms. An expression is derived for the expectation value of the Hamiltonian of the atom, and the variational principle is applied to obtain the relativistic Hartree-Fock equations for the radial functions. The interaction between electrons used is that derived from quantum electrodynamics, treating the coupling of the electron with the radiation field in lowest-order perturbation theory. Since a stationary state of an atom is represented by an antisymmetric state vector, exchange is automatically included. A numerical program is developed to obtain the wave functions and energy eigenvalues for an arbitrary closed-shell atom. The results of numerical calculations which have been carried out using this program are presented and compared with earlier work.

II. DERIVATION OF THE HARTREE-FOCK EQUATIONS

Brown[5] has shown that the expectation value of the Hamiltonian of two bound electrons in states represented by i and j is given by

$$u_{ij}=u_{ii,jj}-u_{ij,ij},$$

where

$$u_{ii,jj}=e^2\int\frac{d^3r_1d^3r_2}{|\mathbf{r}_1-\mathbf{r}_2|}\bar{\psi}_i(\mathbf{r}_1)\gamma_\mu\psi_i(\mathbf{r}_1)\bar{\psi}_j(\mathbf{r}_2)\gamma_\mu\psi_j(\mathbf{r}_2),$$

$$u_{ij,ij}=e^2\int\frac{d^3r_1d^3r_2}{|\mathbf{r}_1-\mathbf{r}_2|}\bar{\psi}_i(\mathbf{r}_1)\gamma_\mu\psi_j(\mathbf{r}_1)\bar{\psi}_j(\mathbf{r}_2)\gamma_\mu\psi_i(\mathbf{r}_2)\times\cos\omega_{ij}|\mathbf{r}_1-\mathbf{r}_2|, \quad (1)$$

and ω_{ij} is the absolute value of the difference between the energies of the electrons. We write the four-component Dirac wave function in the form

$$\psi_{n\kappa m}(\mathbf{r})=\begin{pmatrix}(i/r)G_{n\kappa}(r)\Omega_{\kappa m}(\hat{r})\\(1/r)F_{n\kappa}(r)\Omega_{-\kappa m}(\hat{r})\end{pmatrix}, \quad (2)$$

where the $\Omega_{\kappa m}(\hat{r})$ are two-component normalized spinors

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[1] D. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. **137**, A27 (1965).
[2] See, for example, J. M. Jauch and F. Rohrlich, *Theory of Photons and Electrons* (Addison-Wesley Publishing Company, Inc., Cambridge, Massachusetts, 1955).
[3] I. P. Grant, Proc. Roy. Soc. (London) **A262**, 555 (1961).
[4] Y. K. Kim, Phys. Rev. **159**, 17 (1967).
[5] G. E. Brown, Phil. Mag. **43**, 467 (1952).

which are simultaneous eigenfunctions of orbital and total angular momentum, and of the z component of total angular momentum.[6] The spinor $\Omega_{\kappa m}(\hat{r})$ can be written as

$$\Omega_{\kappa m}(\hat{r})=\sum_{\mu}C(l\tfrac{1}{2}j;\,m-\mu,\,\mu)Y_{l,m-\mu}(\hat{r})\chi^{\mu}, \qquad (3)$$

where $C(l\frac{1}{2}j;\,m-\mu,\,\mu)$ is a Clebsch-Gordan coefficient, Y_{lm} is a spherical harmonic, and χ^{μ} are two-component Pauli spinors. The quantity κ is given by

$$\kappa=\pm(j+\tfrac{1}{2}), \qquad l=j\pm\tfrac{1}{2}.$$

The direct and exchange parts of the interaction can be separated into electric and magnetic terms

$$u_{ii,jj}=e^2(I_{44}+\sum_{\lambda}I_{\lambda\lambda}),$$

$$u_{ij,ij}=e^2(J_{44}+\sum_{\lambda}J_{\lambda\lambda}),$$

where

$$I_{44}=\int\frac{d^3r_1d^3r_2}{|\,\mathbf{r}_1-\mathbf{r}_2\,|}\psi_i^{\dagger}(\mathbf{r}_1)\psi_i(\mathbf{r}_1)\psi_j^{\dagger}(\mathbf{r}_2)\psi_j(\mathbf{r}_2),$$

$$I_{\lambda\lambda}=-\int\frac{d^3r_1d^3r_2}{|\,\mathbf{r}_1-\mathbf{r}_2\,|}\psi_i^{\dagger}(\mathbf{r}_1)\alpha_{\lambda}\psi_i(\mathbf{r}_1)\psi_j^{\dagger}(\mathbf{r}_2)\alpha_{\lambda}\psi_j(\mathbf{r}_2)\times\cos\omega_{ij}\,|\,\mathbf{r}_1-\mathbf{r}_2\,|,$$

$$J_{44}=\int\frac{d^3r_1d^3r_2}{|\,\mathbf{r}_1-\mathbf{r}_2\,|}\psi_i^{\dagger}(\mathbf{r}_1)\psi_j(\mathbf{r}_1)\psi_j^{\dagger}(\mathbf{r}_2)\psi_i(\mathbf{r}_2),$$

$$J_{\lambda\lambda}=-\int\frac{d^3r_1d^3r_2}{|\,\mathbf{r}_1-\mathbf{r}_2\,|}\psi_i^{\dagger}(\mathbf{r}_1)\alpha_{\lambda}\psi_j(\mathbf{r}_1)\psi_j^{\dagger}(\mathbf{r}_2)\alpha_{\lambda}\psi_i(\mathbf{r}_2)\times\cos\omega_{ij}\,|\,\mathbf{r}_1-\mathbf{r}_2\,|. \qquad (4)$$

Substituting the central-field wave functions (2) into the interaction matrix elements (4) with Eq. (3) and the expansions

$$|\,\mathbf{r}_1-\mathbf{r}_2\,|^{-1}=\sum_{lm}\frac{4\pi}{2l+1}\frac{r_<^{\,l}}{r_>^{\,l+1}}Y_{lm}^{*}(\hat{r}_1)Y_{lm}(\hat{r}_2),$$

$$\frac{\cos\omega_{ij}\,|\,\mathbf{r}_1-\mathbf{r}_2\,|}{|\,\mathbf{r}_1-\mathbf{r}_2\,|}=\sum_{lm}\frac{4\pi}{2l+1}K_l(\omega_{ij},r_1,r_2)Y_{lm}^{*}(\hat{r}_1)Y_{lm}(\hat{r}_2), \qquad (5)$$

where

$$K_l(\omega_{ij},r_1,r_2)=-\omega_{ij}(2l+1)j_l(\omega_{ij}r_<)y_l(\omega_{ij}r_>),$$

summing over m_i, and making use of the algebra of the Clebsch-Gordan and Racah coefficients, we obtain for the interaction between an electron and a closed shell

$$\sum_{m_i}I_{44}=(2j_i+1)\mathfrak{F}_0^{E}(i,j),$$

$$\sum_{m_i,\lambda}I_{\lambda\lambda}=0,$$

$$\sum_{m_i}J_{44}=(2j_i+1)\sum_{l}\Lambda^{E}(\kappa_jl\kappa_i)\mathfrak{G}_l^{E}(j,i,\omega_{ij}),$$

$$\sum_{m_i,\lambda}J_{\lambda\lambda}=(2j_i+1)\sum_{l}[\mathfrak{M}_l^{M}(j,i,\omega_{ij})\Lambda^{M}(\kappa_jj\kappa_i)+\mathfrak{L}_l^{M}(j,i,\omega_{ij})\Gamma^{M}(\kappa_jl-\kappa_i)+\mathfrak{L}_l^{M}(i,j,\omega_{ij})\Gamma^{M}(-\kappa_jl\kappa_i)]. \qquad (6)$$

The Slater integrals are defined by

$$\mathfrak{F}_0^{E}(i,j)=\int_0^{\infty}dr\;Y_0(i,r)[G_j(r)^2+F_j(r)^2],$$

$$\mathfrak{G}_l^{E}(j,i,\omega_{ij})=\int_0^{\infty}dr\;Y_l^{E}(j,i,\omega_{ij},r)G_i(r)F_j(r),$$

$$\mathfrak{M}_l^{M}(j,i,\omega_{ij})=2\int_0^{\infty}dr\;Y_l^{M}(j,i,\omega_{ij},r)G_i(r)F_j(r),$$

$$\mathfrak{L}_l^{M}(j,i,\omega_{ij})=\int_0^{\infty}dr\;Y_l^{M}(j,i,\omega_{ij},r)F_i(r)G_j(r), \qquad (7)$$

with

$$Y_l^{E}(j,i,\omega_{ij},r)=r\int_0^{\infty}dr'K_l(\omega_{ij},r,r')\times[G_i(r')G_j(r')+F_i(r')F_j(r')],$$

$$Y_l^{M}(j,i,\omega_{ij},r)=r\int_0^{\infty}dr'K_l(\omega_{ij},r,r')G_j(r')F_i(r'). \qquad (8)$$

The electrostatic and magnetic coupling coefficients are expressed in terms of Clebsch-Gordan and Racah coefficients as follows:

$$\Lambda^{E}(\kappa_2l\kappa_1)=\Lambda(j_2lj_1)\Pi(l_1ll_2),$$

$$\Lambda^{M}(\kappa_2l\kappa_1)=\Lambda(j_2lj_1)\Pi(l_1l+1l_2),$$

$$\Lambda(j_1lj_2)=[C(j_1lj_2;\tfrac{1}{2}0\tfrac{1}{2})]^2/(2j_1+1),$$

$$\Gamma^{M}(\kappa_1l\kappa_2)=\Gamma(\kappa_1l\kappa_2)\Pi(l_1l+1l_2),$$

$$\Gamma(\kappa_1l\kappa_2)=6\sum_{J}[W(1\tfrac{1}{2}j_1l_1;\tfrac{1}{2}J)]^2\Lambda(Jlj_2), \qquad (9)$$

where

$$\Pi(l_1ll_2)=0, \quad l_1+l+l_2 \text{ odd};$$
$$=1, \quad l_1+l+l_2 \text{ even}.$$

The coefficients defined above are given numerically in Tables I and II. Our coefficient $\Lambda(j_1lj_2)$ is equal to one-half the $\Gamma_{j_1lj_2}$ defined by Grant,[3] and we have found his values for $\Gamma_{7/2\,1\,7/2}$ and $\Gamma_{7/2\,3\,7/2}$ to be in error.

We write the total energy of the atom as the sum of

[6] The angular-momentum coupling coefficients and spherical harmonics used are those defined in M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

TABLE I. $\Lambda(j_2lj_1)$. Symmetry relation: $\Lambda(j_2lj_1)=\Lambda(j_1lj_2)$.

j_2	j_1 \ l	0	1	2	3	4	5	6	7	8
1/2	1/2	1/2	1/6							
	3/2		1/6	1/10						
	5/2			1/10	1/14					
	7/2				1/14	1/18				
	9/2					1/18	1/22			
3/2	3/2	1/4	1/60	1/20	9/140					
	5/2		1/10	1/70	1/35	1/21				
	7/2			9/140	1/84	5/252	5/132			
	9/2				1/21	1/99	1/66	9/286		
5/2	5/2	1/6	1/210	4/105	4/315	1/63	25/693			
	7/2		1/14	1/210	1/42	5/462	5/462	25/858		
	9/2			1/21	1/231	4/231	4/429	7/858	7/286	
7/2	7/2	1/8	1/504	5/168	3/616	9/616	75/8008	25/3432	245/10296	
	9/2		1/18	1/462	3/154	9/2002	3/286	7/858	7/1287	49/2431
9/2	9/2	1/10	1/990	4/165	12/5005	9/715	3/715	16/2145	784/109395	49/12155

the zero-order energy and the interaction energy of the electrons

$$E=\sum_j E_{0j}+\sum_{\text{pairs}} U_{ij},$$

where

$$E_{0j}=\int_0^\infty dr\left\{G_j\left[(V_N+1)G_j+\left(\frac{d}{dr}-\frac{\kappa_j}{r}\right)F_j\right]+F_j\left[(V_N-1)F_j-\left(\frac{d}{dr}+\frac{\kappa_j}{r}\right)G_j\right]\right\},$$

and V_N is the Coulomb potential of the nucleus.

Applying the variational principle, incorporating the orthonormality conditions

$$\int_0^\infty (G_{n\kappa}G_{n'\kappa}+F_{n\kappa}F_{n'\kappa})\,dr=\delta_{nn'}, \tag{10}$$

by using Lagrange multipliers λ_{ij}, and setting $\lambda_{jj}=W_j$, we obtain the relativistic Hartree-Fock equations

$$\left(\frac{d}{dr}-\frac{\kappa_j}{r}\right)F_j+(V-W_j)G_j=X_j, \tag{11a}$$

$$\left(\frac{d}{dr}+\frac{\kappa_j}{r}\right)G_j+(2+W_j-V)F_j=Y_j, \tag{11b}$$

where

$$V(r)=V_N(r)+\frac{e^2}{r}\sum_i(2j_i+1)\,Y_0(i,r),$$

$$\begin{aligned}X_j(r)=&\frac{e^2}{r}\sum_i{}'(2j_i+1)\sum_l\{\Lambda^E(\kappa_jl\kappa_i)\,Y_l^E(j,i,\omega_{ij},r)G_i\\&-[\Lambda^M(\kappa_jl\kappa_i)\,Y_l^M(i,j,\omega_{ij},r)+\Gamma^M(\kappa_jl-\kappa_i)\,Y_l^M(j,i,\omega_{ij},r)]F_i\}+\sum{}'\lambda_{ji}G_i,\\Y_j(r)=&-\frac{e^2}{r}\sum_i{}'(2j_i+1)\sum_l\{\Lambda^E(\kappa_jl\kappa_i)\,Y_l^E(j,i,\omega_{ij},r)F_i\\&-[\Lambda^M(\kappa_jl\kappa_i)\,Y_l^M(j,i,\omega_{ij},r)+\Gamma^M(-\kappa_jl\kappa_i)\,Y_l^M(i,j,\omega_{ij},r)]G_i\}-\sum{}'\lambda_{ji}F_i.\end{aligned} \tag{12}$$

The symbol $\sum'_i$ indicates that the sum runs over all orbitals i for which $\kappa_i=\kappa_j$ and $i\neq j$.

III. DESCRIPTION OF THE NUMERICAL PROGRAM

A numerical program has been developed to calculate the wave functions and energy eigenvalues for an arbitrary closed-shell atom. In the numerical work the nucleus has been taken to be a uniformly charged sphere of radius $R=1.2\,A^{1/3}\times10^{-13}$ cm, so that

$$V_N(r)=-Ze^2/r, \qquad r\geq R$$

$$V_N(r)=-3Ze^2/(2R)+Ze^2r^2/(2R^3), \qquad r\leq R,$$

and retardation has been neglected. We do not believe this effect to be large, since retardation enters only in the exchange term, which provides a relatively small correction, and is of second order in the energy differ-

TABLE II. $\Gamma(\kappa_2 l \kappa_1)$. Symmetry relation: $\Gamma(\kappa_2 l \kappa_1) = \Gamma(\kappa_2 l - \kappa_1)$.

κ_2	κ_1 \ l	0	1	2	3	4	5	6	7
−1	1	3/2	1/2						
	2		1/2	3/10					
	3			3/10	3/14				
	4				3/14	1/6			
1	1	1/6	1/2	4/15					
	2	2/3	1/10	1/6	6/35				
	3		4/15	1/14	1/10	8/63			
	4			6/35	1/18	1/14	10/99		
−2	1	2/3	1/2	1/6					
	2	5/12	1/4	13/60	3/28				
	3		1/6	11/70	1/7	5/63			
	4			3/28	29/252	3/28	25/396		
2	1		1/10	3/10	6/35				
	2	3/20	1/4	9/140	3/28	4/35			
	3	2/5	1/14	1/10	1/21	2/30	20/231		
	4		6/35	1/20	9/140	5/132	15/308	10/143	
−3	1		4/15	3/10	1/10				
	2	2/5	1/6	1/10	1/7	1/5			
	3	7/30	1/6	8/105	4/63	31/315	5/99		
	4		1/10	23/210	11/210	65/1386	5/66	35/858	
3	1			1/14	3/14	8/63			
	2		1/14	11/70	1/21	5/63	20/231		
	3	5/42	1/6	4/105	4/63	25/693	5/99	200/3003	
	4	2/7	1/18	1/14	13/462	19/462	25/858	75/2002	70/1287
−4	1			6/35	3/14	1/14			
	2		6/35	3/28	9/140	3/28	15/308		
	3	2/7	1/10	1/14	11/210	19/462	5/66	75/2002	
	4	9/56	1/8	13/280	29/616	23/616	35/1144	475/8008	35/1144

ence ω_{ij}. In addition, we have computed the effect of retardation for a particular case; details are given below.

The limiting form of the kernel in Eq. (8) for $\omega_{ij}=0$ is

$$K_l(0, r, r') = r_<^l / r_>^{l+1}.$$

We can now set the off-diagonal Lagrange multipliers equal to zero. To show that the radial functions will then satisfy the orthogonality conditions, we first multiply Eq. (11a) by G_i and Eq. (11b) by F_i, where i is any orbital except j, for which $\kappa_i=\kappa_j$. We then subtract the equations, interchange i and j in the resulting equation, subtract again, and integrate over r to obtain

$$(W_i-W_j)\int_0^\infty (F_iF_j+G_iG_j)\,dr$$

$$=\int_0^\infty (X_jG_i-X_iG_j+Y_iF_j-Y_jF_i)\,dr.$$

The integrand on the right side of the above equation can be shown to vanish by writing out the functions X_j, X_i, Y_j, and Y_i in the form (12) and replacing the functions $Y_l^E(i, j, 0, r)$ and $Y_l^M(i, j, 0, r)$ by their integral representations (8). We will therefore set the off-diagonal multipliers equal to zero and achieve a considerable simplification in the numerical solution.

The input data consists of the quantum numbers of the electronic shells and previously computed potentials. To begin a calculation, the functions X_j and Y_j were taken to be zero, and the potential V calculated by a relativistic Hartree-Fock-Slater program written by Johnson and Coletta was used. The Hartree-Fock-Slater program used procedures essentially identical to those described by Liberman, Waber, and Cromer,[1] and gave energy eigenvalues in agreement with those reported by these authors.

The solution of the Hartree-Fock equations and the determination of the energy eigenvalues for a given orbital and set of potentials was carried out using a relativistic generalization of a method first employed by Hartree[7] in a nonrelativistic calculation. Let us drop temporarily the subscript j on the radial functions

[7] D. R. Hartree, J. Opt. Soc. Am. **46**, 350 (1956); see also D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley & Sons, Inc., New York, 1957).

TABLE III. Energy eigenvalues for He and Be in rydbergs. (1) Present work; (2) relativistic Hartree-Fock-Roothaan; (3) nonrelativistic Hartree-Fock; (4) experimental.

	(1)	(2)	(3)	(4)
He	1.83589	1.83606[a]	1.836[b]	1.807[b]
Be 1s	9.46601	9.46698[a]	9.466[c]	8.23[d]
Be 2s	0.61862	0.61864[a]	0.6186[c]	···

[a] See Ref. 4.
[b] H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 35, p. 231.
[c] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A150**, 9 (1935).
[d] K. Siegbahn, *Alpha-, Beta-, and Gamma-Ray Spectroscopy* (North-Holland Publishing Company, Amsterdam, 1965), Vol. 1, p. 862.

F_j and G_j. For a given set of potentials and energy these equations have particular solutions $F_L{}^P$ and $G_L{}^P$ and complementary functions $F_L{}^C$ and $G_L{}^C$ satisfying the regularity conditions $F_L \to r^{l+1}$ and $G_L \to r^{l+1}$ at the origin. Similarly, there exist particular solutions $F_R{}^P$ and $G_R{}^P$, and complementary functions $F_R{}^C$ and $G_R{}^P$ satisfying the boundary conditions that the radial functions go to zero as r approaches infinity.

The complementary functions satisfy Eqs. (11) with X_j and Y_j set equal to zero. A solution F and G satisfying both boundary conditions, and continuous everywhere except possibly at the classical turning point r_0 can be formed by setting

$$\left.\begin{aligned} F(r) &= F_R(r) = F_R{}^P(r) + \alpha_R F_R{}^C(r) \\ G(r) &= G_R(r) = G_R{}^P(r) + \alpha_R G_R{}^C(r) \end{aligned}\right\}, \quad r > r_0,$$

$$\left.\begin{aligned} F(r) &= F_L(r) = F_L{}^P(r) + \alpha_L F_L{}^C(r) \\ G(r) &= G_L(r) = G_L{}^P(r) + \alpha_L G_L{}^C(r) \end{aligned}\right\}, \quad r < r_0, \tag{13}$$

where α_R and α_L are any pair of constants. The requirement that α_R and α_L be continuous at r_0 determines α_R and α_L to be

$$\alpha_L = \frac{G_R{}^C(r_0)[F_R{}^P(r_0) - F_L{}^P(r_0)] + F_R{}^C(r_0)[G_L{}^P(r_0) - G_R{}^P(r_0)]}{F_L{}^C(r_0)G_R{}^C(r_0) - F_R{}^C(r_0)G_L{}^C(r_0)},$$

$$\alpha_R = \frac{G_L{}^C(r_0)[F_R{}^P(r_0) - F_L{}^P(r_0)] + F_L{}^C(r_0)[G_L{}^P(r_0) - G_R{}^P(r_0)]}{F_L{}^C(r_0)G_R{}^C(r_0) - F_R{}^C(r_0)G_L{}^C(r_0)}. \tag{14}$$

The solution constructed from Eqs. (13) using the values of α_L and α_R given in Eqs. (14) is continuous everywhere and satisfies the boundary conditions both at the origin and at infinity. Such a solution is not necessarily normalized; the norm of the wave function depends on the energy W. Solutions are computed for different values of W, and the energy eigenvalue, which gives a normalized solution, is determined by successive linear interpolation.

The two first-order differential equations (11) are integrated using the five-point Adams method,[8] chosen because of its stability properties. The Adams method is a standard predict-correct method using as a predictor

$$y_{n+1} = y_n + (h/720)(1901y'_n - 2774y'_{n-1} + 2616y'_{n-2} - 1274y'_{n-3} + 251y'_{n-4}) + (95/288)h^6 y^{(6)}(\xi),$$

and as a corrector

$$y_{n+1} = y_n + (h/720)(251y'_{n+1} + 646y'_n - 264y'_{n-1} + 106y'_{n-2} - 19y'_{n-3}) - (3h^6/160)y^{(6)}(\xi).$$

Here y_n denotes the value of the solution $y(r_n)$ where r_n is the nth mesh point. The point ξ lies somewhere on the interval of integration.

The integration is carried inward from the practical infinity, determined by the condition

$$[V(r) - W]r^2 \approx 300,$$

to the classical turning point. The outward integration is started at the surface of the nucleus, using starting values calculated at points inside the nucleus by a power series.

To have a finer mesh of points near the nucleus, the range of integration is divided into 427 intervals, equally spaced in the variable $t = \ln r$. The mesh is chosen so that the fifth point is on the surface of the nucleus; the integration could then be started with a power series for points inside the nucleus. The last mesh point is fixed at $10^4 \lambda_c$, where λ_c is the electron

TABLE IV. Energy eigenvalues for Ne in rydbergs. (1) Present work; (2) relativistic Hartree-Fock-Roothaan[a]; (3) nonrelativistic Hartree-Fock[b]; (4) experimental x-ray levels.[c]

Shell	j	(1)	(2)	(3)	(4)
1s	1/2	65.607	65.63490	65.546	63.72
2s	1/2	3.872	3.87198	3.861	···
2p	1/2	1.704	1.70568	1.701	1.4
	3/2	1.697	1.69696		

[a] See Ref. 4.
[b] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).
[c] See footnote d, Table III.

[8] F. B. Hildebrand, *Introduction to Numerical Analysis* (McGraw-Hill Book Company, Inc., New York, 1956), pp. 198, 202, 216.

TABLE V. Energy eigenvalues for Ar in rydbergs. (1) Relativistic Hartree-Fock (present work); (2) relativistic Hartree-Fock with retardation (present work); (3) nonrelativistic Hartree-Fock[a]; (4) nonrelativistic Hartree[a]; (5) nonrelativistic Hartree-Fock-Slater[b]; (6) experimental x-ray levels.[c]

Shell	j	1	2	3	4	5	6
$1s$	1/2	238.092	238.088	237.212	237.118	232.54	235.3
$2s$	1/2	24.815	24.816	24.643	22.201	22.865	21.09
$2p$	1/2	19.240	19.243	19.142	17.849	18.207	18.15
	3/2	19.086	19.088				18.01
$3s$	1/2	2.5731	2.5732	2.554	1.912	2.1068	1.98
$3p$	1/2	1.1894	1.1896	1.182	0.834	1.0653	0.88
	3/2	1.1756	1.1758				

[a] R. D. Cowan, A. C. Larson, D. Lieberman, J. B. Mann, and J. Waber, Phys. Rev. 144, 5 (1966).

[b] See Ref. 9.

[c] See footnote d, Table III.

Compton wavelength; the step size Δt varies from 1/32 to 1/28 for $1 \leq Z \leq 92$.

A calculation of the error term of the Adams method formula gives for the K-shell Coulomb radial function

$$F(r) = Ar^{\gamma}e^{-\lambda r},$$

a relative error $|\Delta f/f|$ of order 10^{-10} for r at the classical turning point r_0. The relative error increases somewhat for larger r, reaching a value of approximately 10^{-3} at the practical infinity. However, the absolute value of the error term is nearly the same at this point as at the classical turning point. The numerical-integration routines were also tested on this example for $Z=70$, and the results were found to agree with the above estimates. The Coulomb radial functions were also used to test the integration routines for an inhomogeneous set of equations, by taking

$$X = -20\alpha r^{\gamma-1}e^{-\lambda r},$$

$$Y = 20\alpha r^{\gamma-1}e^{-\lambda r},$$

and

$$V = -90\alpha/r.$$

This set of equations has the same solution as the homogeneous set with $Z=70$.

The power series is terminated when the next term is less than 10^{-0} times the sum. The numerical values for $V=X_j=Y_j=0$ and $\kappa=-1$ were found to agree with the analytic solution

$$F_j = -[(2+W)r]^{-1}[r\cosh(pr) - \sinh(pr)],$$

$$G_j = \sinh(pr)/p,$$

to one part in 10^6.

After solutions continuous everywhere are constructed, using Eqs. (13) and (14), the variation of the energy eigenvalues to produce a closer approximation to the true eigenvalue can be carried out in two ways. First, an error in W large enough to result in radial functions with an incorrect number of nodes is corrected using the "stepwise improvement scheme" or the "range-narrowing scheme," described by Herman and Skillman.[9] Second, if the radial functions have the correct number of nodes, the new eigenvalue is determined by linear interpolation using previous values or W and N. On the second trial integration of an iteration cycle, the value of W used to obtain another value of N for interpolation is $0.95W$.

Modification of the energy is discontinued on any iteration cycle if the interpolation formula gives a change ΔW in the energy such that

$$|\Delta W/W| < 10^{-5}.$$

Using the new radial functions, new potentials are computed using Eqs. (12). The functions $Y_l^E(i,j,0,r)$ and $Y_l^M(i,j,0,r)$ are computed for any pair of orbitals using Bode's integration formula

$$\int_{x_0}^{x_4} f(x)\,dx = (2h/45)(7f_0+32f_1+12f_2+32f_3+7f_4) + (8h^7/945)f^{(6)}(\xi).$$

For the special case $F(r)=re^{-\lambda r}$, the routine gave results in agreement with the analytic solution to seven decimal places. The norm of the wave function was also computed using this formula.

As a remedy for possible instability in the iteration process, the potentials

$$V = \phi V_{\text{calc}} + (1-\phi)V_{\text{old}},$$

$$X_j = \phi X_{j\,\text{calc}} + (1-\phi)X_{j\,\text{old}},$$

$$Y_j = \phi Y_{j\,\text{calc}} + (1-\phi)Y_{j\,\text{old}},$$

$$\phi = 0.375$$

are used in the next cycle. The energy eigenvalues to be used in the first trial integration of the next iteration cycle were calculated using first-order perturbation

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

TABLE VI. Energy eigenvalues for Cu^+ in rydbergs. (1) Present work; (2) nonrelativistic Hartree-Fock[a]; (3) relativistic Hartree[b]; (4) relativistic Hartree-Fock-Slater[c]; (5) nonrelativistic Hartree-Fock-Slater[d]; (6) nonrelativistic Hartree[e]; (7) experimental x-ray levels.[f]

Shell	j	(1)	(2)	(3)	(4)	(5)	(6)	(7)
$1s$	1/2	665.10	658.4	664.8	658.07	650.40	658.0	660.0
$2s$	1/2	83.915	82.30	79.52	80.558	78.87	78.45	80.9
$2p$	1/2	73.117	71.83	70.66	71.180	69.74	69.86	70.0
	3/2	71.676		69.14	69.625			68.5
$3s$	1/2	10.942	10.651	8.978	9.6410	9.355	8.968	8.8
$3p$	1/2	7.4865	7.279	6.012	6.6447	6.429	6.078	5.7
	3/2	7.2936		5.818	6.4470			5.4
$3d$	3/2	1.6193	1.613	1.020	1.4622	1.459	1.195	0.15
	5/2	1.5969		1.000	1.4395			

[a] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).
[b] A. O. Williams, Phys. Rev. **58**, 723 (1940).
[c] See Ref. 1.
[d] See Ref. 9.
[e] D. R. Hartree, Proc. Roy. Soc. (London) A141, 282 (1933).
[f] See footnote d, Table III. The experimental levels quoted are for neutral Cu.

theory. Iteration was continued until

$$\left|\frac{V-V_{\text{old}}}{V_{\text{old}}+e^2/r}\right| \leq 10^{-5}$$

for each value of r.

IV. RESULTS

The numerical results for the energy eigenvalues obtained using the present methods are compared with those from other methods. Results are given for the normal states of the elements He, Be, Ne, Ar, and Cu^+. The energy eigenvalues of He and Be are found to agree closely with those calculated previously using the nonrelativistic Hartree-Fock method. This result is expected, since relativistic effects are completely negligible for these atoms, providing a check on the calculation.

The results for He and Be are shown in Table III, with the nonrelativistic Hartree-Fock results and the experimental values. The remaining discrepancy between calculation and experiment is presumably due to the rearrangement energy and correlation effects.

The energy eigenvalues for neon are shown in Table IV. As the K-shell binding energy is only 63.7 Ry, or approximately 0.00017 times the electron-rest energy, relativistic effects are small for this atom. The nonrelativistic Hartree-Fock eigenvalues were computed using the expansion method, and their authors believed them to be accurate to three significant figures.

The numerical results for He, Be, and Ne presented here are seen to be in substantial agreement with the previous calculations of Kim.[4] The slight differences which do arise are probably due to the difference in numerical technique, and to the effect of finite nuclear size.

The energy eigenvalues for argon are presented in Table V. For the K shell, the difference ΔE between the relativistic and nonrelativistic Hartree-Fock results is 0.9 Ry. The ratio $\Delta E/E$ is thus of the same order of magnitude as the ratio of the binding energy to the rest energy. In general, a relativistic calculation will give a larger binding energy than the corresponding nonrelativistic calculation. The Hartree-Fock and Hartree-Fock-Slater methods give lower energy eigenvalues than the Hartree method.

The magnitude of the effect of retardation was tested for argon by making a calculation with retardation included. The results are presented in column 2 of Table V. It is seen that for all levels the difference is limited to the fifth decimal place.

The energy eigenvalues for Cu^+ are shown in Table VI. Like the eigenvalues for Ar, they are somewhat lower than the relativistic Hartree-Fock-Slater eigenvalues and slightly lower than the nonrelativistic Hartree-Fock eigenvalues. For the K shell, the difference between the relativistic and nonrelativistic eigenvalues is again of the same relative order of magnitude as the ratio of the binding energy to the rest energy of the electron.

Note added in proof. Since the submission of this article for publication, our attention has been called to the work of M. A. Coulthard [Proc. Phys. Soc. (London) **91**, 44 (1967)], in which a relativistic Hartree-Fock calculation is carried out for several atoms, with the magnetic interaction terms omitted. Detailed results are given for mercury.