Analytical Self-Consistent Field Functions for the Atomic Configurations $1s^2$, $1s^2 2s$, and $1s^2 2s^2$*

C. C. J. Roothaan†

Solid State Science Division, Argonne National Laboratory, Lemont, Illinois

Lester M. Sachs

*Solid State Science Division, Argonne National Laboratory, Lemont, Illinois, and
Department of Physics, Illinois Institute of Technology, Chicago, Illinois*

AND

A. W. Weiss

*Laboratory for Molecular Structure and Spectra, Department of Physics,
University of Chicago, Chicago 37, Illinois*

INTRODUCTION

THE generalized SCF formalism developed in a recent paper[1] (hereafter called I), was applied to atomic configurations. We present in this paper the results obtained for the configurations $1s^2$, $1s^2 2s$, and $1s^2 2s^2$ for atoms and ions up to $Z=10$. For these cases we do not need the formalism in its full generality dealing with degenerate orbitals. However, in view of the applications to configurations including p and d orbitals to be presented in subsequent papers, we give here the formulas for the general case.

Our treatment is similar to Watson's[2] calculations on the iron group, and calculations by Allen[2a] on F, F⁻, and Ne. These calculations are based on Nesbet's[3] analysis, which differs from our analysis in the treatment of the off-diagonal Lagrangian multipliers coupling the inner and outer shells; namely, Nesbet's treatment involves certain approximations in the manipulation of these multipliers, whereas our formalism solves the variational problem without any such approximations.

When using the expansion method to obtain SCF orbitals, we do want to know how accurately these orbitals satisfy the Hartree-Fock integro-differential equation. A straightforward test for this is to tabulate (1) $F\phi_i - \epsilon_i\phi_i$ and (2) $F\phi_i/\epsilon_i\phi_i$ as functions of r, where F is the Hartree-Fock operator in differential form, and ϕ_i and ϵ_i are the orbitals and orbital energies found by the expansion method. The expression $F\phi_i - \epsilon_i\phi_i$ should vanish to the number of *decimal places* to which the function ϕ_i represents the Hartree-Fock function. For large values of r the deviation of the expression $F\phi_i/\epsilon_i\phi_i$ from unity should be a measure for the number of *significant figures* given correctly by ϕ_i. A sensitive test for the region $r \to 0$ is the *cusp value*.[4] Namely, for an exact solution of the Hartree-Fock equation,

$$(\lambda+1)(1/f_\lambda)(df_\lambda/dr)_{r=0} = -Z, \qquad (1)$$

where λ is the angular momentum and $r^\lambda f_\lambda(r)$ the radial part of the orbital. For an orbital obtained by the expansion method, the deviation of the left-hand side of Eq. (1) from $-Z$ is a measure for the accuracy of that orbital in the region $r \to 0$.

EVALUATION OF THE MATRIX AND SUPERMATRIX ELEMENTS

The basis functions used are

$$\chi_{p\lambda\alpha} = R_{\lambda p}(r) Y_{\lambda\alpha}(\theta,\phi), \qquad (2)$$

where $Y_{\lambda\alpha}(\theta,\phi)$ are the normalized spherical harmonics in complex form, and the radial functions $R_{\lambda p}(r)$ are given by

$$R_{\lambda p}(r) = [(2n_{\lambda p})!]^{-\frac{1}{2}} (2\zeta_{\lambda p})^{n_{\lambda p}+\frac{1}{2}} r^{n_{\lambda p}-1} e^{-\zeta_{\lambda p} r}. \qquad (3)$$

The functions (2) are the usual normalized nodeless Slater-type functions; we envisage the SCF functions as linear combinations of Slater-type functions with flexible orbital exponents ζ_p and integer values ($\geq \lambda$) for $n_{\lambda p}$.

The matrix elements and supermatrix elements, as defined in Eqs. (45)–(47) of I,[1] can be expressed in terms of integrals over the radial functions only. Before doing so, we introduce separate symbols for the kinetic and potential energy, so that

$$H_{\lambda pq} = -ZU_{\lambda pq} + T_{\lambda pq}. \qquad (4)$$

---

[1] C. C. J. Roothaan, Revs. Modern Phys. **32**, 179 (1960), this issue.

[2] R. E. Watson, Tech. Rept. No. 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (1959); (a) A. M. Karo and L. C. Allen, J. Chem. Phys. **31**, 968 (1959).

[3] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

[4] For a discussion of the cusp for s orbitals, see C. C. J. Roothaan and A. W. Weiss, Revs. Modern Phys. **32**, 194 (1960), this issue. For $\lambda \neq 0$, see P. O. Löwdin, Phys. Rev. **94**, 1600 (1954).

The expressions in terms of radial integrals are

$$S_{\lambda pq} = \int_0^\infty du \cdot u^2 R_{\lambda p}(u) R_{\lambda q}(u),$$

$$U_{\lambda pq} = \int_0^\infty du \cdot u R_{\lambda p}(u) R_{\lambda q}(u), \tag{5}$$

$$T_{\lambda pq} = \tfrac{1}{2} \int_0^\infty du [u^2 R_{\lambda p}'(u) R_{\lambda q}'(u) \\ + \lambda(\lambda+1) R_{\lambda p}(u) R_{\lambda q}(u)],$$

$$\mathscr{J}_{\lambda pq,\mu rs} = \int_0^\infty du \cdot u \int_0^u dv \cdot v^2 \\ \times [R_{\lambda p}(u) R_{\lambda q}(u) R_{\mu r}(v) R_{\mu s}(v) \\ + R_{\mu r}(u) R_{\mu s}(u) R_{\lambda p}(v) R_{\lambda q}(v)], \tag{6}$$

$$\mathscr{K}_{\lambda pq,\mu rs} = \sum_{\nu=|\lambda-\mu|}^{\lambda+\mu} A_{\lambda\mu\nu} \mathscr{K}_{\lambda pq,\mu rs}{}^\nu, \tag{7}$$

$$\mathscr{K}_{\lambda pq,\mu rs}{}^\nu = \tfrac{1}{2} \int_0^\infty du \cdot u^{-\nu+1} \int_0^u dv \cdot v^{\nu+2} \\ \times [R_{\lambda p}(u) R_{\mu r}(u) R_{\lambda q}(v) R_{\mu s}(v) \\ + R_{\lambda q}(u) R_{\mu s}(u) R_{\lambda p}(v) R_{\mu r}(v) \\ + R_{\lambda p}(u) R_{\mu s}(u) R_{\lambda q}(v) R_{\mu r}(v) \\ + R_{\lambda q}(u) R_{\mu r}(u) R_{\lambda p}(v) R_{\mu s}(v)]. \tag{8}$$

In Eq. (7), the summation over ν is to be carried out in steps of 2. The coefficients $A_{\lambda\mu\nu}$ are given by

$$A_{\lambda\mu\nu} = [(\lambda+\mu+\nu+1) A_{\lambda+\mu+\nu}]^{-1} A_{\lambda+\mu-\nu} A_{-\mu+\nu} A_{\mu-\lambda+\nu}, \\ A_\rho = [(\tfrac{1}{2}\rho)!]^{-2} \rho!; \tag{9}$$

ρ is always an even integer.

The expressions for the one-electron integrals, Eqs. (5), are well known[5] and need no further comment. The expressions for the two-electron integrals, Eqs. (6)–(8), however, are much simpler than those commonly used. This is because the supermatrices $\mathscr{J}$ and $\mathscr{K}$ refer to shells rather than orbitals, and sums over subspecies are included in their definitions, Eqs. (47) of I.[1] As a result, the general vector coupling coefficients do not occur in this formulation, but only the much simpler set $A_{\lambda\mu\nu}$ defined by Eqs. (9). As mentioned in I,[1] this relatively simple formulation holds for certain general classes of states, for which the total energy is expressible by Eq. (17) of I. For other cases, a slight generalization is necessary, e.g., for open d, f, etc. shells. The modification for the latter cases requires only new definitions for the coefficients $A_{\lambda\mu\nu}$ in lieu of Eqs. (9), which *do* require the use of the general vector coupling coefficients. We postpone such generalizations to a future publication.

[5] D. R. Hartree, Repts. Progr. Phys. **11**, 113 (1958); *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

For proofs of Eqs. (6)–(9), we use the addition theorem for spherical harmonics,

$$P_\lambda(\cos\theta_{12}) = 4\pi(2\lambda+1)^{-1} \sum_{\alpha=-\lambda}^\lambda Y_{\lambda\alpha}{}^*(\theta_1,\phi_1) Y_{\lambda\alpha}(\theta_2,\phi_2), \tag{10}$$

and the expansion of $r_{12}{}^{-1}$ in terms of Legendre polynomials

$$r_{12}{}^{-1} = \sum_{\lambda=0}^\infty r_>{}^{-\lambda-1} r_<{}^\lambda P_\lambda(\cos\theta_{12}), \tag{11}$$

where

$$r_> = (r_1,r_2)_{\max}, \quad r_< = (r_1,r_2)_{\min}, \quad \cos\theta_{12} = (\mathbf{r}_1 \cdot \mathbf{r}_2)/r_1 r_2.$$

The Coulomb supermatrix element $\mathscr{J}_{\lambda pq,\mu rs}$ represents the electrostatic repulsion of two charge distributions $\Omega_{\lambda pq}$ and $\Omega_{\mu rs}$, defined by [see Eqs. (47) of I]

$$\Omega_{\lambda pq} = (2\lambda+1)^{-1} \sum_{\alpha=-\lambda}^\lambda \bar{x}_{p\lambda\alpha} x_{q\lambda\alpha}; \tag{12}$$

using Eqs. (2) and (10) with $\theta_{12}=0$, $P_\lambda(\cos\theta_{12}) = P_\lambda(1) = 1$, this becomes

$$\Omega_{\lambda pq} = (4\pi)^{-1} R_{\lambda p}(r) R_{\lambda q}(r). \tag{13}$$

Hence we find, using (11),

$$\mathscr{J}_{\lambda pq,\mu rs} = (4\pi)^{-2} \int_0^\infty dr_1 \cdot r_1^2 R_{\lambda p}(r_1) R_{\lambda q}(r_1) \\ \times \int_0^\infty dr_2 \cdot r_2^2 R_{\mu r}(r_2) R_{\mu s}(r_2) \sum_{\nu=0}^\infty r_>{}^{-\nu-1} r_<{}^\nu \\ \times \int\int d\omega_1 d\omega_2 P_\nu(\cos\theta_{12}), \tag{14}$$

where $d\omega_1$ and $d\omega_2$ are infinitesimal solid angles. Carrying out the angular integrations, only the term with $\nu=0$ survives, yielding $(4\pi)^2$, so that

$$\mathscr{J}_{\lambda pq,\mu rs} = \int_0^\infty dr_1 \cdot r_1^2 R_{\lambda p}(r_1) R_{\lambda q}(r_1) \\ \times \int_0^\infty dr_2 \cdot r_2^2 R_{\mu r}(r_2) R_{\mu s}(r_2) r_>{}^{-1} \\ = \int_0^\infty dr_1 \cdot r_1 R_{\lambda p}(r_1) R_{\lambda q}(r_1) \\ \times \int_0^{r_1} dr_2 \cdot r_2^2 R_{\mu r}(r_2) R_{\mu s}(r_2) \\ + \int_0^\infty dr_1 \cdot r_1^2 R_{\lambda p}(r_1) R_{\lambda q}(r_1) \\ \times \int_{r_1}^\infty dr_2 \cdot r_2 R_{\mu r}(r_2) R_{\mu s}(r_2);$$

$\lambda pq \backslash \mu rs$	011	021	022	031	032	033	111	121	122
011	X								
021	X	X							
022	X	X	X						
031	X	X	X	X					
032	X	X	X	X	X				
033	X	X	X	X	X	X			
111	X	X	X	X	X	X	X		
121	X	X	X	X	X	X	X	X	
122	X	X	X	X	X	X	X	X	X

if we reverse the order of integration in the last double integral, Eq. (6) results.

Before we turn to the derivation of the formulas for the exchange supermatrix elements, Eqs. (7)–(9), we discuss the symmetry properties of the matrices and supermatrices which enter the SCF scheme. All our *matrices* are real and symmetrical. Say we deal with a basis set of three s functions ($\lambda=0$) and two p functions ($\lambda=1$); the necessary and sufficient matrix elements of, for instance, the one-electron operator H are collected in the supervector

$$\mathbf{H} = (H_{011}, H_{021}, H_{022}, H_{031}, H_{032}, H_{033}, H_{111}, H_{121}, H_{122}). \quad (15)$$

In I[1] it was noted that the supermatrices were *symmetrical* for the exchange $\lambda pq \leftrightarrow \mu rs$, and *Hermitian* for the *simultaneous* exchange $p \leftrightarrow q$, $r \leftrightarrow s$. In the present case, as may be seen from Eq. (6), $\mathcal{J}_{\lambda pq,\mu rs}$ is *symmetrical* for the *independent* exchanges $p \leftrightarrow q$ and $r \leftrightarrow s$. This stronger symmetry is due to the fact that our basis set is chosen so that we need to consider only *real* orbital coefficient vectors, density matrices, etc. The necessary and sufficient set of elements $\mathcal{J}_{\lambda pq,\mu rs}$ is indicated in Table I; it is the triangular part of a *real symmetrical* matrix, the rows and columns of which are labeled with the supervector indices.

If we use the definition for the exchange supermatrix $\mathcal{R}$ given by the second Eq. (47) of I, then $\mathcal{K}_{\lambda pq,\mu rs}$ is again symmetrical for the exchange $\lambda pq \leftrightarrow \mu rs$, but symmetrical for the *simultaneous* exchange $p \leftrightarrow q$, $r \leftrightarrow s$ only, in contrast to $\mathcal{J}_{\lambda pq,\mu rs}$. Hence we would need, for instance, both $\mathcal{K}_{031,021}$ and $\mathcal{K}_{031,012}$, whereas $\mathcal{J}_{031,021}$ was sufficient. We can, however, use a symmetrized definition for $\mathcal{R}$ which has the same properties as $\mathcal{J}$. Namely, the exchange term in the total energy may be rewritten as follows:

$$\mathbf{D}_T{}^\dagger \mathcal{R} \mathbf{D}_T = \sum_{\lambda pq,\mu rs} D_{T\lambda pq} \mathcal{K}_{\lambda pq,\mu rs} D_{T\mu rs}$$

$$= \tfrac{1}{2} \sum_{\lambda pq,\mu rs} D_{T\lambda pq} (\mathcal{K}_{\lambda pq,\mu rs} + \mathcal{K}_{\lambda pq,\mu sr}) D_{T\mu rs};$$

this is permissible because $D_{T\lambda pq}$ is symmetrical for $p \leftrightarrow q$. The expression

$$\tfrac{1}{2} (\mathcal{K}_{\lambda pq,\mu rs} + \mathcal{K}_{\lambda pq,\mu sr})$$

has the required symmetry; throughout his paper, it is *this* combination which is meant by $\mathcal{R}$.

To derive Eqs. (7)–(9) we take the second Eq. (47) of I,[1] symmetrize it as just discussed, substitute into it the expression for the basis functions, Eq. (2), and use Eqs. (10) and (11); the result is

$$\mathcal{K}_{\lambda pq,\mu rs} = \tfrac{1}{2} (4\pi)^{-2} \int_0^\infty dr_1 \cdot r_1{}^2 \int_0^\infty dr_2 \cdot r_2{}^2$$

$$\times [R_{\lambda p}(r_1) R_{\mu s}(r_1) R_{\lambda q}(r_2) R_{\mu r}(r_2)$$

$$+ R_{\lambda p}(r_1) R_{\mu r}(r_1) R_{\lambda q}(r_2) R_{\mu s}(r_2)]$$

$$\times \sum_{\nu=0}^\infty r_>{}^{-\nu-1} r_<{}^\nu \int \int d\omega_1 d\omega_2 P_\lambda(\cos\theta_{12})$$

$$\times P_\mu(\cos\theta_{12}) P_\nu(\cos\theta_{12}). \quad (16)$$

Now, the *product* of two Legendre functions may be written as a *sum* of Legendre functions according to[6]

$$P_\lambda(x) P_\mu(x) = \sum_{\nu=|\lambda-\mu|}^{\lambda+\mu} (2\nu+1) A_{\lambda\mu\nu} P_\nu(x), \quad (17)$$

where the summation over ν is to be carried out in steps of 2, and the $A_{\lambda\mu\nu}$ are given by Eqs. (9). By substituting the expression (17) into the angular integral in (16) and carrying out the integrations in the usual fashion, we obtain

$$\int \int d\omega_1 d\omega_2 P_\lambda(\cos\theta_{12}) P_\mu(\cos\theta_{12}) P_\nu(\cos\theta_{12}) = (4\pi)^2 A_{\lambda\mu\nu}$$

$$\text{for } \nu = |\lambda-\mu|, \ |\lambda-\mu|+2, \ \cdots, \ \lambda+\mu, \quad (18)$$

all other integrals vanishing. By using this result in Eq. (16), and manipulating the resulting expression in analogous fashion as for the Coulomb supermatrix elements, we obtain the final result expressed by Eqs. (7) and (8).

We now proceed to express the integrals (5), (6), and (8) in terms of elementary functions. By substituting the explicit expression for the radial functions, Eq. (3), into the one-electron integrals (5), we obtain, after some manipulation,

$$S_{\lambda pq} = [V_{2n\lambda p}(\zeta_{\lambda p}) V_{2n\lambda q}(\zeta_{\lambda q})]^{-\frac{1}{2}} V_{n\lambda p + n\lambda q}[\tfrac{1}{2}(\zeta_{\lambda p} + \zeta_{\lambda q})],$$

$$U_{\lambda pq} = 2[V_{2n\lambda p}(\zeta_{\lambda p}) V_{2n\lambda q}(\zeta_{\lambda q})]^{-\frac{1}{2}}$$
$$\times V_{n\lambda p + n\lambda q - 1}[\tfrac{1}{2}(\zeta_{\lambda p} + \zeta_{\lambda q})],$$

$$T_{\lambda pq} = \tfrac{1}{2} \zeta_{\lambda p} \zeta_{\lambda q} [V_{2n\lambda p}(\zeta_{\lambda p}) V_{2n\lambda q}(\zeta_{\lambda q})]^{-\frac{1}{2}}$$
$$\times \{ V_{n\lambda p + n\lambda q}[\tfrac{1}{2}(\zeta_{\lambda p} + \zeta_{\lambda q})] \quad (19)$$
$$- [W_{\lambda, n\lambda p}(\zeta_{\lambda p}) + W_{\lambda, n\lambda q}(\zeta_{\lambda q})]$$
$$\times V_{n\lambda p + n\lambda q - 1}[\tfrac{1}{2}(\zeta_{\lambda p} + \zeta_{\lambda q})]$$
$$+ W_{\lambda, n\lambda p}(\zeta_{\lambda p}) W_{\lambda, n\lambda q}(\zeta_{\lambda q})$$
$$\times V_{n\lambda p + n\lambda q - 2}[\tfrac{1}{2}(\zeta_{\lambda p} + \zeta_{\lambda q})] \},$$

where

$$V_i(x) = x^{-i-1} i!, \quad W_{ij}(x) = 2x^{-1}(j-i-1). \quad (20)$$

[6] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1952), fourth edition, p. 331, example 11.

Similarly, we find for the two-electron integrals (6), and (8),

$$\mathscr{J}_{\lambda pq,\mu rs}=U_{\lambda pq}S_{\mu rs}C_{n_{\lambda p}+n_{\lambda q}-1,\;n_{\mu r}+n_{\mu s}}[(\zeta_{\lambda p}+\zeta_{\lambda q})/(\zeta_{\mu r}+\zeta_{\mu s})]$$
$$+U_{\mu rs}S_{\lambda pq}C_{n_{\mu r}+n_{\mu s}-1,\;n_{\lambda p}+n_{\lambda q}}[(\zeta_{\mu r}+\zeta_{\mu s})/(\zeta_{\lambda p}+\zeta_{\lambda q})],$$

$$\mathscr{K}_{\lambda pq,\mu rs}{}^{\nu}=[V_{2n_{\lambda p}}(\zeta_{\lambda p})V_{2n_{\lambda q}}(\zeta_{\lambda q})V_{2n_{\mu r}}(\zeta_{\mu r})V_{2n_{\mu s}}(\zeta_{\mu s})]^{-\frac{1}{2}}$$
$$\times\{V_{n_{\lambda p}+n_{\mu r}-\nu-1}[\tfrac{1}{2}(\zeta_{\lambda p}+\zeta_{\mu r})]V_{n_{\lambda q}+n_{\mu s}+\nu}[\tfrac{1}{2}(\zeta_{\lambda q}+\zeta_{\mu s})]\cdot C_{n_{\lambda p}+n_{\mu r}-\nu-1,\;n_{\lambda q}+n_{\mu s}+\nu}[(\zeta_{\lambda p}+\zeta_{\mu r})/(\zeta_{\lambda q}+\zeta_{\mu s})]$$
$$+V_{n_{\lambda q}+n_{\mu s}-\nu-1}[\tfrac{1}{2}(\zeta_{\lambda q}+\zeta_{\mu s})]V_{n_{\lambda p}+n_{\mu r}+\nu}[\tfrac{1}{2}(\zeta_{\lambda p}+\zeta_{\mu r})]\cdot C_{n_{\lambda q}+n_{\mu s}-\nu-1,\;n_{\lambda p}+n_{\mu r}+\nu}[(\zeta_{\lambda q}+\zeta_{\mu s})/(\zeta_{\lambda p}+\zeta_{\mu r})]$$
$$+V_{n_{\lambda p}+n_{\mu s}-\nu-1}[\tfrac{1}{2}(\zeta_{\lambda p}+\zeta_{\mu s})]V_{n_{\lambda q}+n_{\mu r}+\nu}[\tfrac{1}{2}(\zeta_{\lambda q}+\zeta_{\mu r})]\cdot C_{n_{\lambda p}+n_{\mu s}-\nu-1,\;n_{\lambda q}+n_{\mu r}+\nu}[(\zeta_{\lambda p}+\zeta_{\mu s})/(\zeta_{\lambda q}+\zeta_{\mu r})]$$
$$+V_{n_{\lambda q}+n_{\mu r}-\nu-1}[\tfrac{1}{2}(\zeta_{\lambda q}+\zeta_{\mu r})]V_{n_{\lambda p}+n_{\mu s}+\nu}[\tfrac{1}{2}(\zeta_{\lambda p}+\zeta_{\mu s})]\cdot C_{n_{\lambda q}+n_{\mu r}-\nu-1,\;n_{\lambda p}+n_{\mu s}+\nu}[(\zeta_{\lambda q}+\zeta_{\mu r})/(\zeta_{\lambda p}+\zeta_{\mu s})]\},$$

$$(21)$$

where

$$C_{\alpha\beta}(t)=(\alpha!\beta!)^{-1}t^{\alpha+1}\int_0^\infty du\cdot u^\alpha e^{-tu}\int_0^u dv\cdot v^\beta e^{-v}. \quad (22)$$

The functions $C_{\alpha\beta}(t)$ can be computed from the recurrence relation

$$C_{\alpha\beta}(t)=(1+t)^{-1}[tC_{\alpha-1,\beta}(t)+C_{\alpha,\beta-1}(t)+\delta_{\beta 0}]. \quad (23)$$

This recurrence relation holds for $\alpha,\beta\geqslant 0$, interpreting terms with a negative index as zero. When using this relation numerically for raising the indices, no serious loss of significant figures can occur, since all the $C_{\alpha\beta}(t)$ are positive, which is obvious from Eq. (22). The proof of Eq. (23) is given in the Appendix.

RESULTS AND DISCUSSION

A digital computer program was written for the IBM 704 at Argonne National Laboratory, which could handle the configurations with s orbitals only. A more general program capable of handling configurations with orbitals with $\lambda\neq 0$ was written for the Remington Rand Univac Scientific 1103A at Wright-Patterson Air Force Base. Although some preliminary results have been obtained with the latter program, we postpone the discussion of those results to a subsequent paper; the results discussed here were all obtained on the IBM 704 at the Argonne National Laboratory. The results for the $1s^2$ configuration presented here had also been obtained earlier with a special two-electron program for the Remington-Rand Univac Scientific 1103 at Wright-Patterson Air Force Base.

The program uses the following input data: (1) m, the number of orbital exponents ζ; (2) p, the number of powers of r for each ζ, the powers themselves being $0, 1, \cdots, p-1$; (3) n_α, n_β, the numbers of occupied

TABLE II. Variation of ζ_1, ζ_2 for Li$^+$, $p=2$. The entries in the Table are the last four significant figures in the energy: $E_{\min}=-7.2364122$ a.u.

$\zeta_2\backslash\zeta_1$	2.0	2.2	2.4	2.6	2.8
4.0	2937	3896	4080	4060	3846
4.2	2813	3936	4110	4079	3815
4.4	2560	3935	4119	4087	3767
4.6	2168	3902	4122	4085	3690
4.8	1620	3840	4118	4074	3592
5.0	0895	3738	4107	4054	3462

orbitals with α and β spin, respectively; (4) Z, the actual nuclear charge; (5) the numerical values of the ζ's; (6) approximate eigenvectors for the occupied orbitals. The program was designed to operate with all the matrix and supermatrix elements in the magnetic core storage of 8192 words. This limited the basis set to 12 functions, which gives rise to 3081 supermatrix elements for both $\mathfrak{J}$ and $\mathfrak{K}$, and much smaller sets for S, U, T, and other assorted quantities. In addition,

TABLE III. Variation of ζ_2 for Li, $\zeta_1=2.4$, $\zeta_2=4.4$, $p=2$. $E_{\min}=-7.4327224$.

ζ_3	0.65	0.66	0.67	0.68	0.69
E	7020	7168	7224	7182	7037

there was a limitation due to the number of functions $C_{\alpha\beta}(t)$ necessary for the construction of $\mathfrak{J}$ and $\mathfrak{K}$; as a result, the program can handle the following combinations of m and p: 1, 6; 2, 6; 3, 4; 4, 2; 5, 1; 6, 1. A single run with a 12-function basis set requires three to 10 minutes, depending on the guess for the eigenvectors, and much less for, say, a 6-function basis set.

After some experimentation for the $1s^22s$ and $1s^22s$ configurations, we found that $m=3$, $p=2$ could yield the SCF total energy to six significant figures or better,[7]

TABLE IV. Variation of ζ_3 for Li$^-$, $\zeta_1=2.4$, $\zeta_2=4.4$, $p=2$. $E_{\min}=-7.4279965$.

ζ_3	0.27	0.28	0.285	0.29	0.30
E	9836	9949	9965	9956	9880

provided we optimized the ζ's. Two of these ζ's apparently represent primarily the $1s$ orbital and the inner loop of the $2s$ orbital; the third ζ is needed to represent the outer loop of the $2s$ orbital. From Hartree's extensive experience,[5] it is known that the $1s$ orbitals are practically independent of whether the $2s$ orbital is absent, singly, or doubly occupied. Armed with these facts, we proceeded as follows:

(1) For the configuration $1s^2$, keeping $m=p=2$, we varied ζ_1 and ζ_2 on a rectangular grid until an energy

---

[7] The only exception to this occurs for Li$^-$, for which $m=3$, $p=2$ yields only four significant figures in the total energy.

TABLE V. Compromise SCF functions for $2 \leqslant Z \leqslant 10$.

Z = 2

ζ	n	$1s^2$ 1s
3.00	0	0.175261
	1	0.010673
1.40	0	0.884315
	1	−0.051269
$-\epsilon$ (a.u.)		0.917946
I (a.u.)		0.917946
Cusp		2.0018
$-E$ (a.u.)		2.861671

Z = 3

ζ	n	$1s^2$ 1s	$1s^2\,2s$ 1s	2s	$1s^2\,2s^2$ 1s	2s
4.40	0	0.133937	0.128169	0.061628	0.133664	0.111961
	1	−0.008925	−0.012275	0.017507	−0.009144	0.044848
2.40	0	0.914304	0.926908	0.039733	0.913953	−0.101615
	1	−0.029575	−0.037651	0.101098	−0.028962	0.222883
0.67	0	...	0.005692	0.010105	...	...
	1	...	−0.002035	−1.043535	...	...
0.285	0	...	...	...	0.001612	−1.055194
	1	...	...	...	−0.001113	0.004754
$-\epsilon$ (a.u.)		2.792361	2.463469	0.079319	2.320989	0.013524
I (a.u.)		2.792361	2.470616	0.196319	2.320989	0.013524
Cusp		3.0113	3.0137	2.9790	3.0111	2.8169
$-E$ (a.u.)		7.236412	7.432722		7.427997	

Z = 4

ζ	n	$1s^2$ 1s	$1s^2\,2s$ 1s	2s	$1s^2\,2s^2$ 1s	2s
6.50	0	0.090576	0.087271	0.040000	0.088737	0.075841
	1	0.006158	0.004118	0.011646	0.004895	0.028953
3.40	0	0.932883	0.938933	0.102410	0.935313	0.064546
	1	−0.020880	−0.026475	0.068967	−0.022712	0.208057
1.20	0	...	0.005943	0.219443	...	...
	1	...	−0.001096	−1.218766	...	...
0.90	0	...	...	...	0.004590	−0.386020
	1	...	...	...	−0.002201	−0.740733
$-\epsilon$ (a.u.)		5.667113	5.102721	0.467844	4.732344	0.309131
I (a.u.)		5.667113	5.120512	0.666145	4.732344	0.309131
Cusp		4.0160	4.0181	4.0008	4.0166	3.9163
$-E$ (a.u.)		13.61130	14.27739		14.57298	

Z = 5

ζ	n	$1s^2$ 1s	$1s^2\,2s$ 1s	2s	$1s^2\,2s^2$ 1s	2s
8.00	0	0.077235	0.074290	0.044364	0.074950	0.076197
	1	0.001760	0.000132	0.012092	0.000370	0.024671
4.40	0	0.942992	0.947348	0.092899	0.945457	0.100824
	1	−0.015453	−0.019849	0.070947	−0.017800	0.196901
1.71	0	...	0.005326	0.331356	...	...
	1	...	−0.000468	−1.307998	...	...
1.42	0	...	...	...	0.005742	−0.202420
	1	...	...	...	−0.002364	−0.922348
$-\epsilon$ (a.u.)		9.541976	8.750132	1.113787	8.185896	0.873807
I (a.u.)		9.541976	8.778937	1.389851	8.185896	0.873807
Cusp		5.0191	5.0201	5.0076	5.0191	4.9675
$-E$ (a.u.)		21.98623	23.37599		24.23756	

Z = 6

ζ	n	$1s^2$ 1s	$1s^2\,2s$ 1s	2s	$1s^2\,2s^2$ 1s	2s
9.50	0	0.066900	0.064265	0.040158	0.064343	0.073559
	1	−0.000681	−0.002034	0.009662	−0.002107	0.021417
5.40	0	0.951308	0.954646	0.088107	0.953819	0.115219
	1	−0.012417	−0.016070	0.056023	−0.015151	0.181766
2.22	0	...	0.004797	0.440327	...	...
	1	...	−0.000143	−1.384259	...	...
1.93	0	...	...	...	0.006343	−0.066932
	1	...	...	...	−0.002390	−1.041633
$-\epsilon$ (a.u.)		14.41689	13.40026	2.012257	12.65066	1.694059
I (a.u.)		14.41689	13.44014	2.365002	12.65066	1.694059
Cusp		6.0208	6.0212	6.0192	6.0203	5.9891
$-E$ (a.u.)		32.36119	34.72606		36.40849	

Z = 7

ζ	n	$1s^2$ 1s	$1s^2\,2s$ 1s	2s	$1s^2\,2s^2$ 1s	2s
11.00	0	0.058772	0.056341	0.045366	0.056014	0.065289
	1	−0.002105	−0.003290	0.011398	−0.003544	0.017043
6.40	0	0.957950	0.960742	0.071379	0.960581	0.126612
	1	−0.010486	−0.013702	0.065051	−0.013522	0.157940
2.72	0	...	0.004414	0.485098	...	...
	1	...	−0.000007	−1.419215	...	...
2.44	0	...	...	...	0.006634	0.056139
	1	...	...	...	−0.002355	−1.138073
$-\epsilon$ (a.u.)		20.29183	19.05186	3.162021	18.12006	2.766718
I (a.u.)		20.29183	19.10280	3.590855	18.12006	2.766718
Cusp		7.0218	7.0219	7.0157	7.0210	7.0075
$-E$ (a.u.)		44.73616	48.32685		51.08231	

Z = 8

ζ	n	$1s^2$ 1s	$1s^2\,2s$ 1s	2s	$1s^2\,2s^2$ 1s	2s
12.50	0	0.052270	0.049983	0.048303	0.049361	0.066281
	1	−0.002955	−0.004029	0.012299	−0.004400	0.016928
7.40	0	0.963254	0.965734	0.058279	0.966047	0.119116
	1	−0.009141	−0.012059	0.069157	−0.012381	0.153934
3.22	0	...	0.004084	0.525134	...	...
	1	...	0.000069	−1.448572	...	...
2.94	0	...	...	...	0.006713	0.128979
	1	...	...	...	−0.002293	−1.195978
$-\epsilon$ (a.u.)		27.16679	25.70418	4.562441	24.59215	4.090744
I (a.u.)		27.16679	25.76618	5.067099	24.59215	4.090744
Cusp		8.0226	8.0224	8.0140	8.0215	8.0081
$-E$ (a.u.)		59.11114	64.17804		68.25771	

Z = 9

ζ	n	$1s^2$ 1s	$1s^2\,2s$ 1s	2s	$1s^2\,2s^2$ 1s	2s
14.00	0	0.047004	0.044986	0.049775	0.044029	0.054391
	1	−0.003450	−0.004373	0.012704	−0.004872	0.012328
8.40	0	0.967475	0.969455	0.047993	0.970326	0.127488
	1	−0.008121	−0.010619	0.070546	−0.011451	0.127278
3.72	0	...	0.003673	0.560359	...	...
	1	...	0.000158	−1.473268	...	...
3.45	0	...	...	...	0.006660	0.227570
	1	...	...	...	−0.002198	−1.263452
$-\epsilon$ (a.u.)		35.04175	33.35696	6.213265	32.06540	5.665442
I (a.u.)		35.04175	33.43000	6.793585	32.06540	5.665442
Cusp		9.0230	9.0225	9.0131	9.0217	9.0228
$-E$ (a.u.)		75.48612	82.27949		87.93405	

Z = 10

ζ	n	$1s^2$ 1s	$1s^2\,2s$ 1s	2s	$1s^2\,2s^2$ 1s	2s
15.50	0	0.042610	0.040635	0.038161	0.039510	0.053432
	1	−0.003762	−0.004643	0.008671	−0.005194	0.011932
9.40	0	0.971012	0.972956	0.052591	0.974094	0.120245
	1	−0.007360	−0.009759	0.047183	−0.010836	0.121903
4.23	0	...	0.003469	0.632319	...	...
	1	...	0.000175	−1.514805	...	...
3.95	0	...	...	...	0.006601	0.281647
	1	...	...	...	−0.002135	−1.302306
$-\epsilon$ (a.u.)		43.91672	42.00995	8.114297	40.53979	7.490705
I (a.u.)		43.91672	42.09403	8.770233	40.53979	7.490705
Cusp		10.0234	10.0228	10.0242	10.0220	10.0235
$-E$ (a.u.)		93.86111	102.6311		110.1110	

TABLE VI. Best SCF functions for $2 \leqslant Z \leqslant 10$.

Z = 2

ζ	n	1s² — 1s
3.00	0	0.457418
	1	0.244272
	2	0.136571
	3	0.094513
	4	0.008192
	5	0.027670
1.40	0	0.000000
	1	0.129851
	2	0.113403
	3	−0.086860
	4	0.025460
	5	−0.002674
−ε (a.u.)		0.917956
I (a.u.)		0.917956
Cusp		2.0019
−E (a.u.)		2.861680

Z = 3

ζ	n	1s² (1s)	1s²2s (1s)	1s²2s (2s)	1s²2s² (1s)	1s²2s² (2s)
4.40	0	−0.000000	0.499766	0.028196	0.501848	0.075238
	1	−0.220023	0.201689	0.007319	0.189087	−0.021164
	2	−0.126397	0.083451	0.002902	0.074281	−0.025592
	3	−0.021018	0.037370	0.004082	0.032005	−0.013139
	4	−0.028489	...	...	...	...
	5	0.015049	...	...		
2.40	0	1.246497	−0.000000	0.122442	−0.000000	0.000000
	1	0.459177	0.322165	0.025246	0.391039	0.382450
	2	−0.675516	−0.049361	0.026322	−0.102103	−0.203580
	3	0.408814	−0.011512	0.011259	0.012513	0.128352
	4	−0.135526	...	...	...	...
	5	0.020320	...			
0.67	0	...	0.033911	0.014681	...	...
	1	...	−0.032212	−1.101788	...	...
	2	...	0.016441	0.078367	...	...
	3	...	−0.003635	−0.035526	...	...
0.285	0	...	...	...	0.000733	−1.266294
	1	...	...	...	−0.001219	0.388390
	2	...	...	...	0.000964	−0.237092
	3	...	...	...	−0.000314	−0.004595
−ε (a.u.)		2.792365	2.463447	0.079318	2.322789	0.014534
I (a.u.)		2.792365	2.470594	0.196323	2.322789	0.014534
Cusp		3.0027	3.0070	3.0062	3.0078	3.0227
−E (a.u.)		7.236415	7.432727		7.428232	

Z = 4

ζ	n	1s² (1s)	1s²2s (1s)	1s²2s (2s)	1s²2s² (1s)	1s²2s² (2s)
6.50	0	0.443327	0.440586	0.081689	0.442306	−0.106320
	1	0.189357	0.195205	0.035570	0.196025	−0.036690
	2	0.059425	0.068732	0.010554	0.069198	−0.006877
	3	0.025014	0.029457	0.005376	0.029984	−0.001767
	4	−0.004885	...	...	...	...
	5	0.000707	...	...	...	...
3.40	0	0.000000	0.000000	0.000000	−0.000000	0.000171
	1	0.533882	0.487708	0.130829	0.494810	−0.303518
	2	−0.168932	−0.161563	−0.011894	−0.161936	0.058670
	3	0.003107	0.022777	0.015755	0.026115	−0.061146
	4	0.019426	...	...	...	...
	5	−0.005592	...			
1.20	0	...	0.027352	0.182542	...	...
	1	...	−0.022703	−1.224015	...	...
	2	...	0.010766	0.031685	...	...
	3	...	−0.002141	−0.016516	...	...
0.90	0	...	...	...	0.006644	0.496479
	1	...	...	...	−0.007953	0.694577
	2	...	...	...	0.004735	−0.050554
	3	...	...	...	−0.001211	0.044122
−ε (a.u.)		5.667116	5.102764	0.467873	4.732670	0.309270
I (a.u.)		5.667116	5.120553	0.666146	4.732670	0.309270
Cusp		4.0028	4.0043	4.0032	4.0041	4.0080
−E (a.u.)		13.61130	14.27740		14.57302	

Z = 5

ζ	n	1s² (1s)	1s²2s (1s)	1s²2s (2s)	1s²2s² (1s)	1s²2s² (2s)
8.00	0	0.461639	0.448595	0.112567	0.460775	0.117108
	1	0.258029	0.205013	0.027197	0.199242	0.054041
	2	0.176207	0.074763	0.000091	0.069294	0.017384
	3	0.137810	0.030916	−0.000003	0.028164	0.007737
	4	0.037801	...	...	...	...
	5	0.047757	...	...	...	...
4.40	0	0.000000	−0.000001	0.000000	0.000000	−0.000000
	1	0.187874	0.351849	0.300086	0.443290	0.207201
	2	−0.453636	−0.081477	−0.080195	−0.123551	0.012615
	3	0.462170	−0.013877	0.071064	0.017767	0.010206
	4	−0.213482	...	...	...	...
	5	0.040873	...	...	...	...
1.71	0	...	0.125970	0.024729	...	...
	1	...	−0.089925	−1.105348	...	...
	2	...	0.035185	−0.062447	...	...
	3	...	−0.006166	0.005804	...	...
1.42	0	...	...	...	0.001179	−0.197772
	1	...	...	...	−0.000443	−0.983398
	2	...	...	...	−0.000185	0.075585
	3	...	...	...	0.000137	−0.032056
−ε (a.u.)		9.541979	8.750137	1.113790	8.185922	0.873823
I (a.u.)		9.541979	8.778943	1.389852	8.185922	0.873823
Cusp		4.9967	5.0046	5.0082	5.0053	5.0025
−E (a.u.)		21.98623	23.37599		24.23758	

Z = 6

ζ	n	1s² (1s)	1s²2s (1s)	1s²2s (2s)	1s²2s² (1s)	1s²2s² (2s)
9.50	0	0.474400	0.533313	0.108615	0.459555	0.105788
	1	0.195068	0.159594	0.030937	0.223948	0.070123
	2	0.071333	0.032675	0.003923	0.085812	0.029392
	3	0.038714	0.008289	0.002561	0.034333	0.013314
	4	0.001165	...	...	...	...
	5	0.008981	...	...	...	...
5.40	0	−0.000000	0.017451	−0.000699	−0.000000	−0.000000
	1	0.441249	0.880749	0.233813	0.249534	0.050414
	2	−0.195623	−0.312327	−0.042908	−0.008724	0.085275
	3	0.077636	0.152329	0.046757	−0.039459	−0.041610
	4	−0.021630	...	...	...	...
	5	0.002943	...	...	...	...
2.22	0	...	−0.593017	0.170852	...	...
	1	...	0.402856	−1.212283	...	...
	2	...	−0.145966	−0.050951	...	...
	3	...	0.024388	0.003938	...	...
1.93	0	...	...	...	0.152639	0.120917
	1	...	...	...	−0.121390	−1.241777
	2	...	...	...	0.051224	0.119930
	3	...	...	...	−0.009813	−0.033566
−ε (a.u.)		14.41689	13.40033	2.012297	12.65062	1.694049
I (a.u.)		14.41689	13.44021	2.365003	12.65062	1.694049
Cusp		6.0020	6.0103	6.0064	6.0047	5.9994
−E (a.u.)		32.36119	34.72606		36.40850	

Z = 7

ζ	n	1s² (1s)	1s²2s (1s)	1s²2s (2s)	1s²2s² (1s)	1s²2s² (2s)
11.00	0	0.483726	0.486051	0.173324	0.510710	0.076037
	1	0.329658	0.187465	−0.043641	0.160686	0.093292
	2	0.181329	0.057554	−0.051667	0.038083	0.047377
	3	0.097099	0.019405	−0.022463	0.011162	0.020769
	4	0.022800	...	...	...	...
	5	0.018714	...	...	...	...
6.40	0	−0.000000	−0.000023	−0.000000	−0.000000	0.000000
	1	−0.097140	0.463619	0.797662	0.680141	−0.183050
	2	0.102628	−0.137653	−0.328748	−0.246970	0.182797
	3	0.010245	0.029486	0.206778	0.097086	−0.105663
	4	−0.021758	...	...	...	...
	5	0.005334	...	...	...	...
2.72	0	...	−0.023679	−0.297734	...	...
	1	...	0.009050	−0.956271	...	...
	2	...	0.000519	−0.138574	...	...
	3	...	−0.000683	0.016855	...	...
2.44	0	...	...	...	−0.266102	0.490948
	1	...	...	...	0.195151	−1.504409
	2	...	...	...	−0.076294	0.174334
	3	...	...	...	0.013598	−0.040179
−ε (a.u.)		20.29183	19.05186	3.162022	18.12011	2.766736
I (a.u.)		20.29183	19.10281	3.590855	18.12011	2.766736
Cusp		7.0012	7.0085	7.0275	7.0105	6.9950
−E (a.u.)		44.73616	48.32685		51.08231	

TABLE VI.—*Continued.*

Z=8 ζ	n	1s² 1s	1s²2s 1s	1s²2s 2s	1s²2s² 1s	1s²2s² 2s
12.50	0	0.490916	0.508584	0.150478	0.520564	0.125861
	1	0.262449	0.183572	−0.029041	0.174232	−0.031133
	2	−0.075741	0.052329	−0.037482	0.046073	−0.037022
	3	−0.149444	0.016647	−0.014409	0.014738	−0.015858
	4	−0.083258	...	...	...	...
	5	−0.058394	...	...	...	...
7.40	0	0.000000	0.000000	−0.000000	0.000000	−0.000000
	1	0.158968	0.527528	0.611948	0.615552	0.502938
	2	1.235800	−0.154423	−0.235503	−0.194008	−0.227788
	3	−1.109943	0.047600	0.150046	0.077870	0.097188
	4	0.444473	...	...	...	...
	5	−0.075629	...	...	...	...
3.22	0	...	−0.139916	−0.053223	...	...
	1	...	0.083134	−1.126041	...	...
	2	...	−0.025213	−0.089833	...	...
	3	...	0.003474	0.009996	...	...
2.94	0	...	...	...	−0.267431	0.082724
	1	...	...	...	0.190808	−1.235532
	2	...	...	...	−0.073026	0.052984
	3	...	...	...	0.012819	−0.018079
−ε (a.u.)		27.16679	25.70416	4.562424	24.59208	4.090721
I (a.u.)		27.16679	25.76616	5.067099	24.59208	4.090721
Cusp		8.0116	8.0091	8.0196	8.0095	8.0280
−E (a.u.)		59.11115	64.17804		68.25771	

Z=9 ζ	n	1s² 1s	1s²2s 1s	1s²2s 2s	1s²2s² 1s	1s²2s² 2s
14.00	0	0.496507	0.505707	0.104220	0.829455	0.622211
	1	0.195498	0.206587	−0.005522	0.448085	0.493860
	2	0.035986	0.066752	−0.016594	0.172047	0.221045
	3	−0.000214	0.022424	−0.005293	0.060943	0.084923
	4	−0.013475	...	...	...	...
	5	−0.003290	...	...	...	...
8.40	0	0.000000	0.000000	0.000000	−0.718260	−1.034748
	1	0.399466	0.395827	0.323193	0.318192	−0.151229
	2	0.039220	−0.077786	−0.113575	0.108552	0.502918
	3	−0.116937	0.013914	0.070940	−0.073506	−0.181980
	4	0.054289	...	...	...	...
	5	−0.009731	...	...	...	...
3.72	0	...	−0.071307	0.325763	...	...
	1	...	0.049249	−1.361125	...	...
	2	...	−0.017450	−0.023285	...	...
	3	...	0.002925	0.001102	...	...
3.45	0	...	...	...	0.000000	−0.000000
	1	...	...	...	0.043768	−0.987677
	2	...	...	...	−0.034097	−0.148813
	3	...	...	...	0.009075	0.032957
−ε (a.u.)		35.04176	33.35692	6.213238	32.06549	5.665469
I (a.u.)		35.04176	33.42996	6.793586	32.06549	5.665469
Cusp		9.0040	9.0073	9.0140	8.9957	8.9243
−E (a.u.)		75.48613	82.27949		87.93404	

Z=10 ζ	n	1s² 1s	1s²2s 1s	1s²2s 2s	1s²2s² 1s	1s²2s² 2s
15.50	0	−0.000000	−0.000001	−0.000000	−0.000000	−0.000000
	1	0.009861	0.074443	−0.120383	0.036173	−0.111155
	2	−0.197848	0.053242	−0.069735	0.028963	−0.063038
	3	−0.197144	0.027463	−0.022126	0.015017	−0.017915
	4	−0.096674	...	...	...	...
	5	−0.058088	...	...	...	...
9.40	0	1.061048	1.051870	0.331420	0.968036	0.414288
	1	−0.154285	−0.388203	0.548671	−0.310659	0.559569
	2	1.306401	0.236094	−0.240153	0.124151	−0.212796
	3	−1.083190	−0.077422	0.161106	−0.067962	0.158253
	4	0.414569	...	...	...	...
	5	−0.067828	...	...	...	...
4.23	0	...	0.026214	−0.023754	...	...
	1	...	0.021212	−1.168941	...	...
	2	...	−0.019783	−0.089115	...	...
	3	...	0.005227	0.007987	...	...
3.95	0	...	...	...	0.335375	−0.382590
	1	...	...	...	−0.231809	−0.892244
	2	...	...	...	0.087142	−0.129215
	3	...	...	...	−0.015221	0.016802
−ε (a.u.)		43.91673	42.00999	8.114323	40.53982	7.490716
I (a.u.)		43.91673	42.09407	8.770233	40.53982	7.490716
Cusp		10.0131	10.0036	10.0237	10.0104	10.0181
−E (a.u.)		93.86112	102.6311		110.1110	

minimum was obtained; Table II gives the results for Li⁺ as an example.

(2) For the configuration $1s^22s$, with $m=3$, $p=2$, we kept ζ_1 and ζ_2 fixed at the optimum values for the $1s^2$

TABLE VII. Radial functions $P(r)$ for Li.

r	1s	2s	r	1s	2s
0	0	0	5.60	0.00025	−0.32350
0.01	0.08988	0.01404	5.80	0.00021	−0.30353
0.02	0.17446	0.02725	6.00	0.00018	−0.28413
0.03	0.25399	0.03966	6.20	0.00016	−0.26540
0.04	0.32872	0.05131	6.40	0.00015	−0.24742
0.05	0.39887	0.06223	6.60	0.00014	−0.23022
0.10	0.68842	0.10690	6.80	0.00013	−0.21385
0.15	0.89284	0.13747	7.00	0.00012	−0.19832
0.20	1.03120	0.15671	7.20	0.00011	−0.18363
0.25	1.11853	0.16688	7.40	0.00011	−0.16979
0.30	1.16666	0.16977	7.60	0.00010	−0.15678
0.35	1.18491	0.16682	7.80	0.00010	−0.14458
0.40	1.18059	0.15921	8.00	0.00009	−0.13317
0.45	1.15945	0.14789	8.20	0.00009	−0.12252
0.50	1.12601	0.13361	8.40	0.00008	−0.11260
0.55	1.08382	0.11701	8.60	0.00008	−0.10338
0.60	1.03565	0.09860	8.80	0.00007	−0.09482
0.65	0.98366	0.07880	9.00	0.00007	−0.08689
0.70	0.92955	0.05796	9.20	0.00006	−0.07956
0.75	0.87460	0.03636	9.40	0.00006	−0.07278
0.80	0.81982	0.01425	9.60	0.00005	−0.06652
0.85	0.76596	−0.00818	9.80	0.00005	−0.06076
0.90	0.71358	−0.03074	10.00	0.00004	−0.05546
0.95	0.66308	−0.05330	10.20	0.00004	−0.05058
1.00	0.61475	−0.07574	10.40	0.00004	−0.04611
1.05	0.56877	−0.09796	10.60	0.00003	−0.04200
1.10	0.52526	−0.11987	10.80	0.00003	−0.03823
1.15	0.48426	−0.14140	11.00	0.00002	−0.03479
1.20	0.44577	−0.16249	11.20	0.00002	−0.03163
1.25	0.40977	−0.18309	11.40	0.00002	−0.02875
1.30	0.37620	−0.20315	11.60	0.00001	−0.02611
1.35	0.34497	−0.22265	11.80	0.00001	−0.02371
1.40	0.31599	−0.24155	12.00	0.00001	−0.02152
1.45	0.28915	−0.25984	12.20	0.00001	−0.01952
1.50	0.26434	−0.27749	12.40	0.00000	−0.01770
1.55	0.24146	−0.29449	12.60	0.00000	−0.01604
1.60	0.22037	−0.31083	12.80	0.00000	−0.01453
1.65	0.20098	−0.32650	13.00	−0.00000	−0.01316
1.70	0.18317	−0.34151	13.20	−0.00000	−0.01191
1.75	0.16682	−0.35585	13.40	−0.00000	−0.01078
1.80	0.15184	−0.36952	13.60	−0.00000	−0.00975
1.85	0.13813	−0.38253	13.80	−0.00001	−0.00882
1.90	0.12558	−0.39488	14.00	−0.00001	−0.00797
1.95	0.11412	−0.40658	14.20	−0.00001	−0.00720
2.00	0.10366	−0.41763	14.40	−0.00001	−0.00651
2.05	0.09411	−0.42805	14.60	−0.00001	−0.00588
2.10	0.08540	−0.43784	14.80	−0.00001	−0.00531
2.15	0.07747	−0.44703	15.00	−0.00001	−0.00479
2.20	0.07025	−0.45561	15.20	−0.00001	−0.00432
2.25	0.06368	−0.46360	15.40	−0.00001	−0.00390
2.30	0.05770	−0.47101	15.60	−0.00001	−0.00352
2.35	0.05227	−0.47787	15.80	−0.00001	−0.00317
2.40	0.04734	−0.48417	16.00	−0.00001	−0.00286
2.45	0.04286	−0.48995	16.20	−0.00001	−0.00258
2.50	0.03880	−0.49520	16.40	−0.00001	−0.00232
2.55	0.03511	−0.49994	16.60	−0.00001	−0.00209
2.60	0.03177	−0.50420	16.80	−0.00001	−0.00188
2.65	0.02874	−0.50798	17.00	−0.00001	−0.00170
2.70	0.02600	−0.51130	17.20	−0.00001	−0.00153
2.75	0.02351	−0.51418	17.40	−0.00001	−0.00137
2.80	0.02126	−0.51663	17.60	−0.00001	−0.00124
2.85	0.01923	−0.51865	17.80	−0.00001	−0.00111
2.90	0.01739	−0.52028	18.00	−0.00001	−0.00100
2.95	0.01572	−0.52152	18.50	−0.00000	−0.00077
3.00	0.01422	−0.52239	19.00	−0.00000	−0.00059
3.05	0.01286	−0.52290	19.50	−0.00000	−0.00045
3.10	0.01163	−0.52307	20.00	−0.00000	−0.00034
3.15	0.01052	−0.52290	20.50		−0.00026
3.20	0.00952	−0.52242	21.00		−0.00020
3.25	0.00861	−0.52164	21.50		−0.00015
3.30	0.00780	−0.52056	22.00		−0.00012
3.35	0.00706	−0.51920	22.50		−0.00009
3.40	0.00640	−0.51758	23.00		−0.00007
3.60	0.00433	−0.50869	23.50		−0.00005
3.80	0.00296	−0.49648	24.00		−0.00004
4.00	0.00205	−0.48161	24.50		−0.00003
4.20	0.00145	−0.46466	25.00		−0.00002
4.40	0.00104	−0.44616	25.50		−0.00002
4.60	0.00077	−0.42656	26.00		−0.00001
4.80	0.00058	−0.40623	26.50		−0.00001
5.00	0.00045	−0.38550	27.00		−0.00001
5.20	0.00036	−0.36466	27.50		−0.00001
5.40	0.00029	−0.34393	28.00		−0.00000

configuration, and varied ζ_3 until an energy minimum was obtained. Table III gives the results for Li as an example.

TABLE VIII. Radial functions $P(r)$ for Be.

r	$1s$	$2s$	r	$1s$	$2s$
0	0	0	3.60	0.00022	−0.42433
0.01	0.14096	0.02569	3.80	0.00011	−0.39027
0.02	0.27089	0.04935	4.00	0.00005	−0.35742
0.03	0.39050	0.07109	4.20	0.00002	−0.32611
0.04	0.50041	0.09101	4.40	0.00001	−0.29654
0.05	0.60125	0.10922	4.60	0.00000	−0.26884
0.10	0.98824	0.17765	4.80	0.00000	−0.24307
0.15	1.22138	0.21530	5.00	0.00000	−0.21923
0.20	1.34508	0.22980	5.20	0.00001	−0.19728
0.25	1.39184	0.22694	5.40	0.00001	−0.17716
0.30	1.38543	0.21118	5.60	0.00001	−0.15879
0.35	1.34317	0.18592	5.80	0.00001	−0.14208
0.40	1.27767	0.15377	6.00	0.00001	−0.12692
0.45	1.19807	0.11679	6.20	0.00001	−0.11320
0.50	1.11093	0.07654	6.40	0.00001	−0.10083
0.55	1.02093	0.03428	6.60	0.00001	−0.08969
0.60	0.93136	−0.00901	6.80	0.00001	−0.07968
0.65	0.84446	−0.05257	7.00	0.00001	−0.07071
0.70	0.76171	−0.09580	7.20	0.00000	−0.06268
0.75	0.68402	−0.13821	7.40	0.00000	−0.05551
0.80	0.61190	−0.17944	7.60	0.00000	−0.04911
0.85	0.54554	−0.21921	7.80	−0.00000	−0.04341
0.90	0.48495	−0.25730	8.00	−0.00000	−0.03834
0.95	0.42995	−0.29356	8.20	−0.00000	−0.03383
1.00	0.38030	−0.32788	8.40	−0.00000	−0.02984
1.05	0.33568	−0.36019	8.60	−0.00000	−0.02629
1.10	0.29574	−0.39044	8.80	−0.00001	−0.02315
1.15	0.26011	−0.41864	9.00	−0.00001	−0.02037
1.20	0.22841	−0.44479	9.20	−0.00001	−0.01791
1.25	0.20029	−0.46890	9.40	−0.00001	−0.01574
1.30	0.17541	−0.49103	9.60	−0.00001	−0.01383
1.35	0.15344	−0.51122	9.80	−0.00001	−0.01214
1.40	0.13407	−0.52953	10.00	−0.00001	−0.01065
1.45	0.11703	−0.54603	10.20	−0.00001	−0.00934
1.50	0.10206	−0.56078	10.40	−0.00001	−0.00819
1.55	0.08892	−0.57386	10.60	−0.00001	−0.00717
1.60	0.07742	−0.58534	10.80	−0.00001	−0.00628
1.65	0.06735	−0.59531	11.00	−0.00001	−0.00550
1.70	0.05856	−0.60382	11.20	−0.00001	−0.00481
1.75	0.05087	−0.61098	11.40	−0.00001	−0.00421
1.80	0.04418	−0.61683	11.60	−0.00001	−0.00368
1.85	0.03834	−0.62147	11.80	−0.00001	−0.00321
1.90	0.03325	−0.62496	12.00	−0.00001	−0.00281
1.95	0.02883	−0.62738	12.20	−0.00000	−0.00245
2.00	0.02499	−0.62878	12.40	−0.00000	−0.00214
2.05	0.02165	−0.62925	12.60	−0.00000	−0.00187
2.10	0.01875	−0.62883	12.80	−0.00000	−0.00163
2.15	0.01623	−0.62759	13.00	−0.00000	−0.00142
2.20	0.01405	−0.62559	13.20		−0.00124
2.25	0.01216	−0.62289	13.40		−0.00108
2.30	0.01052	−0.61953	13.60		−0.00094
2.35	0.00910	−0.61557	13.80		−0.00082
2.40	0.00787	−0.61106	14.00		−0.00071
2.45	0.00680	−0.60603	14.20		−0.00062
2.50	0.00588	−0.60054	14.40		−0.00054
2.55	0.00508	−0.59463	14.60		−0.00047
2.60	0.00439	−0.58833	14.80		−0.00041
2.65	0.00380	−0.58168	15.00		−0.00035
2.70	0.00328	−0.57471	15.20		−0.00031
2.75	0.00284	−0.56747	15.40		−0.00027
2.80	0.00245	−0.55997	15.60		−0.00023
2.85	0.00212	−0.55224	15.80		−0.00020
2.90	0.00183	−0.54432	16.00		−0.00017
2.95	0.00158	−0.53623	16.20		−0.00015
3.00	0.00136	−0.52799	16.40		−0.00013
3.05	0.00117	−0.51962	16.60		−0.00011
3.10	0.00101	−0.51115	16.80		−0.00010
3.15	0.00087	−0.50259	17.00		−0.00009
3.20	0.00075	−0.49397	17.20		−0.00007
3.25	0.00065	−0.48529	17.40		−0.00006
3.30	0.00056	−0.47658	17.60		−0.00006
3.35	0.00048	−0.46785	17.80		−0.00005
3.40	0.00041	−0.45911	18.00		−0.00004

(3) The same as (2), for the configuration $1s^22s^2$. The best ζ_3 for this case is different from the one found in (2). Table IV gives the results for Li⁻ as an example.

(4) Keeping the values of ζ_1, ζ_2, ζ_3 fixed at the optimum values determined in (1), (2), (3), we boosted the value of p to the maximum the program could handle: 6 for $1s^2$, 4 for $1s^22s$, and $1s^22s^2$. At this point, we attempted further ζ variation in a few cases and found that this improved the energy at most by a few units in the eighth significant figure.

The results of what we consider good compromise functions, $p=2$ are listed in Table V. In Table VI are

given the best results we could obtain with the present program. For comparison with previous SCF calculations on Li and Be, we list the numerical SCF functions $P(r) = rR(r)$, obtained from our best expansions, in Tables VII and VIII; in Table IX we do the same for Li⁻. Our functions for Li differ from Fock's[8] in the third decimal place and considerably more for the $1s$ orbital at large r. This may be ascribed to the fact that Fock solved a different variational problem than we did; he determined the $1s$ orbital for Li⁺, and subsequently

TABLE IX. Radial functions $P(r)$ for Li⁻.

r	$1s$	$2s$	r	$1s$	$2s$	r	$2s$
0	0	0	3.60	0.00398	−0.41152	18.50	−0.04146
0.01	0.08990	0.00974	3.80	0.00262	−0.41138	19.00	−0.03798
0.02	0.17449	0.01889	4.00	0.00172	−0.40939	19.50	−0.03479
0.03	0.25403	0.02749	4.20	0.00113	−0.40586	20.00	−0.03185
0.04	0.32876	0.03557	4.40	0.00075	−0.40107	20.50	−0.02915
0.05	0.39892	0.04313	4.60	0.00050	−0.39525	21.00	−0.02668
0.10	0.68850	0.07409	4.80	0.00033	−0.38859	21.50	−0.02440
0.15	0.89294	0.09529	5.00	0.00022	−0.38127	22.00	−0.02231
0.20	1.03132	0.10868	5.20	0.00015	−0.37342	22.50	−0.02040
0.25	1.11866	0.11579	5.40	0.00010	−0.36517	23.00	−0.01864
0.30	1.16680	0.11787	5.60	0.00007	−0.35663	23.50	−0.01702
0.35	1.18505	0.11592	5.80	0.00005	−0.34787	24.00	−0.01554
0.40	1.18072	0.11074	6.00	0.00003	−0.33898	24.50	−0.01418
0.45	1.15956	0.10299	6.20	0.00002	−0.33000	25.00	−0.01293
0.50	1.12611	0.09321	6.40	0.00002	−0.32100	25.50	−0.01179
0.55	1.08390	0.08181	6.60	0.00001	−0.31202	26.00	−0.01074
0.60	1.03571	0.06917	6.80	0.00001	−0.30309	26.50	−0.00979
0.65	0.98371	0.05556	7.00	0.00000	−0.29423	27.00	−0.00891
0.70	0.92958	0.04123	7.20	−0.00000	−0.28549	27.50	−0.00811
0.75	0.87462	0.02637	7.40	−0.00000	−0.27687	28.00	−0.00737
0.80	0.81983	0.01115	7.60	−0.00000	−0.26839	28.50	−0.00670
0.85	0.76595	−0.00431	7.80	−0.00000	−0.26008	29.00	−0.00609
0.90	0.71355	−0.01988	8.00	−0.00001	−0.25193	29.50	−0.00553
0.95	0.66304	−0.03547	8.20	−0.00001	−0.24395	30.00	−0.00502
1.00	0.61469	−0.05101	8.40	−0.00001	−0.23616	30.50	−0.00455
1.05	0.56870	−0.06642	8.60	−0.00001	−0.22856	31.00	−0.00413
1.10	0.52517	−0.08164	8.80	−0.00001	−0.22116	31.50	−0.00374
1.15	0.48415	−0.09664	9.00	−0.00001	−0.21394	32.00	−0.00339
1.20	0.44565	−0.11137	9.20	−0.00001	−0.20693	32.50	−0.00307
1.25	0.40963	−0.12580	9.40	−0.00001	−0.20011	33.00	−0.00278
1.30	0.37604	−0.13990	9.60	−0.00001	−0.19348	33.50	−0.00251
1.35	0.34479	−0.15364	9.80	−0.00000	−0.18705	34.00	−0.00227
1.40	0.31579	−0.16702	10.00	−0.00001	−0.18081	34.50	−0.00206
1.45	0.28894	−0.18001	10.20	−0.00000	−0.17476	35.00	−0.00186
1.50	0.26411	−0.19260	10.40	−0.00000	−0.16889	35.50	−0.00168
1.55	0.24121	−0.20480	10.60	−0.00000	−0.16321	36.00	−0.00151
1.60	0.22012	−0.21658	10.80	−0.00000	−0.15771	36.50	−0.00137
1.65	0.20071	−0.22795	11.00	−0.00000	−0.15239	37.00	−0.00123
1.70	0.18289	−0.23891	11.20	−0.00000	−0.14723	37.50	−0.00111
1.75	0.16653	−0.24946	11.40	−0.00000	−0.14225	38.00	−0.00100
1.80	0.15155	−0.25960	11.60	−0.00000	−0.13743	38.50	−0.00090
1.85	0.13783	−0.26933	11.80	−0.00000	−0.13276	39.00	−0.00081
1.90	0.12528	−0.27866	12.00	−0.00000	−0.12825	39.50	−0.00073
1.95	0.11381	−0.28760	12.20	0.00000	−0.12389	40.00	−0.00066
2.00	0.10334	−0.29614	12.40	0.00000	−0.11968	40.50	−0.00059
2.05	0.09379	−0.30429	12.60	0.00000	−0.11561	41.00	−0.00053
2.10	0.08508	−0.31208	12.80	0.00000	−0.11167	41.50	−0.00048
2.15	0.07715	−0.31949	13.00	0.00000	−0.10787	42.00	−0.00043
2.20	0.06993	−0.32654	13.20		−0.10419	42.50	−0.00039
2.25	0.06336	−0.33324	13.40		−0.10065	43.00	−0.00035
2.30	0.05738	−0.33959	13.60		−0.09722	43.50	−0.00031
2.35	0.05195	−0.34561	13.80		−0.09390	44.00	−0.00028
2.40	0.04702	−0.35130	14.00		−0.09070	44.50	−0.00025
2.45	0.04254	−0.35667	14.20		−0.08761	45.00	−0.00022
2.50	0.03848	−0.36173	14.40		−0.08462	45.50	−0.00020
2.55	0.03479	−0.36649	14.60		−0.08174	46.00	−0.00018
2.60	0.03144	−0.37096	14.80		−0.07895	46.50	−0.00016
2.65	0.02841	−0.37514	15.00		−0.07626	47.00	−0.00014
2.70	0.02567	−0.37905	15.20		−0.07366	47.50	−0.00013
2.75	0.02318	−0.38270	15.40		−0.07115	48.00	−0.00012
2.80	0.02093	−0.38608	15.60		−0.06872	48.50	−0.00010
2.85	0.01890	−0.38922	15.80		−0.06637	49.00	−0.00009
2.90	0.01705	−0.39211	16.00		−0.06411	49.50	−0.00008
2.95	0.01539	−0.39478	16.20		−0.06192	50.00	−0.00007
3.00	0.01388	−0.39721	16.40		−0.05980		
3.05	0.01252	−0.39943	16.60		−0.05776		
3.10	0.01129	−0.40144	16.80		−0.05578		
3.15	0.01018	−0.40324	17.00		−0.05388		
3.20	0.00917	−0.40485	17.20		−0.05203		
3.25	0.00827	−0.40627	17.40		−0.05025		
3.30	0.00745	−0.40751	17.60		−0.04853		
3.35	0.00671	−0.40858	17.80		−0.04686		
3.40	0.00605	−0.40948	18.00		−0.04525		

[8] V. Fock and M. Petrashen, Physik. Z. Sowjetunion 8, 547 (1935).

determined the $2s$ orbital for Li using the Li$^+$ $1s$ orbital. Indeed, a numerical table we obtained for our best Li$^+$ orbital confirmed this. For Be, our orbitals differed from Hartree's[9] by a few units in the last figure he gave.

Generally speaking, we are confident that our SCF orbitals are equivalent to the solutions of the integro-differential Hartree-Fock equations to four decimal places. This is confirmed by the behavior of the fifth figure in the $1s$ orbitals; their tails cross the r axis, decrease to -1×10^{-5}, and then die out as they should. Further confirmation of this accuracy will be obtained when a program for the computation and tabulation of $F\phi_i - \epsilon_i \phi_i$ and $F\phi_i/\epsilon_i \phi_i$, now under construction, is completed. The accuracy of our orbital energies should be at least 4 figures, our total energies 7–8 figures.

---

[9] D. R. Hartree, Proc. Roy. Soc. (London) **A150**, 9 (1935).

APPENDIX

We put in Eq. (22) $e^{-v} = -(d/dv)e^{-v}$ and perform a partial integration with respect to v; the result is

$$C_{\alpha\beta}(t) = C_{\alpha,\beta-1}(t) - (\alpha!\beta!)^{-1}t^{\alpha+1}\int_0^\infty du \cdot u^{\alpha+\beta}e^{-(1+t)u} + \delta_{\beta 0},$$

where the term $C_{\alpha,\beta-1}(t)$ is absent if $\beta=0$. Next, we multiply Eq. (22) by t, put the $te^{-ut} = -(d/du)e^{-ut}$, and perform a partial integration with respect to u; the result is

$$tC_{\alpha\beta}(t) = tC_{\alpha-1,\beta}(t) + (\alpha!\beta!)^{-1}t^{\alpha+1}\int_0^\infty du \cdot u^{\alpha+\beta}e^{-(1+t)u},$$

where the term $tC_{\alpha-1,\beta}(t)$ is absent if $\alpha=0$. Addition of these two equations and division by $1+t$ yields Eq. (23).

Correlated Orbitals for the Ground State of Heliumlike Systems*

C. C. J. ROOTHAAN AND A. W. WEISS

Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, Chicago 37, Illinois

INTRODUCTION

FOR the ground state of atoms, molecules, and solids, the explicit solution of the Schrödinger equation to obtain an accurate wave function is virtually a hopeless task. Instead, one usually chooses a convenient function with adjustable parameters, and determines the best wave function within this class by minimizing the expectation value of the energy, computed from that wave function, with respect to these parameters. The form of the function chosen represents a certain restriction, and it is essential to use physical arguments in choosing such a form; in doing so, we essentially choose a model. The success of such a wave function can, to a certain extent, be judged by comparing the calculated energy with the experimental total energy.

One of the most successful models is the Hartree-Fock approximation,[1-4] in which there occur, instead of adjustable parameters, wholly adjustable undetermined one-electron functions or orbitals. The condition for minimizing the energy leads to nonlinear integro-differential equations for the orbitals, which can be solved by the iterative self-consistent field procedure.[1-4] The total energies obtained by this method are rather good, namely, about 99% of the experimental values or better; also, the lower ionization potentials and electron densities are calculated rather reliably. However, many other physical properties, calculated by the Hartree-Fock function, do not agree nearly as well with experimental data, notably dissociation (or cohesive) energies.

It is well known that the shortcomings of the Hartree-Fock method are due to neglect of the details of the electronic repulsions; the wave function for each individual electron is determined by the potential of the nuclei and that due to the probability density of the other electrons (we ignore the exchange potential, which does not alter this picture materially). On the whole, this allows electrons to come close together more often than is actually the case. The energy correction which would result if this effect is properly taken into account is commonly called the correlation energy.[5] The correlation energy is especially large be-

---

[1] D. R. Hartree, Repts. Progr. Phys. **11**, 113 (1948).
[2] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, New York, 1957).
[3] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).
[4] C. C. J. Roothaan, Revs. Modern Phys. **32**, 179 (1960), this issue.

[5] More precisely, the correlation energy is defined as the difference between the expectation value of the energy of the Hartree-Fock approximation and the correct eigenvalue of the nonrelativistic spin-independent infinite nuclear mass Hamiltonian.