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Hartree-Fock Procedure for Some $nsn's$ ^1S Configurations*

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A numerical Hartree-Fock procedure is described for computing wave functions for $nsn's$ ^1S configurations in which the radial functions for the two s electrons are not assumed to be orthogonal. When the two s electrons are equivalent, this approach corresponds to the unrestricted Hartree-Fock approximation. The procedure was applied to some 2- and 4-electron systems. Results are reported for $1s1s'$ ^1S of He, Li⁺, and Be²⁺ as well as $1s1s'$(^1S)$2sns$ ^1S, $n=2, 3, 4$ of Be. The total energies are compared with those of other approximations, and the transition integrals for the unrestricted approximation are shown to differ only slightly from those of the Hartree-Fock approximation.

I. INTRODUCTION

IN atomic structure calculations, it is usual to assume that the state of an atom can be approximated by an antisymmetric function Ψ constructed from one-electron functions. Furthermore, the one-electron functions are assumed to be products of a radial function $P(nl;r)/r$, a spherical harmonic $Y_l{}^m(\theta,\phi)$, and a spin function, where $nlms$ are the quantum numbers associated with the electron. In the LS-coupling scheme, the orbital angular momenta are coupled to yield a total angular momentum L, and the spin momenta, to yield a total spin S. Such coupling corresponds to combining the spherical-harmonic functions to yield an eigenfunction of the total-angular-momentum operator, and similarly combining the spin functions to yield an eigenfunction of the total spin. Let $|\gamma SL\rangle_{12...N}$ represent an eigenfunction of S and L formed from coupling N electrons by the Racah coupling methods in the order indicated. (Here γ distinguishes different eigenfunctions with the same S and L.) Then

$$\Psi = \mathcal{C} \prod_{i=1}^{N} (1/r_i)P_i(n_il_i; r_i)|\gamma SL\rangle_{12...N}$$

where $\mathcal{C}$ is an antisymmetrizing operator.

So far the form of the radial functions has not been specified. The "best" functions are those for which the energy is stationary. But

$$E=\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle \tag{1}$$

where

$$H=-\tfrac{1}{2}\sum_{i=1}^{N} (\nabla_i{}^2+2Z/r_i)+\sum_{i>j} 1/r_{ij}.$$

Therefore the energy can be expressed entirely in terms of the radial functions $P(nl;r)$. From the fact that the energy must remain stationary with regard to small variations in any one of the radial functions, an equation can be derived for each function. The resulting system of second-order, nonlinear equations determines the Hartree-Fock wave functions.

In order to simplify the evaluation of E according to (1), it is usual to assume that radial wave functions with the same nl quantum numbers are the same, and that they are orthogonal if the angular quantum numbers are the same but the principle quantum numbers different. This greatly reduces the number of permutations which need be considered (see Layzer, Horák, Lewis, and Thompson.[1]) However, for each condition introduced during the evaluation of E, a Lagrange multiplier must be introduced before applying the variational principle. These conditions may restrict the function space of possible solutions, and consequently may affect the value of the energy obtained by this method.

Whenever the antisymmetric function Ψ can be expressed as a single determinant of one-electron functions, the assumption that these form an orthonomal set places no restriction on the generality of the

[1] D. Layzer, Z. Horák, M. N. Lewis, and D. P. Thompson, Ann. Phys. (N. Y.) 29, 101 (1964).

method. This is the case considered by Hartree in his book *The Calculation of Atomic Structures*.[2] On the other hand, Fock[3] realized that the $1s2s\ ^3S$ state was essentially different from the $1s2s\ ^1S$ state in that the orthogonality assumption was not valid for the latter, and therefore he treated the two cases differently. In fact, Sharma and Coulson[4] have shown that the orthogonality assumption leads to equations whose solutions do not become hydrogenic for large values of Z, the atomic number, i.e., the assumption

$$P(nl\,;r) = Z^{1/2}[P^H(nl\,;\rho) + Z^{-1}P_1(nl\,;\rho) + O(Z^{-2})],$$

$$\rho = Zr,$$

leads to a contradiction.

The purpose of this investigation was to consider configurations consisting of a core plus a pair of s electrons which form a ^1S state, and to determine a numerical Hartree-Fock procedure for computing the wave functions for such configurations without assuming orthogonality for the pair of s electrons. When the two s electrons are equivalent, this approach leads to the unrestricted Hartree-Fock (UHF) approximation. Some results are reported for the $1s1s'\ ^1S$ state of He, Li$^+$, and Be^{2+}, and the $1s1s'(^1S)2sns(^1S)\ ^1S$ states of Be. The total energies and the transition integrals obtained from the unrestricted approximation are compared with those determined by other methods.

II. HARTREE-FOCK PROCEDURE FOR CORE+$nsn's$(^1S)

The expression for the total energy as given by Eq. (1) is a homogeneous function of degree zero in each of the radial functions $P(nl\,;r)$. Therefore we may assume without any loss of generality that the radial functions are normalized.

Let i refer to an electron in the core and let summation with respect to i represent a summation over all groups of equivalent electrons in the core. Furthermore, let α and β refer to the two s electrons. Let a, b, c, d be any four electrons in the configuration; then, using Slater's notation,[5] define

$$P_a = P(n_a l_a\,;r),$$

$$Y^k(ab) = Y^k(n_a l_a, n_b l_b\,;r),$$

$$F^k(ab) = F^k(n_a l_a, n_b l_b)\,;\ G^k(ab) = G^k(n_a l_a, n_b l_b),$$

$$R^k(ab\,;cd) = \int_0^\infty (1/r)P_a P_c Y^k(bd)dr,$$

$$\langle a | b \rangle = \int_0^\infty P_a P_b dr,$$

[2] D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley & Sons, Inc., New York, 1957).
[3] V. Fock, Z. Physik **61**, 126 (1930).
[4] C. S. Sharma and C. A. Coulson, Proc. Phys. Soc. (London) **80**, 81 (1962).
[5] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II, p. 17.

$$L_{ab} = \int_0^\infty P_a L P_b dr,$$

where

$$L = d^2/dr^2 + 2Z/r.$$

Now, in deriving an expression for the energy relative to the energy of the core we must include, in addition to the usual terms, the contribution resulting from an interchange of the two s electrons. In this case the space part is symmetric, so that

$$(E - E_{\text{core}})(1 + \langle \alpha | \beta \rangle^2)$$

$$= -\tfrac{1}{2}[L_{\alpha\alpha} + 2\langle \alpha | \beta \rangle L_{\alpha\beta} + L_{\beta\beta}] + F^0(\alpha\beta) + G^0(\alpha\beta)$$

$$+ \sum_{i,k} a_{ik}[F^k(i\alpha) + F^k(i\beta) + 2\langle \alpha | \beta \rangle R^k(i\alpha\,;i\beta)]$$

$$+ \sum_{i,k} b_{ik}[G^k(i\alpha) + G^k(i\beta) + 2\langle \alpha | \beta \rangle R^k(i\alpha\,;\beta i)]. \quad (2)$$

This expression reduces to the usual expression for the energy when $\langle \alpha | \beta \rangle = 0$.

In deriving Eq. (2) we have assumed that

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1, \quad \text{and} \quad \langle i | \alpha \rangle = \langle i | \beta \rangle = 0, \quad \text{if} \quad l_i = 0.$$

Therefore

$$W = E + \lambda_{\alpha\alpha} \langle \alpha | \alpha \rangle + \lambda_{\beta\beta} \langle \beta | \beta \rangle$$

$$+ \sum_i \delta(l_i, 0)[\lambda_{i\alpha} \langle i | \alpha \rangle + \lambda_{i\beta} \langle i | \beta \rangle]$$

must be stationary with regard to variations in P_α and P_β.

Here the λ's are Lagrange multipliers and $\delta(l,0) = 1$ if $l = 0$ and zero otherwise. The variation principle then leads to the equation

$$(L - \epsilon_{\alpha\alpha})P_\alpha + \langle \alpha | \beta \rangle L P_\beta = (2/r)(Y_\alpha P_\alpha + X_\alpha) + \epsilon_{\alpha\beta} P_\beta$$

$$+ (1 + \langle \alpha | \beta \rangle^2)\sum_i \delta(l_i, 0)\lambda_{\alpha i} P_i, \quad (3)$$

where

$$\epsilon_{\alpha\alpha} = -2(1 + \langle \alpha | \beta \rangle^2)\lambda_{\alpha\alpha},$$

$$\epsilon_{\alpha\beta} = -2(E - E_{\text{core}})\langle \alpha | \beta \rangle - L_{\alpha\beta}$$

$$+ 2\sum_{i,k} a_{ik}R^k(i\alpha\,;i\beta) + 2\sum_{i,k} b_{ik}R^k(i\alpha\,;\beta i)$$

$$= \epsilon_{\beta\alpha}, \quad (4)$$

$$Y_\alpha = Y^0(\beta\beta) + \sum_{i,k} a_{ik}Y^k(ii),$$

$$X_\alpha = Y^0(\alpha\beta)P_\beta + \sum_{i,k} b_{ik}[Y^k(i\alpha) + \langle \alpha | \beta \rangle Y^k(i\beta)]P_i$$

$$+ \langle \alpha | \beta \rangle \sum_{i,k} a_{ik}Y^k(ii)P_\beta.$$

A similar equation holds for P_β. Note that $\epsilon_{\alpha\beta} = \epsilon_{\beta\alpha}$ is *not* a Lagrange multiplier but instead is defined by Eq. (4).

Equations for the core wave functions can be derived in a similar manner. They will differ from the usual

equations only by the presence of some extra terms in the exchange resulting from the R^k integrals in Eq. (2).

An expression for $\lambda_{\alpha i}$ and $\lambda_{\beta i}$ can be derived by a procedure similar to that for ordinary Hartree-Fock equations.[6] The operator L is such that $L_{ab}=L_{ba}$; in particular $L_{i\alpha}=L_{\alpha i}$ and $L_{i\beta}=L_{\beta i}$. If we use the Hartree-Fock equations to express each value of L_{ab} in terms of the wave functions and assume $\langle i|\alpha\rangle=\langle i|\beta\rangle=0$, we are led to two equations in the two unknowns, $\lambda_{\alpha i}$ and $\lambda_{\beta i}$. We shall assume that these equations have a unique solution. This will be the case if all s electrons in the core belong to complete groups.

In the Hartree-Fock calculation, it is convenient to consider the ϵ's and the P's as fundamental quantities and express $E-E_{\text{core}}$ in terms of them. Let the right-hand side of Eq. (2) be $H_{\alpha\beta}$ and define

$$F_{ab}=\int_0^\infty P_a(2/r)(Y_bP_b+X_b)dr.$$

Multiplying Eq. (3) by P_α and integrating, we get

$$L_{\alpha\alpha}-\epsilon_{\alpha\alpha}+\langle\alpha|\beta\rangle L_{\alpha\beta}=F_{\alpha\alpha}+\langle\alpha|\beta\rangle\epsilon_{\alpha\beta}, \quad (5)$$

and similarly,

$$L_{\beta\beta}-\epsilon_{\beta\beta}+\langle\alpha|\beta\rangle L_{\alpha\beta}=F_{\beta\beta}+\langle\alpha|\beta\rangle\epsilon_{\alpha\beta}. \quad (6)$$

Adding, solving for $\epsilon_{\alpha\alpha}+\epsilon_{\beta\beta}$, and substituting for $F_{\alpha\alpha}+F_{\beta\beta}$ from their definition, we obtain

$$-\tfrac{1}{2}(\epsilon_{\alpha\alpha}+\epsilon_{\beta\beta})=H_{\alpha\beta}+\langle\alpha|\beta\rangle\epsilon_{\alpha\beta}+F^0(\alpha\beta)+G^0(\alpha\beta),$$

so that

$$(E-E_{\text{core}})(1+\langle\alpha|\beta\rangle^2)=-[\tfrac{1}{2}\epsilon_{\alpha\alpha}+\tfrac{1}{2}\epsilon_{\beta\beta}+\langle\alpha|\beta\rangle\epsilon_{\alpha\beta}$$
$$+F^0(\alpha\beta)+G^0(\alpha\beta)]. \quad (7)$$

Now, multiplying Eq. (3) by P_β and integrating, we get

$$L_{\alpha\beta}-\langle\alpha|\beta\rangle\epsilon_{\alpha\alpha}+\langle\alpha|\beta\rangle L_{\beta\beta}=F_{\beta\alpha}+\epsilon_{\alpha\beta},$$

and similarly

$$L_{\beta\alpha}-\langle\alpha|\beta\rangle\epsilon_{\beta\beta}+\langle\alpha|\beta\rangle L_{\alpha\alpha}=F_{\alpha\beta}+\epsilon_{\alpha\beta}.$$

Adding, and eliminating $L_{\alpha\alpha}+L_{\beta\beta}$ using Eqs. (5) and (6), we obtain an expression for $L_{\alpha\beta}$ which on substitution into (4) results in an expression which reduces to

$$\epsilon_{\alpha\beta}=-\langle\alpha|\beta\rangle(E-E_{\text{core}})-\{R^0(\alpha\alpha;\alpha\beta)+R^0(\beta\beta;\beta\alpha)$$
$$-\langle\alpha|\beta\rangle[F^0(\alpha\beta)+G^0(\alpha\beta)]\}/(1-\langle\alpha|\beta\rangle^2). \quad (8)$$

Finally, on substituting (8) into (7) we obtain

$$E-E_{\text{core}}=-\tfrac{1}{2}(\epsilon_{\alpha\alpha}+\epsilon_{\beta\beta})-\{F^0(\alpha\beta)+G^0(\alpha\beta)$$
$$-\langle\alpha|\beta\rangle[R^0(\alpha\alpha;\alpha\beta)+R^0(\beta\beta;\beta\alpha)]\}/(1-\langle\alpha|\beta\rangle^2). \quad (9)$$

Therefore, given estimates of $\epsilon_{\alpha\alpha}$, $\epsilon_{\beta\beta}$ and the wave functions, Eq. (9) can be solved for $E-E_{\text{core}}$ and (8) for $\epsilon_{\alpha\beta}$. Then the equations for the Lagrange multipliers are solved and Y_α and X_α computed from their definition. With all these functions as known, Eq. (3) can

[6] C. Froese, Phys. Rev. **137**, A1644 (1965).

be rewritten as

$$[L-(2/r)Y_\alpha-\epsilon_{\alpha\alpha}]P_\alpha=f, \quad P_\alpha(0)=P_\alpha(\infty)=0;$$
$$\langle\alpha|\alpha\rangle=1. \quad (10)$$

The latter is solved for P_α and $\epsilon_{\alpha\alpha}$ and the estimate for P_α corrected. Similar equations are solved for the other wave functions and the process repeated until no further significant changes occur. This is essentially the self-consistent field procedure.

III. EQUIVALENT s ELECTRONS

When the two s electrons are in fact equivalent electrons, the procedure just described leads to the unrestricted Hartree-Fock (UHF) approximation for these electrons. The only way in which the case of equivalent electrons differs from that of nonequivalent electrons is in the magnitude of the overlap integral $\langle\alpha|\beta\rangle$. Normally $\langle\alpha|\beta\rangle$ is small, but for equivalent electrons it may be close to unity.

In Eq. (10) the function f includes the term $\langle\alpha|\beta\rangle LP_\beta$, which requires that the estimate P_β be differentiated. Such differentiation emphasizes the errors in the estimate, and when $\langle\alpha|\beta\rangle\simeq1$, the self-consistent-field (SCF) procedure does not converge. Therefore Eq. (3) was transformed to diagonal form so that

$$(L-(2/r)Y_\alpha{}^*-\epsilon_{\alpha\alpha}{}^*)P_\alpha=(2/r)X_\alpha{}^*+\epsilon_{\alpha\beta}{}^*P_\beta$$
$$+(1+\langle\alpha|\beta\rangle^2)\sum_i\delta(l_i,0)\lambda_{\alpha i}{}^*P_i, \quad (11)$$

where, in matrix notation,

$$\begin{pmatrix}\epsilon_{\alpha\alpha}{}^* & \epsilon_{\alpha\beta}{}^*\\ \epsilon_{\beta\alpha}{}^* & \epsilon_{\beta\beta}{}^*\end{pmatrix}$$
$$=\frac{1}{(1-\langle\alpha|\beta\rangle^2)}\begin{pmatrix}1 & -\langle\alpha|\beta\rangle\\ -\langle\alpha|\beta\rangle & 1\end{pmatrix}\begin{pmatrix}\epsilon_{\alpha\alpha} & \epsilon_{\alpha\beta}\\ \epsilon_{\alpha\beta} & \epsilon_{\beta\beta}\end{pmatrix},$$
$$\lambda_{\alpha i}{}^*=(\lambda_{\alpha i}-\langle\alpha|\beta\rangle\lambda_{\beta i})/(1-\langle\alpha|\beta\rangle^2)$$

and

$$Y_\alpha{}^*P_\alpha+X_\alpha{}^*=[Y_\alpha P_\alpha+X_\alpha-\langle\alpha|\beta\rangle(Y_\beta P_\beta+X_\beta)]/$$
$$(1-\langle\alpha|\beta\rangle^2).$$

Notice that the potential and exchange terms now contain about twice as many Y^k integrals as before, so that the faster rate of convergence is offset to some extent by additional computations. In this form the fundamental energy parameters are $\epsilon_{\alpha\alpha}{}^*$, $\epsilon_{\beta\beta}{}^*$, and $\epsilon_{\alpha\beta}$, as given by Eq. (8). Then

$$E-E_{\text{core}}=-\tfrac{1}{2}(\epsilon_{\alpha\alpha}{}^*+\epsilon_{\beta\beta}{}^*)-[F^0(\alpha\beta)+G^0(\alpha\beta)$$
$$+\langle\alpha|\beta\rangle(\epsilon_{\alpha\beta}{}^*+\epsilon_{\beta\alpha}{}^*)]/(1+\langle\alpha|\beta\rangle^2), \quad (12)$$

where

$$\epsilon_{\alpha\beta}{}^*=\epsilon_{\alpha\beta}-\langle\alpha|\beta\rangle\epsilon_{\beta\beta}{}^*, \quad \epsilon_{\beta\alpha}{}^*=\epsilon_{\alpha\beta}-\langle\alpha|\beta\rangle\epsilon_{\alpha\alpha}{}^*.$$

These equations have been left in a somewhat simple form, but in an actual calculation, Eqs. (12) and (8) must be solved for $\epsilon_{\alpha\beta}$ and $E-E_{\text{core}}$.

TABLE I. Results for $1s1s'$ ^1S.

	He	Li$^+$	Be^{2+}
$-E_{total}$	2.87799	7.25147	13.62584
$\langle \alpha|\beta \rangle$	0.87894	0.92808	0.94880
σ_1	-0.185	-0.290	-0.380
σ_2	0.769	0.870	0.959

TABLE II. Comparison of $-E_{total}$ for $1s^2$ ^1S (in a.u.).

	He	Li$^+$	Be^{2+}
1. Exact[a]	2.9037	7.2801	13.6568
2. Configuration interaction			
(i) Analytic[b] (35 config.)	2.9032	7.2792	13.6548
(ii) Z expansion[c]	2.9077	7.2827	13.6577
3. $1s1s'$ (unrestricted)			
(i) Numerical UHF	2.8780	7.2515	13.6258
(ii) Open shell[d]	2.8757	7.2490	13.6230
(iii) Z expansion[e]	2.8718	7.2468	13.6218
4. $1s^2$ Hartree-Fock			
(i) Numerical	2.8617	7.2364	13.6113
(ii) Analytic[f]	2.8617	7.2364	13.6113
(iii) Z expansion[g]	2.8610	7.2360	13.6110

[a] See Ref. 14.
[b] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).
[c] W. B. Sommerville and A. L. Stewart, Proc. Phys. Soc. (London) **80**, 97 (1962).
[d] See Ref. 10.
[e] See Ref. 12.
[f] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).
[g] A. Dalgarno, Proc. Phys. Soc. (London) **75**, 439 (1960).

The present UHF approach for equivalent s electrons is similar to the open-shell method except that in the latter the radial functions are assumed to be simple exponential functions. The results reported in the next two sections show that these two approximations yield total energies which are remarkably similar for 2- and 4-electron systems.

IV. RESULTS FOR $1s^2$ ^1S

Equations (8), (11), and (12) were solved for the $1s1s'$ ^1S state of He, Li$^+$, and Be^{2+}. The numerical integration procedure was the same as that described in an earlier paper.[7] The total energy for He agrees to five decimal places with the value determined earlier by Trefftz, Schlüter, Dettmar, and Jorgens.[8]

In Table I, the total energies, the overlap integral, and the screening numbers σ for each of the two wave functions are reported. Here σ is the Hartree[2] screening number defined as

$$\sigma = Z - (\bar{r}_H/\bar{r}).$$

It is interesting to compare these screening numbers with those from the simple exponential approximation of Hylleraas-Eckart.[9] For He the screening numbers are $\sigma_1 = -0.1832$ and $\sigma_2 = 0.8115$; these correspond closely with our numerical results.

More recently, Shull and Löwdin[10] applied the open-shell method to the atoms H$^-$ to Ne^{8+}. They were able to show that two different orbitals improve the energy, but that the improvement decreases with Z. Hurst et al.[11] have performed similar calculations. Furthermore, Stewart[12] has considered this case from a Z expansion point of view. He assumed first of all that the one-electron orbitals[13] were expanded in powers of $Z^{-1/2}$, and then obtained a Z expansion of the total energy to terms of second order. In this way he was able to show that the unrestricted Hartree-Fock approximation embraces more than 80% of the radial correlation energy.

In Table II, the total energies for $1s1s'$ ^1S of He, Li$^+$,

[7] C. Froese, Can. J. Phys., **41**, 1895 (1963).
[8] E. Trefftz, A. Schlüter, K.-H. Dettmar, and K. Jorgens, Z. Astrophys. **44**, 1 (1957).
[9] E. A. Hylleraas, Z. Physik **54**, 347 (1929); C. Eckart, Phys. Rev. **36**, 878 (1930).
[10] H. Shull and P. O. Löwdin, J. Chem. Phys. **25**, 1035 (1956).
[11] R. P. Hurst, J. D. Gray, G. H. Brigman, and F. A. Matsen, Mol. Phys. **1**, 189 (1958).
[12] A. L. Stewart, Proc. Phys. Soc. (London) **83**, 1003 (1964).
[13] C. A. Coulson, Proc. Phys. Soc. (London) **84**, 511 (1964) has shown that in this case the Hartree-Fock equations have no solution in the form of a Z^{-1} expansion.

and Be^{+2} are compared with those from other approximations, including the exact, nonrelativistic values determined by Pekeris.[14] All the unrestricted approximations (UHF, open shell, second-order Z expansion) give lower total energies than the Hartree-Fock approximations. Also, the energies for the UHF and open-shell method are always lower than the Z-expansion results and, in turn, the UHF energies are somewhat lower than the open-shell energies, though the difference between them is less than 0.08%. On the whole, the improvement in the total energy in going from a Hartree-Fock to an unrestricted approximation is considerably less than the improvement which can be achieved by the inclusion of configuration interaction. In fact, the UHF improvement is 39.2%, 35.3%, and 33.3% of the configuration interaction improvement for He, Li$^+$, and Be^{+2}, respectively. As noted by Shull and Löwdin, the improvement decreases as Z increases.

In Table III some transition integrals (I_{1snp}) from the unrestricted and restricted Hartree-Fock approximation are compared. Here

$$I_{1snp} = \langle 1s|1s''\rangle\langle 1s|r|np\rangle \quad \text{for} \quad (1s^2\ ^1S) \rightarrow (1s''np\ ^1P)$$
$$= (1/\sqrt{2})(\langle 1s|1s''\rangle\langle 1s'|r|np\rangle + \langle 1s'|1s''\rangle\langle 1s|r|np\rangle)/$$
$$(1+\langle 1s|1s'\rangle^2)^{1/2} \quad \text{for} \quad (1s1s'\ ^1S) \rightarrow (1s''np\ ^1P).$$

From Table III it is evident that the assumption of different orbitals does not change appreciably the value of a dipole matrix element for a transition. Trefftz et al.[8] give a detailed comparison for He of length and velocity forms of the oscillator strengths with values obtained by other methods. No extensive differences were noted between the length and velocity forms. However, there appears to be an error in the

[14] C. L. Pekeris, Phys. Rev. **112**, 1649 (1948); **115**, 1216 (1959).

TABLE III. A comparison of I_{1snp} for He sequence.

	He		Li$^+$		Be^{2+}	
	UHF	HF	UHF	HF	UHF	HF
$1s^2\,^1S \to 1s2p\,^1P$	0.5221	0.4984	0.3901	0.3846	0.3038	0.3018
$\to 1s3p\,^1P$	0.2597	0.2498	0.1826	0.1806	0.1374	0.1367
$\to 1s4p\,^1P$	0.1637	0.1578	0.1128	0.1117	0.0840	0.0836

TABLE IV. Overlap integrals and screening numbers for some Be states.

State	$\langle 1s\|1s'\rangle$	$\langle 2s\|ns\rangle$	σ_{1s}	σ_{1s}'	σ_{2s}	σ_{ns}
$1s1s'2s2s'\,^1S$	0.95441	0.91399	−0.241	0.962	1.331	2.103
$1s1s'2s3s\,^1S$	0.95505	0.10637	−0.206	0.892	1.396	2.518
$1s1s'2s4s\,^1S$	0.95508	0.05603	−0.203	0.892	1.384	2.657

length form of the $(1s^2\,^1S) \to (1s2p\,^1P)$ transition. Table III gives a value of 0.2583 for the oscillator strength for two equivalent $1s$ electrons and 0.2834 for two different $1s$ electrons. The latter agrees fairly well with the value of 0.2793 quoted by Trefftz *et al.*, but the former differs appreciably from their value of 0.4390.

V. RESULTS FOR $1s1s'(^1S)2sns(^1S)$ OF Be

The $1s1s'(^1S)2sns(^1S)$ configuration is of special interest in that it represents a case where the core also consists of a pair of s electrons coupled to form a ^1S state. Then the procedure described in this paper must essentially be applied twice, once for each pair of electrons. However, in computing $E-E_{core}$, not only must the two outer electrons be interchanged but also the two inner ones. Let a, b, c, d refer to the four electrons, where ab and cd are each coupled to form a ^1S state. Then

$$(E-E_{ab})(1+\langle c|d\rangle^2)(1+\langle a|b\rangle^2)$$
$$= (1+\langle a|b\rangle^2)\{-\tfrac{1}{2}[L_{cc}+2\langle c|d\rangle L_{cd}+L_{dd}]+F^0(cd)$$
$$+G^0(cd)\}+\sum F^0(ij)-\tfrac{1}{2}G^0(ij)+\langle c|d\rangle[R^0(ij;ij')$$
$$-\tfrac{1}{2}R^0(ij;j'i)]+\langle a|b\rangle\{R^0(ij;i'j)-\tfrac{1}{2}R^0(ij;ji')$$
$$+\langle c|d\rangle[R^0(ij;i'j')-\tfrac{1}{2}R^0(ij;j'i')]\}\}, \quad (13)$$

where the summation is over the four permutations of $\{i,i'\}=\{a,b\}$ and $\{j,j'\}=\{c,d\}$. Since the problem is symmetric with respect to the pairs of electrons ab and cd, a similar equation holds for $(E-E_{cb})$. Equation (13) can also be written as $E-E_{ab}=E_{cd}+I$, where I represents the interactions between the two pairs of electrons, and the energy for a pair is given by Eq. (2) without any electrons in the core. Equations (8) and (9) or (8) and (12) (which can be shown to apply in this case as well) provide a means of computing $E-E_{ab}$ and $E-E_{cd}$, but

$$E=E_{ab}+E_{cd}+I$$
$$= (E-E_{ab})+(E-E_{cd})-I.$$

The latter expression can be used to determine the total energy.

The four-electron case also differs from the two-electron one in that Lagrange multipliers must now be introduced into the Hartree-Fock equations to ensure orthogonality of the outer functions with the inner ones. The fact that $L_{ij}=L_{ji}$ leads to four equations in the four unknown Lagrange multipliers. These equations are singular if $\langle a|b\rangle=1$, $\langle c|d\rangle=1$, or $\langle a|b\rangle=\langle c|d\rangle$. Intuitively, one can argue that the solutions of the

Hartree-Fock equations would not result in any of these conditions, though, as Z increases, the overlap integral does approach unity, which tends to make the convergence of the Hartree-Fock iterations somewhat more critical. For cases such as $1s1s'(^1S)2s3s\,^1S$, no difficulties were encountered using the diagonal form of the equations, as given by Eq. (11). However, for $1s1s'(^1S)2s2s'\,^1S$ the estimates that are generated during the self-consistent field procedure would occasionally be such that $\langle 1s|1s'\rangle \simeq \langle 2s|2s'\rangle$, which sets up violent oscillation in the values for the Lagrange multipliers. In order to avoid this situation, initial estimates were chosen so that the singularity conditions were not encountered at first and then the estimates were allowed to change only slowly. In fact the corrected estimate was taken to be a normalized linear combination of the previous estimate and the solution of the differential equation with a weighting factor of 0.75 and 0.25, respectively. Furthermore, the Lagrange multipliers were recomputed each time a new estimate was formed. This greatly increased the amount of computation involved, and the degree of self-consistency finally achieved (0.0018) was not up to the usual standards (0.000002). In view of the fact that the overlap integrals for the $1s1s'$ and $2s2s'$ functions are likely to be closer to unity and closer to each other for higher Z values, only the $2sns\,^1S$, $n=2, 3, 4$, states of Be were attempted. The overlap integrals and the screening numbers are given in Table IV. Again, it is interesting to note the considerable difference in the screening of the otherwise equivalent electrons.

In Fig. 1, the wave functions from the unrestricted approximation are compared with the Hartree-Fock functions for $1s^22s^2$ of Be. It is interesting to note that, in the region of the main maximum, the wave function for an equivalent pair is approximately the average of the wave functions in the unrestricted approximation. This explains why the transition integrals in Table V for the two approximations differ only slightly.

In Table VI the total energies for the states of Be are compared for a variety of approximations. Again, the

TABLE V. A comparison of some transition integrals I_{2snp} for Be.

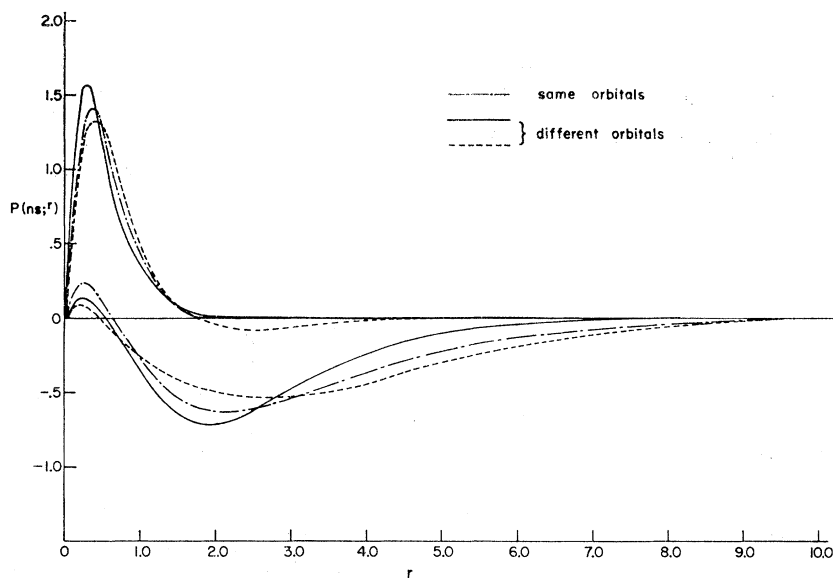| Transition	UHF	HF
$(2s^2\,^1S) \to (2s2p\,^1P)$	−2.6667	−2.6486
$\to (2s3p\,^1P)$	−0.7366	0.7536
$\to (2s4p\,^1P)$	−0.3561	−0.3679

FIG. 1. A comparison of wave functions for Be from the $1s^2 2s^2$ and $1s'1s''2s'2s''$ approximations.

TABLE VI. A comparison of $-E_{total}$ for states of Be.

	$1s^2 2s^2$	$1s^2 2s3s$	$1s^2 2s4s$
1. Exact[a]	14.6674	14.4182	14.3700
2. Configuration interaction			
(i) Analytic[a] (55 config.)	14.6609		
(ii) Analytic HF[b]			
(2 configurations)	14.6165		
(iii) Z expansion[c]	14.5879		
3. $1s1s'(^1S)2sns(^1S)$ (unrestricted)			
(i) Numerical UHF	14.588	14.3745	14.3330
(ii) Open shell[d]	14.5815		
4. $1s^2 2sns\ ^1S$ HF			
(i) Numerical HF	14.5730	14.3622	14.3197
(ii) Analytic HF[e]	14.5730		
(iii) Z expansion[f]	14.5215		

[a] See Ref. 15 and *Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. Circ. No. 467 (U. S. Government Printing and Publishing Office, Washington, D. C., 1952).
[b] See Ref. 20.
[c] See Ref. 1 and D. Layzer, Ann. Phys. (N. Y.) 8, 271 (1959).
[d] See Ref. 15.
[e] See Table II footnote f.
[f] C. Froese, Astrophys. J. 141, 1206 (1965).

open-shell method applied to $1s1s'(^1S)2s2s'(^1S)$ by Brigman, Hurst, Gray and Matsen[15] gives an energy

[15] G. H. Brigman, R. P. Hurst, J. D. Gray, and F. A. Matsen, J. Chem. Phys. 29, 251 (1958).

remarkably close to the unrestricted Hartree-Fock energy. On the other hand, the UHF approximation has done little to improve the energy over the usual Hartree-Fock energy. The percentage of the total correlation energy taken into account by allowing different electrons to occupy different orbitals is 15.9%, 22.0%, and 26.4%, respectively, for the three states. This is small compared to He, where 38.8% of the correlation was accounted for. Obviously the unrestricted Hartree-Fock approximation can only account for some of the radial correlation and none of the angular correlation. In the $2s^2$ configuration, the latter is the more important and, by allowing for interactions with only one other configuration, namely $2p^2\ ^1S$, Watson[16] was able to account for 46.1% of the total correlation. Hartree-Fock calculations with configuration interactions are considerably simpler than the unrestricted calculations, particularly for cases such as $1s1s'(^1S)2s2s'(^1S)$, where Lagrange multipliers cause difficulties. In view of these facts, the unrestricted approximation is not recommended in general for equivalent electrons, but the procedure as outlined is suggested for those cases where a pair of nonequivalent s electrons couple to form a ^1S state.

[16] R. E. Watson, Ann. Phys. (N. Y.) 13, 250 (1961).