

# Single-configuration descriptions of atomic ground and excited states: Ground states of He, Li, and Be

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A formulation of the spin-coupled model (a generalized valence-bond model) for calculating wave functions based on the use of nonorthogonal orbitals is presented, permitting ground, valence excited, multiply excited, and core-valence excited states to be obtained using a first-order iterative scheme. A primary goal is to provide a simple single-configurational model combining visuality (e.g., readily yielding the one-particle density function) with accuracy, while allowing the variational minimum of the single-configuration function for a given basis set to be obtained automatically for almost any kind of state. The theory and its application to the ground-state properties of He, Li, and Be are presented here using even-tempered and Clementi-Roetti basis sets. Uniform scaling of the basis exponents leads to closely parallel energy profiles for both spin-coupled and full configuration-interaction (FCI) calculations. The difference in energies as a function of scale factor is considerably smaller than the corresponding difference between restricted Hartree-Fock and FCI calculations. Each energy profile displays a global minimum and one or more local minima, and, for the associated values of the scale factor, the calculated atomic properties show little variation in magnitude.

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## I. INTRODUCTION

A generalized form of the valence-bond (VB) wave function — known as a “spin-coupled” wave function, after Gerratt and Lipscomb [1] — has had successful single-configuration applications combining accuracy and a compact form. Removal of the orthogonality constraints between the singly occupied orbitals,  $\phi_k$  ( $k = 1, 2, \dots, N$ ), where  $N$  is the number of electrons, necessarily leads to a VB multideterminantal wave function — even at the one-configuration level — if the overall wave function is to remain an eigenfunction of  $\hat{S}^2$ . The flexible forms of the  $\phi_k$  impart a “split-shell” characteristic to the spin-coupled wave function [2] important for improving the treatment of electron correlation. The alternative procedure of regaining some of the lost correlation energy in the Hartree-Fock model involves extensive configuration interaction, with the loss of a compact, physically suggestive wave function. Much has already been said during development and subsequent application of the single-configuration spin-coupled wave function with the focus firmly on the ground states of atoms and molecules — see, for example, the review by Cooper, Gerratt, and Raimondi [3]. A multistructural approach within the spin-coupled formalism has been proposed by Gerratt and co-workers for dealing with excited states [4]. However, the nonorthogonality of the basis makes the evaluation of matrix elements a nontrivial matter.

In the spin-coupled model, the main problem in determining the energy and other properties lies in the enumeration of the  $N!$  permutations in the antisymmetrizer which all yield contributions to each matrix element. Gallup [5], Junker and Klein [6], and others have devel-

oped methods for handling this problem which involve grouping the permutations together — typically by using some sort of coset expansion. Ladner and Goddard [7], Harris [8], and Gerratt [9], on the other hand, prefer to use slightly different group-theoretical techniques in which each permutation is, in essence, considered separately.

The method developed here is similar to that of the latter authors, but differs in important practical details. In this work, a simple first-derivative variational principle is applied to the optimization of a single-configuration spin-coupled wave function. The procedure involves selecting an orbital,  $\phi_i$ , which is to be optimized and then taking an expansion for this orbital over a set of primitive atomic orbitals,  $\{\zeta_j : j = 1, 2, \dots, m\}$ . It is an important feature of the model that by working in a *mixed*  $\zeta_j, \phi_k$  basis (where  $\phi_k$  span the set,  $\{\phi_k : k = 1, 2, \dots, i-1, i+1, \dots, N\}$ ), it is not necessary to expand over the same set of primitive atomic orbitals for each  $\phi_i$  in the iterative optimization procedure. The determination of the optimum orbital expansion coefficients requires the evaluation of matrix elements involving a mixed basis whose members are nonorthogonal — this leads to an eigenvalue problem whose roots form a “stack” of total  $N$ -electron energies, which are upper bounds to the ground and singly excited states of the same symmetry; each such state involves a product of  $N-1$  orbitals occupied in the ground state from  $N-1$  stacks and one orbital associated with the  $i$ th stack. While the orbitals from the  $i$ th stack are not themselves mutually orthogonal, orthogonality is an inherent property of the previously described  $N$ -electron states associated with the  $i$ th stack.

This situation is quite different from that described in the work of Gerratt and co-workers who, evidently, maintain a more conventional self-consistent-field-like formalism in which the orbital eigenvalue problem involves an effective one-electron Hamiltonian — thus paralleling traditional approaches to single-configuration methods, but differing from them in that each electron has its own effective Hamiltonian. The net result is that, unlike our approach of using a mixed basis, the orbitals of a given stack are mutually orthogonal, and their eigenvalues may be regarded as orbital energies. However, this does not automatically lead to an orthogonality condition between the ground state and any of the possible singly excited states. On the other hand, as in our approach, the orbitals belonging to different stacks are nonorthogonal.

It is clear therefore that models based on the use of effective one-electron Hamiltonians for determining orbitals in spin-coupled theory lead to a fundamentally different way of handling excited states from that implicit in the method described here. As will be discussed elsewhere, the present work essentially provides an extension of the work of Davidson [10] on the singly excited states of two-electron systems.

The theoretical approach is described in the following sections, where expectation values for spin-free and spin-dependent operators are derived; an efficient scheme for determining optimum wave-function parameters is described in detail, and the resulting wave functions are then used to determine radial moments and radial density functions from the appropriate spin or spinless one-electron density functions. The optimum wave-function parameters themselves are determined primarily by the choice of scale factor: the approach adopted here requires the initial study of ground-state energy profiles in order to obtain the optimum compromise basis set for providing an adequate description of both ground and excited states.

## II. THEORY

The theory described in this section is based on the use of a single spatial configurational wave function, but with all spin couplings included:

$$\Psi_{SM} = \sqrt{N!} \mathcal{A} \Phi \Theta_S^N \quad (1)$$

where  $\Phi = \phi_1(1)\phi_2(2)\cdots\phi_N(N)$ ,  $\Theta_S^N = \sum_{j=1}^{f_S^N} C_j \theta_j^N$  and

$$\mathcal{A} = \frac{1}{N!} \sum_{P \in S_N} \varepsilon_P P$$

$$\left\| \begin{array}{cccc} S_{11} & S_{21} & \cdots & S_{N1} \\ S_{12} & S_{22} & & \\ \vdots & & \ddots & \\ S_{1N} & \cdots & S_{NN} & \end{array} \right\| = \sum_{\substack{i=1 \\ j \neq i}}^N \sum_{j=1}^N \cdots \sum_{\substack{t=1 \\ t \neq 1, j, \dots}}^N S_{i1} S_{j2} \cdots S_{tN} \quad (4)$$

with elements  $S_{ij} = \langle \phi_i | \phi_j \rangle$ ;  ${}^+U$  is the analogous permanent with elements  $U_S^N((i, j))$ . Dot notation is used in (3b) as the ordered sets  $\{[U_S^N(P)]_{kj} : P \in S_N\}$  and

and  $f_S^N$  denotes the number of linearly independent (Kotani) spin functions,  $\theta_j^N$ , associated with the chosen value of  $S$ , the total spin quantum number.

### A. Matrix elements of spin-free operators

For the wave function (1), the spin-free operator  $\hat{O}$  has a matrix element given by

$$\begin{aligned} \langle \Psi | \hat{O} | \Psi \rangle &= \sum_{j,k} C_j^* C_k \langle \mathcal{A} \Phi \theta_j^N | \hat{O} | \Phi \theta_k^N \rangle \\ &= \sum_{j,k} \sum_{P \in S_N} [U_S^N(P)]_{kj} C_j^* C_k \langle P^r \Phi | \hat{O} | \Phi \rangle, \quad (2) \end{aligned}$$

where  $P = P^r P^\sigma$  acts on electron coordinates, and

$$\varepsilon_P P^\sigma \theta_k^N = \sum_{t=1}^{f_S^N} [U_S^N(P)]_{tk} \theta_t^N$$

with  $\langle \theta_t^N | \theta_k^N \rangle = \delta_{tk}$  ( $S, M$  assumed fixed).

The evaluation of (2) is an  $N!$  process, and its success depends upon the efficient production and storage of both the  $U(P)$  matrices and the relevant integrals  $\langle P^r \Phi | \hat{O} | \Phi \rangle$ . The approach used here depends upon the fact that each  $P \in S_N$  may be written as a product of transpositions, and the problem reduces to finding a systematic way of generating the sequence of  $P$  [or  $U(P)$ ] in a prescribed order from particular products of transpositions,  $(i, j)$ .

Three choices for  $\hat{O}$  are now considered: the unit operator; a one-electron operator  $\sum_{i=1}^N O_1(i)$  and a two-electron operator  $\sum_{i < j}^N O_2(ij)$  to demonstrate how Eq. (2) may be expressed in terms of permanent [2] expansions.

#### 1. The unit operator

Equation (2) may be written in the form

$$\begin{aligned} \langle \Psi | \Psi \rangle &= \sum_{j,k} \sum_{P \in S_N} [U_S^N(P)]_{kj} C_j^* C_k \langle P^r \Phi | \Phi \rangle \\ &= \sum_{j,k} C_j^* C_k \Delta_{kj} = \mathbf{C}^\dagger \mathbf{\Delta} \mathbf{C}, \quad (3a) \end{aligned}$$

where

$$\Delta_{kj} = \sum_{P \in S_N} [U_S^N(P)]_{kj} \langle P^r \Phi | \Phi \rangle = {}^+U_{kj} \cdot {}^+S \quad (3b)$$

and  ${}^+S$  is the permanent of overlap integrals:

$\{\langle P^r \Phi | \hat{O} | \Phi \rangle : P^r \in S_N\}$  may be regarded very loosely as the “coordinates” of two vectors in the permutation vector space [11]. Each term in the expansion (4) is charac-

terized by an  $N$ -tuple of integers  $(i, j, \dots, t)$  corresponding to the particular permutation whose inverse occurs in the sum over  $P$  ( $P$  acts on electronic coordinates) required in the evaluation of  $\Delta_{kj}$ . Equation (3a) thus involves the simultaneous resolution of two permanents—a process that can be performed in the same block of program, even though the expansion of  ${}^+U$  involves extra column manipulations (see the Appendix).

2. One- and two-electron operators

Consider the evaluation of the following expression:

$$O_1(i) = \sum_{P \in S_N} U_S^N(P) \langle P^r \Phi | \hat{O}_1(i) | \Phi \rangle.$$

If (4) is written in the form

$$\begin{vmatrix} S_{11} & S_{21} & \cdots & S_{N1} \\ \vdots & \vdots & & \vdots \\ S_{1i} & S_{2i} & \cdots & S_{Ni} \\ \vdots & \vdots & & \vdots \\ S_{1N} & S_{2N} & \cdots & S_{NN} \end{vmatrix} = \left\langle \begin{vmatrix} S_{11} & S_{21} & \cdots & S_{N1} \\ \vdots & \vdots & & \vdots \\ \phi_1(i) & \phi_2(i) & \cdots & \phi_N(i) \\ \vdots & \vdots & & \vdots \end{vmatrix} \middle| \phi_i(i) \right\rangle$$

then,  $O_1(i) = {}^+U \cdot {}^+F(i)$ , where

$${}^+F(i) = \left\langle \begin{vmatrix} S_{11} & S_{21} & \cdots & S_{N1} \\ \vdots & \vdots & & \vdots \\ \phi_1(i) & \phi_2(i) & \cdots & \phi_N(i) \\ \vdots & \vdots & & \vdots \end{vmatrix} \middle| \hat{O}_1(i) | \phi_i(i) \right\rangle = \begin{vmatrix} S_{11} & S_{21} & \cdots & S_{N1} \\ \vdots & \vdots & & \vdots \\ O_{1i} & O_{2i} & \cdots & O_{Ni} \\ \vdots & \vdots & & \vdots \\ S_{1N} & \cdots & S_{NN} \end{vmatrix}.$$

The elements of  $O_1(i)$  may also be written as

$$(O_1(i))_{kl} = \sum_{\mu=1}^N D_1(\mu, i | k, l) O_{\mu i}, \tag{5}$$

where the  $D_1(\mu, i | k, l)$  coefficients, which are elements of a supermatrix (spatial indices are to the left of the vertical line and spin indices are to the right), are formed from sums of  $[U_S^N(P)]_{kl}$  times a string of  $N - 1$  overlap integrals. Thus, the expectation value of a (spinless) one-electron operator is given by

$$\begin{aligned} \langle \Psi | \hat{O}_1 | \Psi \rangle / \langle \Psi | \Psi \rangle &= \langle \Psi | \sum_{i=1}^N \hat{O}_1(i) | \Psi \rangle / \langle \Psi | \Psi \rangle \\ &= \sum_{k,l} C_k^* C_l (O_1)_{kl} / \langle \Psi | \Psi \rangle \\ &= C^\dagger O_1 C / C^\dagger \Delta C, \end{aligned} \tag{6}$$

where, using (5),

$$O_1 = \sum_{i=1}^N {}^+U \cdot {}^+F(i) = \sum_{i=1}^N O_1(i) = \sum_{\mu,i} D_1(\mu, i) O_{\mu i}$$

with  $[D_1(\mu, i)]_{kl} = D_1(\mu, i | k, l)$  and  $D_1(\mu, i) = C^\dagger D_1(\mu, i) C$

A similar row insertion process (see also the work of Jucys [2] where the use of the overlap permanent and the technique of row insertion was initiated for a more limited kind of wave function) can be used for evaluating matrix elements of  $\hat{O}_2$ : for if  ${}^+G(ij)$  is defined by

$${}^+G(ij) = \left\langle \begin{vmatrix} S_{11} & S_{21} & \cdots \\ \vdots & \vdots & \\ \phi_1(i) & \phi_2(i) & \cdots \\ \vdots & \vdots & \\ \phi_1(j) & \phi_2(j) & \cdots \\ \vdots & \vdots & \end{vmatrix} \middle| \hat{O}_2(ij) | \phi_i(i) \phi_j(j) \right\rangle = \left\langle \begin{vmatrix} S_{11} & S_{21} & \cdots \\ \vdots & \vdots & \\ Q_{1i}(i) & Q_{2i}(i) & \cdots \\ \vdots & \vdots & \\ V_{1j}(j) & V_{2j}(j) & \cdots \\ \vdots & \vdots & \end{vmatrix} \right\rangle,$$

where  $Q_{1i}(i) = \phi_1(i) \phi_i(i)$ ;  $V_{pj}(i) = \int \phi_p(j) \hat{O}_2(ij) \phi_j(j) d\tau_j$ , then  $O_2(ij) = {}^+U \cdot {}^+G(ij)$  and

$$\left\langle \Psi \middle| \sum_{i,j=1}^N \hat{O}_2(ij) \middle| \Psi \right\rangle / \langle \Psi | \Psi \rangle = \langle \Psi | \hat{O}_2 | \Psi \rangle / \langle \Psi | \Psi \rangle = C^\dagger O_2 C / C^\dagger \Delta C, \tag{7}$$

where

$$\mathbf{O}_2 = \sum_{i,j=1}^N {}^+U \cdot {}^+G(ij) = \sum_{i,j=1}^N \mathbf{O}_2(ij).$$

As far as the actual evaluation of the numerators of (6) and (7) are concerned, it is possible to use either a simple, but time-consuming, method or a more elaborate scheme based on the hierarchical properties of density matrices. In the former method, both numerators may be built up from the overlap strings,  $OV = S_{a1}S_{b2}S_{c3} \cdots S_{tN}$ , which arise in the simultaneous permanent resolution of  ${}^+U \cdot {}^+S$  (which is, itself, required in the evaluation of  $\langle \Psi | \Psi \rangle$ ). In particular, the various contributions to either  $\mathbf{C}^\dagger \mathbf{O}_1 \mathbf{C}$  or  $\mathbf{C}^\dagger \mathbf{O}_2 \mathbf{C}$  may be found by multiplying each  $OV$  by either  $\mathbf{C}^\dagger \mathbf{U}(P) \mathbf{C} \langle \phi_\alpha(1) | \hat{O}_1(1) | \phi_\beta(1) \rangle / S_{\alpha\beta}$  or

$$\mathbf{D}_N \cdot P^r [\phi_{\mu 1}(1) \phi_{\mu 2}(2) \cdots \phi_{\mu N}(N)] \cdot \phi_{\nu 1}(1) \phi_{\nu 2}(2) \cdots \phi_{\nu N}(N)$$

is a component of the spinless  $N$ th-order density function,  $\rho_N$ . Successive integrations of those components of  $\rho_N$ , over the spatial coordinates of one electron, then yields a sequence of relations between the density matrices  $\mathbf{D}_N$  and  $\mathbf{D}_{N-1}, \dots, \mathbf{D}_2$  and  $\mathbf{D}_1$  as given by Eq. 3.11 of Pyper and Gerratt [12]. However, because the electron labels occupy a fixed sequence  $1, 2, \dots, N$ , the orbital labels defining each  $\mathbf{D}_{N-1}$  will vary according to the choice of  $\mathbf{D}_N$  and  $S_{\mu_N \nu_N}$ . Repeated use of the recursion relation for  $\mathbf{D}_\nu$  ( $\nu = N-1, \dots, 2, 1$ ) therefore enables (3a), (6), and (7) to be written as

$$\begin{aligned} \sum_{\mu, \nu=1}^N \mathbf{D}_1(\mu, \nu) S_{\mu\nu}, \\ \sum_{\mu, \nu=1}^N \mathbf{D}_1(\mu, \nu) O_{\mu\nu}, \\ \sum_{\mu, \nu, \sigma, \tau=1}^N \mathbf{D}_2(\mu\nu, \sigma\tau) \langle \mu\nu | \hat{O}_2 | \sigma\tau \rangle, \end{aligned} \quad (8)$$

respectively; where, for example, from (5) and (2),

$$\begin{aligned} \mathbf{D}_1(\mu, \nu) &= \sum_{k,l} C_k^* C_l D_1(\mu, \nu | k, l) / \mathbf{C}^\dagger \Delta \mathbf{C} \\ &= \mathbf{C}^\dagger \mathcal{D}_1(\mu, \nu) \mathbf{C} / \mathbf{C}^\dagger \Delta \mathbf{C}. \end{aligned} \quad (9)$$

The elements of  $\mathbf{D}_2$  may be derived in an analogous way to that used for defining the elements of  $\mathbf{D}_1$ : for, from (7),

$$\begin{aligned} (\mathbf{O}_2)_{kl} &= \left( \sum_{i,j=1}^N \mathbf{O}_2(ij) \right)_{kl} \\ &= \sum_{\mu, \nu, \sigma, \tau=1}^N D_2(\mu\nu, \sigma\tau | k, l) \langle \mu\nu | \hat{O}_2 | \sigma\tau \rangle. \end{aligned}$$

$\mathbf{C}^\dagger \mathbf{U}(P) \mathbf{C} \langle \phi_\alpha(1) \phi_\gamma(2) | \hat{C}_2(12) | \phi_\beta(1) \phi_\delta(2) \rangle / S_{\alpha\beta} S_{\gamma\delta}$ , respectively, for all  $S_{\alpha\beta}, S_{\gamma\delta}$  contained in the given overlap string. This technique falters, of course, when any of the  $S_{ij}$  are very small or equal to zero: situations which arise in the single-configuration model only if either  $\phi_i$  or  $\phi_j$  possess different symmetry characteristics—in such cases it is more sensible to use a group function formalism from the start.

Although the scheme just described is not very efficient, it does provide a useful independent check on the results of more elaborate calculations: notably, the hierarchical density-matrix method which starts from  $N!$  of the  $N$ th-order density matrices

$$\mathbf{D}_N(\mu_1 \mu_2 \cdots \mu_N, \nu_1 \nu_2 \cdots \nu_N) = \mathbf{C}^\dagger \mathbf{U}_S^N(P) \mathbf{C} / \mathbf{C}^\dagger \Delta \mathbf{C},$$

where

Thus,

$$\begin{aligned} \mathbf{D}_2(\mu\nu, \sigma\tau) &= \sum_{k,l} C_k^* C_l D_2(\mu\nu, \sigma\tau | k, l) / \mathbf{C}^\dagger \Delta \mathbf{C} \\ &= \mathbf{C}^\dagger \mathcal{D}_2(\mu\nu, \sigma\tau) \mathbf{C} / \mathbf{C}^\dagger \Delta \mathbf{C}. \end{aligned} \quad (10)$$

The construction of the hierarchy used here, for producing the elements of  $\mathbf{D}_1$  and  $\mathbf{D}_2$ , is a little different from that of Gerratt [9], in that only those intermediate  $\mathbf{D}_N$  ( $N \neq 1, 2$ ) matrices are produced which are required in forming all the density-matrix elements appearing in (9). The particular choice of paths in this hierarchy is not unique and may be chosen to minimize computer storage requirements; however, because so few intermediate density matrix elements are formed, the subset of paths required for an  $(N-2)$ -electron system is not contained in the  $N$ -electron hierarchy. On the other hand, if the  $N$ - and  $(N-1)$ -electron systems have the same values of  $f_S^N$  ( $N$  even), then it is possible to use the  $N$ -electron hierarchy for both systems providing a null orbital is incorporated in the analysis for the latter system.

The detailed mode of construction of the hierarchy is illustrated in Fig. 1 for the example of a five-electron system, where  $f_{\frac{5}{2}}^5 = 5$ . The  $5! \mathbf{D}_5(PQRST, 12345)$  elements — designated in the figure by  $\mathbf{D}_5(\cdots \cdots, 12345)$  — are generated in a “natural” order, which is determined by the generation of the  $\mathbf{U}_S^N(P)$  from  ${}^+U$ : in particular, the values of  $PQRST$  range from 12345 to 54321. The subset of  $3(5!)$   $\mathbf{D}_4$  elements, required to form the necessary  $\mathbf{D}_3$ , is formed from the  $\mathbf{D}_5$  by successive application of (8) with  $S_{N5}, S_{N3}$ , and  $S_{N4}$ ; a further application of (8), using  $S_{M4}, S_{M2}$ , and  $S_{M1}$  (where  $T$  assumes, of course, a different value in general for each element of  $\mathbf{D}_4$ ) then yields four blocks of  $\mathbf{D}_3$  elements, each block containing 60 elements. Further reduction to  $\mathbf{D}_2$ , and then to  $\mathbf{D}_1$ , is made using the overlap integrals indicated in Fig. 1. It is clear, moreover, that each limb of the hierarchy involves producing  $5!/(5-\nu)!$  elements of  $\mathbf{D}_{\nu-1}$  from each block of  $\mathbf{D}_5$  elements.

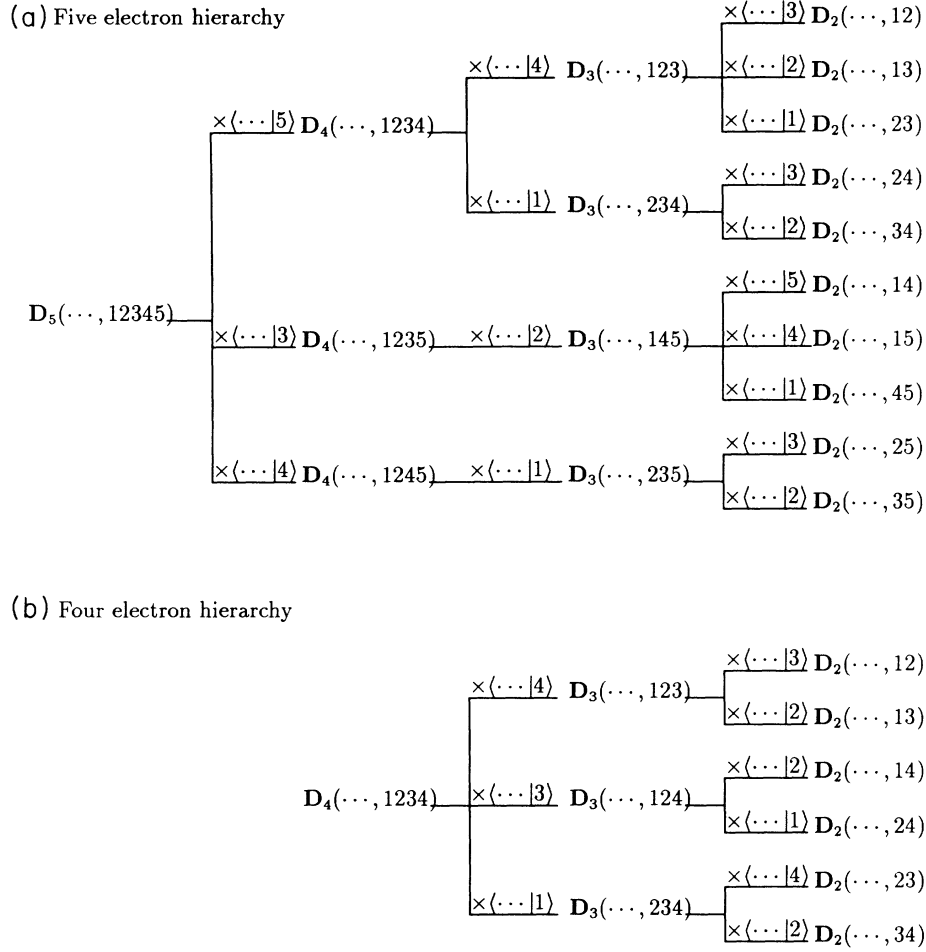


FIG. 1. Possible four- and five-electron density-matrix hierarchy descent paths.

## B. Matrix elements of spin-dependent operators

The matrix elements of one- and two-electron spin-dependent operators may be expressed in terms of the elements of the spinless density supermatrices, with elements  $D_1(\mu, \nu | k, l)$  and  $D_2(\mu\nu, \sigma\tau | k, l)$ , respectively, introduced in the preceding section. Although Gerratt [9] has considered the evaluation of such matrix elements

for one-electron operators — but using a slightly different approach — he has not considered the explicit evaluation of two-electron operators.

Consider, first, the one-electron operator

$$\hat{O}_1 = \sum_{i=1}^N \hat{O}_1^\sigma(i) \hat{O}_1^r(i)$$

with expectation value,  $\bar{O}_1$ :

$$\begin{aligned} \bar{O}_1 &= \sum_i^N \sum_{k,l} C_k^* C_l \sum_{P \in S_N} \langle P^r \Phi | \hat{O}_1^r(i) | \Phi \rangle \langle P^\sigma \theta_k^N | \hat{O}_1^\sigma(i) | \theta_l^N \rangle / \mathbf{C}^\dagger \Delta \mathbf{C} \\ &= \sum_i^N \sum_{k,l} C_k^* C_l \sum_{t=1}^{f_S^N} \left( \sum_{P \in S_N} [\mathbf{U}_S^N(P)]_{tk} \langle P^r \Phi | \hat{O}_1^r(i) | \Phi \rangle \right) \langle \theta_t^N | \hat{O}_1^\sigma(i) | \theta_l^N \rangle / \mathbf{C}^\dagger \Delta \mathbf{C}. \end{aligned} \quad (11)$$

The matrix element over the spin functions may be evaluated by decoupling the last electron from the Kotani spin functions,  $\theta_q^N$ , using Eqs. 4.2 of Kotani and coauthors [13], and by using the identity

$$\langle \theta_t^N | \hat{O}_1^\sigma(i) | \theta_l^N \rangle = \langle (i, N) \theta_t^N | \hat{O}_1^\sigma(N) | (i, N) \theta_l^N \rangle$$

the integration may be performed over the spin coordinates of electron  $N$ :

$$\begin{aligned}
\langle \theta_t^N | \hat{O}_1^\sigma(i) | \theta_t^N \rangle &= \sum_{q,r} [\mathbf{U}_S^N((i, N))]_{qt} [\mathbf{U}_S^N((i, N))]_{rt} \langle \theta_q^N | \hat{O}_1^\sigma(N) | \theta_r^N \rangle \\
&= \left[ \{ \mathbf{U}_S^N((i, N)) \}^\dagger \boldsymbol{\Omega}^1 \mathbf{U}_S^N((i, N)) \right]_{tl} = [\boldsymbol{\Xi}_N(i)]_{tl}.
\end{aligned} \tag{12}$$

The form of the matrix  $\boldsymbol{\Xi}_N(i)$  clearly depends on the form of  $\hat{O}_1^\sigma(N)$ : for example, with  $\hat{O}_1^\sigma(N) = \hat{S}_z(N)$ , the (diagonal) matrix  $\boldsymbol{\Omega}^1$  has elements

$$\boldsymbol{\Omega}_{pp}^1 = \begin{cases} -M/(2S+2) & \text{for } p = 1, 2, \dots, f_{S+\frac{1}{2}}^{N-1}, \\ M/2S & \text{for } p = f_{S+\frac{1}{2}}^{N-1} + 1, \dots, f_S^N. \end{cases}$$

Thus, on using (5), (9), and (12), Eq. (11) may be written as

$$\begin{aligned}
\bar{O}_1 &= \sum_{k,l} C_k^* C_l \sum_{\mu,i} \left( \sum_{t=1}^{f_S^N} D_1(\mu, i|t, k) [\boldsymbol{\Xi}_N(i)]_{tl} \right) \mathbf{O}_{\mu i} / \mathbf{C}^\dagger \boldsymbol{\Delta} \mathbf{C} \\
&= \sum_{\mu,i} [\mathbf{C}^\dagger \mathcal{D}_1(\mu, i) \boldsymbol{\Xi}_N(i) \cdot \mathbf{C}] \cdot \mathbf{O}_{\mu i} / \mathbf{C}^\dagger \boldsymbol{\Delta} \mathbf{C} = \sum_{\mu,i} \bar{\mathbf{D}}_1(\mu, i) \mathbf{O}_{\mu i} = \text{tr}(\bar{\mathbf{D}}_1 \mathbf{O}).
\end{aligned} \tag{13}$$

The expectation value for the two-electron spin-dependent operator follows in an analogous manner:

$$\begin{aligned}
\bar{O}_2 &= \langle \Psi | \sum_{i<j}^N \hat{O}_2^\sigma(ij) \hat{O}_2^r(ij) | \Psi \rangle / \langle \Psi | \Psi \rangle \\
&= \sum_{k,l} C_k^* C_l \sum_{i<j}^N \sum_{t=1}^{f_S^N} \left( \sum_{P \in S_N} [\mathbf{U}_S^N(P)]_{tk} \langle P^r \Phi | \hat{O}_2^r(ij) | \Phi \rangle \right) \langle \theta_t^N | \hat{O}_2^\sigma(ij) | \theta_t^N \rangle / \mathbf{C}^\dagger \boldsymbol{\Delta} \mathbf{C}.
\end{aligned}$$

This time the spin integration is performed after applying the permutation  $(i, N)(j, N) = Q_{ij}$ , say, to the intergrand, followed by a decoupling of the last two electrons in each  $\theta_q^N$ . The full details are given elsewhere [11], and the result may be written in the form

$$\begin{aligned}
\langle \theta_t^N | \hat{O}_2^\sigma(ij) | \theta_t^N \rangle &= \sum_{q,r} [\mathbf{U}_S^N(Q_{ij})]_{qt} [\mathbf{U}_S^N(Q_{ij})]_{rt} \langle \theta_q^N | \hat{O}_2^\sigma(N-1, N) | \theta_r^N \rangle \\
&= \left[ \{ \mathbf{U}_S^N(Q_{ij}) \}^\dagger \boldsymbol{\Omega}^2 \mathbf{U}_S^N(Q_{ij}) \right]_{tl} = [\boldsymbol{\Xi}_N(ij)]_{tl}.
\end{aligned}$$

Hence, using (11),

$$\begin{aligned}
\bar{O}_2 &= \sum_{k,l,i,j,t,\mu,\nu} C_k^* C_l D_2(\mu\nu, ij|t, k) [\boldsymbol{\Xi}_N(ij)]_{tl} \langle \phi_\mu \phi_\nu | \hat{O}_2^r | \phi_i \phi_j \rangle / \mathbf{C}^\dagger \boldsymbol{\Delta} \mathbf{C} \\
&= \sum_{\mu,\nu,i,j} [\mathbf{C}^\dagger \mathcal{D}_2(\mu\nu, ij) \boldsymbol{\Xi}_N(ij) \mathbf{C}] \cdot \langle \phi_\mu \phi_\nu | \hat{O}_2^r | \phi_i \phi_j \rangle / \mathbf{C}^\dagger \boldsymbol{\Delta} \mathbf{C} = \sum_{\mu,\nu,i,j} \bar{\mathbf{D}}_2(\mu\nu, ij) \langle \phi_\mu \phi_\nu | \hat{O}_2^r | \phi_i \phi_j \rangle.
\end{aligned} \tag{14}$$

Once again, the form of the (again diagonal)  $\boldsymbol{\Omega}^2$  matrix depends upon the choice for  $\hat{O}_2^\sigma(N-1, N)$ : for example, with  $\hat{O}_2^\sigma(N-1, N) = \hat{S}_z(N-1)\hat{S}_z(N)$ ,

$$\boldsymbol{\Omega}_{pp}^2 = \begin{cases} \frac{S+2M^2+1}{4(S+1)(2S+3)} & \text{for } p = 1, 2, \dots, f_{S+1}^{N-2}, \\ -\frac{S+2M^2+1}{4(2S+1)(S+1)} & \text{for } p = f_S^{N-2} + 1, \dots, f_{S+1}^{N-2} + f_S^{N-2}, \\ \frac{S-2M^2}{4S(2S+1)} & \text{for } p = f_{S+1}^{N-2} + f_S^{N-2} + 1, \dots, f_{S+1}^{N-2} + 2f_S^{N-2}, \\ \frac{2M^2-S}{4S(2S-1)} & \text{for } p = f_{S+1}^{N-2} + 2f_S^{N-2} + 1, \dots, f_S^N. \end{cases}$$

Here the labeling of the  $f_S^N$  spin functions,  $\theta_q^N$ , reflects the parentage of the  $N$ -electron states.

### III. OPTIMIZATION OF WAVE-FUNCTION PARAMETERS

As noted earlier, the orbitals  $\phi_i$  are expanded over a basis of  $m$  primitive atomic orbitals,  $\zeta_j$ , of the Slater type:

$$\phi_i = \sum_j^m d_{ji} \zeta_j.$$

No restrictions are placed on the expansion coefficients  $d_{ji}$ , other than that of orbital normalization. The process of optimizing the orbital  $\phi_i$  involves starting from an arbitrary initial guess at the "other"  $d_{jr}$  ( $r \neq i$ ) then expanding  $\phi_i$  over its  $m$  basis functions, keeping the other  $N - 1$  orbitals fixed

$$\Psi = \mathcal{A} \phi_1 \cdots \phi_{i-1} \left( \sum_j d_{ji} \zeta_j \right) \phi_{i+1} \cdots \phi_N \Theta_S^N = \sum_j d_{ji} \Upsilon_j.$$

For a given choice of  $\mathbf{C}$ , application of the first-order variation theorem to determine the linear parameters,  $d_{ji}$ , leads to the standard expression for the secular equation

$$\mathbf{H}_{pq} = \sum_{P \in \mathcal{S}_N} \mathbf{C}^T \mathbf{U}_S^N(P) \mathbf{C} \langle P^r \phi_1 \phi_2 \cdots \zeta_p \cdots \phi_N | \hat{H} | \phi_1 \phi_2 \cdots \zeta_q \cdots \phi_N \rangle. \quad (16)$$

Matrix elements of this type are formed in an unconventional *mixed* basis of  $\phi_i$ 's and  $\zeta_p$ 's, where the one- and two-electron integrals,  $h_{kl}$  and  $g_{klk'l'}$ , respectively, appearing in the expression

$$\mathbf{H}_{pq} = \sum_{k,l} h_{kl} \mathbf{D}_1(k,l) + \sum_{k,l,k',l'} g_{klk'l'} \mathbf{D}_2(kl,k'l')$$

are either partially or fully transformed from the  $\zeta$  basis to the  $\phi$  basis, depending on whether or not they involve the orbital  $\phi_i$ , which is replaced by  $\zeta_p$  on the right and  $\zeta_q$  on the left.

Solution of the secular problem yields new  $d_{ji}$ . One- and two-electron integrals are updated (in the  $\phi$  basis) with the new  $d_{ji}$  — a process which may be accomplished in highly efficient "partial summation" stages involving only those integrals that require the new coefficients. In addition, the possibility exists within the formalism to expand each of the  $\phi_i$  over a different subset of basis functions. The two- and four-index transformation routines that embody these features are so efficient that they do not limit the speed of the calculation: the principal limiting factor as  $N$  increases is concerned with the formation of matrix elements.

The updated one- and two-electron integrals are used in the formation of a new potential in which the next orbital, in turn, is optimized. Since this potential never involves any contribution from the orbital being optimized, no ambiguities are encountered in the formation of the potential for an open-shell system: a situation which

in matrix notation:

$$\mathbf{H} \mathbf{d} = \mathbf{S} \mathbf{d} \mathcal{E},$$

where the matrix elements of the Hamiltonian and unit operators are given by

$$\mathbf{H}_{pq} = \langle \Upsilon_p | \hat{H} | \Upsilon_q \rangle \quad \text{and} \quad \mathbf{S}_{pq} = \langle \Upsilon_p | \Upsilon_q \rangle,$$

respectively. Overlap may be removed from the problem by transforming with  $\mathbf{S}^{-1/2}$  then defining  $\mathbf{d} = \mathbf{S}^{-1/2} \mathbf{d}'$ ,

$$\mathbf{H}' \mathbf{d}' = \mathbf{d}' \mathcal{E}$$

and

$$(\mathbf{d}')^\dagger \mathbf{H}' \mathbf{d}' = \mathcal{E}, \quad (15)$$

or in homogeneous form

$$(\mathbf{H}' - \mathcal{E}) \mathbf{d}' = 0;$$

for nontrivial solutions,  $\mathbf{d}$ , it is required that

$$|\mathbf{H}' - \mathcal{E}| = 0,$$

thus by diagonalizing  $\mathbf{H}'$  the eigenvalues  $\mathcal{E}$  and eigenvectors  $\mathbf{d}$  are obtained.

The first step in determining the  $d_{ji}$  involves substituting for the  $\Upsilon_p$  and  $\Upsilon_q$  in the Hamiltonian matrix elements above:

should be contrasted with restricted Hartree-Fock (RHF) calculations where the constraint of orbital double occupancy makes it necessary to form a suitably averaged potential for the case of open-shell systems in order to facilitate solution of the "pseudolinear" variational equations.

Each orbital optimization yields a "stack" of  $m$   $N$ -electron states — important properties of which are given in the analysis below. As discussed in the Introduction, each energy state on a stack is associated with an  $N$ -electron wave function which yields an upper bound to an appropriate excited state — different stacks yield different excited states and it is only the lowest energy state that is optimal for the spin-coupled calculation on the ground state. Thus, for example, in the case of beryllium four stacks are obtained with a structure as shown in Fig. 2, and in a ground-state calculation the orbital corresponding to the *lowest* eigenvalue of each stack is occupied — it is these orbitals that define the new potential in successive cycles of the iterative procedure.

It follows from the relation between  $\mathbf{d}$  and  $\mathbf{d}'$  that

$$\mathbf{d}^\dagger \mathbf{S} \mathbf{d} = (\mathbf{d}')^\dagger \mathbf{S}^{-1/2} \mathbf{S} \mathbf{S}^{-1/2} \mathbf{d}' = (\mathbf{d}')^\dagger \mathbf{d}' = \mathbf{1}$$

and, from (15),

$$\mathbf{d}^\dagger \mathbf{H} \mathbf{d} = (\mathbf{d}')^\dagger \mathbf{S}^{-1/2} \mathbf{H} \mathbf{S}^{-1/2} \mathbf{d}' = (\mathbf{d}')^\dagger \mathbf{H}' \mathbf{d}' = \mathcal{E},$$

demonstrating that wave functions with a single orbital replacement from orbitals in the same "stack" are orthogonal and satisfy the generalized Brillouin-like condition

$$\sum_{P \in S_N} \mathbf{C}^\dagger \mathbf{U}_S^N(P) \mathbf{C} \langle P^r \phi_1 \phi_2 \cdots \phi_i \cdots \phi_N | \hat{O} | \phi_1 \phi_2 \cdots \phi_j \cdots \phi_N \rangle = \delta_{ij} \mathbf{O}_{ii},$$

where  $\hat{O} = \hat{H}, \hat{1}$  — a set of conditions which also holds for the optimum  $\mathbf{C}$ .

Thus the definition of the  $\phi_i$  differs substantially from that of Gerratt, since matrix elements of the operators  $\hat{H}$  and  $\hat{1}$  are found to vanish between all spin eigenfunctions differing by a single orbital replacement at convergence.

The optimum spin-coupling weights are found by expanding the wave function over the representation for the chosen set of spin functions. By analogy with the orbital situation, Hamiltonian matrix elements are of the form

$$\mathbf{H}_{pq} = \sum_{P \in S_N} [\mathbf{U}_S^N(P)]_{pq} \langle P^r \Phi | \hat{H} | \Phi \rangle.$$

The coefficients,  $\mathbf{C}^T \mathbf{U}_S^N(P) \mathbf{C}$  in (16) for all permutations  $P$  of the symmetric group, are re-formed with the new coupling weights. In this work, energy minimization is a two-stage process of spin-then-space optimization — such a scheme allows the progress of the calculation to be easily monitored as at each cycle in the iteration the total energy is output  $N + f_S^N$  times. Instabilities such as lack of monotonic convergence in the sequence of eigenvalues at each cycle is usually indicative of inappropriate initial guessed form for the  $N$  orbitals. In practice, convergence is facilitated by first permitting only the maximally paired spin eigenfunction to be included. If convergence is very slow, which is indicative of local minima in the energy hypersurface, then this can be ameliorated by first selecting the second or third root of the  $N$ th orbital secular problem to obtain a better set of starting orbitals. The advantage of this latter procedure is that the tightly bound (core) orbitals are then very close to their optimal forms in the ground state.

#### IV. RESULTS

In this section, the variation in selected atomic properties with a single basis exponent scaling factor,  $a$ , is

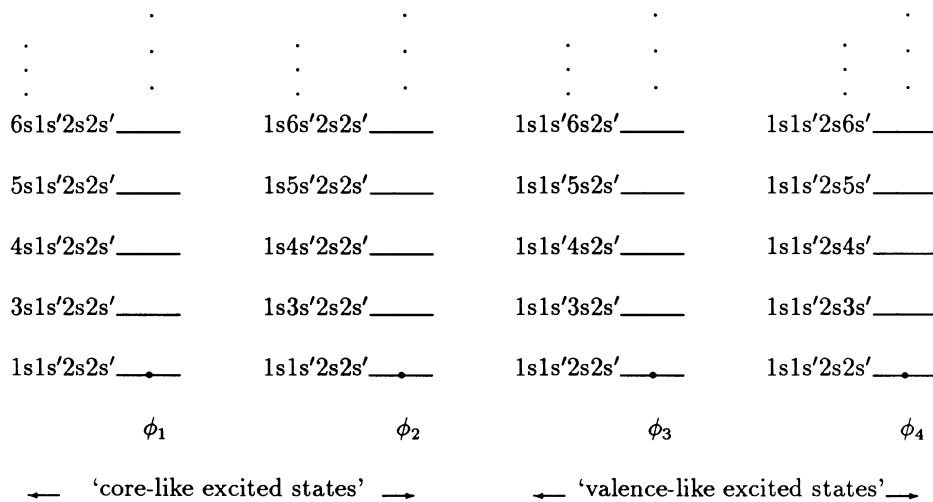


FIG. 2. A schematic diagram of stack  $N$ -electron eigenvalues and associated orbital configurations obtained during the spin-coupled energy minimization procedure for the ground state of the beryllium atom, with orbital occupation as indicated by  $\bullet$ .

investigated. The atoms He, Li, and Be are considered (which include both open- and closed-shell systems) together with different types of Slater-type orbital (STO) basis set, and the results from spin-coupled calculations are compared with those of RHF and full configuration-interaction (FCI) calculations using the same basis sets. The basis sets selected here are those of Clementi and Roetti [14] (CR), where the exponents are individually optimized for the ground-state RHF wave functions of each atom, and even-tempered sets [15] ( $Um$ ) of 1s primitives, where the exponents  $k_i$  are defined in geometric progression by the two parameters  $a$  and  $b$ ,

$$k_i = ab^{i-1}, \quad i = 1, 2, \dots, m.$$

In the present calculations,  $b$  is assigned the value 1.5, and medium and large basis sets are covered by the two choices  $m = 6$  and  $m = 10$ : basis sets are referred to as U6 and U10, respectively. Such an investigation is concerned with the abilities of the basis to describe different regions of an atom, with a primary goal of finding clues as to the best compromise basis set for describing both ground and excited states.

Spin-coupled total energies,  $E_{SC}$ , for the ground states of the three species under consideration, are given in Table I for optimized values of  $a$  for each of the three basis sets used here; optimized energies,  $E_{FCI}$ , obtained from full CI calculations using the same scaled basis sets are also given in the table. The variation of  $E_{SC}$  and  $E_{FCI}$  with  $a$  shows that the two energies closely parallel each other, thus displaying a similar pattern to that observed in analogous calculations on the lowest  $^3S$  excited states of heliumlike species [16]. Also, on going from RHF to spin-coupled to full CI wave functions (i.e., as the amount of electron correlation admitted by the model increases) the position of the global energy minimum moves to larger  $a$  — perhaps a result of the increased radial cor-



relation allowing the orbitals to become more spatially contracted.

For each global minimum some properties of the spinless density, and in the case of lithium the spin densities, in the ground state are shown in Table II. The properties include radial moments, the charge density at the nucleus,  $\rho(r)_{r=0}$ , and the density cusp ratio

$$\left\{ \frac{1}{\rho(r)} \frac{\partial \rho(r)}{\partial r} \right\}_{r=0}$$

The same properties are evaluated at each of the minima appearing in the energy profile of the lithium atom using a U10 basis, for both the  $\alpha$ - and  $\beta$ -spin density functions derived from the spin-coupled wave functions (Table III).

## V. DISCUSSION

The discussions on this paper may be grouped into three main areas—those of theory, implementation, and results. In the theory sections, permanent expansions are used for evaluating the matrix elements of spin-dependent and spin-free one- and two-electron operators. The variational procedure involves the construction of a hierarchy for producing the one- and two-electron density matrices; the choice of hierarchy is not unique and this may be exploited in maximizing the computational efficiency of the calculation. The method is computationally different from both the generalized VB methodology of Leasure and Balint-Kurti [17] and the previously cited spin-coupled approach of Gerratt and co-workers. Cen-

TABLE I. Global and local energy minima in the functions of spin-coupled, restricted Hartree-Fock and full-CI ground-state energies ( $E_{SC}$ ,  $E_{RHF}$ , and  $E_{FCI}$ , respectively) with scale factor  $a$  for the atoms helium, lithium, and beryllium using Clementi-Roetti [14] (CR) basis sets and even-tempered sets of six and ten  $1s$  STO's (U6 and U10, respectively). The scale factors for the global minimum are shown boxed.

Basis	Atom	$E_{RHF}$ (a.u.)	$a$	$E_{SC}$ (a.u.)	$a$	$E_{FCI}$ (a.u.)	$a$	
CR	He	-2.86167927	0.3529	-2.87787867	0.4075			
		-2.86167936	0.6169	-2.87798745	<b>0.6100</b>	-2.87894321	0.6111	
		-2.86167991	<b>0.9994</b>	-2.87796885	0.9814	-2.87897476	<b>0.9771</b>	
	Li	-7.43272569	<b>0.9993</b>	-7.44645289	0.7605	-7.44691569	1.0396	
		-7.43173544	1.8064	-7.44663593	<b>1.7783</b>	-7.44740592	<b>1.7933</b>	
	Be	-14.57302076	<b>0.9994</b>	-14.58924957	0.7751			
				-14.58950307	<b>1.2384</b>	-14.59179248	<b>1.2109</b>	
	U6	He	-2.86167931	0.4229				
			-2.86167973	0.6607	-2.87798444	0.5590		
-2.86168000			<b>0.9461</b>	-2.87799653	0.9262	-2.87898820	0.9933	
-2.86167997			1.4056	-2.87799671	<b>1.3794</b>	-2.87900494	<b>1.3780</b>	
Li		-7.43267577	<b>0.5922</b>	-7.44715918	<b>0.6220</b>	-7.44807703	<b>0.6181</b>	
Be		-14.57190851	<b>0.7705</b>	-14.58980868	<b>0.7914</b>	-14.59089389	<b>0.7881</b>	
U10		He	-2.86167936	0.0829	-2.87798939	0.1067		
			-2.86167991	0.1390				
			-2.86168000	0.1894	-2.87799669	0.1797		
	-2.86168000		0.2829	-2.87799680	0.2770			
	-2.86168000		<b>0.4228</b>	-2.87799681	0.4160			
	-2.86168000		0.6318	-2.87799681	<b>0.6205</b>	-2.87902283	0.6475	
	-2.86168000		0.9432	-2.87799680	0.9251	-2.87902371	<b>0.9254</b>	
	-2.86167998		1.4039	-2.87799677	1.3765	-2.87902366	1.3711	
	Li	-7.43272403	0.1336	-7.44755385	0.1688			
		-7.43272624	<b>0.2297</b>	-7.44756520	0.2735			
		-7.43272582	0.3720	-7.44756616	0.3783	-7.44864496	0.3937	
		-7.43272534	0.5750	-7.44756637	<b>0.5751</b>	-7.44865465	<b>0.5760</b>	
Be	-14.57301857	0.1915	-14.59049589	0.2306				
	-14.57302289	<b>0.3159</b>						
	-14.57302263	0.4900	-14.59051131	<b>0.4841</b>	-14.59175732	0.5052		
	-14.57302225	0.7541	-14.59050961	0.7422	-14.59176696	<b>0.7426</b>		

TABLE II. Radial moments  $\langle r^n \rangle$ , charge density at the nucleus  $\rho(r)_{r=0}$ , and the density cusp ratio of the spinless density functions for the atoms helium and beryllium, using Clementi-Roetti [14] (CR) basis sets and even-tempered sets of six and ten  $1s$  STO's (U6 and U10, respectively) scaled to optimize the respective spin-coupled ground-state energies. In the case of the lithium-atom ground state, the properties of the  $\alpha$ - and  $\beta$ -spin density functions are tabulated. The scale factor for the global minimum is chosen for each case.

Atom	Basis	$a$	$\langle r^{-2} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^3 \rangle$	$\langle r^4 \rangle$	$\rho(r)_{r=0}$	Cusp
He	CR	0.6100	12.0371	1.8681	2.4181	4.0297	8.2422	3.6266	1.9944
	U6	1.3794	12.0382	1.8681	2.4179	4.0269	8.2208	3.6303	2.0041
	U10	0.6205	12.0381	1.8681	2.4179	4.0273	8.2238	3.6296	2.0023
Li ( $\alpha$ )	CR	1.7783	15.3619	4.4350	18.0199	92.5009	547.58	6.9155	2.8113
	U6	0.6220	15.4026	4.4124	17.7558	89.9554	524.03	7.0634	3.0249
	U10	0.5751	15.3954	4.4500	18.2156	94.5782	568.93	7.0411	2.9825
Li ( $\beta$ )	CR	1.7783	14.8278	0.5756	0.4515	0.4560	0.6108	6.6942	2.8137
	U6	0.6220	14.8573	0.5755	0.4513	0.4506	0.5559	6.8236	3.0161
	U10	0.5751	14.8610	0.5753	0.4508	0.4490	0.5440	6.8153	2.9824
Be	CR	1.2384	57.6513	6.1272	17.2440	62.2055	261.39	35.4338	4.0072
	U6	0.7914	57.6483	6.1355	17.3424	63.0948	268.82	35.4221	4.0031
	U10	0.4841	57.6682	6.1573	17.5562	63.7846	281.57	35.4638	4.0075

tral to the effectiveness of the first-order iterative procedure described in this paper is a method for partially updating the one- and two-electron integrals.

The advantage of the present scheme is that it provides a computationally attractive approach to the determination of electronic wave functions for *both* ground and excited states—especially core-valence excited states. Conventionally, such excited states require either the inclusion of fictitious particles to inhibit variational collapse or the use of multiconfigurational formalisms, thus losing the physically appealing form of a single-configurational wave function.

An important aspect of this approach is that, unlike multiconfigurational schemes, it permits the use of different basis sets for different electronic states: this is a useful requirement, as the results show that the optimum ground-state wave function is associated with a basis set which is likely to be too contracted for an acceptable description of excited states. The implementation of the method does not require the formation of an effective one-electron Hamiltonian to determine the optimum orbitals — as in the work of Gerratt [9]; instead, the use of a *mixed* basis yields  $N$  stacks of  $N$ -electron energy states at convergence; these have the property that the associated wave functions are noninteracting on each stack.

TABLE III. Radial moments  $\langle r^n \rangle$ , charge density at the nucleus  $\rho(r)_{r=0}$ , and the density cusp ratio of the  $\alpha$ - and  $\beta$ -spin density functions using an even-tempered basis set of ten  $1s$  STO's (U10) scaled to optimize the spin-coupled energy at local minima in the energy  $E_{SC}$  for the ground state of the lithium atom. The scale factors for the global minimum are shown boxed.

Spin	$a$	$\langle r^{-2} \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^3 \rangle$	$\langle r^4 \rangle$	$\rho(r)_{r=0}$	Cusp
$\alpha$	0.1688	15.3997	4.4498	18.2119	94.5186	568.0936	7.0599	3.0235
	0.2735	15.3950	4.4498	18.2149	94.5792	568.9626	7.0401	2.9896
	0.3783	15.3961	4.4498	18.2119	94.5170	568.0237	7.0482	3.0132
	<b>0.5751</b>	15.3954	4.4500	18.2156	94.5782	568.9297	7.0411	2.9825
$\beta$	0.1688	14.8655	0.5753	0.4509	0.4514	0.6201	6.8351	3.0264
	0.2735	14.8604	0.5753	0.4508	0.4492	0.5478	6.8139	2.9888
	0.3783	14.8616	0.5753	0.4508	0.4491	0.5449	6.8220	3.0125
	<b>0.5751</b>	14.8610	0.5753	0.4508	0.4490	0.5440	6.8153	2.9824

In addition, each stack energy is an upper bound to an appropriate singly excited state.

The results presented in this paper indicate that calculated atomic properties are relatively insensitive to the choice of optimum scale factor, and are of good quality (accuracy of the kind obtained by Jitrik and Bunge [18] of Hylleraas quality is not an objective). However, by a physically motivated extension to the model, doubly excited structures involving orbitals of higher  $l$ , or terms involving the interelectronic coordinates, may be incorporated into the wave function to provide angular correlations.

## VI. CONCLUSION

In summary, a single-configuration spin-coupled formalism is presented for ground states. Calculations on He, Li, and Be show how ground-state properties are relatively insensitive to scaling of the atomic basis-set exponents. The combination of this feature with the stability of the formalism against variational collapse opens the way for an extension of its application to physically motivated good-quality calculations of valence-excited, multiply excited, and core-excited states.

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APPENDIX: EXPANSION OF THE PERMUTATION PERMANENT OF ORDER FOUR

The resolution of the permanent of transpositions

$$\begin{vmatrix} E & (12) & (13) & (14) \\ E & E & (23) & (24) \\ E & E & E & (34) \\ E & E & E & E \end{vmatrix}$$

does not yield the set of permutations for the symmetrizer if the expansion is carried out in the normal

way; however, a mode of resolution — analogous to that achieved by a left-coset expansion of the symmetrizer — is achieved by the following procedure: in the process of the usual resolution, if the *ij*th element in the current row from which the expansion is being made has an entry (*i j*) other than *E*, then columns *i* and *j* are interchanged in the rows beneath (it is important in this row interchange procedure to note that the column labeling is global, in the sense that although column *i* may have been moved into the position of column 1, it is still treated as column *i* insofar as the interchange procedure is concerned); the final multiplication of transpositions is taken in reverse order. This latter procedure is necessary to ensure that the permutations defined through the *N*-tuples in the expansion of the overlap permanent, are exactly paralleled in the expansion of the permutation permanent — thereby ensuring that the  $U_S^N(P)$  matrices are generated in sequence required.

The expansion of the permanent associated with the group of permutations  $S_4$  therefore takes the form

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$$\begin{aligned} & \begin{vmatrix} E & (12) & (13) & (14) \\ E & E & (23) & (24) \\ E & E & E & (34) \\ E & E & E & E \end{vmatrix} = E \begin{vmatrix} E & (23) & (24) \\ E & E & (34) \\ E & E & E \end{vmatrix} + (12) \begin{vmatrix} E & (23) & (24) \\ E & E & (34) \\ E & E & E \end{vmatrix} + (13) \begin{vmatrix} (23) & E & (24) \\ E & E & (34) \\ E & E & E \end{vmatrix} + (14) \begin{vmatrix} (24) & E & (23) \\ (34) & E & E \\ E & E & E \end{vmatrix} \\ & \quad \textcircled{1} \textcircled{2} \textcircled{3} \textcircled{4} \qquad \textcircled{2} \textcircled{3} \textcircled{4} \qquad \textcircled{2} \textcircled{3} \textcircled{4} \qquad \textcircled{3} \textcircled{2} \textcircled{4} \qquad \textcircled{4} \textcircled{2} \textcircled{3} \\ & = E \begin{vmatrix} E & (34) \\ E & E \end{vmatrix} + (23) \begin{vmatrix} E & (34) \\ E & E \end{vmatrix} + (24) \begin{vmatrix} (34) & E \\ E & E \end{vmatrix} \\ & \quad \textcircled{3} \textcircled{4} \qquad \textcircled{3} \textcircled{4} \qquad \textcircled{4} \textcircled{3} \\ & + (12)E \begin{vmatrix} E & (34) \\ E & E \end{vmatrix} + (12)(23) \begin{vmatrix} E & (34) \\ E & E \end{vmatrix} + (12)(24) \begin{vmatrix} (34) & E \\ E & E \end{vmatrix} \\ & \quad \textcircled{3} \textcircled{4} \qquad \textcircled{3} \textcircled{4} \qquad \textcircled{4} \textcircled{3} \\ & + (13)(23) \begin{vmatrix} E & (34) \\ E & E \end{vmatrix} + (13)E \begin{vmatrix} E & (34) \\ E & E \end{vmatrix} + (13)(24) \begin{vmatrix} E & (34) \\ E & E \end{vmatrix} \\ & \quad \textcircled{3} \textcircled{4} \qquad \textcircled{3} \textcircled{4} \qquad \textcircled{3} \textcircled{4} \\ & + (14)(24) \begin{vmatrix} (34) & E \\ E & E \end{vmatrix} + (14)E \begin{vmatrix} (34) & E \\ E & E \end{vmatrix} + (14)(23) \begin{vmatrix} (34) & E \\ E & E \end{vmatrix} \\ & \quad \textcircled{4} \textcircled{3} \qquad \textcircled{4} \textcircled{3} \qquad \textcircled{4} \textcircled{3} \\ & = E + (34) + (23) + (243) + (234) + (24) + (12) + (34)(12) + (132) + (1432) + (1342) \\ & \quad + (142) + (123) + (1243) + (13) + (143) + (24)(13) + (1423) + (1234) + (124) \\ & \quad + (134) + (14) + (1324) + (23)(14). \end{aligned}$$


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