

Multiconfigurational Wavefunction Optimization Using the Unitary Group Method

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Abstract

We have successfully used graphical unitary group methods to implement efficiently both multiconfigurational self-consistent field and configuration interaction *ab initio* quantum chemical computer programs. We indicate how these group theoretic methods improve efficiency and we demonstrate their utility on the ground and excited states of a model problem for which a full-configuration interaction calculation can be performed.

I. Introduction

Using the exponential- i -lambda (EIL) method [1] for wavefunction optimization and the graphical unitary group method [2] for the calculation of one- and two-particle density matrix elements, we have performed multiconfiguration self-consistent field (MCSCF) calculations on the ground and excited states of the Be atom at several levels of sophistication as a model calculation. We show how the global convergence problems of the EIL method may be overcome in these cases. We further show that although completely flexible configuration selection is not easily achieved within the unitary group formalism which we have implemented, limited distinct row tables based only on occupation restrictions are easily constructed. The resulting configuration lists are neither so large that chemical insights are lost nor are they so restrictive that chemical accuracy is sacrificed. We show how the graphical unitary group method may be used to construct efficiently the matrix elements required in the EIL MCSCF method without explicitly performing the two-particle density matrix construction. Because the EIL method possesses very good local convergence properties, not only accurate energy expectation values but also very accurate MCSCF wavefunctions are reported.

The MCSCF wavefunction is a multiconfiguration wavefunction:

$$|\psi^{mc}\rangle = \sum_K C_K |K\rangle \quad (1)$$

where both the configuration mixing coefficients C_K and the orbitals are optimized to give the lowest energy expectation value. A property of the MCSCF wavefunction is that it satisfies the generalized Brillouin theorem [3] (GBT):

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$$\langle \psi^{mc} | [H, i^\dagger j] | \psi^{mc} \rangle = 0 \quad (2)$$

for all electron creation and annihilation operator pairs i^\dagger and j . Not only have accurate potential surfaces been reported using the MCSCF approach, but several procedures including the one-particle Green function [4], two-particle Green function [5], the time-dependent Hartree-Fock (HF) approach to linear response theory [6], gradient techniques for molecular geometry optimization [7], and the coupled cluster method [8] are being extended to allow for MCSCF reference states. Some of these procedures allow for a much simpler implementation if the GBT is assumed to be valid. Thus, it is important to have a procedure which allows the calculation of very accurate wavefunctions (within the orbital basis and configuration basis chosen) to be obtained efficiently and as general as possible a configuration space.

We first give a short review of the unitary group method and of the EIL orbital optimization procedure. We discuss our implementation of these two methods and finally discuss the results of applying these methods to the Be atom.

2. Review of the Graphical Unitary Group Method

We first review the unitary group method as we have implemented it for our EIL MCSCF program and for our CI program. In particular, we refer to the graphical unitary group approach as developed by Shavitt. With this method, the orbital occupation and spin-coupling information needed for the specification of a configuration is represented by a particular walk between the head and tail of Shavitt graph. A limited configuration list is specified by placing restrictions on the Shavitt graph which corresponds to the full-configuration list. These restrictions correspond to deleting certain vertices within the graph or to deleting certain arcs between the vertices within the graph. The vertices of the Shavitt graph are labeled with three integers which correspond to the level in the graph and the A and B values of a Paldus array [9]. A vertex of a Shavitt graph corresponds to a distinct row. The tabular listing of all distinct rows along with the forward and backward chaining indices and various other information is called a distinct row table. If a slight generalization is made to the Shavitt graph which allows multiple vertices with identical A and B values but with different arcs connecting to these multiple vertices, then a completely arbitrary configuration list may be specified. Extensions of this type have previously been used for the purpose of limiting the configuration list to correspond to single irreducible representation of the point group of the molecule [10] and to restrict the configuration list to correspond to the HF interacting space [11]. Since the effort involved in the construction and use of the one- and two-particle density matrix contributions increases as the size of the distinct row table (DRT) and also as the number of configurations specified by the DRT, there is a trade-off of efficiency between increasing the complexity of the DRT and reducing the number of configurations with this approach.

The N -particle basis of configurations specified in the unitary group method is called the Gelfand-Tsetlin basis. These configurations are equivalent, within

a phase factor, to configurations constructed using the geneological procedure. Grabenstetter [12] has developed a very efficient projection procedure for calculating the coefficients of primitive spin functions which span the space of the geneological spin functions. If desired, the configurations specified by the unitary group method could be expressed in terms of Slater determinants using this procedure. This is useful for calculating the reduced density matrices of the spin orbital basis which, in turn, are needed for properties which depend explicitly on the spin (e.g., spin density). The one- and two-particle reduced density matrix elements required for spin-free operators, on the other hand, may be calculated directly using the unitary group formalism because the generators of the unitary group may be expressed in terms of spin-traced components of the electron creation and annihilation operators

$$\begin{aligned}
 P_{ji}^{(1)} &= \langle \psi^{\text{mc}} | i_{\alpha}^{\dagger} j_{\alpha} + i_{\beta}^{\dagger} j_{\beta} | \psi^{\text{mc}} \rangle = \langle \psi^{\text{mc}} | e_{ij} | \psi^{\text{mc}} \rangle \\
 P_{jl,ik}^{(2)} &= \sum_{\substack{\sigma, \sigma' \\ = \alpha, \beta}} \langle \psi^{\text{mc}} | i_{\sigma}^{\dagger} k_{\sigma'}^{\dagger} l_{\sigma} j_{\sigma} | \psi^{\text{mc}} \rangle \\
 &= \langle \psi^{\text{mc}} | e_{ij} e_{kl} - \delta_{jk} e_{il} | \psi^{\text{mc}} \rangle \\
 &= \langle \psi^{\text{mc}} | e_{ij,kl} | \psi^{\text{mc}} \rangle
 \end{aligned} \tag{3}$$

where e_{ij} is taken to be a generator of the unitary group and $e_{ij,kl}$ the generator product defined in Eq. (3). This approach is slightly different from that of previous workers who maintained the difficulty of density matrix evaluation using the unitary group formalism [11]. These density contributions are very easy to calculate within the unitary group formalism; the density matrix elements in the spin orbital basis, on the other hand, at present require using either the symmetric group formalism [13] or a transformation of the wavefunction to a different basis such as that performed by the Grabenstetter procedure.

The generator matrix element evaluation between configurations $|m\rangle$ and $|m'\rangle$, $\langle m' | e_{ij} | m \rangle$, is performed by constructing valid loops within the Shavitt graph [14]. These loops correspond to all possible differences in configurations that have nonzero contributions to the generator matrix elements. By using mathematical induction, Shavitt demonstrated that these matrix elements are the products of segment values of different levels within the loop. These segment values depend only on the shape of the loop at the given level and on the B value of one of the arcs at the given level (Shavitt used the arc of the ket line). Recently using spin-recoupling algebra, Boyle and Paldus [15] have expressed the $\langle m' | e_{ij,kl} | m \rangle$ matrix elements in a form which allows this same factorization. Except for the summation over singlet and triplet coupled intermediate states, this form of the two-particle density matrix contribution is just as simple to evaluate as for the simple generator matrix elements. Shavitt [16] has expressed these segment values within the graphical representation of the Gelfand-Tsetlin basis. The expression for these $\langle m' | e_{ij,kl} | m \rangle$

$$\langle m' | e_{ij,kl} | m \rangle = \left[\prod_{p \in S_1} W(T_p, b_p) \right] \left\{ \sum_{x=0,1} \left[\prod_{p \in S_2} W_x(T_p, b_p) \right] \right\} \tag{4}$$

involves the product of segment values (W) where the indices do not overlap the summation of the products of segment values which correspond to the two spin couplings ($x = 0, 1$) where the indices do overlap. It should be mentioned that several loop types have nonzero contributions for only one of these spin couplings in the overlap range. These segment values allow the evaluation of $\langle m' | e_{ij,kl} | m \rangle$ to be performed just as the $\langle m' | e_{ij} | m \rangle$ evaluation is performed. All loops are constructed which can contribute to these density contributions and the product of the segment values are accumulated appropriately. Since some loops require the accumulation of two separate products, the two-particle density contributions require at most twice the effort of the simple generator matrix element evaluation. Except for the use of the recoupling formalism, our matrix element evaluation is similar to the "loop-driven" procedure of Brooks and Schaefer. Since the matrix elements of the Hamiltonian in the Gelfand-Tsetlin basis involve these matrix elements,

$$\langle m' | \hat{H} | m \rangle = \sum_{ij} h_{ij} \langle m' | e_{ij} | m \rangle + \frac{1}{2} \sum_{ijkl} (ij|kl) \langle m' | e_{ij,kl} | m \rangle \quad (5)$$

where the h_{ij} and $(ij|kl)$ are the one- and two-electron integrals within the orbital basis, they may be used directly in both the CI matrix element construction and later in the density matrix element construction.

We now discuss briefly the types of configuration required for MCSCF wavefunctions. Although this subject has been previously discussed, [17] we wish to emphasize that configurations required for large-scale CI calculations are not typically the same as those required for MCSCF calculations. Configurations for large-scale CI calculations are usually chosen to give the lowest energy, at a particular geometry, given a set of molecular orbitals and a few dominant configurations. The molecular orbitals used are usually SCF orbitals for one of the dominant configurations. Since the Hamiltonian operator involves only one- and two-particle excitation operators, the configurations in the CI calculation are usually chosen to include the single and double excitations from the dominant configurations. Single excitations are said to be for "orbital relaxation" effects and double excitations are said to be for the "electron correlation." At various geometries, as the dominant configurations change, the configurations included in the CI calculation are also changed to obtain the lowest possible energy for the number of configurations included. This is important because the effort involved is dependent on the dimension of the CI secular problem. The configurations required for MCSCF calculations, on the other hand, are usually chosen to describe both equilibrium molecular geometries and molecular distortions far away from equilibrium geometries. The nature of the electronic states of these systems far from equilibrium is such that not only single and double excitations (relative to the dominant configurations near equilibrium) may be required but also sometimes higher-order excitations. This is particularly true if the molecular distortions involve the breaking of several bonds or the breaking of a multiple bond. Since "orbital relaxation" is accounted for in the orbital optimization process, single excitations sometimes lose their importance compared to these

higher excitations. Fortunately, the higher excitations that are required usually only involve a limited number of molecular orbitals. In order to obtain a consistent level of approximation over the molecular potential surface, the MCSCF configuration list typically includes more varied types of configuration but involves fewer orbitals than the configuration list of a CI calculation. The configurations required for MCSCF calculations then are usually chosen to be flexible enough to describe consistently the desired electronic state over a large range of molecular distortions, whereas configurations chosen for CI calculations are chosen to give the best possible energy over a limited range of molecular distortions.

These configuration lists for MCSCF calculations are relatively easy to construct within the graphical unitary group method since they are described well in terms of only occupation restrictions. This is in contrast to the HF interacting space limitations (which involve not only occupation restrictions but also spin-coupling restrictions) that are needed with larger CI calculations to limit the number of configurations. Cumulative orbital occupation restrictions are achieved simply by deleting vertices from the Shavitt graph which are in violation of these imposed restrictions. Examples of the restrictions which are used in typical MCSCF calculations are (1) specifying certain orbitals to remain doubly occupied in all configurations, (2) specifying certain orbitals to remain at least singly occupied in all configurations, (3) specifying a set of orbitals to be at most singly occupied in any configuration, and (4) specifying a set of orbitals in which to make all possible excitations with a given number of electrons. This last case will be referred to as a "full-valence CI" calculation because it shares several properties with full-CI calculations. There are, of course, many other occupation restrictions that can easily be applied when required by a particular molecular system.

The choice of orbitals and configurations which should be included in MCSCF calculations is usually achieved by performing several CI calculations at various geometries in order to determine the basic configurations. Then the orbitals are optimized for these configurations, new CI calculations are performed with these orbitals, new configurations are selected, and the process is repeated until a sufficient level of precision is obtained with the MCSCF wavefunction. Because these steps are often repeated many times, it is necessary to construct DRTs easily for the MCSCF wavefunction evaluation and the corresponding DRTs for the larger CI calculations which include the configurations in the MCSCF space and the most important excitations from this space. For this configuration selection procedure, we have found that DRTs are most easily constructed if the orbitals are ordered within the DRT such that orbitals with similar occupation restrictions are grouped together. Within this occupation grouping, orbitals of the same symmetry should be adjacent in the DRT in order to keep the number of distinct rows as small as possible. For example, all the orbitals that are restricted to be doubly occupied might be placed at the bottom of the DRT, followed by the group of orbitals in which a full-valence CI with the remaining electrons is to be allowed, followed by the group of orbitals which may share at most two electrons, and

finally followed by the group of orbitals which share at most one electron. The construction of these types of limited DRTs requires only the point group symmetry information, a limited amount of occupation restriction information, and the ordering information of the orbitals included in the DRT.

3. Review of EIL Wavefunction Optimization Method

The exponential- i -lambda (EIL) wavefunction optimization [1] is achieved by expressing a trial MC wavefunction in terms of a given MC wavefunction as

$$|\psi^{mc'}\rangle = e^{i\hat{\Lambda}}e^{i\hat{S}}|\psi^{mc}\rangle$$

$$\hat{\Lambda} = \sum_{r>s} \kappa_{(rs)}i(r^\dagger s - s^\dagger r) = \sum_{r>s} \kappa_{(rs)}\hat{T}_{rs}$$

$$\hat{S} = \sum_{n \neq mc} A_n i(|\psi^n\rangle \langle \psi^{mc}| - |\psi^{mc}\rangle \langle \psi^n|) = \sum_n A_n P_n \quad (6)$$

and optimizing the κ and A parameters such that they extremize the energy of the MC wavefunction. The $e^{i\hat{S}}$ operator allows for modification of the current MC wavefunction within the MC configuration space; the $e^{i\hat{\Lambda}}$ operator allows for mixing of the orbitals used in the configuration construction within the molecular orbital basis. The commutator expansion for the energy expectation is truncated to include overall second-order terms in the $\hat{\Lambda}$ and \hat{S} operators

$$E(\kappa, A) = \langle \psi^{mc} | \hat{H} + [H, i\hat{\Lambda}] + \frac{1}{2}[[\hat{H}, i\hat{\Lambda}], i\hat{\Lambda}] + [\hat{H}, i\hat{S}] + \frac{1}{2}[[\hat{H}, i\hat{S}], i\hat{S}] + [[\hat{H}, i\hat{\Lambda}], i\hat{S}] + \dots | \psi^{mc} \rangle \quad (7)$$

The necessary (but not sufficient) condition for energy minimization is that the first derivatives with respect to the κ and A parameters are all zero when evaluated with the current wavefunction.

$$0 = \partial E / \partial \kappa_{rs} = \langle \psi^{mc} | [\hat{H}, i\hat{T}_{rs}] + \frac{1}{2}([[\hat{H}, i\hat{T}_{rs}], i\hat{\Lambda}] + [[\hat{H}, i\hat{\Lambda}], i\hat{T}_{rs}]) + [[\hat{H}, i\hat{T}_{rs}], i\hat{S}] | \psi^{mc} \rangle$$

$$0 = \partial E / \partial A_n = \langle \psi^{mc} | [H, i\hat{P}_n] + \frac{1}{2}([[\hat{H}, i\hat{P}_n], i\hat{S}] + [[\hat{H}, i\hat{S}], i\hat{P}_n]) + [[\hat{H}, i\hat{\Lambda}], i\hat{P}_n] | \psi^{mc} \rangle \quad (8)$$

This leads to a set of linear equations which may be expressed in matrix notation as

$$\begin{pmatrix} \mathbf{B} & \mathbf{C} \\ \mathbf{C}^\dagger & \mathbf{M} \end{pmatrix} \begin{pmatrix} \boldsymbol{\kappa} \\ \mathbf{A} \end{pmatrix} = - \begin{pmatrix} \mathbf{W} \\ \mathbf{W}' \end{pmatrix}$$

$$B_{pqrs} = \frac{1}{2}(\langle [[\hat{H}, i\hat{T}_{pq}], i\hat{T}_{rs}] + [[\hat{H}, i\hat{T}_{rs}], i\hat{T}_{pq}] \rangle)$$

$$C_{pq,n} = C_{n,pq}^\dagger = \langle [[\hat{H}, i\hat{T}_{pq}], i\hat{P}_n] \rangle$$

$$M_{nn'} = \frac{1}{2}(\langle [[\hat{H}, i\hat{P}_n], i\hat{P}_{n'}] + [[\hat{H}, i\hat{P}_{n'}], i\hat{P}_n] \rangle)$$

$$W_{pq} = \langle [\hat{H}, i\hat{T}_{pq}] \rangle$$

$$W'_n = \langle [\hat{H}, i\hat{P}_n] \rangle \quad (9)$$

If the orthogonal states used in the construction of the \hat{S} operator are the eigenstates of the Hamiltonian operator within the MC configuration space, the \mathbf{W} vector is zero and the \mathbf{M} matrix is diagonal. If the mixing coefficients are fully optimized on every iteration, the A parameters need not be explicitly calculated. This allows the κ parameters to be calculated from the partitioned form of Eq. (9),

$$\mathbf{B}'\kappa = (\mathbf{B} - \mathbf{C}\mathbf{M}^{-1}\mathbf{C}^\dagger)\kappa = -\mathbf{W} \quad (10)$$

The effect of the $e^{i\hat{A}}$ operator on an MC wavefunction is to express the MC wavefunction in a new molecular orbital basis where the new molecular orbitals are obtained from

$$\phi' = \phi(e^{-\mathbf{K}}) \quad (11)$$

where $K_{rs} = \kappa_{(rs)}$ and $K_{sr} = -\kappa_{(rs)}$. Since the orbital transformation is calculated from a truncated expression of the energy, these transformations must be repeated until convergence is reached. At convergence the \mathbf{W} vector [the generalized Brillouin theorem (GBT) terms] is zero, the \mathbf{K} matrix is zero, and the orbital transformation matrix is a unit matrix. Since derivatives of the second-order terms in the energy are included in the solution of the κ parameters, the wavefunction and the energy should display second-order convergence. In practice, it has been shown that this method displays true second-order local convergence in both the wavefunction and the energy. However, the method does not show adequate global convergence when the initial orbitals are far from correct [18]. This requires that some care be taken with the initial orbital preparation to ensure that the $(\mathbf{B} - \mathbf{C}\mathbf{M}^{-1}\mathbf{C}^\dagger)$ matrix (the Hessian matrix) has all positive eigenvalues. The \mathbf{B} matrix is the hessian matrix with frozen mixing coefficients. The $(\mathbf{C}\mathbf{M}^{-1}\mathbf{C}^\dagger)$ matrix which is subtracted from the \mathbf{B} matrix accounts for the coupling between the change of the orbitals and the change of the mixing coefficients with every iteration. The $(\mathbf{C}\mathbf{M}^{-1}\mathbf{C}^\dagger)$ matrix may be regarded as the second-order Rayleigh-Schrödinger perturbation theory correction to the \mathbf{B} matrix to account for this coupling.

If the spin orbital basis is assumed to consist of the Cartesian product of an orthonormal spatial orbital basis and the electron spin basis (α, β) , the single excitation operators of the \hat{A} operator may be expressed as the generators of the unitary group of the previous section:

$$\hat{T}_{rs} = i(e_{rs} - e_{sr})$$

The elements of the \mathbf{B} matrix, \mathbf{C} matrix, and \mathbf{W} vector may then be expressed in terms of the e_{ij} and $e_{ij,kl}$.

$$\begin{aligned} B_{pq,rs} = & 2h_{qs}\langle e_{pr} \rangle + 2h_{pr}\langle e_{qs} \rangle - 2h_{qr}\langle e_{ps} \rangle - 2h_{ps}\langle e_{qr} \rangle \\ & + \left(\sum_{sp}^H + \sum_{ps}^H \right) \delta_{qr} + \left(\sum_{rq}^H + \sum_{qr}^H \right) \delta_{ps} - \left(\sum_{rp}^H + \sum_{pr}^H \right) \delta_{qs} - \left(\sum_{qs}^H + \sum_{sq}^H \right) \delta_{pr} \\ & - 2 \sum_{ij} \langle ij|qr \rangle \langle e_{ps,ij} \rangle - 2 \sum_{ij} \langle qj|ir \rangle \langle e_{pj,is} \rangle \end{aligned}$$

$$\begin{aligned}
& +2 \sum_{ij} (qj|is) \langle e_{pj,ir} \rangle + 2 \sum_{ij} (ij|qs) \langle e_{pr,ij} \rangle \\
& +2 \sum_{ij} (pj|ir) \langle e_{qj,is} \rangle + 2 \sum_{ij} (ij|pr) \langle e_{qs,ij} \rangle \\
& -2 \sum_{ij} (ij|ps) \langle e_{qr,ij} \rangle - 2 \sum_{ij} (pj|is) \langle e_{qj,ir} \rangle \\
& +2 \sum_{ij} (ip|jr) \langle e_{iq,js} \rangle - 2 \sum_{ij} (is|jp) \langle e_{ir,jq} \rangle \\
& -2 \sum_{ij} (ir|jq) \langle e_{is,jp} \rangle + 2 \sum_{ij} (iq|js) \langle e_{ip,jr} \rangle \\
& - \left(\sum_{sq}^Y + \sum_{qs}^Y \right) \delta_{pr} - \left(\sum_{rp}^Y + \sum_{pr}^Y \right) \delta_{sq} + \left(\sum_{sp}^Y + \sum_{ps}^Y \right) \delta_{rq} + \left(\sum_{rq}^Y + \sum_{qr}^Y \right) \delta_{sp} \\
& W_{rs} = 2 \sum_{rs}^H - 2 \sum_{sr}^H - 2 \sum_{sr}^Y + 2 \sum_{rs}^Y
\end{aligned}$$

where

$$\begin{aligned}
\sum_{rs}^H & \equiv \sum_i^H h_{is} \langle e_{ri} \rangle \\
\sum_{rs}^Y & \equiv \sum_{ijk}^Y (si|jk) \langle e_{ri,jk} \rangle \\
C_{(rs),n} & = -2 \langle \psi^{mc} | [\hat{H}, i\hat{T}_{rs}] | \psi^n \rangle \\
& = 2 \sum_i h_{ir} \langle \psi^{mc} | e_{is} + e_{si} | \psi^n \rangle \\
& - 2 \sum_i h_{is} \langle \psi^{mc} | e_{ri} + e_{ir} | \psi^n \rangle \\
& + 2 \sum_{ijk} (ir|jk) \langle \psi^{mc} | e_{is,jk} + e_{kj,si} | \psi^n \rangle \\
& - 2 \sum_{ijk} (ik|sj) \langle \psi^{mc} | e_{rj,ik} + e_{ki,jr} | \psi^n \rangle \\
M_{nn'} & = 2(E^n - E^{mc})\delta_{nn'} \quad (12)
\end{aligned}$$

The elements of the **B** matrix and **W** vector are expressed in terms of the one- and two-electron integrals of the current molecular orbital basis and in terms of the one- and two-particle reduced density matrix elements of the current MC wavefunction. However, the **C** matrix requires the e_{ij} and $e_{ij,kl}$ matrix elements in the MC configuration basis along with the mixing coefficients for the excited states in the MC basis. The **C** matrix may be constructed using the partial sum

$$C_{rs,n} = -2 \sum_a \left(\sum_b U_{b,mc} \langle b | [\hat{H}, i\hat{T}_{rs}] | a \rangle \right) U_{a,n}$$

$$= -2 \sum_a C'_{rs,a} U_{a,n} \quad (13)$$

where the \mathbf{U} matrix contains the eigenvectors of the CI problem in the MC space. This avoids some difficulties in the \mathbf{C} matrix construction but the individual e_{ij} and $e_{ij,kl}$ matrix elements in the MC (Gelfand-Tsetlin) basis are still required.

4. Comments on the Implementation of the Unitary Group-EIL Method

From the above discussion, the \mathbf{B} matrix and \mathbf{W} vector could thus be constructed either from the density matrices of the current MC wavefunction or from the individual e_{ij} and $e_{ij,kl}$ contributions just as required in the \mathbf{C} matrix construction. Our approach to the \mathbf{B} matrix and \mathbf{W} vector construction is a compromise between these two extremes. Instead of completely calculating the one- and two-particle density matrices, we calculate all the contributions to a particular density matrix element that result from a single loop. This makes the \mathbf{B} matrix and \mathbf{W} vector construction much more efficient than if constructed from individual density contributions arising from a configuration pair, while avoiding the computational problems of the two-particle density matrix construction. The two-particle density matrix for a typical MCSCF wavefunction is a sparse matrix, the size of which is the fourth power of the number of molecular orbitals, and its construction is usually performed using methods similar to the two-electron integral transformation. For CI wavefunctions calculated from a large number of configurations, these sorting methods will be more efficient for the \mathbf{B} matrix and \mathbf{W} vector than the approach we have taken. We have chosen this simpler approach because the \mathbf{C} matrix evaluation step cannot make use of these more efficient methods and its construction becomes the dominant time factor with larger configuration spaces. In fact, even for some smaller problems (30–100 configurations) the \mathbf{C} matrix construction becomes more significant than the \mathbf{B} matrix or \mathbf{W} vector construction because the former step cannot even make use of the efficiency of the density contributions calculated from a single loop. The \mathbf{C} matrix construction also requires all eigenvectors and eigenvalues of the CI problem in the MC configuration space and thus it appears that this method is limited, for practical reasons, to relatively small dimensions of the MC space (< 200).

For these larger problems then, a reasonable approach might be to neglect completely the coupling between the orbital changes and the mixing coefficient changes and to construct the one- and two-particle density matrix elements needed for the \mathbf{B} matrix and \mathbf{W} vector using these sorting procedures. The convergence of this approximation has been shown to be inferior to the complete second-order procedure, which includes the perturbation corrections calculated from the \mathbf{C} matrix, and to be unsuitable for wavefunction calculation [1,18]. It would be a viable approach, however, for energy optimization since the energy converges to chemical significance (10^{-4} – 10^{-6} hartree) in a reasonable number of iterations with this approximation even though the errors of the wavefunction are still significant (GBT terms are also 10^{-4} – 10^{-6}).

Since both the CI calculation within the MC configuration space and the matrix elements required for the EIL wavefunction optimization require the e_{ij} and $e_{ij,kl}$ matrix elements for every MCSCF iteration, we use the same indexing tape (or formula tape) twice during each iteration. This indexing tape contains, for each loop, the value of the e_{ij} or $e_{ij,kl}$ matrix element and its indices, the loop head, the loop tail, the sum of the segment weights of the bra arcs of the loop, and the sum of the segment weights of the ket arcs of the loop. This information, along with the reverse lexical index array and the reverse lexical offsets in the DRT, allows the efficient calculation of all pairs of configuration indices which share the loop. These configuration indices are used in the CI part of each iteration in the construction of the CI matrix (or of matrix times vector when the diagonalization is performed directly) and later for the contribution of that loop to the one- and two-particle density matrix elements needed for the \mathbf{B}' matrix and \mathbf{W} vector construction.

The e_{ij} and $e_{ij,kl}$ indices determine uniquely the required integrals during the CI part of each iteration. For smaller CI calculations and for the CI calculation within each MCSCF iteration, the CI matrix is explicitly constructed and diagonalized using standard procedures. For larger CI calculations the desired eigenvalues and eigenvectors are calculated using Liu's modification [19] of Davidson's procedure [20]. The required matrix times vector operations are performed directly from the indexing tapes without the explicit Hamiltonian matrix element construction. This aspect of the calculation has been considered by previous workers.

Because a single e_{ij} or $e_{ij,kl}$ may be combined with many different integrals to form contributions to several \mathbf{B} and \mathbf{C} matrix and \mathbf{W} vector elements, we currently construct the \mathbf{B} and \mathbf{C} matrices and \mathbf{W} vector with a single reading of the integral file and with multiple passes of the indexing file. In most cases it is possible to determine very early if all required integrals for a particular density contribution are not available in core and proceed to the next contribution. When the indexing file has been processed for the currently available integrals, new integrals are made available and the indexing file is again processed. When all integrals have been processed, the final transformation for the \mathbf{C} matrix is performed using the eigenvectors of the excited states of the CI calculation in the MC configuration space. The perturbation corrections are then added to the \mathbf{B} matrix and the κ parameters are evaluated by solving the required linear equations.

Since the \mathbf{B}' matrix is symmetric, only the lower triangle needs to be calculated. Efficient procedures exist for solving the required linear equations which require no space beyond the storage of the lower triangle of the \mathbf{B}' matrix itself. It is also useful to determine the inertia (the number of positive, zero, and negative eigenvalues) of the \mathbf{B}' matrix to ensure that the desired solution (all positive eigenvalues) has been found. The inertia can be determined with little extra effort during the solution of the linear equations. This is done without diagonalizing the \mathbf{B}' matrix and without evaluating the eigenvalues explicitly [21]. Since the square of the skew-symmetric \mathbf{K} matrix is a negative semidefinite Hermitian

matrix, the orbital transformation may be evaluated without approximation by using the cosh-sinh expansion of Dalgaard and Jørgensen [1]:

$$e^{-\mathbf{K}} = \mathbf{V}(\cos \mathbf{d})\mathbf{V}^\dagger - \mathbf{KV}(\sin \mathbf{d})\mathbf{d}^{-1}\mathbf{V}^\dagger$$

where

$$\begin{aligned} (\mathbf{KK}) &= \mathbf{V} \mathbf{d}^2 \mathbf{V}^\dagger & \mathbf{d}^2 \text{ diagonal} \\ \mathbf{d} &\equiv \text{Sqrt}(-\mathbf{d}^2) \end{aligned} \quad (14)$$

This requires the diagonalization of the Hermitian matrix (\mathbf{KK}) instead of the skew-symmetric matrix \mathbf{K} .

Inspection of the two-electron integrals required for the CI matrix in the MC space, the \mathbf{B} matrix, \mathbf{C} matrix, and \mathbf{W} vector reveal that only integrals with at most two indices which belong to molecular orbitals that are unoccupied in all configurations need to be calculated. Elbert [22] has recently improved the standard transformation method by arranging the steps such that a partial sum is used more efficiently. A minor rearrangement of the Elbert procedure which places all DO loops involving molecular indices outside of the innermost DO loops which involve atomic orbital indices allows not only the efficient use of the partial sum but also efficient occupation checking to be performed during the integral transformation. If only the required integrals are transformed for each iteration, the integral transformation time may be reduced by approximately half that required for the complete integral transformation. This is partially the result of the fact that the configurations required for MCSCF wavefunctions involve the occupation of only relatively few molecular orbitals. The integral transformation time is usually the most significant part of each iteration (50–90%) even for some of the larger configuration spaces. The efficiency of the integral transformation step is thus an important factor in the efficiency of the wavefunction optimization procedure.

5. Discussion and Results

We have applied the EIL wavefunction optimization procedure using the unitary group method as outlined in the previous sections to the ground state and first excited 1S state of the Be atom. The atomic integrals of the $5s-4p$ contracted Gaussian basis of Table I were calculated using the MOLECULE integral program [23] within the D_{2h} subgroup. If a complex atomic orbital basis had been used, these results could have been duplicated with fewer configurations than are required in these reported calculations. We chose the Be atom as a test case for our wavefunction optimization procedure because the full-CI calculation with this orbital basis (1148 configurations) is within the capabilities of our CI program and because Be is a very correlated system which requires several configurations to describe adequately both the ground and excited states. We can determine in a systematic manner the effect of the configurations included in the MC space on the correlation energy of the electronic states and compare this directly to the total correlation energy within our orbital basis. The goal of

TABLE I. Atomic Gaussian basis for Be.

Basis Fn	Exponent	Contraction Coefficient
1s	1264.5857	0.001945
	189.9368	0.014835
	43.1590	0.072090
	12.0987	0.237154
	3.8063	0.469199
	1.2729	0.356520
2s	0.7478	1.0
3s	0.2200	1.0
4s	0.0823	1.0
5s	0.0300	1.0
1p	3.1965	0.055980
	0.7478	0.261551
	0.2200	0.793972
2p	0.0500	1.0
3p	0.0125	1.0
4p	0.0031	1.0
E(SCF)		= -14.56681165 au
E(Full CI-ground state)		= -14.61758566 au
E(Full CI-'S excited state)		= -14.35451305 au

the MCSCF wavefunction optimization procedure for this system is to optimize the orbitals for a given configuration list and produce the best approximation possible to the corresponding exact energy with this orbital basis obtained from the full-CI calculation. For most molecular systems it is possible to produce very good approximations to not only ground states but also excited states with only a few configurations. In fact, the MCSCF approach has been advocated for this reason since the chemical interpretation of wavefunctions consisting of relatively few configurations is more straightforward than the corresponding interpretation of wavefunctions consisting of large numbers of configurations. Although this is a valid point in favor of the MCSCF approach, our emphasis is on obtaining a MC wavefunction for which the GBT is satisfied.

In Table II we report the results of several ground- and excited-state calculations at different levels of approximation. These different levels of approximation consist of including different configurations and different numbers of configurations in the MC space. The final entry in Table II is the full-CI result within the orbital basis. The first row of Table II contains the results for the single-configuration $1s^2 2s^2$. When the eigenvectors of the one-electron Hamiltonian matrix (the kinetic and nuclear attraction terms within the atomic orbital basis) used directly in the EIL procedure as starting orbitals, the \mathbf{B}' matrix had two negative eigenvalues and these orbitals were thus unsatisfactory for the orbital optimization procedure. Using these same orbitals, a natural orbital iteration was then performed using the $1s^2 2s^2$ configuration and all of its single excitations as the CI reference space. The single excitations allow for the orbital relaxation effects in this CI wavefunction. The eigenvectors of the one-particle

TABLE II. Energies (a.u.) of lowest two 1S states of Be.

Row	# conf.	Grnd. State	Excited State
1	1	-14.566811	
2	4	-14.608494	
3	6	-14.609877	-14.344191
4	13	-14.609932	-14.344411
5	15	-14.609928	-14.346596
6	24	-14.609928	-14.346609
7	15	-14.615178	-14.344466
8	24	-14.615897	-14.344522
9	27	-14.615902	-14.344528
10	37	-14.616480	-14.348719
11	36	-14.615533	-14.346576
12	69	-14.616270	-14.346656
13	106	-14.617567	-14.354009
14	1148	-14.617586	-14.354513

density matrix of this CI wavefunction were used to obtain a new set of orbitals. In this case, this orbital improvement procedure is equivalent to one step of the iterative natural orbital SCF optimization procedure. These orbitals were then used in the EIL optimization and were found to produce a positive definite \mathbf{B}' matrix. The convergence criterion for these calculations was that the sum of the squares of the GBT terms should be less than 10^{-30} . This ensures that the largest error in the wavefunction is less than 10^{-15} . The energy converges to chemical significance when $\sum W_{rs}^2$ is much larger (10^{-5} – 10^{-6}) than this more stringent wavefunction convergence criterion. Since true second-order convergence is displayed by the EIL orbital optimization procedure, three or four fewer iterations are required for energy convergence than are required for wavefunction convergence. For this single-configuration calculation, energy convergence was achieved in three iterations and the wavefunction converged in six iterations of the EIL method. Since the unitary group procedure is not restricted with regard to spin or the number of open shells, this approach could be generally used for closed or open-shell single-configuration wavefunction optimization. If there are linearly independent spin functions, either a choice of spin coupling could be used for single-configuration orbital optimization or all of the spin functions which have identical orbital occupancies could be included. This latter type of limited MCSCF wavefunction is equivalent to a generalized valence bond (GVB) wavefunction where the optimum spin function is calculated. For the single-configuration calculations, no coupling of the orbital changes with mixing coefficient changes needs to be calculated (i.e., no \mathbf{C} matrix is required) and the method displays true second-order convergence. It could also be mentioned at this point that no numerical difficulties are encountered until machine precision (10^{-17} – 10^{-19} in our case) in the convergence of the wavefunction is reached. This implies that the matrix element evaluation and solution of the resulting linear equations is, in general, numerically stable.

The second row of Table II gives the results for a four-configuration MCSCF

calculation. These configurations are the SCF configuration mentioned in the preceding paragraph along with the $1s^2 1p_x^2$, $1s^2 1p_y^2$, and $1s^2 1p_z^2$ configurations. All three of these configurations are required to obtain the correct 1S combination. If a complex atomic orbital basis had been used, these results could have been duplicated with only two configurations. For this calculation, the SCF orbitals calculated from the single $1s^2 2s^2$ configuration were used as starting orbitals. The \mathbf{B}' matrix with these initial orbitals had three negative eigenvalues. A first-order CI calculation was performed which included these four configurations and all single excitations from these four configurations. The orbitals which diagonalized the resulting one-particle density matrix were then used as starting orbitals for the EIL procedure. With these orbitals, the \mathbf{B}' matrix had one negative eigenvalue. The iterative natural orbital procedure was repeated with these orbitals and the new set of orbitals was used in the EIL procedure. These orbitals were sufficient to produce a positive definite \mathbf{B}' matrix. Energy convergence (10^{-4} hartree) was then reached on the third EIL iteration and the wavefunction converged on the seventh EIL iteration.

The third row in Table II gives the results for the ground and first excited state for a six-configuration MC space. This space included the four configurations from row 2 and the single and double excitations from the $2s$ orbital into the $3s$ orbital. The dominant component of the excited state is the $1s^2 2s 3s$ configuration and these configurations appear to give a good description of this excited state. The starting orbitals were the four MC orbitals obtained from the previous calculation reported on row 2. Two iterations were required for the energy to converge to 10^{-6} and a total of six EIL iterations were required for the wavefunction to reach convergence for the ground state. For the excited state, again only two iterations were required for energy convergence and a total of five iterations were required for the GBT terms to be less than 10^{-15} . Although the individual state energies are in error by 0.01 hartree, the energy difference of the two states is only 0.002 hartree in error when compared to the full-CI results of row 14. This indicates that the limited MCSCF method applied to different states has the capability of giving consistent descriptions to the different states. The DRT for this configuration list has the restriction that the $1s$ orbital is doubly occupied in all configurations.

The results of further exploratory CI calculations indicated through natural orbital occupation numbers that the remaining s orbitals were the next most important orbitals to include in configurations within a MC space. Row 4 of Table II shows the results of including the $4s$ and $5s$ orbitals, still with the restriction that the $1s$ orbital remain doubly occupied. This 13-configuration calculation shows only a modest improvement in the energies over the results of row 3. The occupation numbers of the MCSCF orbitals indicated that only one of these orbitals—the $4s$ —had any significant occupation after the orbital optimization procedure.

Row 5 shows the results of including a second p orbital in the configurations in the MC space. The $4s$ orbital was also kept in order to determine the relative importance of the $4s$ and $2p$ orbitals. For this 15-configuration calculation, the

$2p$ orbitals were found to be unimportant for the ground state. In fact the $5s$ orbital in the previous calculation was more important to the ground-state energy than was the $2p$ orbital. However, the $2p$ orbitals are seen to be important for the excited-state description. Row 6 is the result of including the $3p$ orbital along with the $4s$ and $2p$ orbitals into the valence space. These results are very close to the results in row 5 indicating that the $3p$ orbitals are not important for either the ground-state or the excited-state description. The 15-MC calculation of row 5 then includes all the important correlation effects for the electrons in the $2s$ orbital for both the ground and excited states. The energy difference of the two states is seen to be only 0.00026 hartree in error when compared with the energy difference of the full-CI results. The starting orbitals for these calculations were obtained from one iteration of the natural orbital method. The first-order wavefunctions were calculated from the appropriate MC configuration space and all single excitations from these configurations. The initial orbitals for these CI calculations were the 6-MC orbitals from the results of row 3. It should be pointed out that these calculations have redundant variables (orbital pairs for which the GBT is always satisfied and which produce zero eigenvalues of the \mathbf{B}' matrix) that have been removed from the orbital optimization step.

Since all of the $2s$ correlation energy has been obtained with the inclusion of the $4s$ and $2p$ orbitals in the valence space, the remaining correlation energy involves the electrons that have been constrained to the $1s$ orbital. Row 7 of Table II shows the results of allowing all single and double excitations from the SCF configuration into the $3s$ and $1p$ orbitals. The DRT for these configurations was constructed with the constraint that the $3s$ and $1p$ orbitals share, at most, only two electrons. The energy of the ground state was lowered by 0.006 hartree from the 6-MC result of row 3. The energy of the first excited state, however, was lowered only 0.0003 hartree. The 24-MC list of row 8 was obtained by constraining the $1p$ orbitals to share at most only two electrons. This 24-MC space may also be described as a full-valence CI with four electrons in the $1s$, $2s$, and $3s$ orbitals, and then all double excitations from these configurations into the $1p$ orbitals. Row 8 shows that these added configurations again preferentially lower the ground-state energy. Row 9 gives the results of the four electron full-valence CI calculation in all six valence orbitals. The three configurations included in this calculation that were not included in the calculation of row 8 are the configurations which have only p orbitals occupied. These configurations contributed so little to the energy that all further MCSCF calculations were constrained to have at least two s electrons in every configuration.

The inclusion of the $4s$ and $5s$ orbitals was again investigated with the results given in row 10. This 37-MC space included all single and double excitations from the SCF configuration into the $3s$, $4s$, $5s$, and $1p$ orbitals. Compared to row 7, it appears that the $4s$ and $5s$ orbitals are now important for the excited state as well as the ground state.

Row 11 shows the results of including the $1s$ correlation and of including the $2p$ orbitals into the valence. This configuration list includes all single and double excitations from the SCF configuration into the $3s$, $1p$, and $2p$ orbitals. Consistent

with our earlier observation, the $2p$ orbitals are not as important to the ground-state description as the $4s$ and $5s$ orbitals. Row 12 gives the results for the full-valence CI with the $1s$, $2s$, and $3s$ orbitals along with all double excitations from these orbitals into the $1p$ and $2p$ orbitals. This 69-MC calculation shows that the ground state is still preferentially stabilized by the inclusion of these configurations in the MC space.

The results of the final MCSCF calculation performed in this study are reported in row 13 of Table II. This MC configuration space included the full-valence CI configuration space of the $1s$, $2s$, and $3s$ orbitals along with all single and double excitations into the $4s$, $5s$, $1p$ and $2p$ orbitals. The energy of the ground state for this MC space is only in error by 1.9×10^{-5} hartree and the error of the excited state is 5.0×10^{-4} hartree when compared to the full-CI result.

These calculations show that the unitary group method may be used effectively in the construction of configuration lists for multiconfiguration reference spaces. The configuration lists used in this study range from 1 (the SCF configuration) to slightly over 100 at which time the full-CI results are reproduced to within 0.3 kcal/mole. Of course this level of precision is not possible for larger systems; but the energies of the ground state and first excited state were systematically improved using various configuration lists produced from occupation restrictions. These occupation restrictions are readily employed using the distinct row table representation. In the calculations reported here, the generalized Brillouin theorem is satisfied to less than 1.0×10^{-15} for all orbital pairs. The calculation of the MCSCF wavefunction was performed using a wavefunction optimization method that displayed local second-order convergence for all the reported calculations.

Several calculations were attempted, however, that did not result in convergence to the correct solution. In several instances, negative eigenvalues persisted after several first-order wavefunction and natural orbital calculations. A study of these global convergence problems of the EIL method has been performed elsewhere [18]. It should be emphasized that in all cases where initial orbitals produced a positive definite Hessian matrix, second-order convergence to the energy minimum was observed. In the results reported here, initial orbitals were obtained from an appropriate first-order wavefunction using orbitals from previous converged results. As noted, this process sometimes had to be repeated several times before suitable starting orbitals were found.

6. Summary and Conclusions

MCSCF calculations have been performed for the ground and first excited 1S states of Be atom using several configuration lists. These configuration lists were constructed using the graphical unitary group formalism. This formalism is flexible enough to allow wavefunction optimization for several small MC spaces of 1-30 configurations which were shown to describe the ground and excited states, and for larger MC spaces of 30-106 configurations. The 106-configuration calculation reproduces the full-CI result to chemical accuracy. Although we

report that several calculations had convergence difficulties because of the global convergence problems of the EIL method, initial orbitals obtained from the iterative natural orbital method were found sufficient to result in convergence for the cases studied in this report. Local second-order convergence was observed for these cases and the final wavefunctions obtained were accurate to 1.0 (10^{-15}). The required matrix elements for CI calculations and the MCSCF wavefunction optimization were calculated efficiently using the unitary group method.

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