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AN INTRODUCTION TO GUGA IN THE COLUMBUS PROGRAM SYSTEM

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INTRODUCTION

The COLUMBUS Program System is a collection of Fortran programs for performing general multiconfiguration self-consistent-field (MCSCF) and multireference single- and double-excitation configuration interaction (MRSDCI) wave function optimization based on the graphical unitary group approach (GUGA). A general discussion of the COLUMBUS Program System, along with numerous references for further details, may be found in Ref. 1. The purpose of this paper is to describe at an introductory level how wave functions are specified and characterized in the COLUMBUS Program System in terms of the unitary group, and in particular, using the graphical representation as proposed by Shavitt.

THE GRAPHICAL UNITARY GROUP APPROACH

The unitary group has long been used by chemists and physicists in the study of angular momentum coupling, and discussions may be found in almost any standard group theory textbook². In electronic structure theory, the usefulness of the unitary group arises from the ability to compute matrix elements of the form $\langle m | E_{pq} | n \rangle$ and $\langle m | e_{pqrs} | n \rangle$ in which the individual elements of the many-electron expansion basis $|n\rangle$ are each eigenfunctions of the electron spin operators S^2 and S_z . Such spin-adapted many-electron basis functions are called Configuration State Functions (CSFs). The subscripts in these matrix elements label the orbital basis set. These matrix elements are called coupling coefficients. The operators E_{pq} and e_{pqrs} may be written in terms of spin-orbital electron creation and annihilation operators.

$$E_{pq} = a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta} \quad (1)$$

$$e_{pqrs} = E_{pq}E_{rs} - \delta_{rq}E_{ps} = \sum_{\alpha,\sigma} a_{p\sigma}^\dagger a_{q\sigma}^\dagger a_{r\sigma} a_{s\sigma} \quad (2)$$

General electronic operators may be written in terms of these primitive operators which are called, respectively, *generators* and *normal-order generator products*; in this way the generators and generator products form an operator basis. For example, the usual electronic hamiltonian operator may be written as

$$H = \sum_{p,q} h_{pq} E_{pq} + \frac{1}{2} \sum_{p,q,r,s} g_{pqrs} e_{pqrs} \quad (3)$$

The numbers h_{pq} and g_{pqrs} are the operator expansion coefficients. For the hamiltonian operator in particular, they are the integrals of the one-electron and two-electron repulsion parts of the electronic hamiltonian operator over the orthonormal orbital basis functions. From such operator expansions, it is clear that arbitrary matrix elements between wave functions may be reduced to summations over coupling coefficients. Again using the hamiltonian as an example,

$$\begin{aligned} \langle \Psi_a | H | \Psi_b \rangle &= \sum_{p,q} h_{pq} \langle \Psi_a | E_{pq} | \Psi_b \rangle + \frac{1}{2} \sum_{p,q,r,s} g_{pqrs} \langle \Psi_a | e_{pqrs} | \Psi_b \rangle \\ &= \sum_{\substack{p,q \\ m,n}} h_{pq} c_m^a c_n^b \langle m | E_{pq} | n \rangle + \frac{1}{2} \sum_{\substack{p,q,r,s \\ m,n}} g_{pqrs} c_m^a c_n^b \langle m | e_{pqrs} | n \rangle \end{aligned} \quad (4)$$

The coefficients c_m^a and c_n^b are the expansion coefficients for the two wave functions in the CSF basis. A more complete discussion of these aspects of wave function expansions, along with details of the computation of the coupling coefficients, may be found in References 3-8 and references therein. More recent formal developments have extended the use of the unitary group approach to spin-dependent operators⁹⁻¹¹, and the reader is referred in particular to the contributions of Kent and Schlesinger in these proceedings¹² for further discussion.

In order to understand such wave functions, operators, and matrix elements, it is necessary to characterize the orbital basis, the CSF expansion space, and the CSF expansion vectors. The orbital basis is the most fundamental, as it determines the operator expansion terms and the nature of each individual CSF. The nature of the wave function is then determined through the CSF expansion coefficients.

In the COLUMBUS Program System, the orbitals are usually determined by the MCSCF procedure. This involves choosing a CSF expansion space for the MCSCF wave function, and optimizing simultaneously the shape of the individual orbitals and the CSF expansion coefficients. The details of this CSF selection and wave function optimization process have been reviewed elsewhere³. The MCSCF wave function is chosen to be sufficiently flexible in order to account qualitatively for much of the change in the wave function over the course of a chemical reaction. This includes bond-breaking and bond-reforming processes, near-degeneracy effects, and any corresponding spin-recoupling effects. It does not account quantitatively for the "dynamical" electron correlation effects. For these energy contributions, a very flexible large-scale MRSDCI wave function is used. Although there is no rigorous separation of the total electronic energy into these separate contributions, it has proven useful nonetheless to consider separately these different types of interactions.

The MRSDCI wave function expansion usually employed in the COLUMBUS Program System consists of all single- and double-excitations from each of the MCSCF expansion CSFs. For this reason, the MCSCF expansion space is called the *reference* space for the CI wave function. In some cases, it is useful to apply numerical selection procedures to this reference space, the result being that only a subset of the MCSCF

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expansion space is used in the generation of the large-scale MRSDCI wave function. The choice of single and double excitations ensures that all CSFs that interact directly through the hamiltonian with any of the reference CSFs are included in the final wave function expansion. Only the CSF expansion coefficients are varied in the MRSDCI wave function; the orbitals are held fixed as determined by the previous MCSCF optimization procedure.

Because both the MCSCF and the MRSDCI wave function are expanded in terms of CSFs that are constructed using the unitary group approach and with the same molecular orbital basis, it is straightforward to measure the overlap between the two wave functions and to ensure that the most important components of the wave function have been included into the reference space. Understanding the type of contribution to the wave function provided by a particular CSF depends on the orbital occupation pattern and on the coupling of the individual electrons.

Expansion CSFs in the unitary group approach are constructed in a recursive manner in which orbitals, which may be empty, singly occupied, or doubly occupied, are added individually to intermediate expansion terms which, by construction, are themselves spin eigenfunctions. This is sometimes called a *genealogical* construction scheme, since the nature of a final expansion CSF is described in terms of its orbital occupation and spin-coupling *ancestry*, in which the addition of orbitals corresponds to ancestral generations. This genealogical analogy suggests a graphical representation of this ancestry, and this graphical representation is the basis of GUGA.

The quantities of importance in these intermediate expansion terms are the orbital level i , the cumulative number of electrons up to that level N_i , and the cumulative electron spin S_i . For historical reasons, the nonnegative integer quantities a_i and b_i are used instead of the physical quantities N_i and S_i . The interrelation between the two sets of values is given by $N_i = 2a_i + b_i$ and $b_i = 2S_i$. An individual expansion CSF can be represented by a Paldus tableau⁵, which is a vertical collection of the a_i and b_i for each orbital level. A *Shavitt graph* is a graphical representation of these same quantities⁴. Each triple (i, a_i, b_i) is called a *distinct row* and corresponds to a vertex of the graph. In general discussions, the terms *distinct row* and *vertex* are often used interchangeably. The connections in the Shavitt graph between these vertices are called *arcs*, and are constrained to be one of the four physically allowed ways of adding an orbital: empty, singly occupied such that the cumulative spin is increased, singly occupied such that the cumulative spin is decreased, and doubly occupied. These four possibilities are assigned the integer values 0, 1, 2, and 3 respectively, and are called *steps*. A CSF then corresponds to a directed *walk* from the *tail* to the *head* of the Shavitt graph along the arcs. The graph tail is a fictitious distinct row $(i, a_i, b_i) = (0, 0, 0)$ added for completeness; the graph head is determined by the number of orbitals, total number of electrons, and total spin state. For a particular CSF, the collection of steps for all the orbital levels is called the *step vector*. A step vector and a Paldus tableau contain exactly the same information, and for a given CSF in one representation it is straightforward to construct the other representation. Step vectors are written either vertically, as is a Paldus tableau, or horizontally, with a bra-ket notation. Conventionally, the vertical axis of a Shavitt graph corresponds to the orbital level. The different a values are denoted by large horizontal spacings, with increasing values to the left, and the b values associated with each of the corresponding a values are denoted with smaller horizontal spacings, with increasing values to the left. The actual spacings are arbitrary, but it is convenient for the relative a and b spacings to be chosen so as to avoid overlap of the arcs. If a uniform spacing for the a and b increments is used in the pictorial representation of a Shavitt graph, then the arcs corresponding to the four allowed steps have four distinct slopes. A Shavitt graph is stored in a computer in tabular form and this representation is called a *distinct row table* (DRT). An example of a DRT is given in Ref. 4 along with further discussions of these aspects of GUGA. When the distinction is unimportant, the terms *Shavitt graph* and *DRT* are used interchangeably.

In specifying MCSCF, and subsequent MRSDCI, expansion spaces, it is often convenient to begin conceptually with a full-CI expansion space, and to then place restrictions on the allowed orbital occupations or spin-couplings in order to arrive at the final desired CSF expansion space. This is somewhat in contrast to most single-reference or SCF based approaches in which the expansion space is defined in terms of excitations, or excitation-level, relative to the SCF wave function. Furthermore, it is most convenient if these occupation and spin restrictions are expressed in terms of *cumulative* values, since in this case there is a direct correspondence to the arcs and vertices of the Shavitt graph. In this manner, MCSCF and MRSDCI expansion spaces may be defined simply by removing particular arcs and vertices from the Shavitt graph corresponding to the full-CI expansion space. The practical advantage of this approach is that the chaining indices, which determine the lexical ordering of the individual CSFs, may be computed in such a way as to retain the sequential numbering of the expansion CSFs. When this is not possible, an *indexing vector* is required to map between the lexical indices, as determined by the DRT, and the smaller number of CSF indices associated with the final expansion space. A *skip-vector* is one such type of indexing vector in which positive entries represent final expansion CSF indices whereas negative entries correspond to deleted walks. The value of the negative entry in such a skip-vector gives the number of consecutive entries that must be skipped in order to get to the next retained entry. For simplicity in the following discussion, it will be assumed that the indexing vector is unnecessary, and consequently the lexical index and final CSF index will be identical.

In order to determine the lexical index of a CSF expansion term, it is necessary to compute *arc weights*. These are integer quantities associated with each arc in the Shavitt graph⁴. A detailed discussion of the chaining indices will not be given. However, the following features are particularly important. The arc weights themselves are computed recursively, so that the overall effort depends only on the number of distinct rows and not on the total number of walks. In fact, many of the advantageous features of GUGA follow from the ability to formulate operations in terms of manipulations of distinct rows rather than of individual expansion CSFs. (With optimistic assumptions regarding distinct row reuse, the total number of distinct rows scales only as the logarithm of the number of expansion CSFs.) The lexical index of a CSF expansion term is computed simply by adding together the weights of the arcs associated with the corresponding walk (along with an additional +1 offset value). Although it is trivial to generate the entire CSF list (e.g. in terms of step vectors or primitive Slater determinants) from the underlying DRT, it is not always trivial to generate the underlying DRT from an arbitrary list of Slater determinants. For this reason, the DRT representation is used in the COLUMBUS Program System as the primary data structure, and the step vectors are generated on-the-fly only when necessary.

There is some arbitrariness in the computation of the arc weights, and this results in some arbitrariness in the ordering of the expansion CSFs. The following conventions are used in the COLUMBUS Program System. The arc weights are denoted by the array elements y_{dk} in which d labels the step (i.e. 0, 1, 2, or 3) and k labels the vertex (distinct row). The number of distinct paths from vertex k to the head of the Shavitt graph is the number of *upper walks* from that vertex, and is stored in the array element $\bar{x}_k$. The computation of the y_{dk} and $\bar{x}_k$ begins at the graph head and proceeds down, level by level, to the graph tail. For a particular vertex, the arc weights are computed in the order

$$\begin{aligned} y_{3k} &= 0 \\ y_{2k} &= y_{3k} + \bar{x}_{l_{3k}} \\ y_{1k} &= y_{2k} + \bar{x}_{l_{2k}} \\ y_{0k} &= y_{1k} + \bar{x}_{l_{1k}} \\ \bar{x}_k &= y_{0k} + \bar{x}_{l_{0k}} \end{aligned}$$

The chaining index array element l_{dk} is the label of the vertex connected to the current vertex k by the step d . This procedure is demonstrated graphically in Fig. 1.

Fig. 1 Example of arc weight computation with the conventions used in the COLUMBUS Program System. The computation of the entire set of arc weights proceeds by levels from the head of the Shavitt graph to the tail.

In Fig. 1, and in the figures that follow, the upper walk values $\bar{x}_i$ values are the circled integers placed directly at the vertices, and the arc weights y_{ijk} are within the rectangles associated with the arcs. These conventions have been adopted in order to provide for the most straightforward association of expansion CSFs in MCSCF and MRSDCI wave functions in the COLUMBUS Program System.

In order to demonstrate how the above concepts apply to the wave function expansion space for a chemical situation, several CSF expansion spaces for the methyl radical, CH_3 , will be considered. This is one of the sample calculations included in the COLUMBUS Program System distribution files¹³. We first examine how various MCSCF wave function expansions can be defined using GUGA. The simplest MCSCF wave function is the single configuration SCF wave function appropriate for the neighborhood of the equilibrium geometry. For simplicity, and not to diminish the importance of this aspect in general, we will ignore spatial symmetry for this discussion. Orbitals that are restricted to be doubly occupied in all CSFs in an MCSCF expansion are conventionally called *inactive*, orbitals that are open shell or variably occupied in the expansion CSFs are called *active*, and orbitals that are unoccupied are called *secondary* or *virtual*. The SCF wave function consists of four inactive orbitals, and one singly occupied active orbital. These inactive orbitals in the SCF wave function may be taken as the carbon 1s core-like orbital, and the three single-bond orbitals localized between the carbon atom and the three hydrogen atoms. At planar geometries near the equilibrium geometry, the active radical orbital is an out-of-plane p-like orbital on the carbon center. The step vector representation for this wave function is [3333100...] where only the first few entries are given explicitly, and the occupied molecular orbitals correspond to the first levels.

When distorted away from the equilibrium geometry, the most important electron correlation effects involve the repulsion between electrons within a single bond. (We will neglect entirely the correlation effects of the core electrons in this discussion, as is typical for such molecular systems. In actual calculations, such inactive orbitals are treated separately, and are not included explicitly in the DRT specification of the remaining active orbitals. For demonstration purposes in this discussion, the inactive orbital will be included in the DRT, but the virtual orbitals will be ignored.) The simplest treatment of this type of correlation involves adding a correlating orbital for each of the bonding orbitals while maintaining the doubly occupied restriction. That is, in an individual CSF, each such orbital is either empty or doubly occupied. Compared to the SCF wave function, three orbitals have been moved from the inactive space into the active space, and three additional

Table 1. Cumulative occupation and spin restrictions for the PPMC expansion space.

level	1	2	3	4	5	6	7	8
OCCMIN	2	2	4	4	6	6	8	9
OCCMAX	2	4	4	6	6	8	8	9
BMIN	0	0	0	0	0	0	0	1
BMAX	0	0	0	0	0	0	0	1

correlating orbitals have been moved from the virtual space into the active space. In this wave function, each pair of electrons in one of the bonding orbitals is then allowed to occupy a correlating orbital in the wave function. This is called a *perfect-pairing multiconfigurational* (PPMC) expansion space. The simplest way to allow this generalization of the wave function expansion space is to group each bonding orbital together with its correlating orbital in the assignment of the levels in the DRT. With this orbital ordering, the original SCF expansion term is represented as [33030301] where only the (potentially) occupied orbitals are specifically denoted. The entire expansion space consists of 8 CSFs. A general way of specifying such occupation and spin restrictions is with the introduction of four vectors, the entries of which specify the minimum and maximum cumulative values allowed for each orbital level. The 8 CSF PPMC expansion corresponds to the following vector entries.

It is clear from Table 1 that a grouping of the orbitals occurs when the cumulative occupation maximum and minimum values are identical. For example, at level 3 there are exactly 4 electrons total, whereas at level 5 there are exactly 6 electrons specified. The result is that exactly 2 electrons have been restricted to occupy the two-orbital subspace corresponding to levels 4 and 5. Similarly, 2 electrons must occupy levels 2-3, 2 electrons must occupy levels 6-7, and 1 electron must occupy level 8. The PPMC expansion further requires the double-occupancy restriction. In general, this restriction may be enforced in several ways. In the above table, the BMAX vector is employed for this purpose. The Shavitt graph corresponding to the PPMC expansion is shown in Fig. 2. The [33030301] walk corresponds to CSF index 1 ($=0+0+0+0+0+0+0+1$). Notice that the step vector [30303031], corresponding to CSF number 8 ($=0+4+0+2+0+1+0+0+1$), is included also in this wave function expansion. This represents a 6-fold excitation relative to the SCF wave function. The fact that such excitations are included even in this simple MCSCF wave function demonstrates dramatically the difference between multireference and single-reference based approaches to the electron-correlation problem. Even the most sophisticated single-reference correlation methods do not yet consider routinely such wave function contributions.

It is well-known that as the C-H bonds are stretched far from equilibrium towards dissociation, the SCF wave function does not separate correctly into the product of the neutral fragment wave functions, but rather it is contaminated with ionic contributions. That is, the dissociation products $\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$, $\text{CH}_3 \rightarrow \text{CH} + 2\text{H}$, and $\text{CH}_3 \rightarrow \text{C} + 3\text{H}$ contain contaminations due to the ions CH_2^+ , CH_2^- , H^+ , H^- , CH^+ , CH^{+2} , CH^- , C^+ , C^{+2} , C^- , C^{-2} , etc. The single configuration SCF wave function is contaminated in this manner, as are excitation-limited single-reference based wave function expansions. The PPMC wave function is sufficiently flexible to eliminate these ionic contributions upon dissociation. This is due to the inclusion of higher excitations relative to the SCF wave function, such as the 6-fold excitation term discussed above, in the wave function expansion. However, with few exceptions, the PPMC wave function generally does not dissociate to the product of wave functions of the correct spin states of the various molecular fragments. The wave function component corresponding to the C atom in the above reaction, for example, will

Level	1	2	3	4	5	6	7	8
OCCMIN	2	2	4	6	6	8	8	9
OCCMAX	2	4	4	6	6	8	8	9
BMIN	0	0	0	0	0	0	0	1
BMAX	0	1	2	3	4	3	2	1

Table 2. Cumulative occupation and spin restrictions for the $(1^22^22^21^1)$ expansion space.

electrons in different bonds. That is, in addition to the *intra*-pair contributions, it includes the most important *inter*-pair contributions³. The Shavitt graph for the GVB-RCI wave function is shown in Fig. 3. Comparison with Fig. 2 shows how the additional expansion space flexibility translates to additional complexity in the graphical representation. The expansion terms involving high-spin intermediates, such as the 7-open-shell CSF $(1^311111222)$ which has CSF index 54 $(=0+17+17+14+5+0+0+0+1)$, contribute relatively little to the wave function near the equilibrium geometry, but they are crucial in describing correctly the 'agments of the various dissociation reactions.

The GVB-RCI wave function also displays an interesting and important property. The orbitals within an orbital pair may be arbitrarily rotated between each other, and there will always exist some conjugate transformation among the CSF expansion coefficients that will restore the wave function back to its original form. The *representation* of the wave function will be different with the two orbital sets (original and rotated), but the energy, electron density, and any other property will be identical for the two wave function representations. Such orbital rotations are called *redundant*, and must be accounted for in the wave function optimization process to avoid numerical difficulties. However, such redundancies may be used to practical advantage in the interpretation of MCSCF wave functions by making particular orbital rotation choices. For example, orbitals may be chosen to diagonalize the corresponding subblock of the 1-particle density matrix, thereby giving a wave function described in terms of its *natural orbitals*. Alternatively, orbitals may be localized, allowing the identification in the expansion space of charge-transfer or Rydberg contributions or other such qualitative characterizations. The orbitals that may be rotated arbitrarily in this manner in a wave function expansion are said to form an *invariant orbital subspace*. The process of choosing specific orbitals within such a subspace is called *orbital canonicalization* or *orbital resolution*. A more extensive discussion of redundant orbital rotations in the context of analytic energy gradients may be found in Ref. 14.

Such subspaces occur commonly in MCSCF wave functions due to the *direct-product* nature of the underlying expansion space. That is, the expansion space may be regarded as a direct product of expansion spaces of the constituent fragments of the molecular system. In the GVB-RCI example above, the 5 "fragments" are the 1-orbital/2-electron core, the three individual 2-orbital/2-electron C-H bonds, and finally the 1-orbital/1-electron radical. Each fragment individually displays orbital rotation invariance, and this invariance is inherited by the final wave function expansion. Borrowing from the traditional atomic shell notation, the above CH_3 expansion could be denoted $(1^2\otimes 2^2\otimes 2^2\otimes 1^1)$, or even more simply as $(1^22^22^21^1)$ in which the direct-product is implicit. Here the boldface numeral is the number of orbitals in the subspace, and the exponent is the number of electrons associated with that fragment.

Generalization of the GVB-RCI wave function involves relaxation of the occupation restrictions. Suppose that the GVB-RCI wave function expansion was determined, for example by comparison with more exact MRSDCI calculations, to be insufficiently flexible in describing the reaction $\text{CH}_3\text{---CH}+\text{H}_2$. A generalization of the wave function expansion that would allow a more accurate treatment of the spin-recoupling involving the two H atoms would be to merge the two 2-orbital/2-electron invariant orbital subspaces into a

Fig. 2. Shavitt graph for the PPMC expansion for the methyl radical corresponding to the occupation and spin restrictions of Table 1. The inactive core orbital is included.

be some mixture of singlet, triplet, and quinter atomic states ($S=0,1,2$). Additional flexibility in the wave function is required to address this problem. The GVB-RCI (Generalized Valence Bond Restricted CI) wave function, also called the FTP (Full InterPair) wave function, is a generalization of the PPMC wave function that allows for the correct spin-state dissociation to molecular fragments³. This wave function has the same orbital subspace occupation restrictions as the PPMC wave function, but is specified by the occupation vector entries given in Table 2. Comparison with Table 1 shows that the OCCMIN and OCCMAX vector entries are unchanged; it is only the BMIN and BMAX entries that have been generalized. The GVB-RCI expansion contains not only the most important correlation contributions between electrons in a single bond, but it also contains the most important correlations between

Fig. 3. Shavitt graph for the $(1^2 2^2 2^2 2^1)$ GVB-RCI expansion for the methyl radical corresponding to the occupation and spin restrictions of Table 2. The orbital subspace occupation restrictions are the same as for the graph of Fig. 2, but the spin restrictions have been completely relaxed.

single 4-orbital/4-electron "fragment". The occupation restriction vectors for this wave function expansion $(1^2 4^4 2^2 1^1)$ are shown in Table 3. Note that as before, the last orbital in each subspace is associated with cumulative minimum and maximum occupations of equal values. This is a general feature, and it allows the straightforward construction of general direct-product expansion spaces by means of OCCMIN and OCCMAX vector entries.

A practical disadvantage of the $(1^2 4^4 2^2 1^1)$ wave function expansion space is that one of the H atoms is treated differently from the other two. This might not be an issue in a different molecular system, but for CH_3 near the equilibrium geometry, this would lead to an imbalanced treatment of the correlation, and to an artificial slight deviation away from the D_{3h} point group symmetry of the exact wave function. The GVB-RCI expansion did not have this undesirable characteristic, due to the equivalent treatment of all three C-H

Table 3. Cumulative occupation and spin restrictions for the $(1^2 4^4 2^2 1^1)$ expansion space.

level	1	2	3	4	5	6	7	8
OCCMIN	2	2	2	4	6	6	8	9
OCCMAX	2	4	6	6	6	8	8	9
BMIN	0	0	0	0	0	0	0	1
BMAX	0	1	2	3	4	3	2	1

bonds. The equivalence can be restored, but only at the cost of a larger expansion space. One possibility is the direct-product expansion $(1^2 6^6 1^1)$. This expansion space is a superset of the previous one, allowing for the correct description of the $\text{CH}_3 \rightarrow \text{CH} + \text{H}_2$ reaction, while restoring the equivalent treatment of the three C-H bonds.

Finally, the other choice is the expansion $(1^2 7^7)$ which is consistent with the occupation restrictions shown in Table 4 and the DRT in Fig. 4. This expansion is called a FORS (Fully Optimized Reaction Space) or a CASSCF (Complete Active Space SCF) expansion space. It also treats the three C-H bonds equivalently while allowing for the correct description of any possible dissociation product. For the ground electronic state of CH_3 at planar conformations, the $(1^2 6^6 1^1)$ and $(1^2 7^7)$ wave functions are identical since point group symmetry requires that the out-of-plane radical orbital be singly occupied. However, at nonplanar conformations, the more general FORS expansion allows that orbital to have arbitrary occupation. Inspection of Fig. 4 shows the structure that becomes apparent with Full-CI type wave function expansions with GUGA.

In the COLUMBUS Program System, the MRSDCI wave function expansion space is determined first by specifying the reference expansion space. This is often the same set of CSFs in which the MCSCF wave function was expanded. In this case, the occupied orbitals in the MCSCF wave function become the internal orbitals in the MRSDCI expansion. The remaining orbitals are called external orbitals, and they are typically allowed to be occupied by, at most, two electrons in the MRSDCI expansion. In constructing a Shavitt graph for the MRSDCI wave function, it is convenient to group the internal orbitals together, conventionally at the top of the DRT, and then to group the external orbitals together by point group symmetry label, conventionally at the bottom of the DRT. Because the total number of orbitals, internal and external, is often quite large, and because the external orbital occupations are relatively simple compared to the internal orbital space, the external orbital space is treated in a simplified manner. If a particular internal walk, which is that part of a walk in the Shavitt graph determined by the internal orbital occupation and spin coupling pattern, is included in the wave function expansion, then all possible external orbital occupations are automatically included. Since the Shavitt graph for the external orbitals is relatively simple, it is never explicitly constructed, but is only treated implicitly. This implicit treatment occurs both during the expansion space specification and during the computationally intensive wave function optimization

Table 4. Cumulative occupation and spin restrictions for the $(1^2 7^7)$ FORS expansion space.

level	1	2	3	4	5	6	7	8
OCCMIN	2	2	2	2	3	5	7	9
OCCMAX	2	4	6	8	9	9	9	9
BMIN	0	0	0	0	0	0	0	1
BMAX	0	1	2	3	4	3	2	1

This simplified treatment of the external orbitals has two important practical implications. First, it restricts to some extent the allowed types of configuration selection that can be done; the COLUMBUS codes allow selection only of individual internal walks, not of individual CSFs. Secondly, due to the ordering by point group symmetry of the external orbitals, the wave function optimization step, which requires the computation of matrix-vector products involving the large sparse hamiltonian matrix with trial vectors, reduces to regular sequences of dense matrix-vector and matrix-matrix products whose dimensions depend on the number of external orbitals. This allows for the efficient treatment of extremely large wave function expansions, with the optimization procedure itself performing at peak computational speed. MRSDCI wave function expansions of 10^6 to 10^7 are now routine with the COLUMBUS Program System on workstations, and with

n	C_n	C_n^2	Vertex	Γ_1	orb_1	Γ_2	orb_2	d
3	-0.96530	0.93180	z^*					3330001
77	0.05682	0.00323	z^*					3030301
20	0.05682	0.00323	z^*					3300031
161	0.05525	0.00305	z^*					1231201
122	-0.05525	0.00305	z^*					1321021
113	0.04680	0.00219	z^*					1331002
37	-0.04473	0.00200	z^*					3120121
2532	-0.03649	0.00133	y	a'	10			13130200
614	0.03649	0.00133	y	a'	10			13310020
298	0.03290	0.00108	z^*					0333001
-								
789121	0.01939	0.00038	w	a'	12			33030001
759531	0.01939	0.00038	w	a''	5			33300001
-								
35113	0.01479	0.00022	x	a'	11	a''	5	113320000
40107	0.01479	0.00022	x	a'	11	a'	12	113230000

Table 5 shows a summary analysis of a large scale MRSDCI wave function optimization on the methyl radical. This table is extracted from the CIPC program listing included in the sample calculations from the COLUMBUS distribution files¹³. Program CIPC performs wave function analysis for large-scale MRSDCI wave functions. The reference space for this expansion is the (12^{77}) space discussed above, with the additional restriction that the core orbital is constrained to be doubly occupied in all expansion CSFs. This "frozen core" restriction is common for such calculations. Again using the "shell" notation, this expansion could be denoted as $(12^{\text{N}_c 77}) \oplus (12^{\text{N}_c 76}) \oplus (12^{\text{N}_c 75})$ where N_c is the number of external orbitals, and the $\oplus$ symbol denotes the union of the respective expansion CSF subsets. By convention, expansion CSFs with no external electrons are called z-walks, those with one external electron are called y-walks, and those with two external electrons are called either w-walks or x-walks, depending on whether the two electrons are coupled to form respectively an intermediate singlet ($a=1, b=0$) or a triplet ($a=0, b=2$). The step-vector entries corresponding to the frozen core orbital are not included in Table 5. The external step vectors consist mostly of zeros, and a compact notation has been adopted in which these step-vector entries have been suppressed. For each expansion CSF, only the step-vector entries for the occupied external orbitals are included, along with their corresponding point group symmetry labels and numerical symmetry-orbital indices. The internal step-vector entries in Table 5 are listed fully, and, in this case, correspond to the MCSCF natural orbitals. This calculation uses a standard cc-pVTZ basis set. The expansion space consists of 1264744 CSFs of $^2A'$ symmetry using C_s point group symmetry (the symmetry element is a vertical reflection plane). The molecular geometry is a nonplanar distortion away from the (planar) equilibrium conformation. See also Refs. 16-17 for more information about this particular wave function.

As is typical for MRSDCI wave functions, the most important CSFs in the wave function, as measured for example by contribution, are members of the reference CSF set. The reference CSFs are the z -walks denoted with an asterisk in column four of Table 5. The next most important terms are seen to be y -walks, a feature that is also common for MRSDCI expansions. The most important x - and w -walks are included also in Table 5 for

comparison. In single-reference wave function expansions based on SCF references, single excitations are usually relatively unimportant due to Brillouin's theorem which guarantees that matrix elements of the form $\langle \text{Ref} | H | \text{SE} \rangle$ vanish numerically. The contribution of a single excitation $|\text{SE}\rangle$ only arises through indirect interaction with other expansion CSFs in the single-reference case. This is not the case for multireference expansions and consequently such matrix elements are numerically nonzero. Recognition of the general importance of the y -walks in multireference expansions leads to the POL-CI (Polarization CI) and so-called FOCI (First-Order CI) wave function expansions in which only the z - and y -walks are included. POL-CI calculations may be performed with the COLUMBUS Program System as a special case of the more general MRSDCI wave function expansion.

SUMMARY

A brief introduction of the COLUMBUS Program System has been given with emphasis on the use of GUGA, DRTs, and Shavitt graphs in the specification of the wave function expansion space and on the subsequent interpretation of the computed wave functions. The notion of genealogical spin-eigenfunctions is central to this presentation, and represents a conceptually simple and straightforward framework for chemists to understand the complexities of spin-eigenfunctions and their physical significance as molecules dissociate into smaller fragments or rearrange into various conformers and isomers. The philosophical differences between traditional single-reference based approaches and the more general multireference based approaches has been discussed. Although it is more difficult in some respects to treat molecular systems in this manner, the simplifications that arise from a cleaner separation of dynamical and nondynamical correlation effects is an important and useful feature. The remaining challenge is twofold. First, these methods must be extended to larger molecular systems and to systems for which relativistic effects must be treated explicitly. This requires the development of new formal methodology and the efficient exploitation of new computer architectures that can meet the computational demands of such systems. The second challenge is to be able to extract chemical insight from such large-scale wave function expansions.

Acknowledgments

The author wishes to thank Professor G. L. Malli, director of the NATO ASI "Relativistic and Electron Correlation Effects in Molecules and Solids", Vancouver, B.C., Canada, August 1992, for the invitation to present this material. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-ENG-38.

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