THE CONSTRUCTION
AND INTERPRETATION
OF MCSCF WAVEFUNCTIONS

Michael W. Schmidt and Mark S. Gordon
Department of Chemistry, Iowa State University, Ames, Iowa 50011;
e-mail: mark@si.fi.ameslab.gov

KEY WORDS: MCSCF optimization, active orbitals, reaction channels, excited states, dynamic correlation, wavefunction interpretation

ABSTRACT
The multiconfiguration self-consistent field (MCSCF) method offers the most general approach to the computation of chemical reactions and multiple electronic states. This review discusses the design of MCSCF wavefunctions for treating these problems and the interpretation of the resulting orbitals and configurations. In particular, localized orbitals are convenient both for selection of the appropriate active space and for understanding the computed results. The computational procedures for optimizing these wavefunctions and the techniques for recovery of dynamical correlation energy are reviewed.

INTRODUCTION
The essence of chemistry involves processes such as the formation and dissociation of chemical bonds, the excitation of an atom or molecule into a higher electronic state, and atomic or molecular ionization, in which electron pairs are separated. Although the end points of such processes (that is, the reactants and products) may frequently be reasonably well described using a simple wavefunction that corresponds to a single Lewis structure, this often cannot be said for the key species in between, such as transition structures, reactive intermediates, and excited electronic states. Such species often must be described with more complex wavefunctions in which several different arrangements of the electrons (electronic configurations) are taken into account.
Methylene, CH₂, provides a simple example of a species that is not sufficiently described by a single electronic configuration.

A qualitative picture of this molecule was provided more than 40 years ago by Walsh (1), who considered the variation of the valence molecular orbitals (MOs) of simple \( \text{AH}_2 \) molecules as a function of the HAH angle. For CH₂, the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) in \( C_2v \) symmetry are \( a_1 \) and \( b_1 \), respectively. The \( a_1 \) MO is a mixture of carbon 2s and 2p\(_z\) atomic orbitals (AOs) at bent HAH angles, but as the angle opens to linear, the 2s contribution diminishes to zero. This loss of 2s character raises the energy of the HOMO as the angle increases. The LUMO is already a pure carbon 2p\(_x\) orbital; to a first approximation, the energy of this orbital is essentially constant as the HAH angle increases. At exactly 180°, the two orbitals merge into a degenerate \( \pi \) MO. This is illustrated in Figure 1. For strongly bent structures, the ground electronic state is a singlet state, with the electronic configuration well described by placing the two electrons in the \( a_1 \) MO. The first excited triplet state is obtained by placing one electron in each of the two MOs. Thus, a qualitatively correct description of these two electronic states may be obtained with single-configuration wavefunctions, restricted closed- and open-shell Hartree-Fock (RHF and ROHF) wavefunctions, respectively:

\[
\Psi_{\text{RHF}} = a_1(\alpha)a_1(\beta) \quad \Psi_{\text{ROHF}} = a_1(\alpha)b_1(\alpha).
\]

As the HAH angle opens toward linear, the ROHF description of the triplet state remains qualitatively correct, but the electronic configuration in which the two electrons are placed in the \( b_1 \) MO becomes increasingly important for the singlet state. In the limit of a linear HAH angle, the qualitatively correct singlet wavefunction is

\[
\Psi = 2^{-1/2}[a_1(\alpha)a_1(\beta) - b_1(\alpha)b_1(\beta)].
\]

Thus, in order to describe the bend potential of the singlet state in a qualitatively
correct manner at all angles, the wavefunction must be written as

\[ \Psi_{\text{TCSCF}} = A[a_1(\alpha)a_1(\beta)] + B[b_1(\alpha)b_1(\beta)], \]

where A and B are variational parameters. The wavefunction in Equation 3 is the simplest example of a multiconfigurational wavefunction. The variational approach must be applied to both the configurational mixing parameters A and B and the MOs themselves (through the atomic expansion coefficients). Because the wavefunction in Equation 3 contains only two electronic configurations, the method used to variationally optimize these wavefunctions is called the two-configuration self-consistent field (TCSCF) method. Singlet CH\(_2\) may be thought of as a simple example of a diradical, and the TCSCF wavefunction is the simplest qualitatively correct wavefunction for a diradical. The percent of diradical character is given by 2B\(^2\).

An analogous example is the ring opening of cyclopropane to trimethylene. As for methylene, at the equilibrium geometry, the ground state of cyclopropane is qualitatively well described by the RHF wavefunction, in which the carbon–carbon (C–C) \(\sigma\) bond is filled. Because the \(\sigma\) and \(\sigma^*\) orbitals become nearly degenerate as the CC bond is broken, trimethylene is a diradical, and the simplest wavefunction that can describe the cyclopropane ring opening in a qualitatively
correct manner is again a TCSCF wavefunction, in which a second configuration occupying the $\sigma^*$ orbital is also included.

The first two cases discussed above are clearly examples of diradicals. Not all cases are so obvious. For example, the ethylene molecule is well described by a single configuration wavefunction, whereas a single configuration description of other group 14 analogs of ethylene becomes less and less appropriate as one proceeds vertically down the periodic table. Both $\text{H}_2\text{C}=$SnH$_2$ and $\text{H}_2\text{Si}=$SiH$_2$ have significant diradical character in the $\pi$ space and therefore significant configurational mixing (2). The same is true for many transition metal–main group multiple bonds (3). Pulay and coworkers (4–6) estimated that single configuration wavefunctions are inadequate descriptions for species that exhibit more than approximately 10% diradical character; that is, species for which the coefficient $B$ in the second term of Equation 3 is greater than approximately 0.23. By this measure, a single-configuration wavefunction is even inappropriate for $\text{CH}_2=$SiH$_2$ (7).

Many chemical processes involve the direct participation of two or more electron pairs. An example of such a case is the isomerization of bicyclobutane to butadiene (8) (Figure 2): Even if this reaction occurs in a concerted manner, it involves the breaking of two CC $\sigma$ bonds and the formation of two CC $\pi$ bonds. Thus, four electrons are involved in the process, as are four orbitals (two $\sigma$ and two $\sigma^*$ MOs in bicyclobutane, which transform into two $\pi$ and two $\pi^*$ MOs in butadiene). A qualitatively correct wavefunction for this process is one that includes at least two pairs of configurations analogous to the pair in Equation 3.

However, it has been emphasized (9–17) that a more useful (and quantitatively more accurate) wavefunction is one that includes all configurations in which the four active electrons are allowed to occupy the four active orbitals in any manner that is consistent with the chosen spin and space symmetry. This added flexibility results in a greater number of configurations in the wavefunction (20 vs 4, in the butadiene example). A multiconfiguration self-consistent field (MCSCF) wavefunction in which the active electrons are distributed in all consistent ways among the active orbitals is called a full optimized reaction

![Figure 2](image_url) The isomerization of bicyclobutane to butadiene.
space (FORS) (9–15) or a complete active space SCF (CAS-SCF) (16, 17) wavefunction. These full configurational space wavefunctions are invariant to unitary transformations among the orbitals in the active space, an appealing feature that is discussed in more detail below.

The general form of a MCSCF wavefunction is

\[ \Psi_{\text{MCSCF}} = \sum_k A_k \Phi_k \]

\[ \Phi_k = A \left\{ \prod_{i \in K} \phi_i \right\} \]

\[ \phi_i = \sum_\mu \chi_\mu C_{\mu i} , \]

which is a linear combination of several configurations [referred to as configuration state functions (CSFs), \( \Phi_k \)]. Each CSF differs in how the electrons are placed in the MOs, \( \phi_i \). The MOs are usually expanded in a basis of AOs, \( \chi_\mu \).

A MCSCF wavefunction is one in which both the configuration mixing coefficients \( A_k \) and the MO expansion coefficients \( C_{\mu i} \) are variationally optimized. Such a wavefunction is therefore distinct from a configuration interaction (CI) wavefunction, in which only the configuration mixing coefficients are variationally optimized. Procedures for optimization of \( A_k \) and \( C_{\mu i} \) are described in the section on Optimization Procedures. The section on Selection of MCSCF Configurations deals with the selection of those orbitals and electrons that are to be active in the MCSCF wavefunction.

It is well known that RHF wavefunctions are invariant (except for sign) to unitary transformations among the doubly occupied orbitals. The same is true for the doubly occupied and separately the singly occupied orbitals in a ROHF wavefunction. This degree of freedom has been exploited to transform the canonical orbitals that are eigenfunctions of the Fock operator into localized MOs that correspond more closely to such Lewis-like concepts as lone pairs and bond orbitals. Since a MCSCF wavefunction is likewise invariant to a unitary transformation of the orbitals that comprise the active space, one can transform this set of orbitals into localized MCSCF MOs. This leads to a useful method for interpreting complex wavefunctions in chemically meaningful terms. This is discussed in the section on Interpretation of MCSCF Wavefunctions.

It is important to think of the MCSCF wavefunction as the analog to a Hartree-Fock wavefunction for systems that do not have simple one-configuration descriptions. Viewed in this way, accurate energetic predictions should not necessarily be expected to emerge from MCSCF treatments. Accurate energies, such as reaction energies and barrier heights for chemical reactions, require
addition of correlation corrections in the same way that such corrections are required for single-configuration Hartree-Fock wavefunctions. It is frequently said that the MCSCF treatment corrects for nondynamical or quasi-degenerate correlation effects within the active space. The additional correlation is then referred to as dynamic correlation. Methods for the computation of dynamic correlation energy for MCSCF wavefunctions are described in the section on Dynamic Correlation Methods.

This review focuses on methodological aspects of MCSCF theory. Although several reviews deal with various aspects of MCSCF, no comprehensive survey exists. Therefore, we attempt to summarize most areas of interest relating to the construction of MCSCF wavefunctions at a single point on the potential energy surface. Fairly complete references to the methodology are given. However, no attempt is made to include all applications of MCSCF theory, and where examples seem appropriate, they are usually from our own group’s work. As a summary, the section on Additional Topics mentions the important subjects of MCSCF potential energy surfaces and molecular properties. We intend to address these topics in a future review.

OPTIMIZATION PROCEDURES

This section reviews in chronological order the various MCSCF wavefunction optimization techniques that have been used. Mathematical formalisms are not presented, though references to the primary literature are provided. Related concepts such as the choice of configurations or treatment of excited states that affected the development of MCSCF algorithms are included in our outline of the four distinct periods in MCSCF methodology.

Optimized Valence Configurations

Although mentioned as early as the 1930s (18, 19), the first practical use of MCSCF wavefunctions was in the mid 1960s with the optimized valence configuration (OVC) model of Wahl, Das, and Gilbert (20–26; see 24 for a bibliography of MCSCF work between the 1930s and the beginning of the OVC era). The optimization problem of Equation 4 was separated into alternating steps: obtaining CI coefficients \( A_k \) by diagonalization of the Hamiltonian, followed by an orbital update. The optimized orbitals \( \mathbf{C}_\mu \) were obtained by a set of coupled Fock matrix diagonalizations by generalizing upon the closed- and open-shell SCF techniques that had recently been devised. Convergence was generally unsatisfactory, and in retrospect we know this was due in part to the authors’ choice of configurations.

The CSFs used in the OVC method (27–30) were selected by importance (measured by the size of \( A_k \) and/or its changing contribution across the potential
Typically, the 5–10 CSFs in an OVC wavefunction included not only several important double excitations within the valence orbital space, but also a few configurations with electrons excited outside this space. The use of selected rather than full classes of configurations while using an unfolded (sequential improvement of orbital and CI coefficients) optimization technique almost assured poor convergence. The process of selecting configurations was laborious, based on several trial calculations, but it taught us a great deal about what kinds of configurations would have large coefficients or were necessary for the proper description of bond breaking. Most applications of the OVC method were limited to diatomics (27–30). It was clear from this work that MCSCF wavefunctions were chemically useful but that more powerful convergence methods were required.

Before going on, it is useful to mention that the generalized valence bond (GVB-PP) method developed by Goddard and coworkers (31, 32) is in some ways quite similar to the OVC model. The perfect pairing GVB wavefunction limits the configurations to pairwise double excitations within the valence orbital space, so the configuration selection is more constrained than in OVC but is thereby made considerably more systematic. Improved orbitals were originally obtained by the orthogonality-constrained basis set expansion (OCBSE) method (32), which diagonalized coupled Fock operators for orbitals in each shell. The MO counterpart to the GVB model is the separated pair independent particle model (33–35), dating from the same time period. This model also uses strongly orthogonal geminals, and the simple nature of the two-particle density matrix in these perfect pairing theories affords a great deal of insight into electron correlation contributions. Use of the GVB model continues to the present time because it is the only MCSCF method able to avoid integral transformations, and considerable progress has been made in replacing the OCBSE orbital update step.

**Generalized Brillouin Theorem**

The need for more reliable convergence led to further explorations (36–40) of the multiconfigurational Fock equations, leading to development of more general MCSCF Lagrange multiplier matrix expressions, along with some experimentation in use of Newton-Raphson optimization techniques. Several of these ideas presaged the developments of the third era of MCSCF programs, but the discovery in 1968 (41, 42) of the generalized Brillouin theorem (GBT) led most workers in the field into an exploration of first-order convergence techniques based on the elimination of single excitations. The optimization problem was usually treated by alternating determination of the CI coefficients with orbital improvements, but these can in fact be folded together (40). This second generation of orbital update methods led to the first reliably convergent polyatomic MCSCF programs.
The GBT (41, 42) demonstrated the equivalence of the convergence criterion exploited by the Fock matrix techniques, namely a symmetric Lagrange multiplier matrix, to the vanishing of certain single excitation matrix elements. The single excitations (SX) are excitations from all configurations of the MCSCF wavefunction, with unrelaxed CI coefficients, and thus possess multiconfigurational character themselves. At convergence, the Hamiltonian matrix elements between the MCSCF wavefunction and the SX space must vanish. This led to several optimization techniques attempting to drive these matrix elements to zero (43–54). The most reliable way to update orbitals proved to be the replacement of the natural orbitals (discussed in detail in the section on Interpretation of MCSCF Wavefunctions) of the MCSCF wavefunction by natural orbitals of the super-CI, as devised by Ruedenberg et al in 1979 (51). The main bottleneck in performing the super-CI, which required Hamiltonian matrix elements between the MCSCF function and all SX functions, was that each SX was a linear combination of as many CSFs as were contained in the MCSCF wavefunction. Thus, each element of the relatively modestly sized super-CI Hamiltonian required computation of a large number of simpler matrix elements, and this typically limited Ruedenberg’s implementation to about 25 MCSCF configurations. Efficient CI techniques (52) increased this number somewhat, but it was clear the demand for larger numbers of configurations was going to be difficult to satisfy. In 1980, however, Roos (53) showed that it is possible to approximate the super-CI Hamiltonian by using Fock matrix elements to approximate some terms in the SX-SX matrix block while still computing exactly the MCSCF-SX elements that according to the GBT are required to vanish. This eliminated the bottleneck of computing matrix elements over individual CSFs, and the resulting super-CI algorithm is still in use.

The 1970s were also a time of further exploration into the types of configurations that should be included in a MCSCF computation. The OVC work had shown that excitations within the valence orbitals (from occupied valence MOs \( \phi_i, \phi_j \) into virtual valence MOs \( \phi_a, \phi_b \)) are important: For example, double excitations such as \( \phi_i^2 \rightarrow \phi_a^2 \) or, less obviously, \( \phi_i^2 \phi_j^2 \rightarrow \phi_i^1 \phi_j^1 \phi_a^1 \phi_b^1 \), are often important, and sometimes single or even triple or higher excitations carry appreciable weight. Even when these other excitations have coefficients small enough that individually they have little influence on the shape of the optimized orbitals, they are sufficiently numerous to make a substantial contribution to the energy. The desire to systematize the generation of the CSFs, and thereby avoid the trial-and-error process involved in OVC configuration selection, led Ruedenberg et al to propose in the period from 1976 to 1982 the full optimized reaction space (FORS) model (9–15). The model included all configurations arising from distributing the active electrons in active orbitals, ensuring that no important configuration could be overlooked. The same conceptual MCSCF wavefunction was termed complete active space (CAS-SCF) in 1980 by Roos.
et al (52), and the two terms are interchangeable. Additional advantages to the use of full active space MCSCF wavefunctions include simplification of the optimization problem (by reducing orbital-CI couplings) and increased interpretability, both of which arise from the invariance of the energy to rotation of the active orbitals.

Although a singlet state with four electrons in four active orbitals has 20 MCSCF configurations, a singlet with 10 electrons in 10 orbitals requires 19,404 CSFs. Thus, the desire to use full active spaces fueled demand for computational techniques that could treat thousands of MCSCF configurations. The late 1970s was also the period when gradients of the potential energy surface were first considered, requiring sharply converged wavefunctions for accurate gradient components. These trends led most workers away from further developments of first-order convergence methods based on SX elimination.

Second Order Methods

The third major era in MCSCF orbital optimization was launched in 1978 by Dalgaard & Jørgensen (55). This work was the first to apply the Newton-Raphson method to general MCSCF wavefunctions, but it has precursors in earlier work on SCF (36) and GVB (31) quadratic convergence. Their formalism possessed quadratic convergence, based on use of the second derivative of the energy with respect to orbital rotation parameters (the orbital Hessian), in addition to the asymmetry of the Lagrangian (the orbital gradient) that is exploited in first-order methods. The method is the standard Newton-Raphson method from numerical analysis, in which the step toward the energy stationary point is the inverse Hessian times the gradient. A key development was the use of an exponential parameterization of the orbital rotation matrix (55), allowing easy identification of the nonredundant optimization parameters. The technique remains the most robust and widely used MCSCF convergence method and has therefore spawned a large primary literature (55–87), as well as several reviews (88–92). A 1980 paper of Siegbahn et al (60) contains a useful comparison of the second-order approach to the SX elimination procedure, as well as explicit formulae for the orbital gradient and Hessian.

Initially, the problem was treated by the heretofore standard procedure of unfolding the optimization of CI coefficients and orbital expansions into two separate steps, applying Newton-Raphson only to the latter, which prevents true quadratic convergence. Soon workers were enlarging the gradient and Hessian to include both orbital and CI terms simultaneously, yielding true second-order convergence (56, 59). Simultaneous improvements in CI methodology, particularly evaluation of the second-order density matrix (62), soon permitted the use of several thousand configurations. Modern programs implementing second-order methodology are highly sophisticated, involving not only extremely good direct CI capability, but also—for example—the Augmented Hessian method.
(67) to avoid inverting the Hessian or the partitioned Hessian (63) or norm extended optimization (79) procedures to avoid storage of the very large CI-CI block of the Hessian. By the mid 1980s, MCSCF computations containing on the order of 200,000 CSFs had been performed (84). Some exploration of third-order procedures has been attempted (73).

Besides its obvious applicability to bond dissociations on ground electronic surfaces, MCSCF offers a general variational approach to excited-state surfaces. Although excited states that differ from the ground state in spin or spatial symmetry can sometimes be treated at the SCF level, a general treatment requires multiroot capability, namely taking the CI coefficients $A_K$ for the desired state. Although excited-state MCSCF applications started being made in 1969 (93) and continued through the OVC (25, 30) and GBT (46, 48, 49) periods (1973–1977), two advances led to more routine treatment of excited states. One of these was the advent of second-order simultaneous CI and orbital optimization, because these two optimizations are typically more coupled in excited states than in ground states (61, 65). The second was the concept of state averaging, first introduced by Docken & Hinze in 1972 (94), and adopted by Ruedenberg et al in 1979 (51) and Werner & Meyer in 1981 (68). State averaging gives a single set of MCSCF orbitals, optimized in a compromise sense: that is, as an average for two or more electronic states rather than for a single specific state. It thus avoids root flipping (94) (interchanges of close-lying states during MCSCF optimization of the higher state), and frequently some small admixture of the ground state greatly stabilizes the convergence process for excited states. It is often convenient to have the states of interest be expanded from a single set of orbitals, although this is not necessary for computation of the transition density (95–98). State averaging is particularly useful for the computation of nonadiabatic interactions (e.g. spin-orbit or vibronic coupling) among electronic states (99).

First-Order Procedures

Currently, most MCSCF computations are performed with one of the existing second-order programs. There has, however, been a reawakening of interest in first-order methods in the 1990s. It is now clear that very large atomic basis sets, including multiple polarization functions, are needed to obtain accurate energetics using single-reference many-body methods, and surely the same bases are needed in MCSCF applications. Although the second-order methods promise rapid convergence when many CSFs are used, they face a bottleneck in trying to use large, one-electron basis sets. Specifically, a second-order method must transform integrals over two virtual orbital indices, and storage of the orbital hessian and solution of the resulting Newton-Raphson equations also becomes prohibitive.
Accordingly, in 1989, Meier & Staemmler (100) revisited the GBT approach to orbital optimization (CI coefficients are once again obtained by a separate CI diagonalization). They arrange the SX matrix elements \( \langle \Phi | H | \Phi (i \rightarrow a) \rangle \), which should vanish at convergence into a matrix \( B_{ia} \), which is diagonalized to find the improved orbitals. Two additional ideas improve upon the intrinsically linear convergence. Renormalization of the \( B \) elements speeds convergence for active orbitals with occupancy near 2.0 or 0.0, and fast microiterations based on approximated \( B \) elements are added. Standard convergers such as direct inversion in the iterative space (DIIS) may be applied to the microiterations. The computational demand for the orbital update step is the formation of the Lagrangian, which requires a transformation over just one virtual orbital index. Meier & Staemmler’s method (100) was independently programmed by Dupuis et al (101), who comment: “If we can do a traditional SCF calculation, then we can carry out the first-order CAS-SCF calculation.” Our experience with the Dupuis code indicates that convergence is usually obtainable, but that fewer iterations would be desirable.

Accordingly, we (102) recently combined their efficient program for the formation of the Lagrangian, yielding the orbital gradient, with an approximate second-order technique based on an idea of Fischer & Almlöf (103) and achieved a convergence intermediate between first and second order. The idea combines a diagonal guess of the orbital Hessian with Broyden-Fletcher-Goldfarb-Shano (BFGS) updates and avoids explicit storage of the Hessian. Overall time to complete the MCSCF calculation is less than full Newton-Raphson, except perhaps in cases of very large CSF expansions. The program has been in use in our group for one year and is robust provided some care is taken in choosing starting orbitals. The implementation is presently limited to full active spaces because that is normally what is wanted.

**SELECTION OF MCSCF CONFIGURATIONS**

*Full Configurational Spaces*

Reference has already been made to early days when a few carefully selected configurations were used (27–30). This trial-and-error approach has been replaced by the introduction of the full optimized reaction space (FORS) or complete active space SCF (CAS-SCF) models. In the interest of historical accuracy, it should be noted that the idea of restricting MCSCF excitations to valence orbitals was proposed in the valence CI model (104, 105), based on even earlier partitioning of orbitals into internal and external sets (106, 107). The discussion here is limited to the subject of full active spaces, and after a few words reviewing this choice, the majority of this section is dedicated to an attempt to teach a practical approach to active space design.
In the FORS (9–15) or CAS-SCF (16, 17, 52, 65) approach, the electrons and orbitals are partitioned into spectator and active sets. The spectator orbitals are those fairly uninvolved in the chemical process of interest (i.e., those electrons whose bonds are not breaking). Active electrons are those associated with orbitals that undergo substantial changes in electronic structure characteristics during the chemical process of interest. All orbitals are optimized, but electron correlation energy is recovered only for the active electrons. Because all possible configurations distributing the active electrons among the active orbitals are included, the problem of choosing CSFs is converted into a problem of choosing the active orbitals. The number of configurations contained in a MCSCF wavefunction with \( N \) active electrons in \( m \) active orbitals, and total spin coupled to \( S \), is given by the Weyl-Robinson formula (108):

\[
\frac{2S + 1}{m + 1} \left( \begin{array}{c} m + 1 \\ m - 1/2N - S \end{array} \right) \left( \begin{array}{c} m + 1 \\ 1/2N - S \end{array} \right).
\]

The presence of point-group symmetry will reduce the number of CSFs from this value somewhat. We illustrate below an appropriate scheme to identify the correct active space, defined by the values of \( N \) and \( m \).

The choice of the active space for excited-state MCSCF wavefunctions is a problem that cannot currently be regarded as solved. Because excited states typically involve orbitals outside the valence orbitals (e.g., Rydberg orbitals), most applications still involve some trial and error to select the proper orbitals. In early attempts (109), CSFs were selected by scanning a series of CI computations, including a larger number of configurations, and deleting configurations that contributed less than a cutoff value to the energy. Today, the most successful computation of vertical excitation energies is Roos’s restricted active space (RAS) configuration selection (110, 111). Because the excited states typically require enlargement of the active space by one or more orbitals beyond the valence orbitals to account for the excitations, the full CAS set of configurations can become very large. Typically, only one or two electrons populate the newly added orbitals in any of the important configurations, so the RAS method divides the active space into three categories: orbitals with a limited number of vacancies, a fully active orbital set, and orbitals with a limited number of electrons. This subset of the CAS wavefunction encompasses the important configurations while greatly decreasing the total number that must be dealt with. Usually, a number of trial calculations are necessary to determine exactly how to deal with the following problems (17). How many weakly occupied orbitals must be added for a quantitative treatment of all excited states of interest? How many Rydberg basis functions are necessary to account for the Rydberg levels interspersed with the desired valence states? What state weightings in
state-averaged wavefunctions are required to reasonably represent the valence levels and the desired number of Rydberg states?

Active Space Design

The question most frequently asked by new users of MCSCF programs is how to make a reasonable choice of the active space. Two reviews by Roos (16, 17) attempt to teach this by example. The question is of such importance, however, that we devote the remainder of this section to a different approach. We restrict ourselves to molecular valence states arising from ground state AOs.

One approach, which we have used for many years, is an illustrative scheme inspired by GVB diagrams (112). The diagrams allow one to count both the active orbitals and the active electrons. Because they are simply a generalization of ordinary Lewis dot diagrams they are easily learned. The diagrams are in essence a pictorial bookkeeping scheme and include a correct accounting for all spectator valence electrons.

As the simplest possible example, consider the full active space wavefunction for H₂ (Figure 3, left; see legend for details). The orbitals are interpreted as orthogonal MCSCF orbitals, localized onto atoms, as opposed to the overlapping valence bond hybrids in GVB diagrams. A line may be placed between any two such atomic-like orbitals, provided there is only one electron in each. The line may be regarded as an indication of where to construct bonding and antibonding molecular orbitals from the atomic orbitals (Figure 3, right). Orbitals and therefore electrons are most easily counted by drawing the localized atomic-like orbitals, but the MCSCF computations are usually done with symmetry-adapted bonding, nonbonding, and antibonding orbitals. Of course, there are exactly as many of the latter as there are atomic-like orbitals. Finally, because the full active space wavefunction is invariant to transformation of the orbitals, it may be preferable to consider the MCSCF wavefunction as being constructed from

![Figure 3](image-url)

*Figure 3* The full active space wavefunction for H₂. *Circles*, the two active 1s orbitals, which are the valence orbitals of each hydrogen; *dots*, the electron each orbital contributes; *lines*, bonding interactions.
the orthogonal, atomic-like orbitals shown. In this case, the line in the figure is interpreted as representing a bonding interaction, as exhibited by a large positive off-diagonal element in the first-order density matrix (bond-order matrix) (15). Both interpretations of the line contrast with its interpretation in GVB diagrams as denoting an overlap, but as in the GVB diagram they indicate the presence of a bond.

Additional examples are shown in Figure 4 (see legend for details), using valence s and p orbitals, which may be drawn as sp hybrids if appropriate. Inactive electrons excluded from the active space denote doubly occupied orbitals. Figure 4a shows an active space for ethylene, in which four electrons are placed in active \(\sigma, \pi, \pi^*,\) and \(\sigma^*\) orbitals. There are four active orbitals, four active electrons, and eight inactive electrons, for a correct total of 12 valence electrons. This active space is capable of treating the rotation to break the \(\pi\) bond (113), forming the biradical shown (note the absence of a bond line after rotation), or handling the dissociation to two triplet methylenes (11). The active space is clearly unable to treat any reactive channel involving the breaking of a CH bond. The final portion of Figure 4a shows banana bonds formed from fully localized AOs. This diagram is exactly equivalent to the first diagram, as the MCSCF wavefunction is invariant under such orbital transformations (114, 114a). (Because valence bond calculations include only a subset of the full active space configurations, valence bond energies for the \(\sigma-\pi\) and banana structures are different. The lower valence bond energy for the latter has unfortunately resulted in confusing and incorrect interpretations. It is clear that this is an artifact caused by orbital symmetry breaking. The two viewpoints are equivalent if a full active space wavefunction is used).

Figure 4b shows similar \(\pi\) bond systems, but with one nonbonding lone pair on the heteroatom included in the ethylene-like active spaces of \(\sigma, \pi, \pi^*,\) and \(\sigma^*\), enlarging them to six electrons in five orbitals. The active space shown for methanimine is capable of handling the rotation about the \(\pi\) bond, the \(n \rightarrow \pi^*\) valence state, or dissociation to methylene and imidogen (yielding a reasonable ROHF wavefunction for the NH fragment, \(\sigma^2\pi_x^1\pi_y^1\)). Note that in our evaluation of the \(\pi\) bond strength (113), we omitted the lone pair from the active space, as we considered rotation only. Similarly, the active space for formaldehyde encompasses \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) valence states, or a dissociation into \(\text{CH}_2 + \text{O}\). Note that the oxygen has an inert lone pair, mainly of 2s character, in addition to the p lone pair, which is included in the active space. All three 2p orbitals of the dissociated oxygen are active in order to provide a consistent treatment of these degenerate orbitals. The active space shown is not designed to describe isomerization to hydroxycarbene HCOH, as the CH bonds have been placed in the inactive orbital space. An active space of 10 electrons in 9 orbitals would be required to provide a description of the isomerization process that is of comparable accuracy to that for the CO bond processes.
Figure 4  Schematic diagrams for the design of multiconfiguration self-consistent field active spaces. Lines, inactive electrons excluded from the active space, denoting doubly occupied orbitals. See text for additional details.
Figure 4c shows the ring opening of singlet cyclopropylidene to allene (115–117). The active space allows breaking the CC $\sigma$ bond opposite the methylene group. The methylenic singlet state has an initially empty p orbital to correlate the sp$^2$ lone pair. These four orbitals can smoothly change into the p orbitals forming the allene $\pi$ bonds. In particular, there are two active orbitals at the central carbon in both species. Note that it is useful to consider both reactant and product species, making sure that not only are the number of active electrons and orbitals the same, but that one can imagine how one orbital set will transform smoothly into the other during the reaction. If the transition state for the process is known, its molecular and electronic structure can be useful in making this connection between reactants and products.

Figure 4d illustrates the ring opening of bicyclobutane to form butadiene (8). Only two of the four equivalent peripheral bonds must break to form the product, but all four are treated in the same fashion to obtain a consistent description of the reactant. Thus, the active space used for this species is 10 electrons in 10 orbitals. Opening two opposing peripheral bonds gives one unpaired electron on each carbon, which after rearranging and planarizing are able to form the two $\pi$ bonds of the product. The bent bridge bond and the two unbroken peripheral bonds vary smoothly into a reasonable $\sigma$ skeleton in the product. Isoelectronic with bicyclobutane is the bicyclic form of N$_2$O$_2$, a potentially important high-energy fuel (8, 118). The active space used for bicyclobutane is not adequate to describe the isomerization of this species or its dissociation to 2 NO, because one lone pair on each oxygen interacts strongly with the bonds and antibonds as the reaction proceeds. Thus, the active space must include 14 electrons in 12 orbitals in order to obtain smoothly varying reaction paths. This example serves as an emphatic illustration that careful attention must be paid to the behavior of the orbitals involved in the chemistry of interest throughout the reaction surface.

Our final example (Figure 4e) constructs the hypervalent axial bond in PF$_3$Cl$_2$, according to the three-center, four-electron model of Rundle (119) and Musher (120). The central p orbital of phosphorous maps to the lone pair of PF$_3$, whose MCSCF wavefunction contains only a single CSF. Consideration of $d$ orbitals in the pentacoordinated species would have led to an illogical active space.

The examples chosen here illustrate inactive bond pairs and lone pairs and, within the active space, atomic-like orbitals that contribute zero, one, or two active electrons. As a check, the diagram should account for all valence electrons. Because we have depicted equilibrium geometries rather than transition states, the singly occupied orbitals are usually paired in bonds. The one exception shown is the twisted transition state for ethylene rotation, in which the diagram exhibits diradical character. Note that there are always four orbitals around C, N, O, F, P, or Cl, as these atoms possess four valence AOs. These are
partitioned into active and inactive orbitals, depending on the reactive channel of interest. Because each example places some valence electrons into filled spectator orbitals, each active space treats only a subset of the possible reactive channels. Inclusion of all valence orbitals into the active space [Ruedenberg et al.’s full valence space (12)] enables any conceivable reactive channel on the ground-state surface to be explored.

Furthermore, the diagrams contain the necessary information to perform MCSCF computations in terms of symmetry-adapted MOs. Consider the banana bond representation of ethylene, with the standard axis choice of z along the CC bond, and x perpendicular to the molecule. Taken together, the four equivalent localized orbitals form a reducible representation \( \Gamma \), whose characters under the \( D_{2h} \) point-group operations are \( E = 4, C_2(z) = 0, C_2(y) = 0, C_2(x) = 0, i = 0, \sigma_{xy} = 0, \sigma_{xz} = 4, \sigma_{yz} = 0 \). (All four atomic-like orbitals are unmoved by the identity operation and the xz reflection, whereas all other operations interchange the orbitals). Reducing the representation \( \Gamma \) gives four irreducible representations, \( a_g \oplus b_{3u} \oplus b_{2g} \oplus b_{1u} \), which are the formal names in \( D_{2h} \) for the \( \sigma, \pi, \pi^* \), and \( \sigma^* \) orbitals of ethylene. Reducing the two-dimensional \( \sigma \) and two-dimensional \( \pi \) representations shown in the first part of Figure 4a gives the identical result. The diagrams thus contain symmetry information in addition to counting electrons and orbitals.

Our examples were limited to sp block atoms. The extension to transition metals is an easy one, as each metal possesses six valence AOs, the nd, and \((n+1)s\). In some circumstances it has proven necessary to extend the active space to include the valence \((n+1)p\) orbital (121).

To summarize, we have presented a diagrammatic design of active spaces that are a straightforward generalization of the familiar Lewis dot diagrams (which themselves summarize Hartree-Fock electronic structure). With a bit of practice, these diagrams are easily drawn. They permit facile comparison of active spaces for reactants, transition states, and products. At a simple level, they may be regarded as a counting scheme for both orbitals and electrons. However, the full symmetry characteristics of the MCSCF wavefunction can be extracted from the diagrams.

The second most commonly asked question about MCSCF relates to the practical matter of starting orbitals, to which a few general comments may be addressed. Typically, starting orbitals are taken from some single-configuration SCF wavefunction, and the MCSCF computation is therefore performed with symmetry-adapted bonding orbitals rather than with the atomic-like orbitals used to illustrate active space design. It is desirable to improve upon the lowest SCF virtual orbitals, which are typically diffuse in nature, particularly when using first-order convergence methods. A particularly simple procedure, known as modified virtual orbitals (122), is to replace the SCF virtual orbitals with those
from a Fock operator for a highly positive ion. When the molecule contains distinct active regions and spectator regions, it may be advantageous to localize the canonical SCF orbitals into the two regions in order to identify the best starting active orbitals. This can be done under the constraint of preserving orbital symmetry in order to retain the speedups permitted by use of orbital symmetry during the MCSCF computation. Other options for starting orbitals that have been suggested are unrestricted Hartree-Fock (UHF) natural orbitals (4–6) or second-order Møller-Plesset (MP2) natural orbitals (123). Finally, a visualization program (124) that allows examination of the starting orbitals, and a check of the converged orbitals, is essential.

INTERPRETATION OF MCSCF WAVEFUNCTIONS

It is often said that MCSCF wavefunctions are difficult to interpret because they may contain thousands or tens of thousands of CSFs. This is misleading. The most interpretable part of the MCSCF wavefunction is the set of active orbitals, which usually comprises a small subset of the orbital space. When the CSF expansion coefficients are analyzed, this is usually done in terms of the first-order density matrix

$$\rho_{ij} = \sum_J \sum_K A_J A_K \rho_{JK}^{ij},$$

where the so-called structure factors $$\rho_{jk}^{ij} = \langle \Phi_j | \hat{E}_{ij} | \Phi_k \rangle$$ depend on the details of how orbitals i and j are occupied in CSFs J and K. The density matrix thus nicely summarizes the many CI expansion coefficients $$A_K$$ in a few values. Only the active-active block of $$\rho$$ is of interest, as $$\rho_{ij} (i \neq j)$$ vanishes when i or j is a doubly occupied orbital, and $$\rho_{ii} = 2$$ if $$\phi_i$$ is doubly occupied. Thus, judicious choice of the active orbitals can provide important insights, despite the apparently complex nature of the total wavefunction.

Orbital Invariances

It is well known that the RHF wavefunction is unchanged, apart from phase, by orthogonal transformation of the occupied orbitals,

$$\Psi = A \{ \phi_1(1) \phi_2(2) \cdots \phi_N(N) \},$$

$$\phi' = \phi U,$n

$$\Psi' = A \{ \phi'_1(1) \phi'_2(2) \cdots \phi'_N(N) \} = \pm \Psi.$$n

The invariance arises because mixing one doubly occupied orbital with another leaves the determinantal form of Equation 6 unchanged. The orbital transformation U also leaves the RHF density matrix unchanged, $$\rho_{ij} = 2 \delta_{ij}.$$
The FORS or CASSCF MCSCF wavefunction is also invariant under orthogonal transformation of the orbitals, provided \(U\) in Equation 7 is blocked so that the orbital mixing between active orbitals and doubly occupied orbitals is zero. Rotation within the doubly occupied orbitals leaves each individual CSF unchanged, for the same reason the RHF wavefunction is invariant. Mixing among the active orbitals changes a CSF if the two orbitals mixed have different occupation numbers in that particular CSF. For example, if a doubly occupied and a vacant orbital in one CSF are mixed, this CSF is changed. However, the full active space wavefunction will contain two other CSFs, one with both orbitals singly occupied and one with these two orbitals vacant and doubly occupied, respectively. The orbital rotation causes the CI coefficients of these three CSFs to be changed, in a manner that preserves the energy and density of the total wavefunction. We say that the orbital rotation engenders a rotation of the CI coefficients. If only the first-order density matrix for the transformed orbitals \(\phi'\) is needed, this is obtained by

\[
\rho' = U \rho U^\dagger.
\]

In the event that it is desirable to know the updated \(A'_K\) values, it is not necessary to repeat the CI calculation in the rotated orbital basis, as these can be computed from the specific orbital transformation \(U\) (125–127). The rest of this section covers various choices of orbital transformations that are particularly chemically revealing.

The first such orbital set is the natural orbitals (NOs) (128), which are defined by requiring that the density matrix \(\rho'\) in Equation 9 be diagonal. The diagonal elements are known as the natural orbital occupation numbers (NOON), which sum to the total number of electrons in the active space. Because NOs extremize the NOON by diagonalization of \(\rho\), they provide the most compact CSF expansion \(A_K\) possible. The NOON values serve as an indication of the multireference character, which is low if the NOON are near two and zero (states with unpaired electrons will have some NOON near one). A special case was mentioned in the Introduction where the occupation number (2B\(^2\) in Equation 3) of the second orbital was used as a measure of the biradical character of a TCSCF calculation. The presence of occupation numbers between 0.1 and 1.9 indicates considerable multireference character. A natural orbital is usually delocalized over the active region of the molecule, into a bonding or antibonding shape.

Another useful orbital choice is the localized MOs (LMOs). The invariance of the closed shell wavefunction expressed in Equation 8 permits transformation to orbitals closely resembling chemical concepts, such as bonds and lone pairs. Lennard-Jones & Pople exploited this in their equivalent orbitals (129), and in the intervening years a number of different mathematical criteria have been...
proposed to localize orbitals. The two most commonly used are maximization of the orbital self energy sum (130),
\[ \sum_i [ii\mid ii] , \]
and maximization of the separation of orbital centroids (131),
\[ \sum_i |\langle i\mid r\mid i \rangle|^2 , \]
which are commonly referred to as the Ruedenberg and Boys localizations, respectively, although both were proposed in the original paper by Edmiston & Ruedenberg (130).

Although LMOs have most commonly been used for Hartree-Fock wavefunctions, the application of localization criteria are considerably more general. A mathematical criterion such as maximizing the sums in Equations 10 or 11 can be applied to any set of orbitals, in particular to the orbitals defining the MCSCF wavefunction.

Some Examples

Figure 5 shows Ruedenberg-type MCSCF LMOs for H\(_2\) and PF\(_3\)Cl\(_2\), which should be compared with the schematic active space diagrams shown in Figures 3 and 4c. Clearly, the result of the MCSCF optimization and the diagrams initially used to design the wavefunction correspond closely! Note that the localized active orbitals remain orthogonal, by virtue of using an orthogonal transformation in Equation 7, leading to the presence of orthogonalizing tails in the LMOs. The diagonal density matrix elements shown reflect the electron occupancy of the LMO and permit a population analysis of the active electrons. The off-diagonal elements, which are termed bond orders, are indicative of bonding or antibonding interactions (positive or negative sign) between the LMOs.

LMOs and their corresponding density matrix from Equation 9 were used to interpret the origin of a barrier for the symmetry allowed hydrogen exchange reaction between ethane and ethylene (15) and to understand the extent of aromaticity in a number of X\(_3\)Y\(_3\)H\(_6\) analogs of benzene (132). For example, in benzene the bond order element connecting nearest neighbor (ortho) \(\pi\) LMOs is 0.620, but the para interaction is antibonding, \(-0.279\). The presence of resonance in benzene is revealed by this antibonding interaction, as well as by a diminution of the ortho interaction relative to ethylene, where the LMO \(\pi\) bond order is 0.897.

It is sometimes useful to extract information from the CI expansion coefficients directly, rather than from their summary in the density matrix. The
Figure 5  Ruedenberg-type localized orbitals for multiconfiguration self-consistent field wavefunctions. The electron occupation numbers are shown below, and the bond orders are between orbitals. Note that more than 1.5\textsuperscript{e−} are transferred to the axial Cl atoms in PF\textsubscript{3}Cl\textsubscript{2}. The PCl bond order is weak, and moreover there is an antibonding interaction between the two Cl atoms of −0.239. These results may be compared with the PCl bond order 0.958 found in a two configuration self-consistent field wavefunction for the model compound PCIF\textsubscript{2}.

following two equivalent full valence MCSCF wavefunctions for H\textsubscript{2}

\[ \psi_{\text{NO}} = 0.9940\sigma_{g}^{2} - 0.1097\sigma_{u}^{2} \]

\[ \psi_{\text{LMO}} = 0.7804S_{L}^{1}S_{R}^{1} + 0.4421S_{L}^{2} + 0.4421S_{R}^{2} \]

are constructed from the bonding and antibonding NOs, and left (S\textsubscript{L}) and right (S\textsubscript{R}) hydrogen LMOs, respectively. The first form shows RHF dominance at the equilibrium distance, whereas the second shows 61\% (0.7804\textsuperscript{2}) covalent and 39\% ionic character. Of course symmetry dictates that the two ionic configurations H\textsuperscript{−}H\textsuperscript{+} and H\textsuperscript{+}H\textsuperscript{−} have equal contributions in this homonuclear case. The second expansion is an example of what has been termed the MCSCF/LMO/CI
Figure 6 Valence bond structures. (top and bottom) The $\pi$ and $\sigma$ electronic structures, respectively. Solid line, covalent structure; one electron is contributed by both M and E. Arrow, ionic structure; both electrons are possessed by the atom at the base of the arrow, denoting a dative bond. Resonance structures A, E, and I are overall neutral. Resonance structures B, G, and H are termed nucleophilic, as their formal charge on E is negative. Conversely, resonance structures C, D, and F are termed electrophilic.

method. The large ionic character in the H$_2$ LMO CI expansion is due to the use of orthogonal orbitals. The ionic contribution can be made to vanish, apparently, by permitting the orbitals to be nonorthogonal in a valence bond model. A very good exploration of MO versus valence bond pictures of H$_2$ has been given by Hurley (133).

Another, more realistic example of the MCSCF/LMO/CI analysis is the case of double bonds between transition metals (M) and main group elements (E) (3). The active space used was the four orbitals directly involved in the double bond, so only two d orbitals of M are active. The orbitals were localized separately within the $\sigma$ and $\pi$ spaces, to avoid the formation of banana bonds. Of the 20 configurations in a 4-electron, 4-orbital active space, the 9 valence bond structures in Figure 6 are found to be important.

The nine chemically sensible structures in Figure 6 always comprise 95% of the wavefunction, with only very small admixtures of the remaining structures, which contain 0, 1, 3, or 4 electrons in the $\sigma$ orbitals. Resonance structures in which E acts as a $\sigma$-donor should be much more important than those in which it acts as an $\sigma$-acceptor. Similarly, M $\rightarrow$ E back-bonding resonance structures should be more prevalent in the $\pi$ bonds. Finally, for the coordination of main group fragments to early, high-valent transition metals, resonance structures that are nucleophilic and neutral should dominate over electrophilic resonance structures. As one goes to lower-valent complexes, this trend is expected to start to reverse. Each of these chemically intuitive expectations is supported by the MCSCF/LMO/CI analysis.
For the systems \( H_2M = EH_2 \), with \( M = Ti, Zr, Hf, Nb, \) or \( Ta \) and \( E = C \) or \( Si \), the covalent structure \( A \) together with the \( \sigma \)-ylide structure \( D \) account for 60–80% of the total wavefunction. Before this type of MCSCF/LMO/CI analysis, the \( \sigma \)-ylide resonance structure had not been suspected as a major contributor to alkylidene \( (E = C) \) compounds, which were typically discussed in terms of Fischer carbenes, structure \( A \), or Schrock carbenes, structure \( F \). Table 1 contains a breakdown of these 10 molecules in terms of contributions from neutral, nucleophilic, and electrophilic structures.

It is worth noting that for \( E = Si \), the species are multiconfigurational in character. For the five metals considered, the NOON of the \( \pi^* \) orbital varies from 0.19 to 0.44. This observation is not limited to multiple bonds involving transition metals. \( E = E' \) double bonds (with \( E, E' = Si, Ge, Sn \)) also exhibit significant multiconfigurational (i.e. diradical) character and are generally nonplanar (2). Further details about the nature of main-group transition metal multiple bonding, including the effect of Cl substitution, and an analysis of \( M/E \) triple bonds can be found in the original papers and in a recent review (3).

The active orbitals of a full valence space wavefunction can be localized by an external criterion that maximizes the overlap between the s and p orbitals of the free atom, with the MCSCF localized molecular orbital (13). The resulting LMOs typically have overlap with the true atomic orbital in excess of 0.95, showing the great extent to which molecular wavefunctions are composed from their constituent atoms. Further, the molecular MCSCF configurations built

<table>
<thead>
<tr>
<th>Determinants</th>
<th>Ti</th>
<th>Zr</th>
<th>Nb</th>
<th>Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>M = E</td>
<td>44.6</td>
<td>36.5</td>
<td>40.0</td>
<td>32.8</td>
</tr>
<tr>
<td>M ( \doteq ) E</td>
<td>3.8</td>
<td>2.6</td>
<td>4.7</td>
<td>2.9</td>
</tr>
<tr>
<td>M ( \doteq ) E</td>
<td>1.9</td>
<td>9.7</td>
<td>5.5</td>
<td>14.1</td>
</tr>
<tr>
<td>M ( \doteq ) E</td>
<td>34.6</td>
<td>36.2</td>
<td>31.5</td>
<td>30.9</td>
</tr>
<tr>
<td>M ( \doteq ) E</td>
<td>8.2</td>
<td>7.3</td>
<td>8.6</td>
<td>6.8</td>
</tr>
<tr>
<td>M ( \doteq ) E</td>
<td>0.3</td>
<td>2.6</td>
<td>1.6</td>
<td>6.3</td>
</tr>
<tr>
<td>M ( \doteq ) E</td>
<td>5.4</td>
<td>2.6</td>
<td>5.7</td>
<td>3.1</td>
</tr>
<tr>
<td>M ( \doteq ) E</td>
<td>0.2</td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>M ( \doteq ) E</td>
<td>0.8</td>
<td>2.3</td>
<td>2.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Neutrophilic</td>
<td>53.6</td>
<td>46.1</td>
<td>50.6</td>
<td>42.7</td>
</tr>
<tr>
<td>Nucleophilic</td>
<td>36.8</td>
<td>48.5</td>
<td>38.6</td>
<td>51.4</td>
</tr>
<tr>
<td>Electrophilic</td>
<td>9.4</td>
<td>5.3</td>
<td>10.8</td>
<td>6.1</td>
</tr>
</tbody>
</table>

*Nucleophilic structures are defined as those with \( M^+E^- \) ionicity. Electrophilic means \( M^+E^+ \).*
from these very atomic-like orbitals can be transformed into products of atomic
(and ionic) states, as if these were the exact s and p orbitals of the free atoms
(134, 134a). Expression of the MCSCF CSFs in terms of these ground- and
excited-state products offers a chance to follow electronic structure changes
across a potential surface in terms of these states. For example, the barrier on
the C\(^2\Sigma^+\) surface of CH is found to occur in the region in which the asymptotic
\(^1\text{D}\) state of C changes to \(^1\text{S}\) character, before ultimately becoming predominately
a \(^3\text{P}\) state atom at \(R_{\text{eq}}\) (135).

The interpretation of the CI expansion based on orthogonal LMOs in terms
of covalent and ionic contributions, or the analysis of molecular MCSCF wave-
functions in terms of atomic states seems reminiscent of valence bond terminol-
y. Two recent attempts to analyze MCSCF wavefunctions in valence bond
terms have been made. Although both use the acronym CASVB, they take rather
different approaches. In the first, the active orbitals are localized by one of the
procedures described here, either retaining orthogonality (136) or not (136a).
The wavefunction is then reexpressed in terms of these orbitals, combined with
nonorthogonal Rumer spin functions. The systems considered (136) include
benzene, where the occupation of Dewar structures was found to be about half
that for Kekule structures. The second approach (137) generates nonorthogonal
orbitals, to maximize the covalent valence bond contribution to the full MCSCF
wavefunction. This procedure was applied to CH\(_2\), CH\(_4\), and O\(_3\).

DYNAMIC CORRELATION METHODS

Although the MCSCF wavefunction has sufficient flexibility to model the large
changes in electronic structure that can occur during chemical reactions, its
energy unfortunately does not possess sufficient accuracy. It is common for
barrier heights or overall reaction thermodynamics to be in error by 10–15
kcal/mol or even more. The origin of the error is clear: Many of the valence
electrons have been treated as filled closed-shell orbitals with no recovery of
correlation energy, whereas the active electrons have only a partial recovery of
correlation.

Since the 1960s (106), correlation energy has been divided into near-de-
generacy and dynamical contributions, based on a partitioning of orbitals into
internal and external sets. The internal orbitals are the valence orbitals, some
of which have been included in the active region. Excitations of electrons
within the active region involve relatively small promotion energies, and hence
the term near-degeneracy is applied to this portion of the correlation energy.
Excitation of the active electrons or inert valence electrons into the external
(or virtual) orbitals of the MCSCF wavefunction accounts for the remaining
correlation energy, which is termed dynamic. Recovery of dynamic correlation
energy is needed to improve upon MCSCF energetics. This section describes four alternatives for dynamic correlation corrections: multireference (MR)-CI, empirical corrections, MR-PT, and cluster approaches.

**MR-CI**

The most obvious approach to dynamic correlation, and therefore the first that received significant attention for molecular calculations, is MR-CI, using the MCSCF as the reference wavefunction. The immediate problem is that there are very many configurations in such a CI. The smallest conceivable systematic MR-CI is the first-order CI (FOCI) (104, 105, 138), in which no more than one electron is promoted from the MCSCF configurations into the external orbital space. A subset of FOCI, restricting the reference configurations to those present in a GVB calculation, is termed a polarization CI (POL-CI) (139). Next, one can add all configurations in which two electrons are promoted to external orbitals, and this is called by analogy the second-order CI (SOCI). Early workers (104, 107) tried to decrease the size of the SOCI by including only those double excitations with a direct Hamiltonian matrix element with one of the MCSCF configurations, terming this extended CI. Our experience is that FOCI energies are not necessarily a systematic improvement over MCSCF energies, but that SOCI provides accurate energetics (113). Unfortunately, SOCI is difficult to apply to any but the smallest molecules, as the number of configurations rapidly becomes enormous. The most commonly used MR-CI program is probably that of Werner & Knowles (140–142), whose determinant-based internally contracted scheme facilitates extending the correlation treatment to the valence inactive electrons. A 1996 paper (142a) on CSF-based MR-CI is also of note, and contains additional references to the MR-CI literature.

**Empirical Corrections**

A semiempirical correction for dynamical correlation energy known as the intra-atomic correlation correction (IACC) was developed by Lam et al (134) and Schmidt et al (134a) (Ruedenberg’s group). The IACC method uses the MCSCF wavefunction expressed in the atomic/ionic product state function basis described in the previous section. The known correlation energies of the free atoms and ions are added to the diagonal elements of the Hamiltonian in this atomic product basis. This empirically adjusted Hamiltonian improves the potential curves of four out of five valence states of the CH radical (134a). However, the IACC model is most easily applied when the full valence space is active, and as yet there is no extension to polyatomic systems.

Another empirical correction known as scaled external correlation (SEC) (135) applies to the MR-CI energy rather than to the MCSCF energy. The correction formula is intended to account for AO basis set truncation as well as...
the omission of excitation levels higher than two. It is given by
\[ E(SEC) = E(MR-CI) + \frac{E(MR-CI) - E(MCSCF)}{F}. \]
Here the scale factor \( F \) is found to vary with the basis set used and is generally obtained by calibration against experimental energy differences.

**MR-PT**

The most successful method to date for recovery of dynamical correlation energy in MCSCF wavefunctions is second-order perturbation theory. We give only a few references from the period prior to 1987 (143–145), whereas numerous treatments have since been proposed (146–177). The most widely applied of these methods is CASPT2 (149–152), and several reviews of its effectiveness are available (178–181). These multireference perturbation theory methods differ in how the Hamiltonian is partitioned, as well as in how the MCSCF orbitals are canonicalized. Because an excellent review of the theoretical differences between most of these methods is available (167), the comparison here is primarily numerical. Second-order results seem accurate enough for predictive chemistry, but some work at third-order has been attempted (146, 152, 153, 163, 166).

At second order, perturbation theory consists of single and double excitation contributions and hence is expected to resemble SOCl in the recovery of dynamical correlation energy. It is, however, much more efficient, requiring about the same amount of computation as determination of the underlying MCSCF wavefunction (178) and thus can be applied almost routinely. Implementation of CASPT2 requires construction of the third-order density matrix, as well as integrals with two virtual orbital indices (179). This places a limit on the size of the active space comparable to that for the underlying MCSCF computation.

The most systematic tests of accuracy at second order have employed the CASPT2 approach. Computations on a comprehensive test set of molecules (178) show CASPT2 reproduces bond distances to 0.01 Å and atomization energies to within 3–6 kcal/mol per broken electron pair (systematically underestimating these). This means an isogyric (spin conserving) reaction energy is expected to be accurate to 3 kcal/mol, provided an adequate atomic basis set is used. Vertical excitation energies for a variety of organic molecules are reproduced within 0.2 eV, with only a few exceptions (181). Clearly, these levels of accuracy are sufficient for reliable prediction of chemical results. A limited study of properties at second order exists (169). A recent study of several diatomics indicates third-order CASPT3 dissociation energies and frequencies are more accurate than the second-order results (152).

Less systematic information is available on the accuracy of the other multireference perturbation treatments. However, it is customary to compare each method with a full CI benchmark on methylene (182). Table 2 gathers the
Table 2  Total energies and singlet-triplet splitting of CH₃ for various second-order multireference perturbation theories

<table>
<thead>
<tr>
<th>Method</th>
<th>Reference</th>
<th>(^1\text{A}_1)</th>
<th>(^3\text{B}_1)</th>
<th>Splitting (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>Authors</td>
<td>-38.886297</td>
<td>-38.927947</td>
<td>26.14</td>
</tr>
<tr>
<td>MP2</td>
<td>Authors</td>
<td>-38.996127</td>
<td>-39.024889</td>
<td>18.05</td>
</tr>
<tr>
<td>MCSCF</td>
<td>Authors</td>
<td>-38.945529</td>
<td>-38.965954</td>
<td>12.82</td>
</tr>
<tr>
<td>FOCI</td>
<td>Authors</td>
<td>-38.980168</td>
<td>-39.003242</td>
<td>14.48</td>
</tr>
<tr>
<td>SOCI</td>
<td>Authors</td>
<td>-39.025804</td>
<td>-39.044928</td>
<td>12.00</td>
</tr>
<tr>
<td>CASPT2D</td>
<td>150</td>
<td>-39.011773</td>
<td>-39.036804</td>
<td>15.71</td>
</tr>
<tr>
<td>CASPT2N</td>
<td>150</td>
<td>-39.013078</td>
<td>-39.037664</td>
<td>15.43</td>
</tr>
<tr>
<td>CASPT2 (g3)</td>
<td>151</td>
<td>-39.013049</td>
<td>-39.033686</td>
<td>12.95</td>
</tr>
<tr>
<td>CASPT3</td>
<td>152</td>
<td>-39.023397</td>
<td>-39.044195</td>
<td>12.30^b</td>
</tr>
<tr>
<td>GMP3</td>
<td>153</td>
<td>-39.023222</td>
<td>-39.04338</td>
<td>12.65^b</td>
</tr>
<tr>
<td>MRMP2, (F_{\text{av}})</td>
<td>159</td>
<td>-39.011715</td>
<td>-39.036886</td>
<td>15.79</td>
</tr>
<tr>
<td>MRMP2, (F_{\text{hs}})</td>
<td>159</td>
<td>-39.011715</td>
<td>-39.033025</td>
<td>13.37</td>
</tr>
<tr>
<td>GVVPT3</td>
<td>163</td>
<td>-39.023090</td>
<td>-39.042709</td>
<td>12.31^b</td>
</tr>
<tr>
<td>MCQDPT</td>
<td>165</td>
<td>-39.011978</td>
<td>-39.037028</td>
<td>15.72^c</td>
</tr>
<tr>
<td>MROPT1</td>
<td>167</td>
<td>-39.012836</td>
<td>-39.037929</td>
<td>15.75</td>
</tr>
<tr>
<td>MROPT2</td>
<td>167</td>
<td>-39.013328</td>
<td>-39.032886</td>
<td>12.27</td>
</tr>
<tr>
<td>ZTE-EN2</td>
<td>176</td>
<td>-39.027388</td>
<td>-39.048230</td>
<td>13.08</td>
</tr>
</tbody>
</table>

^aRestricted open-shell RMP2 theory (182a, 182b).
^bThis is a result at third order.
^cComputed by the authors using H Nakano’s code (165). The value in the table is not found in Reference 165 itself; we have used this computer code to calculate it according to Reference 165’s formalisms.

available total energies and singlet-triplet gaps. The zero-order MCSCF wavefunction used in all cases is the full valence space, specifically six electrons in six orbitals. Unfortunately, this standard test case is one where the MCSCF result is already quite good, and thus many second-order splittings are worse than the MCSCF result.

No two multireference methods give the same result, although the total energies are reasonably similar. The average dynamical correlation energy recovered for the singlet state is 81% and for the triplet, 85%. These values are comparable to single-reference MP2, which usually recovers about 80% of the total correlation energy (183). [Here, 78% (singlet) and 69% (triplet) of the total correlation energy is recovered by single reference MP2.] Of course, some correlation is already picked up by the MCSCF wavefunction. In this instance, the near-degeneracy correlation recovered by the MCSCF is 42% (singlet) and
27% (triplet) of the total. SOCI is of course more accurate than perturbation theory, recovering 98% (singlet) and 97% (triplet) of the dynamical correlation energy. Because the different multireference perturbation treatments give similar total energies, we might speculate that their accuracy is about the same as that of CASPT2, namely 3–6 kcal/mol per electron pair. However, more extensive numerical tests of the competing methods, of the sort CASPT2 has been subjected to, would be highly desirable.

As we have mentioned, one strength of MCSCF is its ability to treat excited states. Applying the perturbative treatment to each state separately might give reversed state orders, if the two MCSCF states are energetically close. This is unphysical if the states are of the same symmetry, but such problems can be circumvented by application of quasidegenerate perturbation theory (QDPT). Various possible approaches have been reviewed recently by Malrieu (171). We summarize one such approach, not only to indicate how QDPT treats several states on an equal footing, but to illustrate the types of computations involved in second-order theories.

In Nakano’s implementation of QDPT (165), a model space is chosen by selecting the desired roots from the Hamiltonian evaluated over the MCSCF configurations. In most circumstances, state averaging over all states included in the model space is used during determination of the MCSCF orbitals. Denoting the MCSCF states included in the model space as \( \alpha, \beta \), the effective Hamiltonian is

\[
\langle \alpha | H_{\text{eff}} | \beta \rangle = E_{\text{MCSCF}}^{\beta} \delta_{\alpha\beta} + \sum_X \langle \alpha | V | X \rangle \langle X | V | \beta \rangle / (E^{\beta} - E^{X}_X),
\]

where the sum \( X \) is over singly and doubly excited configurations, into the external orbital space of the MCSCF. The final term of Equation 12 is symmetrized in \( \alpha \) and \( \beta \) when applied to off-diagonal elements. In second quantization notation, the perturbation is

\[
V = \sum_p \sum_q \sum_r \sum_s \[pq|rs\] \hat{E}_{pq,rs} + \sum_p \sum_q \sum_r \sum_s \[pq|rs\] \hat{E}_{pq,rs}.
\]

The zero-order energy from the unperturbed Hamiltonian is

\[
E_K^{\alpha} = \langle K | H^0 | K \rangle, \quad H^0 = H - V.
\]

The orbitals are canonicalized by diagonalizing the closed shell-like Fock operator \( F \) within the filled, active, and virtual blocks,

\[
F_{pq} = h_{pq} + \sum_r \sum_s \rho_{rs} \left( [pq|rs] - \frac{1}{2} [pr|qs] \right).
\]

where \( \rho \) is the state-averaged first-order density matrix. This yields the orbital energies \( \varepsilon \) appearing in the perturbation (Equation 13), and makes \( H^0 \) a sum
of one-electron operators. Efficient computation (165) of the matrix elements appearing in Equation 12 requires generation of the third-order density matrix over active orbitals, as well as transformed integrals with two virtual orbital indices. Evaluation of Equation 12 is much more efficient than MR-CI, as matrix elements of the type $\langle X | H | X' \rangle$ are not needed. In the single-reference limit, this Hamiltonian partitioning and orbital canonicalization choice reduce to normal MP2 for a closed shell and to the OPT1 variant (184) of restricted high-spin open-shell perturbation theory.

Note that $H_{\text{eff}}$ contains off-diagonal corrections, as well as single-state corrections to the diagonal terms. Diagonalization of $H_{\text{eff}}$ yields simultaneously corrected energies at second order for all states included in the model space. Care must be taken to include all relevant states in the model space. Nakano (165) illustrates the merit of this “perturb first, diagonalize last” approach near an avoided crossing of two $3\Sigma^+_g$ states in LiF.

**MR-CC**

Other approaches to the problem of dynamical correlation include the averaged coupled-pair functional (ACPF) (185–187), and the related multireference version of the coupled electron pair approximation (MRCEPA) (188–191). These methods attempt to correct for the unlinked cluster terms that prevent size-extensivity in MR-CI. Some work in the application of coupled-clusters (CC) methodology to multireference systems has been attempted in recent years (192–202). The success of single-reference CC methods ensures that a great deal of additional work on MR-CC programs is to be expected in the future.

**ADDITIONAL TOPICS**

This review focused on the problem of generating a MCSCF wavefunction at a single point on a potential energy surface, its interpretation, and the options for recovering its dynamic correlation energy. Modern quantum chemistry requires more global knowledge of potential energy surfaces, and naturally there is a large body of information related to MCSCF surfaces.

Because MCSCF wavefunctions are especially useful for exploring the details of potential energy surfaces, particularly through reactive channels, it is important to have analytic first- and second-derivatives for MCSCF wavefunctions. The computation of these derivatives of the MCSCF energy with respect to nuclear degrees of freedom is a fundamental requirement for exploring these potential surfaces.

A description of the interaction of two or more electronic states (for example, as a result of surface crossings or avoided crossings) requires MCSCF wavefunctions as a starting point. The determination of spin-orbit coupling or
vibronic coupling matrix elements is most conveniently accomplished using MCSCF wavefunctions that are averaged over the states of interest: that is, using state-averaged MCSCF wavefunctions. One then needs at least the first derivatives of SA-MCSCF wavefunctions with respect to the atomic coordinates. Transitions between different electronic states can be caused by radiation, vibronic coupling, or spin-orbit coupling, and these subjects are closely related to nuclear derivative theory.

Derivatives of the electronic energy with respect to parameters other than nuclear degrees of freedom are also important in chemistry. Examples include polarizabilities and magnetic properties. Miscellaneous topics include the extended Koopmans’ theorem and the occurrence of orbital symmetry breaking.

Because time and space do not permit the inclusion of this material in this review, we intend to survey these topics in a second chapter next year.

ACKNOWLEDGMENTS

We have benefited for many years from the expertise of Professor Klaus Ruedenberg in the area of MCSCF theory and gratefully take this opportunity to thank him for sharing this with us. In addition, we thank Dr. Michel Dupuis for providing us with several generations of MCSCF orbital optimization codes. The work presented here is a composite of efforts supported by the Air Force Office of Scientific Research, the National Science Foundation, and the Ames Laboratory of the Department of Energy.

Literature Cited

17. Roos BO. 1992. In Lecture Notes in


264 SCHMIDT & GORDON

124. For example, Brett Bode’s MacMolPlt, available from http://www.msg.ameslab.gov/GAMESS/GAMESS.html
164. Hoffmann MR. 1995. See Ref. 204, pp. 1166–90.
266 SCHMIDT & GORDON


# Annual Review of Physical Chemistry

## Volume 49, 1998

### CONTENTS

- **MOLECULES IN OPTICAL, ELECTRIC, AND MAGNETIC FIELDS:**
  - A Personal Perspective, A. D. Buckingham 0
  - SPECTROSCOPY OF ATOMS AND MOLECULES IN LIQUID HELIUM, J. Peter Toennies, Andrei F. Vilesov 1
  - Structure and Transformation: Large Molecular Clusters as Models of Condensed Matter, Lawrence S. Bartell 43
  - The Shuttle Glow Phenomenon, Edmond Murad 73
  - Ultrafast Solvation Dynamics Explored by Femtosecond Photon Echo Spectroscopies, Wim P. de Boeij, Maxim S. Pshenichnikov, Douwe A. Wiersma 99
  - Chemical Reaction Dynamics Beyond the Born-Oppenheimer Approximation, Laurie J. Butler 125
  - Explosives Detection: A Challenge for Physical Chemistry, Jeffrey I. Steinfeld, Jody Wormhoudt 203
  - The Construction and Interpretation of MCSCF Wavefunctions, Michael W. Schmidt, Mark S. Gordon 233
  - Molecular Electronic Spectral Broadening in Liquids and Glasses, Anne B. Myers 267
  - Scanning Tunneling and Atomic Force Microscopy Probes of Self-Assembled, Physisorbed Monolayers: Peeking at the Peaks, Leanna C. Giancarlo and, George W. Flynn 297
  - Proton-Coupled Electron Transfer, Robert I. Cukier, Daniel G. Nocera 337
  - Nanocrystal Superlattices, C. P. Collier, T. Vossmeyer, J. R. Heath 371
  - Computational Approach to the Physical Chemistry of Fullerenes and Their Derivatives, Wanda Andreoni 405
  - OPTICAL STUDIES OF SINGLE MOLECULES AT ROOM TEMPERATURE, X. Sunney Xie, Jay K. Trautman 441
  - HIGH RESOLUTION SPECTROSCOPY IN THE GAS PHASE: Even Large Molecules Have Well-Defined Shapes, David W. Pratt 481
  - Computer Simulations with Explicit Solvent: Recent Progress in the Thermodynamic Decomposition of Free Energies, and in Model, Ronald M. Levy, Emilio Gallicchio 531
  - INTERFACES AND THIN FILMS AS SEEN BY BOUND ELECTROMAGNETIC WAVES, Wolfgang Knoll 569