

## Modern valence bond representations of CASSCF wavefunctions

Thorstein Thorsteinsson<sup>1</sup>, David L. Cooper<sup>1</sup>, Joseph Gerratt<sup>2</sup>,  
Peter B. Karadakov<sup>2</sup>, Mario Raimondi<sup>3</sup>

<sup>1</sup> Department of Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, UK

<sup>2</sup> School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK

<sup>3</sup> Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via Golgi 19, I-20133 Milano, Italy

Received May 5, 1995/Accepted January 14, 1996

**Abstract.** Exact transformations of “ $N$  electrons in  $N$  orbitals” CASSCF structure spaces are examined that lead to modern valence bond representations, in which the total wavefunction is dominated by covalent structures built from a common product of *nonorthogonal* orbitals. The resulting descriptions of the electronic structure may be compared directly with those that arise in the spin-coupled (or *full-GVB*) approach. Using singlet methylene, methane and ozone as representative examples, various overlap-based and energy-based criteria are investigated for generating modern VB representations of “ $N$  in  $N$ ” CASSCF wavefunctions, which we denote CASVB.

**Key words:** CASSCF – Spin-coupled – VB – CASVB

### 1 Introduction

Complete active space self-consistent field (CASSCF) calculations, as implemented in many of the standard *ab initio* packages of quantum chemistry, are now essentially routine. Such a wavefunction consists of all configurations of the appropriate spatial symmetry and total spin which may be generated by distributing  $N$  electrons in  $m$  orthogonal orbitals [1]. Simultaneous optimisation of the orbitals and of the configuration interaction coefficients typically leads to reliable energy surfaces and molecular properties, although CASSCF calculations are more often used as the precursors for more sophisticated treatments that take better account of (mostly dynamical) electron correlation.

One obvious drawback of multiconfiguration SCF approaches is the difficulty of interpretation. Most chemists do not “feel comfortable” with large numbers of configuration interaction (CI) coefficients. Similarly, the (equivalent) natural orbital representation, obtained by diagonalising the one-particle density matrix, presents the problematic interpretation of fractional orbital occupation numbers. On the whole it is usually far from straightforward to extract *simple*, chemically appealing descriptions from CASSCF wavefunctions. The same is not true of those

modern forms of *ab initio* valence bond (VB) theory that are based on the full optimisation of nonorthogonal orbitals and of the associated spin-coupling pattern.

Of course, a CASSCF wavefunction is invariant under linear transformations of the defining orbitals, and so we may choose to transform the orbitals to a non-orthogonal set that is similar to those which arise in VB theory. We have introduced the mnemonic CASVB for a CASSCF wavefunction represented in this way. For any (nonsingular) linear transformation of the active orbitals

$$\{\phi^{\text{CASVB}}\} = \{\phi^{\text{CASSCF}}\} \mathbf{O}, \quad (1)$$

there exists a corresponding transformation of the structure space

$$\{\Phi^{\text{CASVB}}\} = \{\Phi^{\text{CASSCF}}\} \mathbf{T}(\mathbf{O}), \quad (2)$$

in which  $\{\Phi^{\text{CASSCF}}\}$  is the row-vector of  $N_{\text{CAS}}$  CAS structures (configurations) defined in terms of the orbitals  $\{\phi^{\text{CASSCF}}\}$ , and  $\{\Phi^{\text{CASVB}}\}$  is the corresponding row-vector defined in terms of the  $\{\phi^{\text{CASVB}}\}$ . Essentially this problem has been considered by Malmqvist in Ref. [2], in the context of the so-called ‘‘CASSCF state interaction method’’ [3]. The key to an efficient solution of this problem involves writing the orbital transformation as a product of  $m \times m$  simple ‘‘updates’’ of the form

$$\mathbf{O}_{\mu\nu}(\lambda): \phi_\nu \rightarrow \phi_\nu + \lambda \phi_\mu. \quad (3)$$

The corresponding structure transformations are particularly simple to evaluate. A complete description of this scheme may be found in Ref. [2]. Further details of our specific implementation [4] for use in orbital optimisation will be published separately. This paper is concerned with the insights gained from the CASVB interpretations, but we stress that the *practicality* of this approach lies in the efficient transformation of the structure space.

An important role in the resurgence of interest in valence bond approaches has been played by spin-coupled (SC) theory [5]. The SC wavefunction consists of a single product of spatial orbitals and a normalised total spin function. Each singly occupied orbital is typically expressed as a completely general linear combination of basis functions stemming from all the nuclear centres, and the total spin function is expanded in the full spin space. It has become clear that an  $N$ -electron SC wavefunction, based on a single product of  $N$  singly occupied fully optimised nonorthogonal orbitals, has much in common with the analogous ‘‘ $N$  in  $N$ ’’ CASSCF description, based on all configurations which may be obtained by distributing  $N$  electrons in  $N$  orbitals. It seems likely that the space spanned by the  $N$  nonorthogonal orbitals of an SC wavefunction must be very similar to that spanned by the  $N$  orthogonal orbitals of the  $N$  in  $N$  CASSCF wavefunction. There are various pieces of evidence:

- SC potential energy and molecular property surfaces are found to be parallel to, and close to, the equivalent CASSCF results.
- Particularly for small values of  $N$ , the SC energy is usually only a few millihartree above the CASSCF energy.
- A full-CI calculation based on all distributions of the  $N$  electrons in the  $N$  spin-coupled orbitals leads to a solution in which the covalent part, i.e. the original single spatial configuration, is strongly dominant. Adding additional ‘‘ionic’’ configurations, in which one or more orbitals is doubly occupied, does not alter the basic qualitative picture.

All of this suggests that an  $N$ -electron SC calculation could be viewed as an excellent approximation to the analogous many-configuration  $N$  in  $N$  CASSCF wavefunction. Given also that it has usually proved very straightforward to extract much chemical and physical insight from SC calculations, it seems very worthwhile to seek CASVB representations which resemble the corresponding spin-coupled description.

The structure of this paper is as follows. Section 2 presents an overview of those features of the CASSCF and SC methods which are particularly relevant to the present work. Section 3 describes various criteria which might be used for selecting the orbital transformation  $\mathcal{O}$  in Eq. (1). Various results are discussed in Sect. 4 for three representative systems: singlet methylene, methane and ozone. Further discussion is presented in Sect. 5, with emphasis on the relationship with previous work and on the computational effort associated with the various CASVB criteria. We present our overall conclusions in Sect. 6.

## 2 The CASSCF and SC wavefunctions

In both the CASSCF and SC approaches, the orbital space is partitioned as follows:

- frozen core,
- optimised core,
- active orbitals,
- virtual orbitals.

The frozen core consists of doubly occupied orbitals which are *not* optimised in the calculation. These orbitals, which are typically taken to be the lowest-lying MOs from an SCF calculation, can be removed from the problem by means of simple modifications of the one-electron integrals [6]. The optimised core orbitals are also doubly occupied in all structures, but these orbitals are relaxed during the optimisation procedure. Due to the simple form of the core wavefunction, the core orbitals may be chosen as an orthonormal set and the active and virtual orbitals orthogonalised on the core, without loss of generality.

In the present paper, a spin-coupled configuration will be taken to mean a function of the general form

$$\Psi_{\text{SC}} = \mathcal{A}(\varphi_1^2 \varphi_2^2 \cdots \varphi_n^2 \Theta_{\text{pp}}^{2n} \phi_1 \phi_2 \cdots \phi_N \Theta_{\text{SM}}^N), \quad (4)$$

in which the  $\{\phi_\mu\}$  are the so-called spin-coupled orbitals and  $\Theta_{\text{SM}}^N$  is a normalised  $N$ -electron spin function (i.e. eigenfunction of  $\hat{S}^2$  and  $\hat{S}_z$ ). The  $\{\varphi_i\}$  are the (orthogonal) doubly occupied core orbitals and  $\Theta_{\text{pp}}^{2n}$  is the corresponding perfectly paired spin function for the  $2n$  core electrons. The total spin function  $\Theta_{\text{SM}}^N$  for the “active” electrons is expanded in the full spin space of dimension [7]

$$f_S^N = \frac{(2S + 1)N!}{(\frac{1}{2}N + S + 1)!(\frac{1}{2}N - S)!} \quad (5)$$

according to

$$\Theta_{\text{SM}}^N = \sum_{k=1}^{f_S^N} c_{S_k} \Theta_{\text{SM};k}^N, \quad (6)$$

in which the  $c_{sk}$ 's may be termed "spin-coupling coefficients". The merits of different choices of spin basis for spin-coupled wavefunctions are reviewed in Refs. [8, 9] the most commonly used being the Kotani, Rumer and Serber schemes [7]. Kotani spin functions may be generated by successive coupling of the spins of *individual* electrons, according to the usual rules for combining angular momenta, whereas the Serber spin functions correspond to the successive coupling of the spins (singlet or triplet) of *pairs* of electrons. The Rumer spin basis is based on coupling together singlet pairs of electrons in  $f_S^N$  linearly independent ways, and corresponds closely to classical VB notions of electron pairing. Rumer spin functions, unlike those from the Kotani or Serber schemes, are nonorthogonal.

The CASSCF wavefunction is constructed as a full-CI expansion of all  $N$  active electrons in all  $m$  active orbitals. By considering the possible spatial occupations, and for each of these the allowed modes of spin-coupling, the length of this expansion can be shown to be

$$N_{\text{CAS}}(N, m, S) = \frac{2S + 1}{m + 1} \binom{m + 1}{\frac{1}{2}N - S} \binom{m + 1}{\frac{1}{2}N + S + 1}, \quad (7)$$

commonly referred to as the Weyl formula [10]. Any full-CI wavefunction is invariant under (nonsingular) linear transformations of the defining orbitals, and our aim in this paper is to exploit this to suggest alternative representations of the active CASSCF orbital set.

It is instructive to compare the spin-coupled and CASSCF wavefunctions from the point of view of the number of variational degrees of freedom. Identical partitioning of the orbital spaces will be assumed and so we restrict ourselves to the "N in N" type of CASSCF wavefunction. The number of variational parameters associated with the core-active, core-virtual and active-virtual orbital rotations must of course be the same in the two cases. The difference between the two methods lies solely in the definition of the "active" part of the wavefunction. In this part the CASSCF wavefunction simply has  $N_{\text{CAS}} - 1$  free parameters, because all active-active orbital rotations are redundant. In comparison the spin-coupled wavefunction generally has  $f_S^N - 1$  linear parameters associated with variations in the spin-coupling and  $m \times (m - 1)$  nonlinear orbital parameters, although some of these may become redundant in special cases. The relationship between the two wavefunction parameter sets is quite complicated, and depends on the orbital representation chosen for the CASSCF. It will always be true, however, that the spin-coupled parameter space is a subspace of the CASSCF parameter space. As an illustration, we show in Table 1 the number of "active" variational degrees of freedom for varying number of electrons and spin. The large difference between the two sets of numbers, particularly for higher numbers of electrons, highlights the interpretational advantages of the spin-coupled wavefunction. The fact that the spin-coupled wavefunction continues to perform satisfactorily over this range is evidence that the method is probably physically sound as far as describing *non-dynamical* correlation effects is concerned.

The small difference in the active parts of the wavefunctions, caused by the relative lack of flexibility of the spin-coupled wavefunction, is likely to induce small changes in the core, active and virtual orbital spaces (and then further relaxation of the active part of the wavefunction). The magnitudes of these effects are likely to be closely related in most cases, with the possible exception of systems exhibiting near-singularities in the core-active, core-virtual or active-virtual orbital rotation

**Table 1.** Number of free variational parameters for “ $N$  in  $N$ ” CASSCF and spin-coupled wavefunctions not including orbital rotations involving core or virtual orbitals

| $N$ | $S$           | CAS     | SC   |
|-----|---------------|---------|------|
| 2   | 0             | 2       | 2    |
| 2   | 1             | 0       | 0    |
| 3   | $\frac{1}{2}$ | 7       | 7    |
| 4   | 0             | 19      | 13   |
| 4   | 1             | 14      | 14   |
| 5   | $\frac{1}{2}$ | 74      | 34   |
| 6   | 0             | 174     | 34   |
| 6   | 1             | 188     | 38   |
| 7   | $\frac{1}{2}$ | 783     | 55   |
| 8   | 0             | 1763    | 69   |
| 8   | 1             | 2352    | 83   |
| 9   | $\frac{1}{2}$ | 8819    | 113  |
| 10  | 0             | 19403   | 131  |
| 10  | 1             | 29699   | 179  |
| 11  | $\frac{1}{2}$ | 104543  | 241  |
| 12  | 0             | 226511  | 263  |
| 12  | 1             | 382238  | 428  |
| 13  | $\frac{1}{2}$ | 1288286 | 584  |
| 14  | 0             | 2760614 | 610  |
| 14  | 1             | 5010004 | 1182 |

parameter sets. An analogous discussion would apply to more general VB and CASSCF wavefunctions, with differing numbers of active orbitals and active electrons.

### 3 CASVB criteria

We start by rewriting the CAS wavefunction in the form

$$\Psi_{\text{CAS}} = C_{\text{cov}} \Psi_{\text{cov}} + C_{\text{ion}} \Psi_{\text{ion}}, \quad (8)$$

in which all the wavefunctions are normalised, but  $\Psi_{\text{cov}}$  (covalent) and  $\Psi_{\text{ion}}$  (ionic) are unlikely to be orthogonal. In this expression, the symbol  $\Psi_{\text{cov}}$  represents a wavefunction of the general form of Eqs. (4) and (6), i.e. a linear combination of  $f_S^N$  structures built from a common orbital product. It proves convenient to define a projection matrix  $\mathbf{P}_{\text{cov}}$  which is diagonal with 1's in the positions relevant to the  $f_S^N$  covalent structures and zeroes elsewhere.

In the present work, we have examined two categories of criteria for choosing the orbital transformation, one of them overlap-based and the other energy-based. In the first of these, we find the orbital transformation  $\mathbf{O}$  which maximises

$$S_{\text{cov}} = \frac{\langle \Psi_{\text{CAS}} | \Psi_{\text{cov}} \rangle}{\langle \Psi_{\text{cov}} | \Psi_{\text{cov}} \rangle^{1/2}}. \quad (9)$$

In the other,  $\mathbf{O}$  is chosen so as to minimise

$$E_{\text{cov}} = \frac{\langle \Psi_{\text{cov}} | \hat{H} | \Psi_{\text{cov}} \rangle}{\langle \Psi_{\text{cov}} | \Psi_{\text{cov}} \rangle}. \quad (10)$$

In either case, the CI coefficients for the covalent structures, i.e. the analogues of the  $c_{Sk}$ 's in Eq. (6), are the relevant entries in the vector  $\bar{c} = \mathbf{P}_{\text{cov}} \mathbf{T}^{-1}(\mathbf{O}) \mathbf{c}$ , in which  $\mathbf{c}$  is the original CASSCF CI vector. Of course, we could instead choose to treat the spin-coupling coefficients as further parameters to be varied in the optimisation of  $S_{\text{cov}}$  or  $E_{\text{cov}}$ . We have used superscripts  $s$ ,  $e$  and  $c$  to indicate the source of the spin-coupling coefficients:

- $s$  maximise  $S_{\text{cov}}$ ,
- $e$  minimise  $E_{\text{cov}}$ ,
- $c$  directly from the CASSCF CI vector appropriate to  $\{\phi^{\text{CASVB}}\}$ .

Such considerations lead naturally to four criteria for choosing  $\mathbf{O}$ :

- CASVB1 maximise  $S_{\text{cov}}^s$  with respect to  $\mathbf{O}$  and to the spin-coupling coefficients ( $\bar{c}$ ),
- CASVB2 maximise  $S_{\text{cov}}^c$  with respect to  $\mathbf{O}$ , extracting  $\bar{c}$  from the CI vector appropriate to  $\{\phi^{\text{CASVB}}\}$  according to  $\mathbf{P}_{\text{cov}} \mathbf{T}^{-1} \mathbf{c}$ ,
- CASVB3 minimise  $E_{\text{cov}}^e$  with respect to  $\mathbf{O}$  and to the spin-coupling coefficients ( $\bar{c}$ ),
- CASVB4 minimise  $E_{\text{cov}}^c$  with respect to  $\mathbf{O}$ , extracting  $\bar{c}$  from the CI vector appropriate to  $\{\phi^{\text{CASVB}}\}$  according to  $\mathbf{P}_{\text{cov}} \mathbf{T}^{-1} \mathbf{c}$ .

We can, of course, also envisage various ‘‘mixed’’ schemes, such as maximising  $S_{\text{cov}}^e$ :  $\mathbf{O}$  would be chosen so as to maximise  $S_{\text{cov}}$  and  $\bar{c}$  so as to minimise  $E_{\text{cov}}$ .

For CASVB1, the covalent part of the CAS wavefunction takes the form

$$C_{\text{cov}} \Psi_{\text{cov}} = \{\Phi^{\text{CASSCF}}\} \mathbf{T}(\mathbf{O}) \mathbf{P}_{\text{cov}} \bar{c}. \quad (11)$$

The quantity to be maximised with respect to the choice of  $\mathbf{O}$  (and hence  $\mathbf{T}$ ) and with respect to the  $f_S^N$  spin-coupling coefficients in  $\mathbf{P}_{\text{cov}} \bar{c}$  is

$$S_{\text{cov}}^s = \frac{\mathbf{c}^\dagger \mathbf{S} \mathbf{T} \mathbf{P}_{\text{cov}} \bar{c}}{(\bar{c}^\dagger \mathbf{P}_{\text{cov}} \mathbf{T}^\dagger \mathbf{S} \mathbf{T} \mathbf{P}_{\text{cov}} \bar{c})^{1/2}}, \quad (12)$$

in which  $\mathbf{S}$  is the overlap matrix in the *original*  $\{\Phi^{\text{CASSCF}}\}$  basis. For CASVB2, we maximise

$$S_{\text{cov}}^c = \frac{\mathbf{c}^\dagger \mathbf{S} \mathbf{T} \mathbf{P}_{\text{cov}} \mathbf{T}^{-1} \mathbf{c}}{((\mathbf{T}^{-1} \mathbf{c})^\dagger \mathbf{P}_{\text{cov}} \mathbf{T}^\dagger \mathbf{S} \mathbf{T} \mathbf{P}_{\text{cov}} \mathbf{T}^{-1} \mathbf{c})^{1/2}} \quad (13)$$

with respect only to the choice of  $\mathbf{O}$  (and hence  $\mathbf{T}$ ).

The quantity to be minimised for CASVB3 is

$$E_{\text{cov}}^e = \frac{\bar{c}^\dagger \mathbf{P}_{\text{cov}} \mathbf{T}^\dagger \mathbf{H} \mathbf{T} \mathbf{P}_{\text{cov}} \bar{c}}{\bar{c}^\dagger \mathbf{P}_{\text{cov}} \mathbf{T}^\dagger \mathbf{S} \mathbf{T} \mathbf{P}_{\text{cov}} \bar{c}}, \quad (14)$$

in which  $\mathbf{H}$  is the hamiltonian matrix in the *original*  $\{\Phi^{\text{CASSCF}}\}$  basis. For CASVB4, we minimise

$$E_{\text{cov}}^c = \frac{(\mathbf{T}^{-1} \mathbf{c})^\dagger \mathbf{P}_{\text{cov}} \mathbf{T}^\dagger \mathbf{H} \mathbf{T} \mathbf{P}_{\text{cov}} \mathbf{T}^{-1} \mathbf{c}}{(\mathbf{T}^{-1} \mathbf{c})^\dagger \mathbf{P}_{\text{cov}} \mathbf{T}^\dagger \mathbf{S} \mathbf{T} \mathbf{P}_{\text{cov}} \mathbf{T}^{-1} \mathbf{c}}. \quad (15)$$

The definition of CASVB3 is somewhat special, because the resulting  $\Psi_{\text{cov}}$  must correspond *exactly* with the outcome of a spin-coupled calculation in which the active orbitals are expanded only in the space defined by the active CASSCF orbitals, and in which the (frozen) core orbitals are taken from the CASSCF wavefunction. Of course, this  $\Psi_{\text{cov}}$  does not correspond to the fully variational SC wavefunction defined in Eq. (4). The CAS and SC active spaces are likely to differ, and so the SC-like wavefunction obtained from such a restricted calculation would not be optimal with respect to active–virtual orbital rotations. Similarly, the freezing of the core also means that this wavefunction would not be optimal with respect to core–active and core–virtual rotations.

It was a useful test of the newly developed code for CASVB3 that it produced a wavefunction identical to that obtained with our existing spin-coupled programs, provided the various restrictions were imposed. In fact, the procedure used to minimise  $E_{\text{cov}}^e$  could be extended so as to obtain the “proper” variational spin-coupled wavefunction. The spin-coupling coefficients, i.e.  $\bar{c}$ , can be transformed to the basis of CAS structures according to

$$\bar{c}_{\text{CAS}} = T\bar{c}, \quad (16)$$

after which the (orthogonal) orbitals can be reoptimised with respect to the core–active, core–virtual and active–virtual rotations, using standard CASSCF procedures, but keeping the CI coefficients ( $\bar{c}_{\text{CAS}}$ ) fixed. The new orbital space can then be transformed according to the definition of CASVB3, and the whole two-step procedure repeated until self-consistency is reached. While this may not be the most elegant approach, it can be implemented with very little programming effort. Also, given that the CASSCF and (fully optimised) spin-coupled orbitals span very similar spaces, this iterative two-step procedure should converge very rapidly. A scheme of this general type has been implemented by Murphy and Messmer [11], who investigated a hierarchy of correlated VB wavefunctions, of increasing complexity, with emphasis on obtaining a large proportion of the correlation energy recovered by the CASSCF wavefunction. They suggested that the so-called “orbital-relaxed” GVB wavefunction (GVB/R) represents the best compromise between compactness and total energy. Such a wavefunction consists of  $f_S^N$  covalent structures, as in the SC model, but with different orbital products for each mode of spin coupling. The intrinsic overcompleteness of such a description was not a problem in any of the examples they examined, because of symmetry relations between the orbitals in different structures.

## 4 Results for representative systems

All the CASSCF [12, 13] calculations described in the present work were carried out with MOLPRO [14], employing basis sets taken from the basis function library associated with the program. The spin-coupled and nonorthogonal CI calculations, and the CASVB transformations themselves, used our own codes. We describe in turn our results for singlet methylene, for methane and for ozone. Each of these systems illustrates different features of the CASVB representation.

### 4.1 Singlet methylene

The geometry adopted for the  $^1A_1$  state of  $\text{CH}_2$  of  $r_{\text{CH}} = 1.117 \text{ \AA}$  and  $\theta(\text{HCH}) = 102.4^\circ$  was taken from the work of Bauschlicher and Taylor [15].

Correlation-consistent pVTZ basis sets due to Dunning [16] were used for C/H, consisting of (10s5p2d/5s2p) Cartesian gaussians contracted to [4s3p2d/3s2p]. We carried out “6 in 6” CASSCF calculations, with one (optimised) core orbital,  $1a_1$ , which corresponds to the carbon  $1s^2$  core. The six active MOs are  $2a_1$ ,  $1b_2$ ,  $3a_1$ ,  $1b_1$ ,  $2b_2$ , and  $4a_1$ , with natural orbital occupation numbers 1.981, 1.977, 1.910, 0.088, 0.023, and 0.021, respectively. The configuration  $1a_1^2 2a_1^2 1b_2^2 3a_1^2$  is strongly dominant, with a weight of 93.49%, and so it might be thought that the SCF picture is basically correct. However, it is well established [15] that a realistic treatment of this state requires at least a two-configuration description of the form  $(\dots 3a_1^2) - \lambda(\dots 1b_1^2)$ .

Spin-coupled calculations, with the same geometry and basis set, were carried out with a  $1a_1^2$  core taken directly from the CASSCF wavefunction, so as to simplify direct comparison. However, the six singly occupied spin-coupled orbitals were not restricted to the CASSCF space, but were instead optimised as completely general linear combinations of the CASSCF active and virtual orbitals. This spin-coupled calculation recovered 92.63% of the 61.59 millihartree of correlation energy incorporated in the CASSCF wavefunction (see Table 2). Much of the remaining 7.37% may be obtained by using the SC orbitals in a nonorthogonal CI calculation with the same list of configurations as in the CASSCF calculation. The resulting energy (labelled SC + CI in Table 2) is within 0.54 millihartree of the CASSCF energy. Although the SC + CI and CASSCF calculations both involve an “ $N$  in  $N$ ” full-CI, the energies do not coincide because of the small differences between the spaces spanned by the SC and CASSCF active orbitals.  $SC^{CAS}$  denotes the restricted calculation, in which the SC orbitals are expanded only in the space of the CASSCF active orbitals. The difference in energy from the full SC calculation (albeit also with a frozen core taken from the CASSCF) is small compared with the difference between SC and CASSCF (see Table 2). Of course, although  $SC^{CAS}$  is energetically inferior to SC,  $SC^{CAS} + CI$  is superior to SC + CI, in that it must reproduce the CASSCF energy.

The spin-coupled description of methylene, calculated with a variety of basis sets, has been presented on numerous occasions, including studies of the singlet–triplet splitting and of the cycloaddition reactions with alkenes [17], of  $XH_2$  neutrals and ions [18], and of the barrierless reaction with  $H_2$  to form  $CH_4$  [19]. Although no such constraints were imposed in the present calculation, we find that the fully-optimised SC orbitals for the singlet state consist of two symmetry-related pairs, which describe the C–H bonds, and two equivalent nonbonding orbitals, as shown<sup>1</sup> in Fig. 1. Orbital  $\phi_1$  takes the form of a distorted  $sp^x$ -like hybrid on carbon, pointing towards one of the hydrogen atoms, and  $\phi_2$  takes the form of a distorted H(1s) function. The corresponding electron spins are predominantly (but not exclusively) singlet coupled. Orbitals  $\phi_3$  and  $\phi_4$  are the counterparts in the other C–H bond.

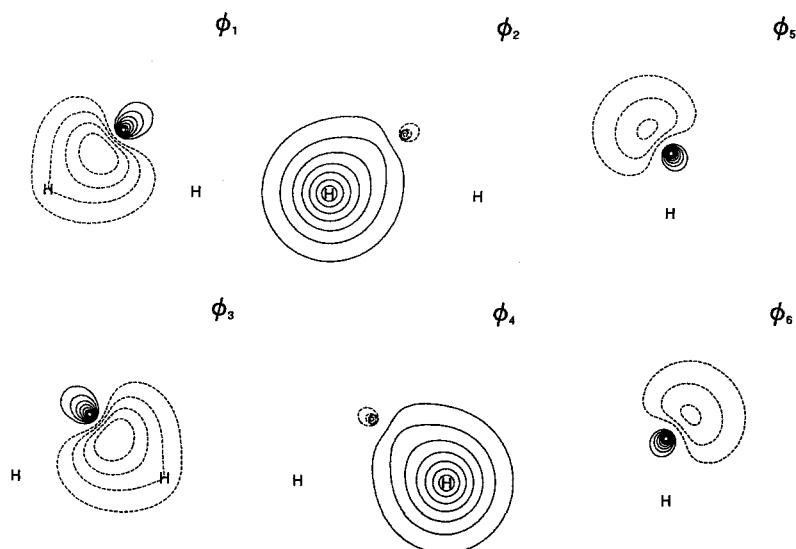
The two nonbonding orbitals ( $\phi_5$  and  $\phi_6$ ) also take the form of pseudo-tetrahedrally arranged  $sp^x$ -like hybrids, but exhibit significantly greater C(2s)

<sup>1</sup> All of the contour plots in the present work depict representations of  $\phi_\mu$ , with positions of the nuclei projected onto the page and indicated by means of their chemical symbols. It is convenient to define  $F_1 = \min(|\phi_{\min}|, \frac{1}{2}|\phi_{\max}|/n_{\text{ctr}})$  and  $F_2 = |\phi_{\max}| -$  we have used  $n_{\text{ctr}} = 7$ . The plots were constructed by requesting  $n_{\text{ctr}}$  equally spaced contour heights (—) between  $F_1$  and  $F_2$ , and a further  $n_{\text{ctr}}$  equally spaced contour heights (---) between  $-F_2$  and  $-F_1$ . Adjacent contour heights differ by  $(F_2 - F_1)/(n_{\text{ctr}} + 1)$ .



**Table 2.** Energies for singlet methylene. Further details of the various calculations are given in the text

| Calculation            | $E/\text{hartree}$ | $(E - E_{\text{CAS}})/\text{millihartree}$ |
|------------------------|--------------------|--|
| SCF                    | -38.891714         | 61.59                                      |
| SC <sup>CAS</sup>      | -38.948156         | 5.15                                       |
| SC                     | -38.948765         | 4.54                                       |
| SC + CI                | -38.952771         | 0.54                                       |
| SC <sup>CAS</sup> + CI | -38.953306         | (0)  |
| CASSCF                 | -38.953306         | (0)  |

**Fig. 1.** SC orbitals singlet methylene. Orbitals  $\phi_1$ – $\phi_4$  are shown in the molecular plane, with  $\phi_5$ – $\phi_6$  in the perpendicular mirror plane

character than do  $\phi_1$  and  $\phi_3$ . This description of the nonbonding electrons differs significantly from the simple SCF picture, in which both electrons occupy essentially a single C( $sp^2$ ) hybrid that points along the  $C_2$  axis, away from the hydrogens. Because of the ways in which  $\phi_5$  and  $\phi_6$  transform into one another under various operations of the molecular point group, the corresponding electrons spins must be exactly singlet coupled in order to give the correct overall symmetry for the molecular state. The SC description of these nonbonding electrons turns out to be especially helpful for understanding various reactions involving singlet methylene [17, 19]. In MO theory terms, the differences between the SCF and SC calculations arise to a first approximation from the incorporation of some ( $\dots 1b_1^2$ ) character, as in the two-configuration SCF description or a CASSCF calculation.

We find that the fully optimised SC orbitals lie predominantly in the space of the active CASSCF MOs. Specifically, just 0.090%, 0.102% and 0.006% of orbitals  $\phi_1$ ,  $\phi_2$  and  $\phi_5$ , respectively, is expanded in the space of the CAS virtual orbitals. Given the success of the fully optimised SC description and the fact that all of our

CASVB criteria are based on transforming the CAS active MOs, it is encouraging that the spaces spanned by SC and CASSCF calculations are so similar. The overlaps between the SC orbitals are reported in Table 3, together with the corresponding quantities for the (renormalised) components of the fully optimised SC orbitals that lie within the CASSCF space. As expected, there is a high overlap ( $>0.8$ ) between  $\phi_1$  and  $\phi_2$ , which constitute one of the C–H bonds. We also observe significant overlaps between the various  $sp^x$ -like hybrids. This is especially true for the nonbonding orbitals, because of the increased C(2s) character. The perfect-pairing spin function is overwhelmingly dominant, contributing 98.81% of the total spin function in the Kotani or Serber basis.

In the present case, all four CASVB criteria prove extremely successful in producing descriptions similar to the spin-coupled picture. The orbital plots are fairly difficult to distinguish by eye (see Fig. 2) but slightly larger variations are discernible in the overlap matrices (see Table 4). Criteria CASVB2 and CASVB4, in which the spin-coupling coefficients are extracted directly from the appropriate CI vector, reproduce most closely the SC results. Criterion CASVB1 and, to a lesser extent, CASVB3, show greater differences, as indicated by the reduced “bond” overlaps,  $\langle \phi_1 | \phi_2 \rangle$ , and the increased “between-bond” overlaps,  $\langle \phi_1 | \phi_3 \rangle$ .

Values of  $S_{\text{cov}}$  and  $E_{\text{cov}}$  for the various CASVB representations are reported in Table 5. As indicated earlier, criteria CASVB1–CASVB4 optimise  $S_{\text{cov}}^s$ ,  $S_{\text{cov}}^c$ ,  $E_{\text{cov}}^e$  and  $E_{\text{cov}}^c$ , respectively.  $\text{SC}^{\text{trunc}}$  is used to denote the set of (renormalised) components of the fully optimised SC orbitals that lie within the space of the CASSCF active orbitals. The largest overlap ( $S_{\text{cov}}^s$ ) is 0.99862 and the best energy ( $E_{\text{cov}}^e$ ) is  $-38.948156$  hartree, but none of the others are very different from these optimal values. Certainly, the energy differences are small compared with the difference between the SC and SC + CI calculations.

Finally, we examine the various sets of spin-coupling coefficients. The singlet coupling of the spins associated with the nonbonding electrons has the consequence that there are only two nonzero values of  $c_{S_k}$  (Eq. (6)). The weights of the perfectly paired spin function are expressed in Table 6 as percentages of the total spin function in the Kotani or Serber bases. As a general trend, we find that the largest weights for perfect pairing arise when the spin-coupling coefficients are those determined by the CASSCF wavefunction ( $\mathbf{P}_{\text{cov}} \mathbf{T}^{-1} \mathbf{c}$ ). The corresponding weight tends to be smallest when  $\bar{e}$  is energy-optimised, but the variation is not so large in this case. The greater importance of the perfectly paired spin function for CASVB2 and CASVB4 (relative to CASVB1 and CASVB3) is associated with some adaptation of the orbitals, so as to increase the overlaps in the bond-forming orbital pairs.

**Table 3.** Overlaps between the SC orbitals of singlet methylene. The lower triangle corresponds to the full calculation, and the upper triangle to the (renormalised) components of the fully-optimised SC orbitals that lie within the CASSCF space.

|          | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\phi_5$ | $\phi_6$ |
|----------|----------|----------|----------|----------|----------|----------|
| $\phi_1$ | 1        | 0.808    | 0.314    | 0.121    | 0.197    | 0.197    |
| $\phi_2$ | 0.806    | 1        | 0.121    | −0.056   | 0.132    | 0.132    |
| $\phi_3$ | 0.314    | 0.120    | 1        | 0.808    | 0.197    | 0.197    |
| $\phi_4$ | 0.120    | −0.055   | 0.806    | 1        | 0.132    | 0.132    |
| $\phi_5$ | 0.197    | 0.132    | 0.197    | 0.132    | 1        | 0.673    |
| $\phi_6$ | 0.197    | 0.132    | 0.197    | 0.132    | 0.673    | 1        |

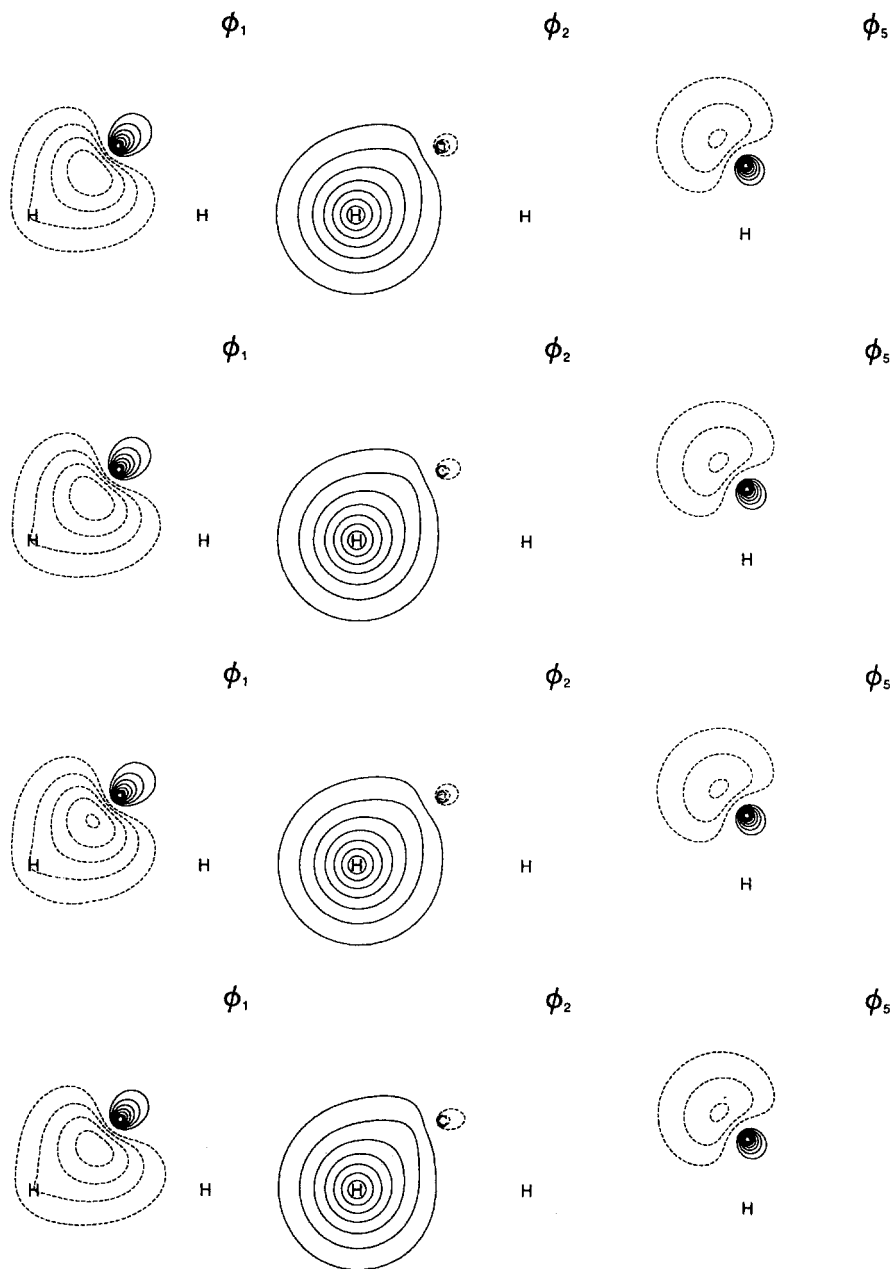


Fig. 2. Symmetry-unique CASVB orbitals for singlet methylene. In order, the four rows correspond to CASVB1–CASVB4

Overall, singlet methylene can be viewed as a straightforward case, for which the correspondence between the SC and CASSCF wavefunctions is fairly clear-cut, and all four CASVB criteria provide very acceptable modern VB representations of the bonding. As we shall now discuss, the same is not true in the case of methane.

**Table 4.** Overlaps between the CASVB orbitals of singlet methylene

| <i>CASVB1</i> |          |          |          |          |          |          |
|---------------|----------|----------|----------|----------|----------|----------|
|               | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\phi_5$ | $\phi_6$ |
| $\phi_1$      | 1        |          |          |          |          |          |
| $\phi_2$      | 0.746    | 1        |          |          |          |          |
| $\phi_3$      | 0.517    | 0.117    | 1        |          |          |          |
| $\phi_4$      | 0.117    | -0.293   | 0.746    | 1        |          |          |
| $\phi_5$      | 0.245    | 0.133    | 0.245    | 0.133    | 1        |          |
| $\phi_6$      | 0.245    | 0.133    | 0.245    | 0.133    | 0.673    | 1        |
| <i>CASVB2</i> |          |          |          |          |          |          |
|               | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\phi_5$ | $\phi_6$ |
| $\phi_1$      | 1        |          |          |          |          |          |
| $\phi_2$      | 0.809    | 1        |          |          |          |          |
| $\phi_3$      | 0.310    | 0.117    | 1        |          |          |          |
| $\phi_4$      | 0.117    | -0.074   | 0.809    | 1        |          |          |
| $\phi_5$      | 0.228    | 0.158    | 0.228    | 0.158    | 1        |          |
| $\phi_6$      | 0.228    | 0.158    | 0.228    | 0.158    | 0.673    | 1        |
| <i>CASVB3</i> |          |          |          |          |          |          |
|               | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\phi_5$ | $\phi_6$ |
| $\phi_1$      | 1        |          |          |          |          |          |
| $\phi_2$      | 0.782    | 1        |          |          |          |          |
| $\phi_3$      | 0.403    | 0.110    | 1        |          |          |          |
| $\phi_4$      | 0.110    | -0.175   | 0.782    | 1        |          |          |
| $\phi_5$      | 0.221    | 0.129    | 0.221    | 0.129    | 1        |          |
| $\phi_6$      | 0.221    | 0.129    | 0.221    | 0.129    | 0.671    | 1        |
| <i>CASVB4</i> |          |          |          |          |          |          |
|               | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ | $\phi_5$ | $\phi_6$ |
| $\phi_1$      | 1        |          |          |          |          |          |
| $\phi_2$      | 0.811    | 1        |          |          |          |          |
| $\phi_3$      | 0.261    | 0.105    | 1        |          |          |          |
| $\phi_4$      | 0.105    | -0.037   | 0.811    | 1        |          |          |
| $\phi_5$      | 0.210    | 0.143    | 0.210    | 0.143    | 1        |          |
| $\phi_6$      | 0.210    | 0.143    | 0.210    | 0.143    | 0.671    | 1        |

**Table 5.** Values of  $S_{\text{cov}}$  and  $E_{\text{cov}}$  for singlet methylene, calculated with various sets of orbitals

| Orbitals            | $S_{\text{cov}}^s$ | $S_{\text{cov}}^e$ | $S_{\text{cov}}^c$ | $E_{\text{cov}}^s$ | $E_{\text{cov}}^e$ | $E_{\text{cov}}^c$ |
|---------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| SC <sup>trunc</sup> | 0.99855            | 0.99855            | 0.99854            | -38.948108         | -38.948111         | -38.948070         |
| CASVB1              | 0.99862            | 0.99814            | 0.99814            | -38.948061         | -38.948066         | -38.946893         |
| CASVB2              | 0.99860            | 0.99859            | 0.99859            | -38.948080         | -38.948085         | -38.948051         |
| CASVB3              | 0.99858            | 0.99858            | 0.99851            | -38.948153         | -38.948156         | -38.947945         |
| CASVB4              | 0.99856            | 0.99856            | 0.99856            | -38.948125         | -38.948129         | -38.948117         |

**Table 6.** Weights  $w_{pp} = (c_{pp})^2$  of the perfectly paired spin function, expressed as percentages of the total spin function in the Kotani or Serber bases

| Orbitals            | $w_{pp}^s$ | $w_{pp}^e$ | $w_{pp}^c$         |
|---------------------|------------|------------|--------------------|
| SC                  |            | 98.81      | 99.22 <sup>a</sup> |
| SC <sup>trunc</sup> | 98.80      | 98.66      | 99.17              |
| CASVB1              | 97.90      | 97.70      | 99.76              |
| CASVB2              | 98.92      | 98.72      | 99.18              |
| CASVB3              | 98.53      | 98.38      | 99.40              |
| CASVB4              | 98.99      | 98.82      | 99.10              |

<sup>a</sup> This value relates to the SC + CI calculation

#### 4.2 Methane

In the calculations on CH<sub>4</sub> (T<sub>d</sub> symmetry,  $r_{CH} = 2.065$  bohr) we adopted the same C/H basis sets as for singlet methylene. The MOs in the CASSCF calculation were partitioned as follows:

- one optimised core orbital ( $\approx C(1s^2)$ ),
- eight active orbitals, to accommodate the eight valence orbitals,
- 52 virtual orbitals.

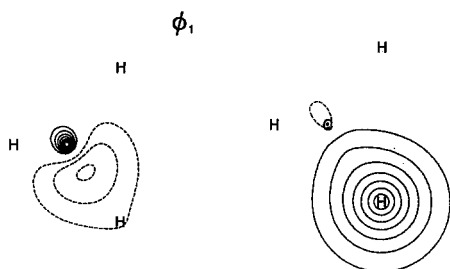
The “8 in 8” CASSCF energy represents an improvement over the SCF description of 83.00 millihartree (see Table 7). The occupation numbers of the first four orbitals are all close to two, and the weight of the configuration in which these MOs are doubly occupied is 96.06%.

An SC calculation was then carried out for the eight valence electrons of CH<sub>4</sub>, with the two core electrons accommodated in the core orbital from the CASSCF calculation, without further relaxation. The SC orbitals were expanded in the full space of the CASSCF active and virtual orbitals. In spite of being based on a single orbital product, the SC energy accounts for 79.06% of the correlation energy recovered by the CAS wavefunction. This is a somewhat lower proportion than that found for methylene (and other six-electron cases) and for the ozone calculations described later, probably on account of the increased number of active electrons and thus the greater difference in the number of variational parameters between the SC and CASSCF methods (see Table 1).

The modern VB description of methane, as revealed by SC theory, is well established [5, 19–21]. Although no such constraints were imposed in the calculation, the converged spin-coupled wavefunction consists of four symmetry-related pairs of orbitals, each associated with a different C–H bond. The symmetry-unique orbitals are shown in Fig. 3. Orbital  $\phi_1$  takes the form of a deformed  $sp^x$ -like hybrid on carbon and orbital  $\phi_2$  resembles a distorted H(1s) function. The overlap between these two orbitals is 0.69 (see Table 8), with predominantly singlet coupling of the corresponding electrons spins. Orbitals  $\phi_3$ ,  $\phi_5$  and  $\phi_7$  are the carbon-based hybrids in the other C–H bonds, and orbitals  $\phi_4$ ,  $\phi_6$  and  $\phi_8$ , respectively, are the hydrogen-based orbitals to which they point. This description is certainly reminiscent of Pauling’s original picture [22] of C( $sp^3$ ) hybrids which overlap with H(1s) functions to form directed covalent bonds. Key differences include the small deformations of the spin-coupled orbitals and the substantial overlaps

**Table 7.** Energies for methane. Further details of the various calculations are given in the text

| Calculation            | $E/\text{hartree}$ | $(E - E_{\text{CAS}})/\text{millihartree}$ |
|------------------------|--------------------|--|
| SCF                    | -40.212541         | 83.00                                      |
| SC <sup>CAS</sup>      | -40.275607         | 19.93                                      |
| SC                     | -40.278158         | 17.38                                      |
| SC + CI                | -40.291257         | 4.28                                       |
| SC <sup>CAS</sup> + CI | -40.295536         | (0)  |
| CASSCF                 | -40.295536         | (0)  |

**Fig. 3.** Symmetry-unique SC orbitals for methane**Table 8.** Symmetry-unique orbital overlaps for methane

| Calculation         | $\langle \phi_1   \phi_2 \rangle$ | $\langle \phi_1   \phi_3 \rangle$ | $\langle \phi_1   \phi_4 \rangle$ | $\langle \phi_2   \phi_4 \rangle$ |
|---------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| SC                  | 0.692                             | 0.529                             | 0.096                             | -0.152                            |
| SC <sup>trunc</sup> | 0.699                             | 0.531                             | 0.096                             | -0.152                            |
| CASVB1              | 0.201                             | 0.916                             | -0.062                            | -0.322                            |
| CASVB2              | 0.783                             | 0.323                             | 0.059                             | -0.109                            |
| CASVB3              | 0.272                             | 0.883                             | -0.038                            | -0.316                            |
| CASVB4              | 0.752                             | 0.370                             | 0.058                             | -0.131                            |

between the different  $sp^x$ -like hybrids (0.52). A more significant difference is that in a classical VB calculation with *strictly* localised orbitals [23], it proves necessary to include ionic structures even to match the SCF energy for the same basis set.

For a high-symmetry system, such as methane, it can be particularly beneficial to express the total spin function  $\Theta_M^N$  in the Serber basis. Each of the  $f_S^N = 14$  Serber functions for  $N = 8$  and  $S = 0$  may be represented by  $((s_{12} s_{34})S_4; s_{56})S_6; s_{78}$  in which  $s_{12}, s_{34}, s_{56}$  and  $s_{78}$  may be 0 or 1 (for singlet or triplet electron pairs) and the  $S_{2p}$  denote the total spin of the first  $p$  electron pairs. We find that there are only four unique nonzero spin-coupling coefficients for  $\text{CH}_4$ , such that

$$\begin{aligned}
 \Theta = & + b_1(((11)2; 1)1;1) \\
 & + b_2(((11)0; 1)1;1) \\
 & - b_3(((10)1; 0)1;1) - b_3(((01)1;0)1;1) - b_3(((00)0;1)1;1) \\
 & - b_3(((10)1;1)0;0) - b_3(((01)1;1)0;0) - b_3(((11)0;0)0;0) \\
 & + b_4(((00)0;0)0;0)
 \end{aligned} \tag{17}$$

with all the  $b_i$  positive. The Serber functions are orthogonal and so the corresponding “weights” of the different modes of spin-coupling are simply  $w_i = (b_i)^2$ , as reported in Table 9. In the case of the full SC calculation, the most important contribution comes from the perfectly paired mode of spin coupling, as one would anticipate, but the other modes make up 10% of the total spin function.

We find for  $\phi_1$  and  $\phi_2$  that 0.35% and 0.56%, respectively, of the orbital lies outside the CASSCF active space. These numbers are somewhat larger than those for singlet methylene, and so it is not surprising that the difference in energy between  $\text{SC}^{\text{CAS}}$  and SC, as well as that between SC + CI and CASSCF (=  $\text{SC}^{\text{CAS}}$  + CI), is larger in the present case (see Table 7).

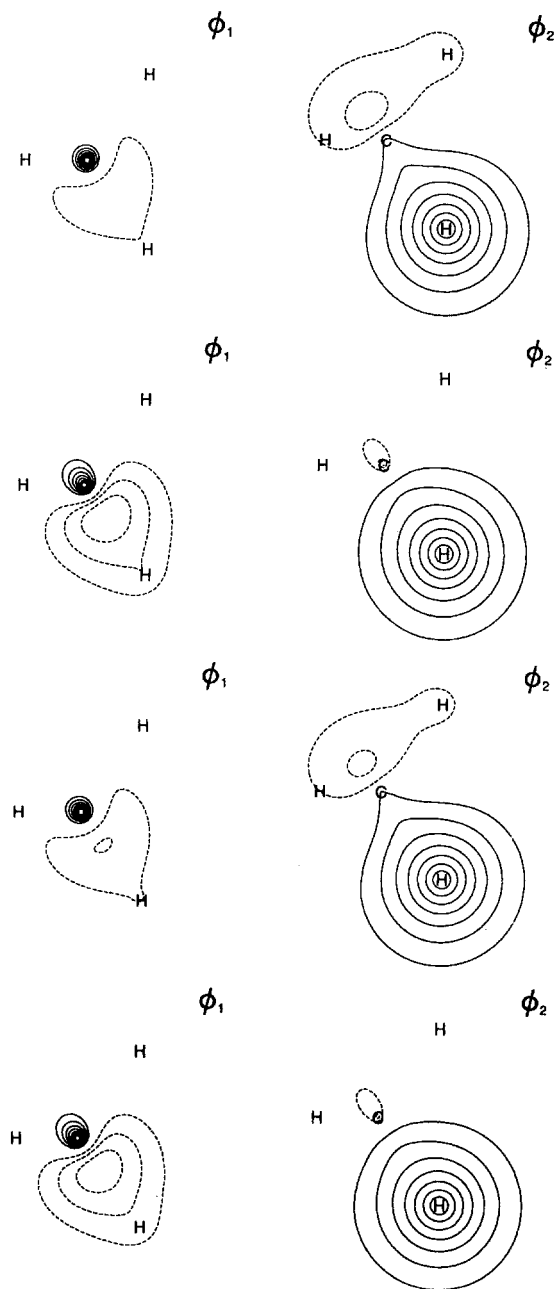
The outcomes of some of the CASVB criteria for methane were far less successful than was the case for singlet methylene. The various symmetry-unique orbitals are plotted in Fig. 4. It can be seen that CASVB2 and CASVB4 produce orbital descriptions which agree qualitatively with those from the full-SC calculation. These criteria suggest slightly more delocalisation of  $\phi_1$  than does SC, and this is reflected in an increased bonding overlap (see Table 8). As before, this may be rationalised from the observation that the weight of the perfectly paired spin function is increased when the spin-coupling coefficients are taken from the CASSCF wavefunction (see Table 9).

On the other hand, CASVB1 and CASVB3 lead to anomalous, “rogue” solutions. Both of these criteria yield extremely localised carbon orbitals,  $\phi_1$ , which have relatively small overlaps (0.20 and 0.27, respectively) with the H(1s) functions,  $\phi_2$ . It is useful to recall that the covalent wavefunction  $\Psi_{\text{cov}}$  determined with CASVB3 must coincide exactly with the  $\text{SC}^{\text{CAS}}$  wavefunction, in which the SC orbitals are restricted to the CASSCF active space. We have previously encountered such anomalous solutions, exhibiting marked differences from the “full” calculation, for a few cases in which the total number of orbital free parameters was severely restricted. It appears that the small components of  $\phi_1$  and  $\phi_2$  that lie outside the CASSCF active space play a very important role in the full-SC calculation.

Looking at the covalent weights and energies listed in Table 10, we see that criteria CASVB1 and CASVB3 give rather good values of  $S_{\text{cov}}$  and  $E_{\text{cov}}$ . Of course, with these orbital sets, the values of  $E_{\text{cov}}$  become nonsensical if the spin-coupling coefficients are taken instead from the CASSCF wavefunction. Although it is difficult to disregard the relative success of CASVB1 and CASVB3 in generating good values for the covalent weights and energies, the orbitals do not conform with the standard classical or modern VB descriptions of the bonding. As such, it seems reasonable to reject the covalent wavefunctions generated by these two criteria as

**Table 9.** Weights in the Serber basis,  $w_i = (b_i)^2$ , for methane (see Eq. (17)) expressed as percentages. The  $w^c$  values for SC orbitals were taken from the SC + CI calculation

| Orbitals                   | $w_1^s$ | $w_2^s$ | $w_3^s$ | $w_4^s$ | $w_1^e$ | $w_2^e$ | $w_3^e$ | $w_4^e$ | $w_1^c$ | $w_2^c$ | $w_3^c$ | $w_4^c$ |
|----------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| SC                         |         |         |         |         | 0.19    | 0.24    | 1.59    | 90.00   | 0.01    | 0.01    | 0.48    | 97.08   |
| $\text{SC}^{\text{trunc}}$ | 0.19    | 0.23    | 1.55    | 90.29   | 0.13    | 0.16    | 1.56    | 90.36   | 0.00    | 0.00    | 0.31    | 98.13   |
| CASVB1                     | 0.83    | 1.04    | 6.72    | 57.82   | 0.79    | 0.98    | 6.64    | 58.37   | 0.13    | 0.16    | 1.09    | 93.17   |
| CASVB2                     | 0.00    | 0.00    | 0.84    | 94.95   | 0.00    | 0.01    | 0.89    | 94.61   | 0.01    | 0.01    | 0.53    | 96.79   |
| CASVB3                     | 0.64    | 0.80    | 5.66    | 64.58   | 0.60    | 0.75    | 5.63    | 64.85   | 0.07    | 0.09    | 0.58    | 96.38   |
| CASVB4                     | 0.00    | 0.00    | 0.82    | 95.08   | 0.00    | 0.01    | 0.87    | 94.77   | 0.01    | 0.01    | 0.50    | 96.99   |



**Fig. 4.** Symmetry-unique CASVB orbitals for methane. In order, the four rows correspond to CASVB1–CASVB4

being anomalous. Starting from these orbital sets, attempts were made with (full) SC calculations to locate analogous local minima or stationary points, but none could be found. It seems that this type of solution simply does not exist for the standard SC calculations. It is interesting to note that the CASVB2 and CASVB4 orbital sets give values of  $S_{\text{cov}}$  and  $E_{\text{cov}}$  which are inferior to those obtained with the



**Table 10.** Values of  $S_{\text{cov}}$  and  $E_{\text{cov}}$  for methane, calculated with various sets of orbitals

| Orbitals            | $S_{\text{cov}}^s$ | $S_{\text{cov}}^e$ | $S_{\text{cov}}^c$ | $E_{\text{cov}}^s$ | $E_{\text{cov}}^e$ | $E_{\text{cov}}^c$ |
|---------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| SC <sup>trunc</sup> | 0.99529            | 0.99529            | 0.99547            | -40.273644         | -40.273646         | -40.271765         |
| CASVB1              | 0.99613            | 0.99612            | 0.99279            | -40.275304         | -40.275325         | -40.236634         |
| CASVB2              | 0.99522            | 0.99521            | 0.99517            | -40.273082         | -40.273085         | -40.272922         |
| CASVB3              | 0.99605            | 0.99605            | 0.98478            | -40.275602         | -40.275607         | -40.243954         |
| CASVB4              | 0.99515            | 0.99515            | 0.99509            | -40.273424         | -40.273427         | -40.273219         |

SC<sup>trunc</sup> set, generated by renormalising the component of the fully optimised SC orbitals which lies inside the CASSCF active space. Nonetheless, it is clear that basing the spin-coupling on the CASSCF CI vector, as in CASVB2 and CASVB4, goes a long way towards alleviating the problem of relatively few free orbital parameters, by restricting  $\Psi_{\text{cov}}$  to physically more realistic regions of the parameter space.

The question arises whether there might be a higher-lying CASSCF solution of  $A_1$  symmetry which has CASVB1 and CASVB3 representations that are consistent with the spin-coupled results. Judging by the SC + CI energy given in Table 7, such a solution could be expected to be around 4 millihartree above the ground state. The first excited state of  $A_1$  symmetry is, however, 28 millihartree above the CASSCF solution we have considered here. So while it might be perfectly feasible to generate CASVB representations of this or higher states, these valence bond descriptions would have little to do with the *ground state* of methane.

### 4.3 Ozone

The calculations on  $O_3$  ( $C_{2v}$  symmetry,  $r = 1.2717 \text{ \AA}$ ,  $\theta = 121.6085^\circ$ ) employed a Huzinaga [24] basis set for oxygen consisting of (10s6p) Cartesian gaussians contracted to [5s3p], and augmented with  $d$  functions with exponent 0.85. Our main interest here is in the four  $\pi$  electrons, by which we mean the electrons which occupy orbitals which are antisymmetric with respect to reflection in the molecular plane. It soon becomes clear that there are two "4 in 4" CASSCF solutions which are very similar in energy. CAS "A" has an active space which consists of three orbitals of  $B_1$  symmetry, and one of  $A_2$ . CAS "B" has an active space which consists of two orbitals of  $B_1$  symmetry, and two of  $A_2$ . Optimising the doubly occupied orbitals of the  $\sigma$ -electron core, the CAS "A" solution is preferred over CAS "B" by 2.4 millihartree. The extent to which this energy difference is due to the different core orbital spaces can be gauged by carrying out further CASSCF calculations in which the core orbitals are frozen as the corresponding SCF orbitals. This gives the same ordering for the two solutions, but the energy difference is now only 0.02 millihartree. The fact that there are near-degenerate solutions in this way, suggests that neither of these "4 in 4" CASSCF wavefunctions is likely to provide a very satisfactory description of the bonding for this system. Nevertheless, it proves instructive to examine the corresponding SC and CASVB representations, as a further test of the various CASVB criteria.

Just as there are two rival CASSCF active spaces, it is possible to converge on two distinct SC wavefunctions. The relative energies of these two solutions, which we also label "A" and "B", depend on the choice of the  $\sigma$ -electron core. With

**Table 11.** Energies for some of the wavefunctions considered for ozone

| Valence (core)   | $E/\text{hartree}$ | $(E_{\text{SCF}}-E)/\text{millihartree}$ |
|------------------|--------------------|--|
| SCF              | -224.319107        | (0)                                      |
| "2 in 2" CAS     | -224.412508        | 93.40                                    |
| "4 in 3" CAS     | -224.416002        | 96.90                                    |
| SC "A" (SCF)     | -224.417478        | 98.37                                    |
| SC "B" (SCF)     | -224.417579        | 98.47                                    |
| CAS "B" (SCF)    | -224.417910        | 98.80                                    |
| CAS "A" (SCF)    | -224.417932        | 98.83                                    |
| SC "B" (CAS "A") | -224.424705        | 105.60                                   |
| SC "B" (CAS "B") | -224.424833        | 105.73                                   |
| CAS "B"          | -224.425112        | 106.01                                   |
| SC "A" (CAS "B") | -224.427020        | 107.91                                   |
| SC "A" (CAS "A") | -224.427173        | 108.07                                   |
| CAS "A"          | -224.427541        | 108.43                                   |
| "4 in 5" CAS     | -224.436532        | 117.43                                   |

orbitals taken from either of the CAS optimised cores, we find that SC solution "A" is preferred over SC solution "B" (see Table 11). The same ordering is found if the core orbitals  $\phi_i$  in Eq. (4) are fully optimised simultaneously with the SC active orbitals, using the techniques developed in Ref. [25]. However, with core orbitals taken from the SCF wavefunction, solution SC "B" lies fractionally lower than SC "A".

The form of the SC "A" orbitals (and the corresponding overlap matrix) depends very little on the specific choice of core. Furthermore, application of any of the CASVB criteria to the CAS "A" wavefunction(s) leads to much the same description. Similarly, the form of the SC "B" orbitals (and the corresponding overlap matrix) depends very little on the specific choice of core, and application of any of the CASVB criteria to the CAS "B" wavefunction(s) leads to much the same description as SC "B". Representative "A-solution" and "B-solution" orbitals are shown in Fig. 5a, b, and the overlap integrals are listed in Table 12. For "A", the mode of spin coupling in the covalent wavefunction is the pairing (2-3, 1-4) (dictated by symmetry given the nature of the orbitals), whereas the overwhelmingly dominant mode for "B" is the pairing (1-2, 3-4). As such, the SC "A" solutions and the CASVB representations of CAS "A" correspond to a singlet diradical. On the other hand, the SC "B" solutions and the CASVB representations of CAS "B" correspond to a "hypervalent" solution in which the central oxygen atom takes part in  $\pi$  bonds with each of its neighbours. The  $\phi_1$  orbitals (and similarly  $\phi_4$ ) differ relatively little between the two types of solution. The hypervalent solution is the one found in previous SC work, which was based on an SCF core [26], but it is now clear that the diradical solution has much the same energy.

The present work has, for obvious reasons, been concerned mostly with "4 in 4" CASSCF descriptions of ozone's  $\pi$  electron system, but we will also briefly consider alternative calculations. The fact that the  $1b_1$ ,  $2b_1$  and  $1a_2$  orbitals are qualitatively similar in the two CASSCF solutions suggests a "4 in 4" calculation. Such a wavefunction gives an improvement of about 10 millihartree over the two "4 in 4" solutions (see Table 11). Alternatively the  $3b_1$  and  $2a_2$  orbitals may *both* be omitted (as they have quite low occupation numbers) leading to a "4 in 3" calculation (even a "2 in 2" calculation is possible). The "4 in 3" wavefunction lies about

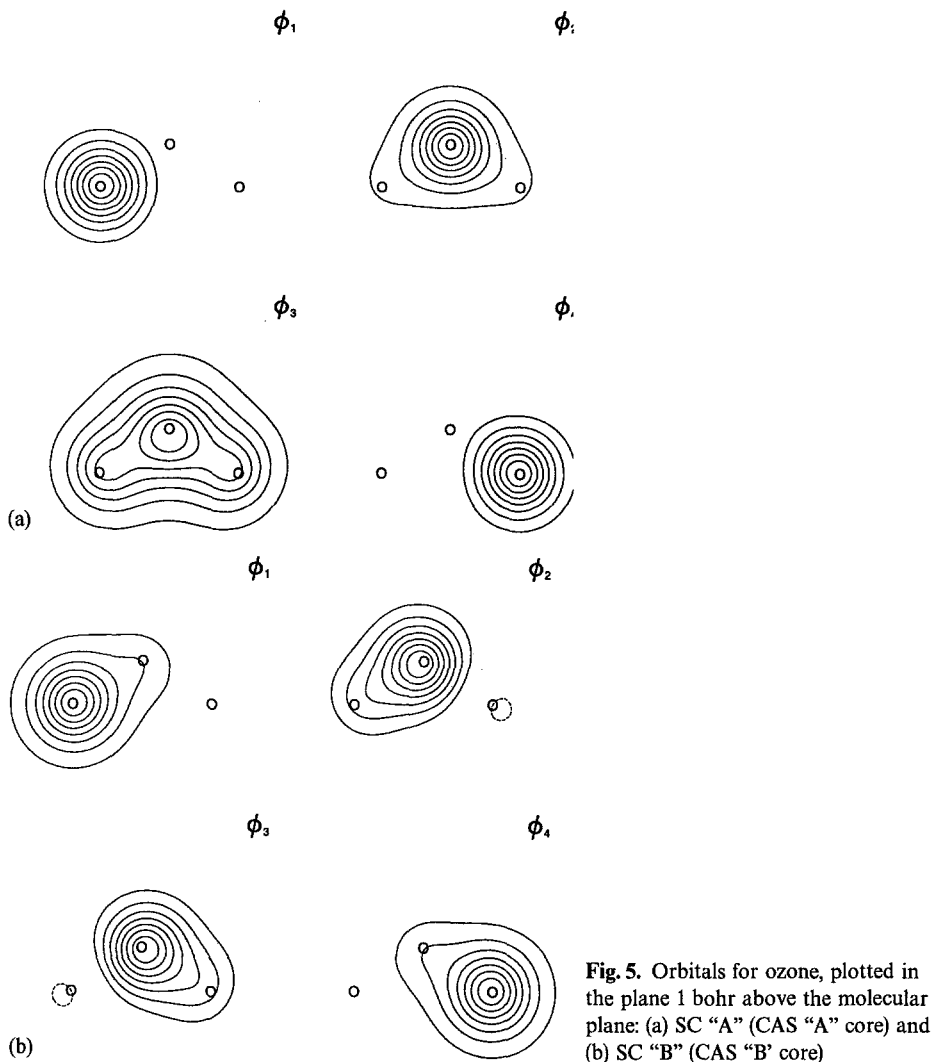


Fig. 5. Orbitals for ozone, plotted in the plane 1 bohr above the molecular plane: (a) SC "A" (CAS "A" core) and (b) SC "B" (CAS "B" core)

Table 12. Symmetry-unique orbital overlaps for ozone

| Calculation           | $\langle \phi_1   \phi_2 \rangle$ | $\langle \phi_1   \phi_3 \rangle$ | $\langle \phi_2   \phi_3 \rangle$ | $\langle \phi_1   \phi_4 \rangle$ |
|-----------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| SC "A" (CAS "A" core) | 0.199                             | 0.470                             | 0.806                             | -0.167                            |
| SC "B" (CAS "B" core) | 0.573                             | 0.106                             | 0.725                             | 0.137                             |

10 millihartree about the two 4 orbital solutions (see Table 11). Thus, the effects of including  $3b_1$  or  $2a_2$  are of the same order of magnitude, and roughly independent of each other. Therefore, from the point of view of CASSCF calculations, there seems to be little reason to prefer a "4 in 4" wavefunction over the "4 in 3" or "4 in 5" cases. An improved valence bond treatment would in contrast to this need at least six active orbitals – although the orbitals on the terminal oxygens are

sufficiently similar in the two types of solution, the central atom has four unique orbitals. As such, an improved modern VB description would necessarily be based on at least two orbital products. These might be obtained either by a generalisation of the CASVB schemes investigated here or by the direct optimisation of a multi-configuration SC wavefunction, as described in Ref. [27].

## 5 Discussion

The invariance of the CASSCF wavefunction to linear transformations of the defining orbitals has inspired a number of “localisation” schemes, analogous to those used for single-determinant SCF wavefunctions. One such strategy involves projecting the optimised orbitals onto the atomic basis functions and then performing a symmetrical orthogonalisation [28]. Another is based on minimising the energy of the perfect-pairing function [29].

A particularly interesting scheme has been presented by McDouall and Robb [30]: the CASSCF CI space is diagonalised using configuration state functions (CSFs) built from *orthogonal* localised orbitals, found as described in Ref. [29], and then the  $f_s^N$  roots of the target SC-like wavefunction are expanded in the space of the  $f_s^N$  eigenvectors with largest projections onto the covalent space. An additional assumption in their scheme is that the expansion coefficients for the covalent structures  $\{\Omega_i\}$  coincide with the corresponding CI coefficients, i.e.

$$\begin{aligned}\Psi^\lambda &= \sum_{i=1}^{f_s^N} c_i^\lambda \Phi_i + \sum_{j=f_s^N+1}^{N_{\text{CAS}}} c_j^\lambda \Phi_j \\ &\equiv \sum_{i=1}^{f_s^N} c_i^\lambda \Omega_i,\end{aligned}\quad (18)$$

in which  $\lambda$  designates different eigenvalues of the CI vectors.

The conventional way of dealing with unitary orbital transformations in CASSCF calculations is of course to equate

$$\mathbf{O} = \exp(\Lambda), \quad (19)$$

in which  $\Lambda$  is anti-Hermitian [31] (i.e. skew-symmetric for real orbital transformations), with a corresponding operator for transforming the structure space [32]

$$\hat{\Lambda} = \exp\left(\sum_r \sum_s \Lambda_{rs} a_r^\dagger a_s\right), \quad (20)$$

where  $a_r^\dagger$  and  $a_s$  are the conventional second-quantisation creation and annihilation operators. The relationship between the transformation of the covalent structures  $\{\Omega_i\}$  in Eq. (18) and the transformation of the orbitals can be written as

$$|\Omega_i\rangle = \hat{\Lambda} |\Phi_i\rangle, \quad i = 1, \dots, f_s^N. \quad (21)$$

This expression cannot usually be solved exactly for the orbital transformation parameters, because the functions  $|\Omega_i\rangle$  are of a more general form than  $\hat{\Lambda} |\Phi_i\rangle$ . McDouall and Robb [30] premultiplied both sides of Eq. (21) by  $\langle \Omega_j |$  and then truncated the exponential in Eq. (20) after the linear term. The orbital parameters could then be related trivially to the coefficients of just the singly ionic structures, i.e. those in which one of the orbitals is doubly occupied.

One of the key differences between the present work and that described in Ref. [30] is that we make no approximations in the transformation of the structure

space. We have concluded from our calculations that the effort associated with the full transformation is not sufficient to warrant such approximations. The method of McDouall and Robb [30] also involves two further approximations: expanding the SC-like wavefunction in the  $f_s^N$  eigenvectors with largest covalent character, and choosing the spin-coupling coefficients to be those of the CI vectors based on *orthogonal* orbitals. These approximations are only likely to be benign for cases in which the localised CASSCF orbitals are very similar to those from a fully nonorthogonal treatment of the system. The schemes which we have explored in the present work are preferable in the sense that they avoid these approximations. Each of our CASVB schemes is also *iterative*. One advantage of an iterative procedure is, of course, that the outcome is less sensitive to the initial choice of orbitals. Suitably localised orthogonal orbitals might reduce the number of iterations, if used as a starting guess, but an initial localisation step is no longer crucial.

As mentioned earlier, the important characteristic of a CASSCF calculation that it is a full-CI expansion (in the given space) has been exploited by Murphy and Messmer [11] to optimise modern VB wavefunctions using standard CASSCF codes. More recently, Malcolm and McDouall [33] have described an iterative variational biorthogonal valence bond (BOVB) approach in which they introduced a dual basis to circumvent the usual problems associated with evaluating matrix elements between configurations built from nonorthogonal orbitals. The variational bound to the BOVB energies holds because of the use of *all*  $N_{\text{CAS}}$  of the “ $N$  in  $N$ ” configurations. Their BOVB procedure is based on a super-CI strategy and it converges when the orbitals satisfy the generalised Brillouin conditions. As such, the BOVB orbitals (and thus the covalent reference function) must coincide with those obtained from an  $\text{SC}^{\text{CAS}}$  calculation, or by applying criterion CASVB3 to the CASSCF wavefunction. It could be interesting to compare the computational costs of the BOVB approach with those of the  $\text{SC}^{\text{CAS}}$  and CASVB3 schemes, especially from the point of view of convergence characteristics. Of course, our implied warnings about the problems of carrying out calculations with a severely restricted total number of orbital free parameters (as in the  $\text{SC}^{\text{CAS}}$  and CASVB3 descriptions of the bonding in methane) apply equally well to the BOVB method.

Our previously published SC calculations for a range of 1,3-dipoles (diazomethane, fulminic acid and nitrene) and some related inorganic molecules ( $\text{O}_3$ ,  $\text{N}_2\text{O}$  and  $\text{NO}_2$ ) [26, 34] were carried out with SCF frozen cores, treating explicitly only four  $\pi$  electrons in each case. We found a hypervalent solution (cf. SC “B” for  $\text{O}_3$ ) for each molecule. Malcolm and McDouall [35] have now studied the same systems using their BOVB codes, treating the same number of active electrons but optimising also the core orbitals. For most of the molecules, they report descriptions that are very similar to those obtained with the SC method. The two exceptions are  $\text{O}_3$  and  $\text{NO}_2$ , for which they obtained the type “A” (diradical) solutions. We have now seen for  $\text{O}_3$  that the two types of description, “A” and “B”, have much the same energy: which one of them is the lowest depends on the particular choice of core orbitals. We find that an analogous situation arises for  $\text{NO}_2$ . It seems clear that future modern VB studies of  $\text{O}_3$  and  $\text{NO}_2$  should be based on larger active spaces.

We turn now to the computational costs associated with applying the different CASVB transformations. For the energy-based criteria, CASVB3 and CASVB4, the limiting factor in our present implementation is not the actual computational effort so much as the storage requirements associated with the hamiltonian matrix, which we transform according to  $T^\dagger HT$ . There is clearly significant scope for improving the present algorithms by forming directly the product of  $H$  and a given

vector, as is done in direct CI calculations [1]. The CPU-intensive part of the present code is essentially a simple matrix multiplication (a one-index transformation of  $\mathbf{H}$ ) so that the computational effort scales as follows [4]:

$$\text{CASVB3: } N_{\text{CAS}}^2 \times \{N(N-1) + f_S^N\},$$

$$\text{CASVB4: } N_{\text{CAS}}^2 \times \{N(N-1) + 1\},$$

in which the factors of  $N_{\text{CAS}}^2$  arise from the transformation of  $\mathbf{H}$ , and the terms in brackets are related to the number of free parameters. For systems with high symmetry,  $\mathbf{H}$  is block-diagonal, and so the scaling properties of both methods are significantly reduced relative to  $N_{\text{CAS}}^2$ . This could make CASVB3, for example, competitive with the cost of carrying out directly an  $\text{SC}^{\text{CAS}}$  calculation.

The overlap-based criteria, CASVB1 and CASVB2, are fundamentally different in the sense that the quantities to be optimised do not require  $\mathbf{H}$ . This makes the algorithms easily applicable to much larger systems than is currently plausible for CASVB3 and CASVB4, or that can be treated with our SC codes. In Table 13, we report values of  $N_L$ , defined as the number of loop iterations associated with one structure transformation of a single CI vector. Values of  $N_L$  for  $S = 0$  are smaller when using Rumer spin functions instead of determinants, but the corresponding loops are slightly more expensive. The overall computational effort scales as follows [4]:

$$\text{CASVB1: } \{N(N-1) + f_S^N + 2\} \times N_L,$$

$$\text{CASVB2: } \{N(N-1) + 2\} \times N_L.$$

**Table 13.** Number of loop iterations ( $N_L$ ) associated with one structure transformation of a single CI vector for CASVB1 and CASVB2.  $N_{\text{det}}$  is the total number of determinants and  $N_{\text{CAS}}$  is the number of CSFs in the CAS space: these values could be reduced by making use of any molecular point group symmetry

| $N$ | $S$           | $N_{\text{CAS}}$ | $N_{\text{det}}$ | $N_L$<br>(determinants) | $N$ (Rumer<br>functions) |
|-----|---------------|------------------|------------------|-------------------------|--------------------------|
| 2   | 0             | 3                | 4                | 8                       | 10                       |
| 2   | 1             | 1                | 1                | 2                       | 2                        |
| 3   | $\frac{1}{2}$ | 8                | 9                | 63                      | 56                       |
| 4   | 0             | 20               | 36               | 216                     | 228                      |
| 4   | 1             | 15               | 16               | 160                     | 162                      |
| 5   | $\frac{1}{2}$ | 75               | 100              | $1.70 \times 10^3$      | $1.44 \times 10^3$       |
| 6   | 0             | 175              | 400              | $4.80 \times 10^3$      | $4.50 \times 10^3$       |
| 6   | 1             | 189              | 225              | $4.95 \times 10^3$      | $5.00 \times 10^3$       |
| 7   | $\frac{1}{2}$ | 784              | 1225             | $3.80 \times 10^4$      | $3.07 \times 10^4$       |
| 8   | 0             | 1764             | 4900             | $9.80 \times 10^4$      | $8.48 \times 10^4$       |
| 8   | 1             | 2352             | 3136             | $1.19 \times 10^5$      | $1.21 \times 10^5$       |
| 9   | $\frac{1}{2}$ | 8820             | 15876            | $7.78 \times 10^5$      | $6.08 \times 10^5$       |
| 10  | 0             | 19404            | 63504            | $1.91 \times 10^6$      | $1.56 \times 10^6$       |
| 10  | 1             | 29700            | 44100            | $2.56 \times 10^6$      | $2.61 \times 10^6$       |
| 11  | $\frac{1}{2}$ | 104544           | 213444           | $1.52 \times 10^7$      | $1.16 \times 10^7$       |
| 12  | 0             | 226512           | 853776           | $3.59 \times 10^7$      | $2.83 \times 10^7$       |
| 12  | 1             | 382239           | 627264           | $5.14 \times 10^7$      | $5.28 \times 10^7$       |
| 13  | $\frac{1}{2}$ | 1288287          | 2944656          | $2.86 \times 10^8$      | $2.15 \times 10^8$       |
| 14  | 0             | 2760615          | 11778624         | $6.60 \times 10^8$      | $5.07 \times 10^8$       |
| 14  | 1             | 5010005          | 9018009          | $9.92 \times 10^8$      | $1.03 \times 10^9$       |

For all four of our CASVB criteria, the cost of a single evaluation of the objective function ( $S_{\text{cov}}$  or  $E_{\text{cov}}$ ) is a small component of the expressions we have just presented, i.e. the overall cost is dominated by the effort required to generate the complete Hessian. As such, it makes sense to find the optimal “update” for a given Hessian (and gradient), even if this requires multiple evaluations of  $S_{\text{cov}}$  or  $E_{\text{cov}}$ .

## 6 Conclusions

The present work exploits the invariance of full-CI expansions under any nonsingular linear transformation of the active orbitals. In particular, we have examined *exact* transformations of the “ $N$  in  $N$ ” CASSCF structure space that lead to modern valence bond representations, in which covalent structures built from a common product of nonorthogonal orbitals dominate the total wavefunction. In addition, we have been able to quantify the very close correspondence between CASSCF and SC calculations. The differences can be associated with

- (1) the different active orbital spaces, and
- (2) the inclusion or exclusion of “ionic” structures.

In all the cases we have examined, the first effect has been rather small, although in the case of methane the small components of the SC orbitals that lie outside the CAS active space lead to a dramatic change in the orbital description. In general, the second factor does not have any major impact on the qualitative interpretation of the wavefunction, as signified, for example, by the relatively small changes in the spin-coupling coefficients when including ionic structures.

We have defined overlap-based (CASVB1 and CASVB2) and energy-based (CASVB3 and CASVB4) criteria for selecting “useful” orbital transformations that lead to SC-like representations of the CASSCF wavefunction. The resulting covalent components ( $\Psi_{\text{cov}}$ ) have overlaps with the full CASSCF wavefunction on the order of 99%.

For singlet methylene, all four CASVB schemes can be used to generate modern VB representations of the bonding that are very similar to the one which emerges from the full-SC calculation. For methane, on the other hand, it turns out to be important to generate the spin-coupling coefficients by transforming the CASSCF CI vector, rather than to treat them as further parameters to be varied in the optimisations. Furthermore, the orbitals which emerge from an SC calculation restricted to the CAS active space do not correspond to the conventional representations of the bonding in  $\text{CH}_4$ , probably because of the rather restricted number of orbital free parameters. This also has ramifications for certain other approaches, such as BOVB [29].

All four CASVB schemes perform very well for ozone, treated as a system with four active  $\pi$  electrons distributed in four orbitals. The SC calculation recovers almost all of the correlation energy incorporated in the CASSCF wavefunction, and the spaces defined by the CASSCF and SC active orbitals are very similar. However, a special feature of this system is that there exist *two* “4 in 4” CASSCF wavefunctions with very similar energy. Correspondingly, there are two sets of CASVB representations, as well as two SC solutions (diradical and hypervalent). As such, neither description alone can be considered an adequate modern VB picture of the bonding in ozone.

Perhaps the most surprising finding is the small difference between the outcomes of the corresponding  $\max(S_{\text{cov}})$  and  $\min(E_{\text{cov}})$  criteria. In view of the relative computational costs, this seems to point to the CASVB1 and CASVB2 schemes as being of greatest practical utility for future work. The CASVB criteria have now been applied to a range of systems, in most cases with excellent results [4]. The particular examples included here have been chosen to illustrate various aspects of the method, not least some of the problems that may occur. It is not significant that the perfect-pairing mode of spin coupling is dominant in the cases presented here, in that excellent results have also been obtained, for example, for the  $\pi$  electrons of benzene [4]. Full details of all the CASVB algorithms will be published separately, together with descriptions of our further applications.

## References

1. For a review of the CASSCF method see, for example: Roos BO (1987) *Adv Chem Phys* 69:399
2. Malmqvist PÅ (1986) *Int J Quant Chem* 30:479
3. Malmqvist PÅ, Roos BO (1989) *Chem Phys Lett* 155:189
4. Thorsteinsson T (1995) Development of methods in spin-coupled theory. PhD thesis, University of Liverpool, UK
5. For a review of applications see, for example: Cooper DL, Gerratt J, Raimondi M (1991) *Chem Revs* 91:929
6. McWeeny R (1954) *Proc R Soc Lond Ser A* 223:306
7. Pauncz R (1979) *Spin eigenfunctions*. Plenum, NY
8. Raos G, Gerratt J, Cooper DL, Raimondi M (1993) *Molec Phys* 79:197
9. Karadakov PB, Gerratt J, Cooper DL, Raimondi M (1995) *Theor Chim Acta* 90:51
10. Paldus J (1976) In: Eyring H, Henderson DG (eds) *Theoretical chemistry: advances and perspectives*, Vol. 2. Academic Press, NY
11. Murphy RB, Messmer RP (1993) *J Chem Phys* 98:7958
12. Werner H-J, Knowles PJ (1985) *J Chem Phys* 82:5053
13. Knowles PJ, Werner H-J (1985) *Chem Phys Lett* 115:259
14. MOLPRO is a package of *ab initio* programs written by H-J Werner and PJ Knowles, with contributions from Almlöf J, Amos R, Elbert S, Hampel K, Meyer W, Peterson K, Pitzer R and Stone AJ
15. Bauschlicher CW, Taylor PR (1986) *J Chem Phys* 85:6510
16. Dunning Jr TH (1989) *J Chem Phys* 90:1007
17. Sironi M, Raimondi M, Cooper DL, Gerratt J (1987) *J Chem Soc Faraday Trans 2* 83:1651
18. Wright SC, Cooper DL, Sironi M, Raimondi M, Gerratt J (1990) *J Chem Soc Perkin Trans 2*, 369
19. Sironi M, Cooper DL, Gerratt J, Raimondi M (1990) *J Am Chem Soc* 112:5054
20. Penotti F, Cooper DL, Gerratt J, Raimondi M (1988) *J Mol Struct (THEOCHEM)* 169:421
21. Hiberty PC, Cooper DL (1988) *J Mol Struct (THEOCHEM)* 169:437
22. Pauling L (1928) *Proc Natl Acad Sci USA* 14:359; Pauling L (1931) *J Am Chem Soc* 53:1367
23. Raimondi M, Campion W, Karplus M (1977) *Molec Phys* 34:1483
24. Huzinaga S (1965) *J Chem Phys* 42:1293
25. Karadakov PB, Gerratt J, Raimondi M, Cooper DL (1992) *J Chem Phys* 97:7635
26. Cooper DL, Gerratt J, Raimondi M (1989) *J Chem Soc Perkin Trans 2*, 1187
27. Penotti FE, to be published; see also: Penotti FE (1993) *Int J Quant Chem* 46:535
28. Ruedenberg K, Schmidt MW, Gilbert MM, Elbert ST (1982) *Chem Phys* 71:41,51,61; Schmidt MW, Lam B, Elbert ST, Ruedenberg K (1985) *Theor Chim Acta* 68:69
29. McDouall JJW, Robb MA (1986) *Chem Phys Lett* 132:319
30. McDouall JJW, Robb MA (1987) *Chem Phys Lett* 142:131
31. Levy B (1969) *Chem Phys Lett* 4:17
32. Thouless DJ (1961) *The quantum mechanics of many-body systems*. Academic Press, NY
33. Malcolm NOJ, McDouall JJW (1994) *J Comp Chem* 15:1357
34. Cooper DL, Gerratt J, Raimondi M, Wright SC (1987) *Chem Phys Lett* 138:296
35. Malcolm NOJ, McDouall JJW (1994) *J Comp Chem* 15:1365