Nonorthogonal weights of modern VB wavefunctions. Implementation and applications within CASVB

Thorstein Thorsteinsson [a] and David L. Cooper [b]

[a] *Department of Chemistry, Chemistry Laboratory IV, Universitetsparken 5, 2100 Copenhagen Ø, Denmark*
[b] *Department of Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 7ZD, UK*

The CASVB approach is a recent development in modern valence bond theory which aims to provide easily visualized, highly accurate representations of very general types of CASSCF wavefunctions. Fully variational optimization may also be performed for quite general types of modern valence bond wavefunction. Numerous definitions of nonorthogonal weights are used to investigate the role of contributions from various types of 'ionic' configurations, taking hexatriene and N_2S_2 as illustrative examples.

1.   Introduction

It is now widely accepted that any approach that seeks realistic molecular wavefunctions within a valence bond (VB) formulation is likely to involve optimization of some or all of the participating orbitals. To distinguish these procedures from earlier, more qualitative treatments, typically based on strictly localized orbitals, we have adopted the term 'modern valence bond theory'. Since a valence bond wavefunction is generally of multideterminantal form, there are many parallels to the multiconfiguration self-consistent field (MCSCF) methods of molecular orbital (MO) theory, such as the restriction to a relatively small 'active space' describing the chemically most interesting features of the electronic structure. This relationship is emphasized further in CASVB [8,36–40], due to the very close connection with the complete active space self-consistent field or CASSCF approach.

Many different factors determine the utility (or otherwise) of any computational procedure. Some points to bear in mind in the present context are computational efficiency, flexibility of the optimization, supporting programs, and the general availability of the codes. For a valence bond procedure, the computational efficiency is to a large extent determined by the strategy for overcoming the nonorthogonality problem. This is achieved in CASVB by a transformation of the valence bond wavefunction to an orthogonal full CI representation. In this sense, a CASVB wavefunction is a particular constrained form of CASSCF wavefunction. While this might not be the 'best' or most elegant solution to this problem, there are unquestionable advantages of such an approach. The possibility for overlap-based optimization, for example, serves to make the valence bond interpretation of CASSCF wavefunctions significantly more

efficient than similar schemes based on variational optimization (see, for example, [7]). Furthermore, the proper utilization of point group symmetry [39], and special techniques for applying the electronic Hamiltonian to full CI vectors [21,32,37,42] combine to make the efficiency of variational optimization also compare favourably with alternative methods presently available.

Computational efficiency is not on its own a useful measure of the practicality of a given method. Regarding the optimization procedure, other significant features in CASVB are the flexible form of the modern VB wavefunctions that can be used – these can be of quite general multiconfigurational form – as well as the possibility of constrained optimization. Constraints attain special importance in VB optimization for removing redundant parameters, imposing partial orthogonality, or symmetry adapting the overall wavefunction [8,39]. Such constraints may avoid linear dependency problems or help convergence towards a particular type of solution.

Although on the increase, the number of researchers employing VB methodology is still very much in the minority. This is understandable in view of the lack of generally available programs, and the significant 'activation barrier' thus associated with undertaking these kinds of studies. To help alleviate this deficiency, our procedures have now been made publicly available as part of the quantum chemistry package MOLPRO[1], in which they are interfaced to a sophisticated CASSCF program [25,41]. We foresee a wider distribution of our code in the near future. An important additional benefit is the number of supporting programs that become available in this way. In principle, all of the impressive technology developed within the CASSCF formalism becomes accessible within a valence bond framework. The most obvious examples include direct evaluation of integrals, one- and two-electron properties, geometry optimization, and the treatment of excited states. All such techniques may be employed without the need for major restructuring of existing codes.

We present in section 4 two new applications of the CASVB approach – *trans*-1,3,5-hexatriene and N_2S_2 – exemplifying various aspects of our method. A recurring theme is the analysis of modern VB wavefunctions by assigning nonorthogonal weights to the constituent structures or spatial configurations. After a brief review of the CASVB strategy, we review in section 3 the commonly employed definitions of nonorthogonal weights and their implementation within our procedure. Finally, we present our main conclusion in section 5.

2. The CASVB strategy

The invariance of certain types of wavefunctions with respect to orbital transformations is utilized in many methods. One important motivation is to facilitate the

---

interpretation of the wavefunction, as for example in the common MO localization schemes [1,2,12–14,16,33], while an important alternative is to speed up the convergence of the total energy or of properties when going to more highly correlated treatments (e.g., methods based on 'natural orbitals' [9,27] or on 'improved virtual orbitals' [23,24]). This invariance also underpins CASVB, with a main aim being to increase the interpretability of CASSCF wavefunctions by utilizing the inherent freedom in the representation of the active orbital set. Related work in this area is discussed in our earlier papers [8,36–40].

Full CI spaces are invariant with respect to (nonsingular) linear transformations of the defining one-electron basis:

$$\{\phi'\} = \{\phi\}\mathbf{O} \quad \Rightarrow \quad \{\Phi'\} = \{\Phi\}\mathbf{T(O)}. \tag{1}$$

In these expressions, the $\{\}$ signify row vectors of orbitals, ϕ, or configuration state functions (or determinants), Φ. In general, the configuration space may contain a core part common to all functions, $\Phi_I = \mathcal{A}(\Phi^{\mathrm{core}} \times \Phi_I^{\mathrm{act}})$, and can then be classified as an 'N electrons in m orbitals' full CI within the active space. The transformation of the full CI space, $\mathbf{T(O)}$, is also linear and, for nonsingular transformations, $\{\mathbf{O}\}$ and $\{\mathbf{T(O)}\}$ form isomorphic groups. Using the basic property $\mathbf{T(O_1 O_2)} = \mathbf{T(O_1)T(O_2)}$, the effects of the full CI transformation can be determined very efficiently (without direct construction) by decomposition of the orbital transformation [28,36,37].

Useful representations of Ψ_{CAS} may be obtained by expressing a trial wavefunction in the form

$$\Psi_{\mathrm{VB}} = \sum_I c_I \Phi_I^{\mathrm{VB}} = \sum_I c_I \big(\{\Phi\}\mathbf{T}(\mathbf{O}^{\mathrm{VB}})\big)_I, \tag{2}$$

and optimizing $\mathbf{O}^{\mathrm{VB}}$ and the structure coefficients, c_I. We have previously considered overlap-based

$$\text{maximize } S_{\mathrm{VB}} = \frac{\langle \Psi_{\mathrm{CAS}} | \Psi_{\mathrm{VB}} \rangle}{\langle \Psi_{\mathrm{VB}} | \Psi_{\mathrm{VB}} \rangle^{1/2}}, \tag{3}$$

or energy-based

$$\text{minimize } E_{\mathrm{VB}} = \frac{\langle \Psi_{\mathrm{VB}} | \widehat{H} | \Psi_{\mathrm{VB}} \rangle}{\langle \Psi_{\mathrm{VB}} | \Psi_{\mathrm{VB}} \rangle}, \tag{4}$$

criteria for the optimization. Both aim to give accurate approximations to CASSCF wavefunctions. Emphasis will be placed in the present account on the overlap criterion, but energy-based optimization is also of significant utility, especially in the context of fully variational applications. The number and the nature of the VB structures in equation (2) may be varied according to the features of a given application. In many cases a sensible choice for the form of Ψ_{VB} will be a single spatial configuration of N singly-occupied orbitals, i.e., a spin-coupled wavefunction

$$\Psi_{\mathrm{VB}} = \mathcal{A}\big(\Phi^{\mathrm{core}} \phi_1^{\mathrm{VB}} \phi_2^{\mathrm{VB}} \cdots \phi_N^{\mathrm{VB}} \Theta_{SM}^N\big). \tag{5}$$

Optimization of this type of wavefunction has formed the basis for applications on a wide variety of molecular systems [6] with a significant degree of success in providing understanding of nondynamical electron correlation effects. The expansion coefficients of the total spin function Θ_{SM}^{N} in the full allowed spin space are termed the spin-coupling coefficients (c_{Sk}).

It proves useful to consider the wavefunction space generated by first-order changes in the valence bond variational parameters. For the orbital parameters we may define

$$\widehat{E}_{\mu\nu}^{\perp} = \widehat{E}_{\mu\nu} - \langle\phi_{\mu}|\phi_{\nu}\rangle\widehat{E}_{\nu\nu}, \tag{6}$$

describing an excitation $\phi_{\nu} \rightarrow \phi_{\mu}$ such that the first-order function

$$\Psi_{\mu\nu} \equiv \widehat{E}_{\mu\nu}^{\perp}\Psi_{\text{VB}} \tag{7}$$

is ensured to be orthogonal to the reference function. We use a similar notation for changes in the structure parameters:

$$\Psi_{I} = \widehat{E}_{I1}^{\perp}\Psi_{\text{VB}}, \quad I = 2, \ldots, N_{\text{VB}}, \tag{8}$$

such that the $\{\Psi_2, \Psi_3, \ldots\}$ form the $(N_{\text{VB}} - 1)$-dimensional orthogonal complement to Ψ_{VB}. For the energy-based criterion this formulation leads to the well-known Brillouin conditions for a stationary point:

$$\frac{\partial E_{\text{VB}}}{\partial c_{\mu\nu}} = 2\langle\Psi_{\text{VB}}|\widehat{H}|\Psi_{\mu\nu}\rangle = 0 \quad \wedge \quad \frac{\partial E_{\text{VB}}}{\partial c_{I}} = 2\langle\Psi_{\text{VB}}|\widehat{H}|\Psi_{I}\rangle = 0, \tag{9}$$

where $c_{\mu\nu}$ and c_{I} are the parameters corresponding to the variations $\widehat{E}_{\mu\nu}^{\perp}$ and $\widehat{E}_{I1}^{\perp}$ (real wavefunctions are assumed here). Closely analogous relations exist for the overlap-based criterion

$$\frac{\partial S_{\text{VB}}}{\partial c_{\mu\nu}} = \langle\Psi_{\text{CAS}}|\Psi_{\mu\nu}\rangle = 0 \quad \wedge \quad \frac{\partial S_{\text{VB}}}{\partial c_{I}} = \langle\Psi_{\text{CAS}}|\Psi\rangle = 0. \tag{10}$$

The overlap-based optimization will, loosely speaking, seek to minimize the contributions in the total CASSCF wavefunction from:

- Structures generated by single orbital replacements from the reference. (In the case of a spin-coupled wavefunction, these may be termed either singly ionic or singly excited structures.)
- Alternative linear combinations of structure coefficients.

Due to the nonorthogonality of structures, however, the coefficients of these structures may be nonvanishing. This raises the question of how sensibly to define weights of the nonorthogonal structures.

3. Definitions of nonorthogonal weights

We review here various definitions of weights for nonorthogonal structures and their implementation within CASVB. In general, we consider a wavefunction given as a linear combination of nonorthogonal structures

$$\Psi = \sum_I c_I \Psi_I, \tag{11}$$

with $(\mathbf{S})_{IJ} = \langle \Psi_I | \Psi_J \rangle$. We wish to assign weights $w(\Psi_I)$ (or just w_I) as measures of the 'importance' of each Ψ_I in this expansion. It is useful to consider some desirable features for such schemes:

(1) Normalization, i.e., $\sum_I w_I = 1$.

(2) Meaningful range, i.e., $\forall I, \; 0 \leqslant w_I \leqslant 1$.

(3) Linearity, i.e., $\forall I, J, \; w(\Psi_I) + w(\Psi_J) = w(\Psi_I + \Psi_J)$.

(4) Correct limit, i.e., $\mathbf{S} = \mathbf{1} \Rightarrow w_I = c_I^2$.

None of the schemes considered here will adhere to all four points.

One of the simplest and most stable schemes for assigning nonorthogonal weights is that due to Chirgwin and Coulson [5]. Restricting one of the summations, in the normalization condition for Ψ, weights may be defined according to

$$w_I = \sum_J c_J^* c_I S_{JI} = \langle \Psi | \Psi_I \rangle c_I. \tag{12}$$

Points 1, 3 and 4 trivially hold in this case; the main problem with Chirgwin–Coulson weights is that they may lie outside the interval [0;1].

The definition of weights is unambiguous when the functions are orthogonal, suggesting that it could be useful to define weights by orthogonalization(s) of the $\{\Psi_I\}$. There are many such schemes that can lead to sensible weights. If, for example, only the weights for a *subset* of functions are of interest, then it could be useful to perform an orthogonalization only of the remaining functions, so that a block-diagonal overlap matrix is defined. This can lead to significant simplifications. Indeed, the overlap-based criterion in equation (3) can be viewed as a partitioning of the CASSCF space according to

$$\Psi_{\text{CAS}} = S_{\text{VB}} \Psi_{\text{VB}} + \left(1 - S_{\text{VB}}^2\right)^{1/2} \Psi_{\text{RES}}^{\perp}, \tag{13}$$

followed by a maximization of the weight for Ψ_{VB}. A similar strategy can be applied to the analysis of VB structures if, for example, the weight of specifically the perfectly paired structure is of interest. In the more general case, in which weights of *all* functions could be of interest, Löwdin's scheme for symmetric orthogonalization [26] is an attractive option. This leads to orthogonalized functions deviating as little as possible, in a root mean square sense, from the original set. Weights defined in this way will adhere to points 1, 2 and 4 listed above. The well known Mulliken [29] and

Löwdin procedures for population analysis are of course just special applications of the Chirgwin–Coulson and symmetrically-orthogonalized weights.

Another procedure of some merit is the 'inverse-overlap scheme' due to Gallup and Norbeck [17,18]. Weights are defined according to

$$w_I = |c_I|^2 / (\mathbf{S}^{-1})_{II}. \tag{14}$$

The diagonal element of $\mathbf{S}^{-1}$ gives a measure of the length of the 'unique' component of Ψ_I,

$$1/(\mathbf{S}^{-1})_{II} = \left\| \Psi_I^\perp \right\|^2, \tag{15}$$

in which $\Psi_I^\perp$ is orthogonal to the other members of the set. The weights defined in this way adhere only to items 2 and 4 above, but are customarily also normalized to unity.

The implementations within CASVB of the nonorthogonal weights just outlined all take advantage of the following simple relation:

$$\mathbf{S} = \mathbf{T}^\dagger(\mathbf{O})\mathbf{T}(\mathbf{O}) = \mathbf{T}(\mathbf{O}^\dagger\mathbf{O}) = \mathbf{T}(\mathbf{s}), \tag{16}$$

where we have used $\mathbf{S}$ for the overlap matrix between structures and $\mathbf{s}$ for the orbital overlaps. In the case where Ψ_{VB} is used in combination with a projection operator (e.g., $\widehat{P}_{\text{SYM}}$ [39]), the expression for $\mathbf{S}$ may be slightly more involved, but it can always be expressed in terms of the two full CI transformations $\mathbf{T}(\mathbf{O}^\dagger)$ and $\mathbf{T}(\mathbf{O})$. Extra care should also be taken when interpreting the results in this case. Of course, $\mathbf{T}(\mathbf{s})$ is not evaluated explicitly, for the same reasons as we avoid direct construction of $\mathbf{T}(\mathbf{O})$. Computation of the overlap matrix between valence bond structures requires N_{VB} applications of $\mathbf{T}(\mathbf{s})$:

$$(\mathbf{S}_{\text{VB}})_{IJ} = \mathbf{c}^{(I)\dagger}\mathbf{T}(\mathbf{s})\mathbf{c}^{(J)}, \tag{17}$$

where the $\mathbf{c}^{(I)}$ are the CI vectors corresponding to valence bond structures Ψ_I. Diagonalization of $\mathbf{S}_{\text{VB}}$ can then give both the inverse and square root of the overlap matrix, which leads to the inverse-overlap and Löwdin-orthogonalized weights, respectively.

Forming explicitly the complete overlap matrix in the full CI structure basis is of course untenable for anything but the smallest active spaces, and the implementation of weights must therefore rely on one or more full CI transformations. For example, in the case of the Chirgwin–Coulson definition of weights, we consider the normalization condition for a vector expressed in the basis of VB structures:

$$\mathbf{c}^\dagger(\mathbf{T}(\mathbf{s})\mathbf{c}) = 1. \tag{18}$$

Partitioning this summation yields all the required weights, so that a *single* full CI transformation is sufficient in this case. This also proves to be the true for Löwdin-orthogonalized weights, in which we require the effect of one application of $\mathbf{S}^{1/2}$:

$$\mathbf{S}^{1/2}\mathbf{S}^{1/2} = \mathbf{S} = \mathbf{T}(\mathbf{s}) \quad \Rightarrow \quad \mathbf{S}^{1/2} = \mathbf{T}(\mathbf{s}^{1/2}). \tag{19}$$

It is clear from this last expression that a symmetric orthogonalization of the full CI structure space is strictly equivalent to a symmetric orthogonalization of the underlying orbital basis.

Evaluation of inverse-overlap weights is somewhat more involved. We introduce the set of vectors $\{\mathbf{c}^{(I)}\}$ such that $\mathbf{c}^{(I)}$ is zero except for $(\mathbf{c}^{(I)})_I = c_I$, so that equation (14) can then be recast in the form

$$w_I = \frac{(\mathbf{c}^{(I)\dagger}\mathbf{c}^{(I)})^2}{\mathbf{c}^{(I)\dagger}\mathbf{S}^{-1}\mathbf{c}^{(I)}}, \quad \left\|\mathbf{c}^{(I)}\right\| \neq 0. \tag{20}$$

Of course, if $\mathbf{c}^{(I)}$ is the zero vector we set $w_I = 0$. In order to consider the case where the $\{\mathbf{c}^{(I)}\}$ do not form a diagonal matrix, we then insert resolutions of the identity, using a unitary transformation, $\mathbf{U}$:

$$w_I = \frac{(\mathbf{c}^{(I)\dagger}\mathbf{U}^{\dagger}\mathbf{U}\mathbf{c}^{(I)})^2}{\mathbf{c}^{(I)\dagger}\mathbf{U}^{\dagger}\mathbf{U}\mathbf{S}^{-1}\mathbf{U}^{\dagger}\mathbf{U}\mathbf{c}^{(I)}} = \frac{(\mathbf{c}'^{(I)\dagger}\mathbf{c}'^{(I)})^2}{\mathbf{c}'^{(I)\dagger}(\mathbf{S}')^{-1}\mathbf{c}'^{(I)}}. \tag{21}$$

This means that provided a general set of vectors, $\{\mathbf{c}'^{(I)}\}$, can *in principle* be brought into diagonal form by a unitary transformation, one may use equation (21) to obtain the corresponding inverse-overlap weights.

For the weights of spatial configurations in the CI expansion, the set $\{\mathbf{c}'^{(I)}\}$ is not diagonal, because each configuration occurs as a combination of several structures, but it is trivial to show that such a diagonalization can in fact be performed. Unfortunately, the associated computational effort becomes substantial for larger active spaces, because an application of $\mathbf{T}(\mathbf{s}^{-1})$ must be carried out for each spatial configuration. This problem can be significantly alleviated by grouping configurations together (for example, according to ionicity or to excitation level). Thus, it is clear that the effort involved is closely connected to the 'resolution' required for the weights.

4. Applications

Trans-1,3,5-hexatriene

As an example of a notionally 'covalent' system, we consider the conjugated hydrocarbon *trans*-1,3,5-hexatriene. This system has been the subject of recent CASSCF and CASPT2 studies [34], as well as some earlier GVB-CI [30,31] and CI [3,4] investigations. The calculations described here employed Dunning's VTZ basis sets [11] for C/H, consisting of (10s5p/5s) Cartesian GTOs contracted to [4s3p/3s], to which were added a d-function on each carbon and a p-function on each hydrogen (exponents $\alpha = 0.8$ and $\alpha = 1.0$, respectively). The geometry used here was that determined by electron diffraction on the ground state [22].

The σ electrons were kept in an (optimized) core in all calculations, while all π electrons were described at the CASSCF level. We consider both '6 in 6' and '6 in 8' CASSCF calculations for the ^1A_g ground state and for the first excited state of ^1A_g symmetry. Energies for the various MO-based calculations are collected in table 1.

Table 1
Energies for various calculations on hexatriene.

Calculation	State	E (hartree)
SCF	1^1A_g	-231.866981
'6 in 6' CASSCF	1^1A_g	-231.949701
'6 in 6' CASSCF	2^1A_g	-231.740642
'6 in 8' CASSCF	1^1A_g	-231.953994
'6 in 8' CASSCF	2^1A_g	-231.745708
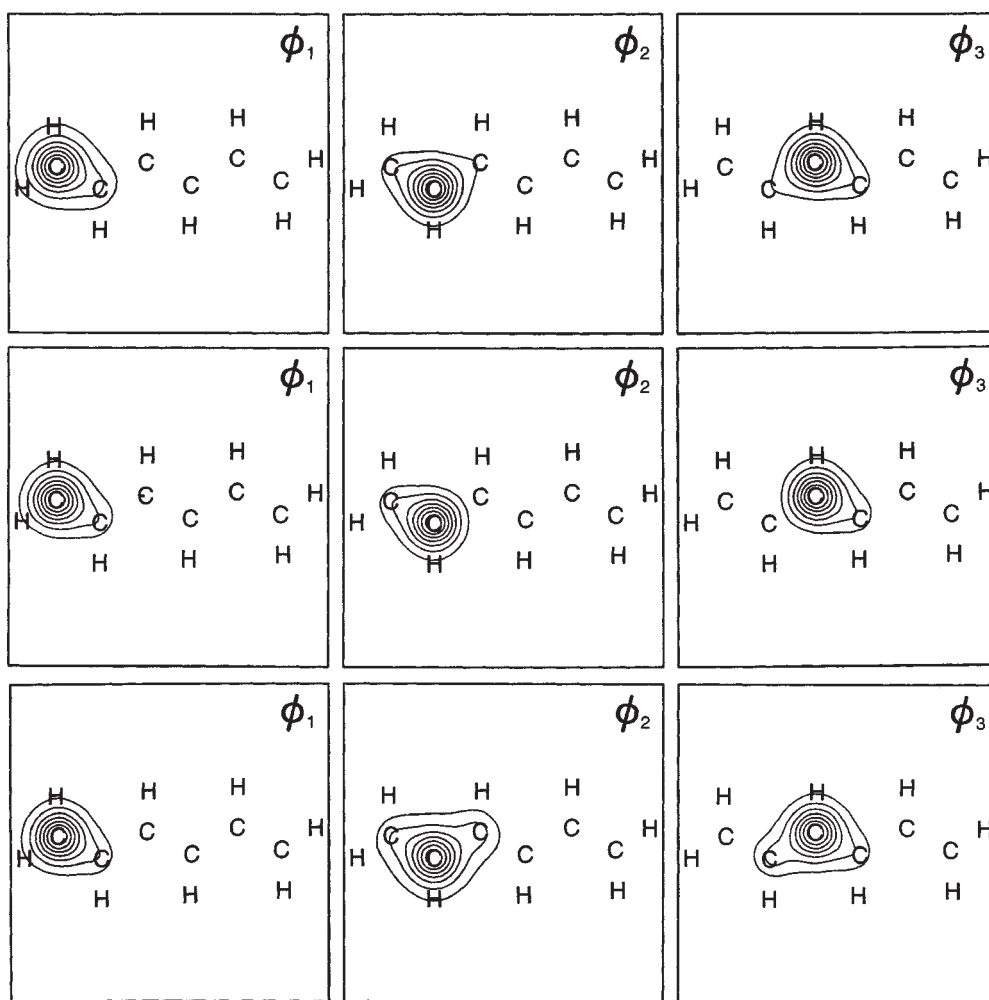
Figure 1. Symmetry-unique CASVB orbitals for the 1^1A_g state of hexatriene. Orbitals ϕ_4, ϕ_5 and ϕ_6 may be generated from ϕ_3, ϕ_2 and ϕ_1 by $\widehat{C}_2$ rotations. The orbitals are plotted 1 bohr above the molecular plane. In sequence the three orbital sets are: unconstrained optimization, optimization with strong orthogonality constraint, optimization with a single perfect-pairing structure.

Table 2

CASVB overlaps and energies for max(S_{VB}) interpretations of '6 in 6' CASSCF calculations. For the 2^1A_g state, the strong orthogonality calculation is based on the pairing (23)(45)(16).

Method of interpretation	S_{VB}	E_{VB} (hartree)
(a) 1^1A_g		
SC	0.999590	−231.948901
SC + Löwdin orthogonalization	0.571618	−231.290334
SC + full orthogonality	0.577851	−231.273492
SC + strong orthogonality	0.993307	−231.939698
SC + perfect pairing	0.997181	−231.945481
(b) 2^1A_g		
SC	0.998517	−231.738354
SC + Löwdin orthogonalization	0.659124	−231.363292
SC + full orthogonality	0.672102	−231.350493
SC + strong orthogonality	0.899971	−231.680931

Table 3

Coefficients and weights of structures based on the Kotani spin basis (all structures are defined with a normalized spin function), for the CASVB interpretations of the '6 in 6' CASSCF wavefunctions. c, i and s refer to Chirgwin–Coulson, inverse-overlap, and symmetrically orthogonalized weights, respectively.

	Ψ_1	Ψ_2	Ψ_3	Ψ_4	Ψ_5
(a) 1^1A_g					
c_{Sk}	0.0035	−0.0341	0.0930	0.0930	0.612
$^c w(k)$	0.0046%	0.10%	0.99%	0.99%	97.92%
$^i w(k)$	0.00031%	0.03%	0.43%	0.43%	99.11%
$^s w(k)$	0.01%	0.11%	1.16%	1.16%	97.54%
(b) 2^1A_g					
c_{Sk}	−0.1507	0.7731	−0.6354	−0.6354	−0.3354
$^c w(k)$	2.34%	40.68%	25.77%	25.77%	5.43%
$^i w(k)$	0.52%	27.03%	24.97%	24.97%	22.51%
$^s w(k)$	3.84%	39.92%	24.07%	24.07%	8.10%

The overlap-based CASVB representation of the '6 in 6' ground state calculation was based on a single-configuration spin-coupled wavefunction. The valence bond description arising from such a treatment consists of localized orbitals on each carbon with some deformation towards the neighbouring carbon centres (see top row of figure 1). The overlap between the modern valence bond and CASSCF wavefunctions, S_{VB}, amounts to 0.999590 (see table 2(a)) which is even higher than we have found for other calculations based on '6 in 6' active spaces. The energy difference $E_{VB} - E_{CAS}$ is accordingly just 0.8 millihartree. The electron spins couple to a very good approximation according to the perfect-pairing mode (12)(34)(56), as indicated by the spin-coupling coefficients and their weights (see table 3(a)). The Chirgwin–Coulson

Table 4

Overlaps between (normalized) orbitals for $\max(S_{VB})$ interpretations of CASSCF wavefunctions for the 1^1A_g state (lower triangle) and 2^1A_g state (upper triangle) of hexatriene.

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
Unconstrained VB ('6 in 6')						
ϕ_1		0.619	0.204	0.118	−0.001	0.061
ϕ_2	0.652		0.557	0.156	−0.119	−0.001
ϕ_3	0.086	0.309		0.605	0.156	0.118
ϕ_4	0.029	0.072	0.641		0.557	0.204
ϕ_5	−0.020	−0.084	0.072	0.309		0.619
ϕ_6	0.006	−0.020	0.029	0.086	0.652	
Unconstrained VB ('6 in 8')						
ϕ_1		0.618	0.206	0.124	0.001	0.066
ϕ_2	0.656		0.562	0.162	−0.125	0.001
ϕ_3	0.094	0.309		0.620	0.162	0.124
ϕ_4	0.041	0.080	0.650		0.562	0.206
ϕ_5	−0.023	−0.093	0.080	0.309		0.618
ϕ_6	0.006	−0.023	0.041	0.094	0.656	
Perfect-pairing VB ('6 in 6') 1^1A_g						
ϕ_1	1					
ϕ_2	0.599	1				
ϕ_3	0.161	0.618	1			
ϕ_4	−0.106	0.135	0.537	1		
ϕ_5	−0.040	0.012	0.135	0.618	1	
ϕ_6	0.003	−0.040	−0.106	0.161	0.599	1

weights in this case agree very well with the weights of the Löwdin-orthogonalized structures, whereas inverse-overlap weights attribute a higher importance to the perfectly paired function. The orbital overlaps for this wavefunction are given in table 4.

The consequences of augmenting the wavefunction with ionic structures may be assessed by evaluating weights of the total CASSCF wavefunction, transformed to the orbital representation defined by $\max(S_{VB})$. We report in table 5(a) the accumulated weights for configurations with the various possible ionicities, analyzing both Ψ_{CAS} and the residual function $\Psi_{RES}^\perp = \Psi_{CAS} - S_{VB}\Psi_{VB}$. Even though the Chirgwin–Coulson weights may fall outside the meaningful range [0;100%], it is nevertheless clear that the covalent configuration strongly dominates, while the contributions from triply ionic structures are negligible. The fact that the weights of the doubly ionic structures dominate the residual vector is consistent with the observation that the optimization of the orbitals tends to minimize contributions from singly ionic structures. The Brillouin-like condition embodied in equation (10) also reduces the Chirgwin–Coulson covalent weight in $\Psi_{RES}^\perp$ to zero (cf. equation (12)). The inverse-overlap weights show qualitative agreement with these findings, except for the non-zero covalent weight in the residual vector. The effect of orthogonalizing the structures can be seen to be very severe in this case. The weight of the covalent configuration falls to 32.8%, which

Table 5

Accumulated weights of configurations in the hexatriene '6 in 6' CASSCF wavefunctions according to their ionicity. The entries '≈ 0' signify zero within numerical accuracy.

Ionicity	Chirgwin–Coulson		Inverse-overlap		Löwdin	
	Ψ_{CAS} (%)	$\Psi_{RES}^{\perp}$ (%)	Ψ_{CAS} (%)	$\Psi_{RES}^{\perp}$ (%)	Ψ_{CAS} (%)	$\Psi_{RES}^{\perp}$ (%)
(a) 1^1A_g						
0	101.28	≈ 0	98.04	2.85×10^{-3}	32.80	7.57×10^{-4}
1	-2.31	1.23×10^{-2}	7.06×10^{-1}	2.85×10^{-2}	45.09	1.17×10^{-2}
2	1.03	6.90×10^{-2}	1.24	5.01×10^{-2}	19.50	5.55×10^{-2}
3	-1.75×10^{-4}	6.63×10^{-4}	1.34×10^{-2}	5.41×10^{-4}	2.61	8.20×10^{-2}
(b) 2^1A_g						
0	112.63	≈ 0	90.98	3.67×10^{-2}	43.63	3.20×10^{-2}
1	-11.98	2.58×10^{-1}	8.74	2.51×10^{-1}	46.44	1.48×10^{-1}
2	-7.08×10^{-1}	3.63×10^{-2}	2.86×10^{-1}	8.22×10^{-3}	9.51	1.13×10^{-1}
3	5.72×10^{-2}	2.01×10^{-3}	5.49×10^{-4}	1.58×10^{-5}	4.23×10^{-1}	3.12×10^{-3}

is clearly not satisfactory when compared to the value obtained with nonorthogonal orbitals.

Orthogonal orbitals are of course often associated with large weights for ionic structures and so, to investigate this proposition further, a max(S_{VB}) optimization was carried out with full orthogonality constraints. The optimal value for S_{VB} becomes 0.577851, corresponding to a covalent weight of 33.39%; this is only slightly better than for the Löwdin-orthogonalized set. All of these orbitals are very tightly localized on individual carbon atoms. The two orbital sets are very similar, with overlaps of 0.997, 0.998 and 0.996 between the respective orbitals 1, 2 and 3. Weights accumulated according to the ionicity of configurations are given in table 6 for the fully orthogonal orbital set. A somewhat less severe type of constraint is that of 'strong orthogonality', in which the bond-forming orbital pairs are allowed to overlap: such an optimization leads to an S_{VB} value of 0.993307, which is quite acceptable. Contour plots of these orbitals are depicted in the second row of figure 1 and it is noticeable that they lack the secondary deformations found previously for orbitals ϕ_2 and ϕ_3. However, ϕ_1 is very similar in the two sets, with an overlap of 0.997; for comparison, the overlaps between the two sets are 0.988 and 0.984 for ϕ_2 and ϕ_3, respectively. Given that deformations along the bond-forming directions are vastly more important than the secondary distortions, it is also natural to expect the corresponding singly ionic structures to dominate in the orthogonal representations of the CASSCF wavefunction. The accumulated weights for the eight structures formed by excitations between bond-forming orbitals are 43.56% (total 44.48%) for the constrained and 41.83% (total 45.09%) for the symmetrically orthogonalized orbital sets. This over-whelming dominance is not surprising in view of the large optimal values for the overlaps between these orbitals; in the strong orthogonality case they amount to $\langle \phi_1 | \phi_2 \rangle = 0.665$, $\langle \phi_3 | \phi_4 \rangle = 0.657$ and $\langle \phi_5 | \phi_6 \rangle = 0.665$. A clear conclusion of this type of analysis must be that Löwdin orthogonalization is too severe to allow a reasonable interpretation of configuration weights, at least in the case of a complete CASSCF wavefunction.

Table 6

Accumulated weights according to the ionicity of configurations in the total $1\,^1A_g$ CASSCF wavefunction. The entry '≈ 0' signifies zero within numerical accuracy. 'F' denotes here the orbital set obtained with full orthogonality constraints, while 'S' denotes the strong-orthogonality orbital set.

Ionicity	Ψ_{CAS} (F)	Chirgwin–Coulson		Inverse-overlap		Löwdin	
	(%)	Ψ_{CAS} (S) (%)	$\Psi^\perp_{RES}$ (S) (%)	Ψ_{CAS} (S) (%)	$\Psi^\perp_{RES}$ (S) (%)	Ψ_{CAS} (S) (%)	$\Psi^\perp_{RES}$ (S) (%)
0	33.39	97.16	≈ 0	74.67	1.03×10^{-3}	33.37	6.68×10^{-5}
1	44.48	4.22	1.21	22.96	1.21	44.49	8.82×10^{-1}
2	19.37	-1.40	1.22×10^{-1}	2.34	1.23×10^{-1}	19.38	4.33×10^{-1}
3	2.76	1.31×10^{-2}	3.27×10^{-3}	3.01×10^{-2}	1.58×10^{-3}	2.76	1.91×10^{-2}

Table 7

CASVB overlaps and energies for $\max(S_{VB})$ interpretations of a '6 in 8' CASSCF ground state calculation for hexatriene. Orbitals $\phi^\perp_7$ and $\phi^\perp_8$ are kept orthogonal to $\{\phi_1 - \phi_6\}$. There are no such restrictions on ϕ_7 and ϕ_8.

Method of interpretation	S_{VB}	E_{VB} (hartree)
SC	0.997807	-231.948743
$SC + (\phi_1 \rightarrow \phi_7) + (\phi_2 \rightarrow \phi_8)$	0.998163	-231.949362
$SC + (\phi_1 \rightarrow \phi^\perp_7) + (\phi_2 \rightarrow \phi^\perp_8)$	0.998145	-231.949343
$SC + (\phi_1 \rightarrow \phi_7) + (\phi_3 \rightarrow \phi_8)$	0.998318	-231.949686
$SC + (\phi_1 \rightarrow \phi^\perp_7) + (\phi_3 \rightarrow \phi^\perp_8)$	0.998301	-231.949627
$SC + (\phi_2 \rightarrow \phi_7) + (\phi_3 \rightarrow \phi_8)$	0.998326	-231.949738
$SC + (\phi_2 \rightarrow \phi^\perp_7) + (\phi_3 \rightarrow \phi^\perp_8)$	0.998295	-231.949704

The strong orthogonality (SO) restriction favours the bonds formed between the carbon pairs 1–2, 3–4 and 5–6, which is also a feature of the perfect-pairing (PP) approximation. Indeed, these two approximations are often invoked together, as in the common GVB-SOPP procedure. To compare the two effects of the SO and PP approximations, we performed a fully-variational optimization with a single, perfectly-paired VB structure. The resulting orbitals are shown in the third row of figure 1. It is noticeable that the secondary deformations of the four central carbon orbitals within the perfect-pairing approximation turn out to be somewhat larger than when the full spin space is included. It therefore seems that the overall exchange interaction between these respective centres becomes unfavourable for too large deformations.

We turn now to the '6 in 8' CASSCF calculation on the hexatriene ground state. Compared to the '6 in 6' CASSCF, this treatment can be viewed as incorporating some degree of predominantly dynamical correlation. We may still choose to interpret the wavefunction using a *single* configuration of spin-coupled form, although some lowering of S_{VB} is of course then to be expected. The value goes down to 0.997807 in this case (see table 7). This is a feature of the superiority of the '6 in 8' CASSCF wavefunction, rather than any reflection of differences between the two VB wavefunc-

Table 8
Accumulated weights in the total '6 in 8' ^1A_g CASSCF wavefunctions according to the number of excitations from $\{\phi_1-\phi_6\}$ into $\{\phi_7, \phi_8\}$.

Excitation level	1^1A_g (%)	2^1A_g (%)
0	99.651	99.515
1	0.197	0.325
2	0.151	0.160
3	1.43×10^{-4}	1.31×10^{-4}
4	4.14×10^{-5}	5.92×10^{-5}

tions. The E_{VB} values can accordingly be seen to be quite similar, -231.948901 vs. -231.948743 hartree.

Within the orbital representation defined by maximizing S_{VB} with the spin-coupled reference, the configurations defining a '6 in 6' CASSCF space using orbitals $\phi_1-\phi_6$ amount to 99.65% of the total '6 in 8' CASSCF wavefunction (table 8). This value can be evaluated exactly by imposing orthogonality between the two orbital sets $\{\phi_1-\phi_6\}$ and $\{\phi_7, \phi_8\}$. Given that the spin-coupled configuration represents 99.56% ($= S_{VB}^2$) of the total wavefunction, we obtain a similar proportion of the '6 in 6' CASSCF – 99.91%, corresponding to an 'S_{VB}' of 0.999553 – as seen in the previous optimization.

It therefore seems that the '6 in 8' CASSCF wavefunction can be viewed, to a good approximation, as the (unchanged) '6 in 6' CASSCF to which has been added configurations corresponding to excitations into orbitals ϕ_7 and ϕ_8. With this in mind, we next augmented the spin-coupled configuration with excitations into these orbitals:

$$\Psi_{VB} = c_1\Psi_{SC} + \widehat{P}_{SYM}^{(1)}\{c_2\widehat{E}_{71}\Psi_{SC} + c_3\widehat{E}_{82}\Psi_{SC}\}, \tag{22}$$

in which $\widehat{P}_{SYM}^{(1)}$ projects onto the A_g irreducible representation [39]. The use of $\widehat{P}_{SYM}^{(1)}$ is equivalent to adding also the configurations generated by excitations $\phi_6 \rightarrow \widehat{C}_2\phi_7$ and $\phi_5 \rightarrow \widehat{C}_2\phi_8$. We maximized S_{VB} with respect to the coefficients defining ϕ_7 and ϕ_8, as well as the structure coefficients for the excited configurations. Both an unconstrained optimization was carried out and an optimization in which orbitals ϕ_7 and ϕ_8 were kept orthogonal to the spin-coupled orbital set. Values for S_{VB} and E_{VB} are shown in table 7, in which excitations from orbital pairs ϕ_1,ϕ_3 and ϕ_2,ϕ_3 are also considered. Allowing nonorthogonality corresponds to incorporating ionic '6 in 6' configurations and will, as such, recover some static correlation effects. However, as can be seen, this effect is relatively minor. All in all the gain upon adding to the wavefunction the two singly excited structures is somewhat disappointing, recovering only a small fraction of the 0.197% attributable to singly excited configurations. In this case, these configurations represent a larger fraction of the total CASSCF wavefunction than can be attributed to the doubly excited configurations – this is in spite of the Brillouin-type condition embodied in equation (10). However, all of the orbital representations of

the CASSCF wavefunction assign uniformly quite small weights to these configurations, and so there is no clear-cut way of augmenting Ψ_{VB}, short of adding a relatively large number of excited structures. This can, on the other hand, be interpreted as an indication that Ψ_{VB} is unlikely to have serious deficiencies in a correlation sense.

For the overlap-based interpretation of the '6 in 6' excited state, a single configuration spin-coupled wavefunction again leads to an adequate description, giving $S_{VB} = 0.998517$ (see table 2(b)). The orbital change relative to the ground state calculation is only minor, and the major effect is a recoupling of the electron spins, i.e., a change of the form given in equation (8). This is in accordance with earlier observations that "the 2^1A_g state ... has the character of the broken-bond valence bond structure ..." [30]. As shown in table 3(b), the weight of the perfect-pairing structure is now quite small, as is to be expected on orthogonality grounds. The orbitals are shown in figure 2, with the corresponding overlaps in table 4. It is clear that the deformations in the directions 1–2, 3–4 and 5–6 are still substantial, although the other nearest neighbour overlaps have increased significantly.

There is no longer any obvious pairing scheme between the orbitals, and so there is no straightforward way of selecting appropriate strong orthogonality or perfect-pairing approximations. The pairing scheme (23)(45)(16) seems to be the best candidate, since this leads to the greatest weight of the perfect-pairing structure (54.77%) and it also yields the optimal strong orthogonality solution. The S_{VB} value is, however, significantly inferior to the corresponding ground state result (see table 2(b)). The non-zero orbital overlaps are $\langle \phi_2|\phi_3 \rangle = 0.649$, $\langle \phi_4|\phi_5 \rangle = 0.649$ and $\langle \phi_1|\phi_6 \rangle = -0.017$. Imposing the perfect-pairing mode of spin coupling also seems to be too severe a restriction for this system, and leads to linear dependence in the orbital set.

The Chirgwin–Coulson and inverse-overlap analyses of the CASSCF residual vector suggests a dominance of the singly ionic structures, with higher ionicities being orders of magnitude less important (see table 5(b)). As one would expect, the configurations generated by excitations between neighbouring centres dominate, with the larger weights arising from the 2→1 and 3→4 (and symmetry-related) excitations; these account for 0.16% (Chirgwin–Coulson) or 0.08% (inverse-overlap). Performing the corresponding five configuration optimization then leads to an S_{VB} value of 0.998927 with a corresponding energy of -231.738914 hartree.
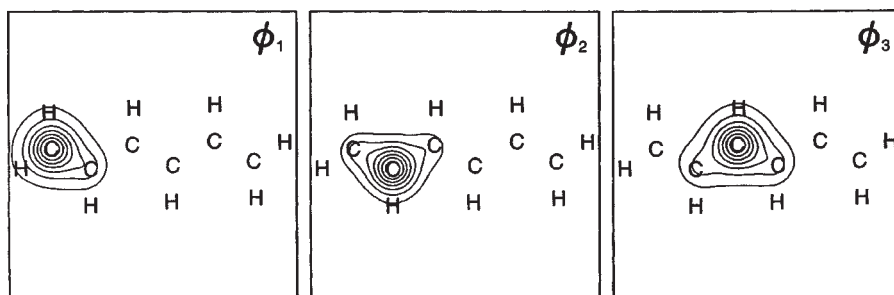

Figure 2. Symmetry-unique CASVB orbitals for the 2^1A_g state of hexatriene.

For the '6 in 8' excited state calculation a similar picture emerges as for the ground state. The S_{VB} value achieved with Ψ_{VB} of spin-coupled form was in this case 0.996067, with a corresponding energy of -231.738079 hartree. Accumulated weights for the CASSCF solution are given in table 8, according to the number of excitations into orbitals ϕ_7 and ϕ_8. As before, the overlap between Ψ_{VB} and the '6 in 6' part of this wavefunction is very similar to the true '6 in 6' result: $S_{VB} = 0.998493$ (see table 2(b)). However, while the remaining part of the wavefunction is clearly dominated by single and double excitations, the distribution of weights for these configurations is highly uniform.

N_2S_2

N_2S_2 is a system for which significant charge separation might be expected. It is also of interest due to the rival bonding schemes that have been suggested – we show three such models in figure 3. The spin-coupled description of N_2S_2 has recently been considered by Gerratt et al. [19], who proposed a singlet diradical structure, resembling (a) in figure 3. A different diradical description was considered by Harcourt and Skrezenek [20,35], in which the long bond is formed between the nitrogen centres (structure (b) in figure 3). A third possibility – (c) in figure 3 – was suggested by Findlay et al. [15]. It involves one sulfur centre taking part in two double bonds, with a lone pair on the other sulfur atom. We describe here the various CASVB descriptions of this system, as well as the role played by the ionic configurations.

We assumed a square geometry for S_2N_2 with S–N bond lengths of 165.4 pm (as in [19]) and used a DZP basis set due to Dunning [10]. The molecule was oriented with N atoms lying on the x-axis and S atoms on the y-axis. We concentrate here on the description of the 6 valence π electrons, keeping all σ electrons and the four $S(2p_z)$ electrons as (optimized) core. The three rival models in figure 3 may be characterized according to the transformation properties of the active orbitals:
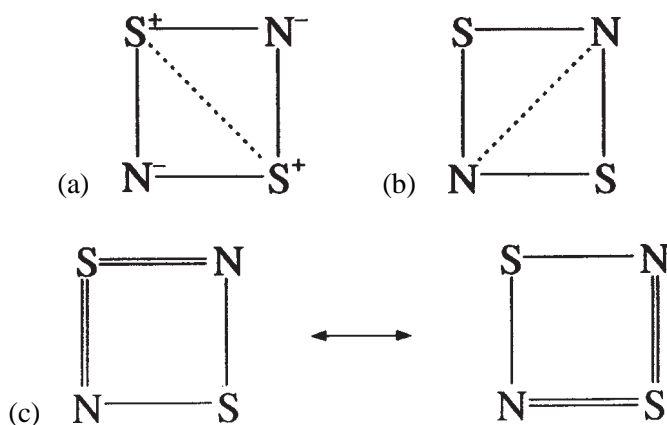

Figure 3. Lewis structures for N_2S_2.

(a) $3 \times B_{1u} + B_{2g} + 2 \times B_{3g}$;

(b) $3 \times B_{1u} + 2 \times B_{2g} + B_{3g}$;

(c) $3 \times B_{1u} + 3 \times B_{2g} + 3 \times B_{3g} + 3 \times A_u \rightarrow$ CASSCF: $2 \times B_{1u} + B_{2g} + 2 \times B_{3g} + A_u$.

The valence bond orbitals do not transform as individual irreducible representations, but the full set of orbitals must form a basis for a representation of the molecular point group. Since (c) involves two configurations, this strictly requires twelve active orbitals but, in order to facilitate direct comparison between the different models, this was reduced to six by use of the symmetry projection operator described later.

The symmetry distribution of active orbitals appropriate to the S–S diradical structure (a) leads to the lowest '6 in 6' CASSCF solution. Energies for the various MO-based calculations are collected in table 9, in which we refer to this wavefunction as CASSCF a. The CASVB interpretation of this wavefunction reproduces the spin-coupled picture [19], giving an S_{VB} value of 0.999827 and $E_{VB} = -903.847542$ hartree. The orbitals are shown in figure 4.

The alternative N–N diradical structure (b) may also be obtained in a very straightforward manner by interpretation of the CASSCF solution b. The orbitals are shown in figure 5. It is noticeable how similar the two diradical descriptions become when rotated by 90°. The energy of this alternative CASSCF solution lies about 8.6 millihartree higher than the lowest solution and so, in spite of a high S_{VB} of 0.999799, the modern VB energy ($E_{VB} = -903.838825$ hartree) is somewhat higher than that for the S–S diradical structure.

As shown in table 9, we find that CASSCF wavefunction c lies very close in energy to solution a. The six CASVB orbitals are shown in figure 6 – they define one of two equivalent valence bond configurations. The optimization was carried out using the symmetry projection operator $\widehat{P}_{SYM}^{(A_g + B_{2u})}$ [39] to ensure correct overall symmetry with respect to reflection in $x = 0$. In addition, the spin function was restricted to be of perfect-pairing form, in order to avoid linear dependency problems. This appears to be the consequence of the very localized orbitals associated with the same sulfur atom. We found that allowing partial triplet coupling of the electron spins corresponding to *either* of the orbital pairs led to almost identical orbitals. In spite of this restriction on the mode of spin coupling, the overlap with the CASSCF wavefunction was very acceptable ($S_{VB} = 0.999523$) leading to an energy within 2 millihartree of solution a ($E_{VB} = -903.845939$ hartree).

Table 9
Energies for various calculations on N_2S_2.

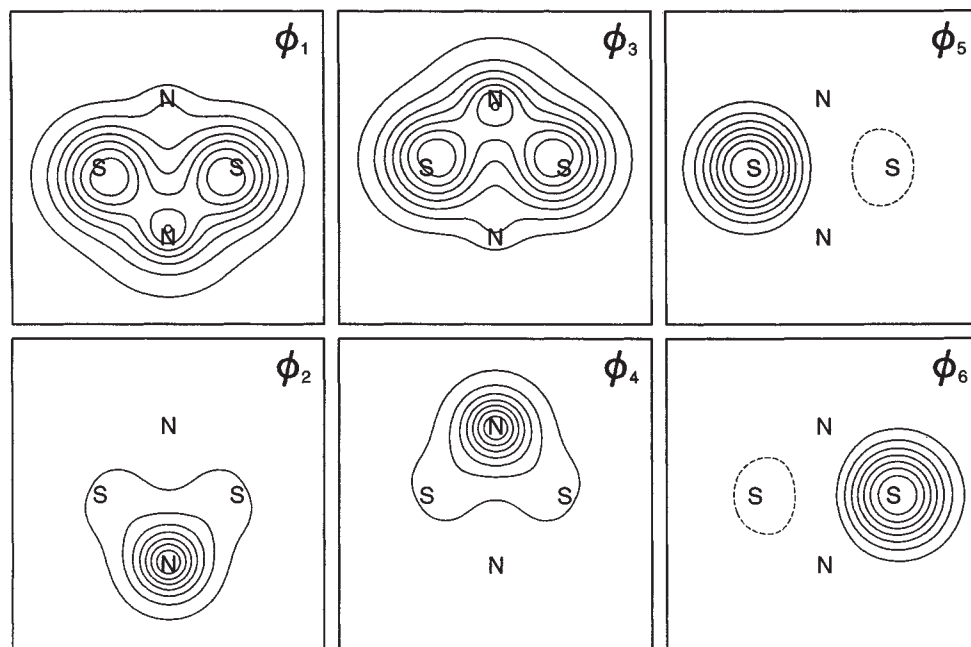| Calculation	E (hartree)
SCF	-903.784035
CASSCF b	-903.839551
CASSCF c	-903.847628
CASSCF a	-903.848173

Figure 4. CASVB orbitals from the interpretation of the CASSCF a N_2S_2 solution.
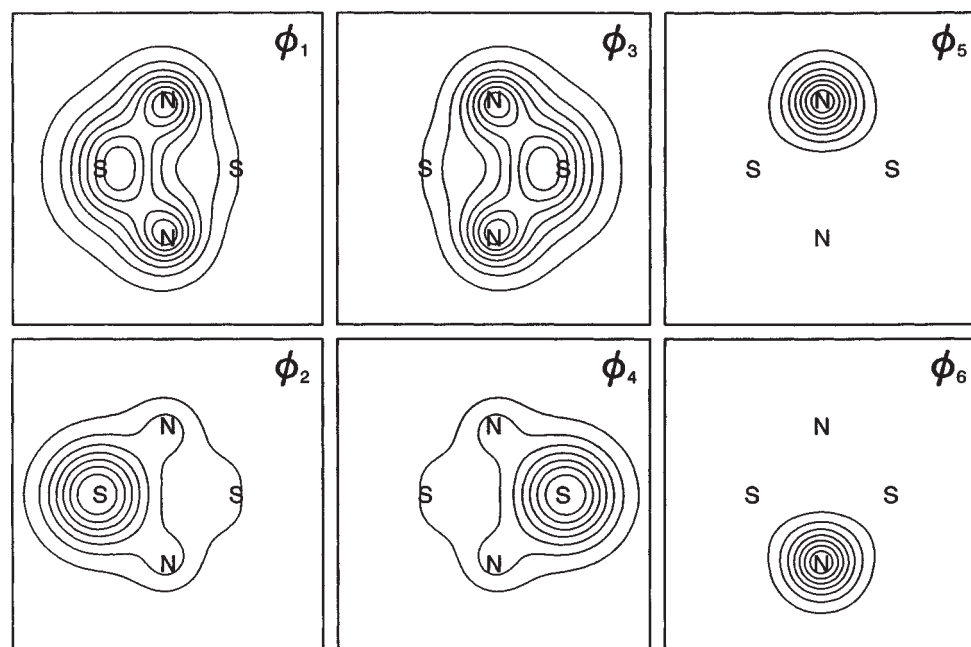
Figure 5. CASVB orbitals from the interpretation of the CASSCF b N_2S_2 solution.
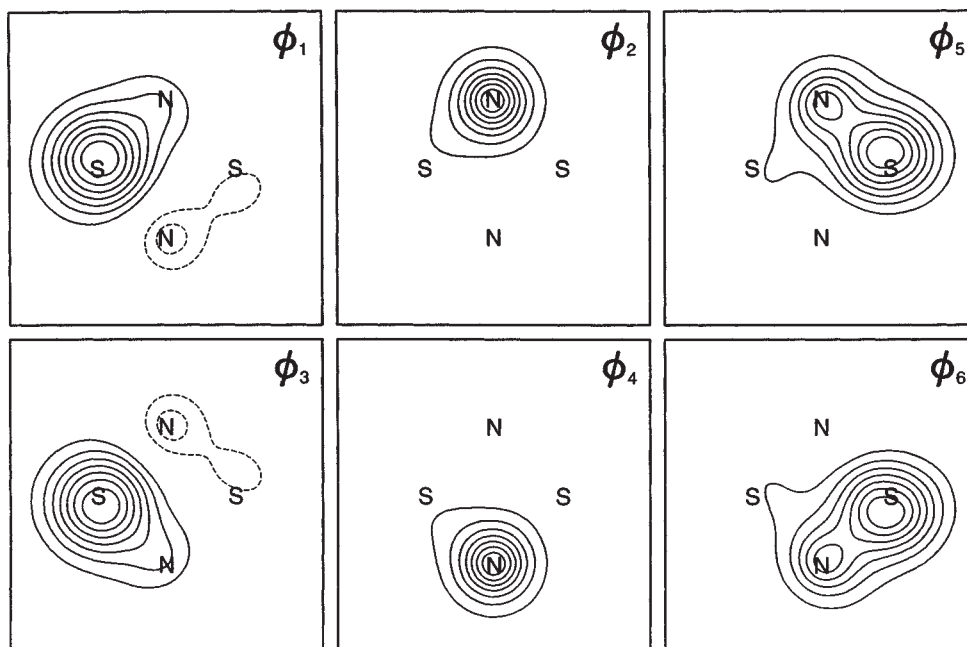
Figure 6. CASVB orbitals from the interpretation of the CASSCF c N_2S_2 solution.

It seems clear that an S–S diradical structure is, in fact, a very good description for calculations with 6 active π orbitals, but alternatives a and c lie far too close in energy to allow definitive statements to be made. In any case, all three models could play important roles in more extensive computational treatments and, particularly, for different molecular geometries. The various overlap matrices are reported in table 10, with structure coefficients and weights in table 11. An important feature is the occurrence of negative overlaps for the S–S and N–N diradical orbital pairs, with nodal planes between the two participating centres, so that for none of these descriptions can there be any question of cross-ring bonding.

We now consider the analysis of the CASSCF vector a, for which the CASVB picture corresponds to significant charge separation, although the distinct three-centre nature of orbitals ϕ_1 and ϕ_3 serves to distribute the charge somewhat more evenly than is suggested by scheme (a) in figure 3. Weights for the various ionicities are shown in table 12. Of particular note is the very low covalent weight in the total CASSCF wavefunction with the inverse-overlap definition. The sum of the (unnormalized) inverse-overlap weights turns out to be just 2.21×10^{-3}%, signifying very short 'unique' components for all configurations (cf. equation (15)). For comparison, the corresponding sum of weights for the residual vector represents 4.76% of this vector. Those configurations in which ϕ_5 and/or ϕ_6 become doubly occupied are by far the most important, but the overall contribution from ionic structures is very small. With increasing (nondynamical) correlation there is a tendency to homogenize the charge distribution, as is to be expected. The two configurations $\phi_5\phi_5\phi_6\phi_6\phi_1\phi_2$ and

Table 10
Overlap matrices for the overlap-based interpretations of N_2S_2.

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
CASVB solution a						
ϕ_1	1					
ϕ_2	0.767	1				
ϕ_3	0.832	0.488	1			
ϕ_4	0.488	0.330	0.767	1		
ϕ_5	0.338	0.123	0.338	0.123	1	
ϕ_6	0.338	0.123	0.338	0.123	-0.595	1
CASVB solution b						
ϕ_1	1					
ϕ_2	0.444	1				
ϕ_3	0.649	-0.114	1			
ϕ_4	-0.114	-0.058	0.444	1		
ϕ_5	0.237	0.590	-0.105	0.034	1	
ϕ_6	-0.105	0.034	0.237	0.590	0.610	1
CASVB solution c						
ϕ_1	1					
ϕ_2	0.886	1				
ϕ_3	0.704	0.506	1			
ϕ_4	0.506	0.442	0.886	1		
ϕ_5	0.391	0.200	0.391	0.200	1	
ϕ_6	0.391	0.200	0.391	0.200	-0.355	1

Table 11
Coefficients and weights of structures based on the Kotani spin basis (structures are defined with a normalized spin function), for the CASVB interpretations of the '6 in 6' CASSCF N_2S_2 solutions a and b, respectively. Structures 1–3 are disallowed by symmetry. c, i and s refer to Chirgwin–Coulson, inverse-overlap, and symmetrically orthogonalized weights, respectively.

	Solution a			Solution b	
	Ψ_4	Ψ_5		Ψ_4	Ψ_5
c_{Sk}	0.1578	0.8464		0.1218	0.8297
$^c w(k)$	4.94%	95.06%		0.84%	99.16%
$^i w(k)$	0.84%	99.16%		0.09%	99.91%
$^s w(k)$	10.97%	89.03%		2.33%	97.67%

$\phi_5\phi_5\phi_6\phi_6\phi_3\phi_4$ attain the overall largest Chirgwin–Coulson and inverse-overlap weights in the residual vector (1.34×10^{-2}% and 3.68×10^{-3}% each, respectively) and performing a three configuration optimization that includes these gives $S_{VB} = 0.999879$.

Within the Chirgwin–Coulson definition, the singly ionic configurations dominate the residual vector, and so we investigated calculations in which the SC reference was augmented by configurations generated by single excitations. Adding the configuration

Table 12

Accumulated weights according to the ionicity of configurations in the total CASSCF a wavefunction for N_2S_2. The entry '≈ 0' signifies zero within numerical accuracy.

Ionicity	Chirgwin–Coulson		Inverse-overlap		Löwdin	
	Ψ_{CAS} (%)	$\Psi_{RES}^{\perp}$ (%)	Ψ_{CAS} (%)	$\Psi_{RES}^{\perp}$ (%)	Ψ_{CAS} (%)	$\Psi_{RES}^{\perp}$ (%)
0	126.69	≈ 0	27.60	9.12×10^{-4}	17.39	2.01×10^{-3}
1	-24.16	2.35×10^{-2}	21.42	9.94×10^{-3}	47.74	1.10×10^{-2}
2	-2.07	1.38×10^{-2}	50.87	2.36×10^{-2}	30.41	1.90×10^{-2}
3	-4.56×10^{-1}	-2.76×10^{-3}	1.10×10^{-1}	5.10×10^{-5}	4.46	2.48×10^{-3}

generated by the excitation $\phi_1 \to \phi_5$ (and symmetry-related counterparts) led to $S_{VB} = 0.999853$. The corresponding excitation(s) $\phi_2 \to \phi_5$ led to $S_{VB} = 0.999865$, and the combination of both types of excitation gave $S_{VB} = 0.999973$. It should be noted that while these excitations each represent four configurations, the number of variational parameters is only increased by one each time. This can be seen in relation to a total number of 12 symmetry preserving SC parameters as opposed to 55 CASSCF parameters associated with the active space. The extra computational effort involved in this enlargement of the wavefunction is minimal within the CASVB strategy, and it leads to an *extremely* accurate representation of the CASSCF solution.

5. Conclusions

Considering the various definitions of weights, it is clear that for realistic cases the change involved in an orthogonalization (even if symmetric) of the full functional space is too severe to lead to a complete set of sensible weights. We have shown that this is closely related to the inability of orthogonal orbitals to yield compact VB wavefunctions of reasonable quality. For the analysis of the CASSCF vector, the relative magnitudes of the weights change dramatically, but also for the analysis of VB structures an appreciable equalization of the weights can be observed. The Chirgwin–Coulson and inverse-overlap definitions generally show better agreement in this case, although inverse-overlap weights tend to attribute greater importance to the dominant components. Both the Chirgwin–Coulson weights and inverse-overlap populations behave somewhat erratically in the analysis of the total CASSCF vector, but this behaviour largely disappears for the 'residual vector', $\Psi_{RES}^{\perp} = \Psi_{CAS} - S_{VB}\Psi_{VB}$.

Analysis of the residual wavefunction, $\Psi_{RES}^{\perp}$, using either the Chirgwin–Coulson or inverse-overlap scheme, thus seems to be a useful strategy for gaining a further understanding of the important correlation effects in CASVB, and related, calculations. The two definitions generally show excellent qualitative agreement, but the evaluation of Chirgwin–Coulson weights is, of course, computationally cheaper. The relative importance of configurations of varying ionicity or excitation level can be assessed with confidence. Strongly dominating configurations can suggest useful ways of augmenting the first-order function, as was illustrated by the case of N_2S_2. Conversely, one

may argue that with reasonably good values of S_{VB}, the absence of such components increases one's confidence in the quality of the modern valence bond description.

Finally, it is clear that a flexible approach to valence bond calculations is of paramount importance in the study of chemical bonding. Within the CASVB approach, particularly important features in this respect include:

- choice of transformation properties of the active space (as a direct sum of irreducible representations);
- single- or multiconfigurational wavefunctions;
- use of symmetry projection operators;
- flexible constraints (e.g., to ensure correct wavefunction symmetry).

A single configuration wavefunction of spin-coupled form remains a natural starting point for the majority of applications, but a systematic approach is clearly required in order to assess with confidence the relative importance of rival descriptions. This, and the systematic way in which further correlation may be incorporated, are strong points in favour of the CASVB procedure.

References

[1] S.F. Boys, Rev. Mod. Phys. 32 (1960) 296.
[2] S.F. Boys, in: *Quantum Theory of Atoms Molecules and the Solid State*, ed. P.-O. Löwdin (Academic Press, New York, 1966) p. 253.
[3] R.J. Cave and E.R. Davidson, Chem. Phys. Lett. 148 (1988) 190.
[4] R.J. Cave and E.R. Davidson, J. Phys. Chem. 92 (1988) 614.
[5] B.H. Chirgwin and C.A. Coulson, Proc. Roy. Soc. Lond. Ser. A 201 (1950) 196.
[6] D.L. Cooper, J. Gerratt and M. Raimondi, Chem. Rev. 91 (1991) 929.
[7] D.L. Cooper, J. Gerratt, M. Raimondi, M. Sironi and T. Thorsteinsson, Theoret. Chim. Acta 85 (1993) 261.
[8] D.L. Cooper, T. Thorsteinsson and J. Gerratt, Int. J. Quantum Chem. 65 (1997) 439.
[9] E.R. Davidson, J. Chem. Phys. 37 (1962) 577.
[10] T.H. Dunning, Jr., J. Chem. Phys. 55 (1971) 716.
[11] T.H. Dunning, Jr., Chem. Phys. 90 (1989) 1007.
[12] C. Edminston and K. Ruedenberg, J. Chem. Phys. 43 (1963) S97.
[13] C. Edminston and K. Ruedenberg, Rev. Mod. Phys. 35 (1963) 457.
[14] C. Edminston and K. Ruedenberg, in: *Quantum Theory of Atoms Molecules and the Solid State*, ed. P.-O. Löwdin (Academic Press, New York, 1966) p. 263.
[15] R.H. Findlay, M.H. Palmer, A.J. Downs, R.G. Edgell and R. Evans, Inorg. Chem. 19 (1980) 1307.
[16] J.M. Foster and S.F. Boys, Rev. Mod. Phys. 32 (1960) 300.
[17] G.A. Gallup and J.M. Norbeck, Chem. Phys. Lett. 21 (1973) 495.
[18] G.A. Gallup, R.L. Vance, J.R. Collins and J.M. Norbeck, Adv. Quantum Chem. 16 (1982) 229.
[19] J. Gerratt, S.J. McNicholas, P.B. Karadakov, M. Sironi, M. Raimondi and D.L. Cooper, J. Am. Chem. Soc. 118 (1996) 6472.
[20] R.D. Harcourt and F.L. Skrezenek, J. Mol. Struct. (Theochem) 36 (1987) 203.
[21] R.J. Harrison and S. Zarrabian, Chem. Phys. Lett. 158 (1989) 393.
[22] W. Haugen and M. Traetteberg, Acta Chem. Scand. 20 (1966) 1726.
[23] S. Huzinaga and C. Arnau, Phys. Rev. A 1 (1970) 1285.

[24] S. Huzinaga and C. Arnau, J. Chem. Phys. 54 (1971) 1948.

[25] P.J. Knowles and H.-J. Werner, Chem. Phys. Lett. 115 (1985) 259.

[26] P.-O. Löwdin, Ark. Mat. Astr. Fysik 35A (1947) 9.

[27] P.-O. Löwdin and H. Shull, J. Chem. Phys. 25 (1956) 1035.

[28] P.Å. Malmqvist, Int. J. Quantum Chem. 30 (1986) 479.

[29] R. Mulliken, J. Chem. Phys. 23 (1955) 1833, 2343.

[30] M.A.C. Nascimento and W.A. Goddard III, Chem. Phys. Lett. 60 (1979) 197.

[31] M.A.C. Nascimento and W.A. Goddard III, Chem. Phys. 53 (1980) 265.

[32] J. Olsen, B.O. Roos, P. Jørgensen and H.J.Aa. Jensen, J. Chem. Phys. 89 (1988) 2185.

[33] J. Pipek and P.G. Mezey, J. Chem. Phys. 90 (1989) 4916.

[34] L. Serrano-Andrés, M. Merchán, I. Nebot-Gil, R. Lindh and B.O. Roos, J. Chem. Phys. 98 (1993) 3151.

[35] F.L. Skrezenek and R.D. Harcourt, J. Am. Chem. Soc. 106 (1984) 3934.

[36] T. Thorsteinsson, Development of methods in spin-coupled theory, Ph.D. thesis, University of Liverpool (1995).

[37] T. Thorsteinsson and D.L. Cooper, Theoret. Chim. Acta 94 (1996) 233.

[38] T. Thorsteinsson, D.L. Cooper, J. Gerratt, P.B. Karadakov and M. Raimondi, Theoret. Chim. Acta 93 (1996) 343.

[39] T. Thorsteinsson, D.L. Cooper, J. Gerratt and M. Raimondi, Theoret. Chim. Acta 95 (1997) 131.

[40] T. Thorsteinsson, D.L. Cooper, J. Gerratt and M. Raimondi, in: *Quantum Systems in Chemistry and Physics: Trends in Methods and Applications*, eds. R. McWeeny, J. Maruani, Y.G. Smeyers and S. Wilson (Kluwer, Dordrecht, 1997).

[41] H.-J. Werner and P.J. Knowles, J. Chem. Phys. 82 (1985) 5053.

[42] S. Zarrabian, C.R. Sarma and J. Paldus, Chem. Phys. Lett. 155 (1989) 183.