Biorthogonal valence bond descriptions of electronic structure

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Summary. A valence bond approach based on nonorthogonal orbitals in a biorthogonal representation is presented. While the scheme suffers from the lack of a variational bound on the energy functional, it is shown that with a suitable optimization of the orbitals reliable molecular wavefunctions can be obtained. A review of the background theory is given emphasizing the similarity of this approach to the familiar spin-free unitary group formulation of quantum chemistry. The details of the computer implementation are discussed and the method is illustrated with model calculations on HF, H_2O and F_2O_2.

1. Introduction

The rivalry between the molecular orbital (MO) and valence bond (VB) descriptions of electronic structure is an old one. At the qualitative level, both approaches provide insights into particular areas of chemistry. For example, the MO approach has historically been the standard model for discussing molecular spectra, while many VB concepts (such as hybridization, electron pair bonds etc) have provided an enduring basis for discussions of bonding and structure. However, at the quantitative level the popularity of MO approaches has overshadowed that of VB schemes. The reasons for the acceptance of MO methods are well known and clearly dominated by considerations of computer implementation. This has led ultimately to a body of quantitative data which allows the MO theory to be tested and validated.

The methodology associated with the VB theory is very much more demanding from a computational point of view and has worked against the development of 'black-box' approaches such as are commonplace among MO based models of electronic structure. In spite of this, a number of groups have pursued and developed *ab initio* VB schemes and applied them with great success to a variety of chemical problems. In particular the generalized valence bond (GVB) method of Goddard and coworkers [1–5] has found very wide application, albeit in the so-called "strong orthogonality–perfect-pairing" (SO-PP) approximation. In the

SO-PP scheme each doubly occupied orbital of a single determinant Hartree–Fock wavefunction is replaced by two distinct orbitals which are allowed to overlap with each other but remain orthogonal to all other orbitals; this defines the SO condition. The PP condition then imposes a further restriction by including only a single spin-coupling scheme for the electrons. The SO-PP restrictions lead to dramatic simplifications in the calculations, enabling the GVB-SO-PP scheme to be applied to quite large systems.

The classical VB theory, in which the wavefunction of a molecule is constructed from the wavefunctions of the constituent atoms has been discussed by Simonetta et al. [6]. A displeasing facet of the classical VB approach is the need to include vast numbers of ionic configurations in the molecular wavefunction in order to achieve quantitative accuracy; an achievement which is won at the cost of any simple interpretation of the resulting wavefunction. This problem was first addressed by Coulson and Fischer [7], who showed that the ionic configurations could be eliminated by allowing the orbitals to deform away from their atomic forms. The Coulson–Fischer approach was generalized into the spin-coupled valence bond (SCVB) theory by Gerratt [8]. In SCVB all possible spin-pairings associated with a single spatial configuration of orbitals are optimized simultaneously with the orbitals. Subsequent developments in methodology [9, 10] led to a variety of applications [11–13] of SCVB which showed it to be competitive with the complete active space self consistent field (CASSCF) procedures of MO theory, while retaining the all important interpretability associated with the best VB wavefunctions through the use of a single spatial configuration. More recently, McWeeny [14] has put forward a spin-free form of classical VB theory based on overlap enhanced atomic orbitals. This scheme appears to lie somewhere between the approach of Simonetta et al. [6] and the SCVB in that only a small number of classical VB structures are included in the wavefunction and the orbitals are mixed according to the strength of their overlaps [15, 16]. Finally, the work of Gallup and coworkers should be mentioned in the context of classical VB theory, a thorough review of which may be found in [17].

From the previous discussion, it would seem that the VB theory is well served by practitioners. Nevertheless, VB calculations beyond the SO-PP type approximations are still very demanding for many-electron systems. The purpose of this work is to suggest an approach which is capable of eliminating some of the bottlenecks associated with traditional VB methods but does not require SO-PP type restrictions.

2. Theory

The main difficulty in VB calculations arises from the use of nonorthogonal orbitals in constructing many-electron wavefunctions. This leads to the well known $N!$ dependence of matrix elements (where N is the number of electrons). A solution to this problem was first suggested by Moshinsky and Seligman [18], who considered the use of nonorthogonal orbitals in the second quantization formalism. By defining creation and annihilation operators for nonorthogonal orbitals, the usual anticommutation relations are modified to:

$$\{a_{i\sigma}, a_{j\tau}\} = 0 \tag{1a}$$

$$\{a_{i\sigma}^{+}, a_{j\tau}^{+}\} = 0 \tag{1b}$$

$$\{a_{i\sigma}^{+}, a_{j\tau}\} = \delta_{\sigma\tau} S_{ij} \tag{1c}$$

where $a_{i\sigma}^+$ and $a_{i\sigma}$ denote creation and annihilation operators, respectively. In Eq. (1), σ and τ are spin labels corresponding to the orbitals i and j, and S_{ij} is the spatial overlap integral between i and j:

$$S_{ij} = \int \phi_i(1)^* \phi_j(1) \, dr_1 = \langle i \mid j \rangle \qquad (2)$$

Provided that the orbitals are linearly independent, the inverse of the overlap matrix $(T = S^{-1})$ may be found. It is then possible to define another linearly independent orbital basis $\{\tilde{\Phi}\}$, which is said to be *dual* or biorthogonal to the primary orbital basis $\{\Phi\}$, through the transformation:

$$\tilde{\Phi} = \Phi T = \Phi S^{-1} \qquad (3a)$$

$$|\tilde{i}\rangle = \sum_k |k\rangle T_{ki} \qquad (3b)$$

In what follows all quantities expressed in the dual basis will be denoted by a tilde. The transformation in Eq. (3) bestows on the primary and dual bases the property of biorthogonality:

$$\langle \tilde{i} \mid j \rangle = \delta_{ij} \qquad (4)$$

The same transformation may be applied to the Fock space operators $a_{i\sigma}^+$ and $a_{i\sigma}$ to define dual operators $\tilde{a}_{i\sigma}^+$ and $\tilde{a}_{i\sigma}$. However, it is only necessary to consider dual annihilation operators, defined by:

$$\tilde{a}_{i\sigma} = \sum_k a_{k\sigma} T_{ki} \qquad (5)$$

which leads to the modified anticommutation relations:

$$\{\tilde{a}_{i\sigma}, \tilde{a}_{j\tau}\} = 0 \qquad (6a)$$

$$\{a_{i\sigma}^+, a_{j\tau}^+\} = 0 \qquad (6b)$$

$$\{a_{i\sigma}^+, \tilde{a}_{j\tau}\} = \delta_{\sigma\tau}\delta_{ij} \qquad (6c)$$

which are equivalent to those for orthogonal orbitals. The conventional molecular hamiltonian can now be expressed as:

$$\hat{H} = \sum_{ij} \sum_{\sigma\tau} \langle \tilde{i}\sigma | \hat{h} | j\tau \rangle a_{i\sigma}^+ \tilde{a}_{j\tau} + \frac{1}{2} \sum_{ijkl} \sum_{\sigma\tau\varrho\varepsilon} (\tilde{i}\sigma j\tau \mid \tilde{k}\varrho l\varepsilon) a_{i\sigma}^+ a_{k\varrho}^+ \tilde{a}_{l\varepsilon} \tilde{a}_{j\tau} \qquad (7)$$

where $\hat{h}$ contains the usual one-electron operators:

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_A^{\text{nuclei}} \frac{Z_A}{r_{iA}} \qquad (8a)$$

and

$$\langle \tilde{i}\sigma | \hat{h} | j\tau \rangle = \int \tilde{\phi}_i(1)^* \hat{h}\phi_j(1) \, dr_1 \int \sigma(1)^*\tau(1) \, d\omega_1 \qquad (8b)$$

$$(\tilde{ij} \mid \tilde{k}l) = \int \tilde{\phi}_i(1)^* \tilde{\phi}_k(2)^* \frac{1}{r_{12}} \phi_j(1)\phi_l(2) \, dr_1 \, dr_2 \int \sigma(1)^*\varrho(1) \, d\omega_1 \int \tau(2)^*\varepsilon(2) \, d\omega_2$$

$$(8c)$$

where r denotes the spatial variable and ω the spin variable, and the integrals over the one- and two-electron operators have the dual basis to the left and the primary basis to the right of the operator.

To make the connection with the familiar unitary group form of the hamiltonian in Eq. (7), it is necessary to consider the operators:

$$\tilde{E}_{ij}^{\sigma\tau} = a_{i\sigma}^+ \tilde{a}_{j\tau} \tag{9}$$

which satisfy the same commutation relations as the unitary group operators [19]:

$$[\tilde{E}_{ij}^{\sigma\tau}, \tilde{E}_{kl}^{\varrho\varepsilon}] = \delta_{jk}\delta_{\tau\varrho}\,\tilde{E}_{il}^{\sigma\varepsilon} - \delta_{il}\delta_{\sigma\varepsilon}\,\tilde{E}_{jk}^{\tau\varrho} \tag{10}$$

but do not possess a hermitian condition and so:

$$(\tilde{E}_{ij}^{\sigma\tau})^\dagger \neq \tilde{E}_{ji}^{\tau\sigma} \tag{11}$$

hence the group generated by $\tilde{E}_{ij}^{\sigma\tau}$ is $GL(2n)$ rather than $U(2n)$ (where n is the number of orbitals). To obtain operators for subgroups of $GL(2n)$ it is necessary to contract over the orbital or spin indices in the usual manner [20] to obtain:

$$\tilde{E}_{ij} = \sum_\sigma \tilde{E}_{ij}^{\sigma\sigma} \tag{12a}$$

$$(\tilde{E}_{ij})^\dagger \neq \tilde{E}_{ji} \tag{12b}$$

$$\tilde{E}^{\sigma\tau} = \sum_i \tilde{E}_{ii}^{\sigma\tau} \tag{12c}$$

$$(\tilde{E}^{\sigma\tau})^\dagger = \tilde{E}^{\tau\sigma} \tag{12d}$$

The condition in Eq. (12d) is a consequence of the summation over all orbital indices in Eq. (12c). The operators $\tilde{E}_{ij}$ and $\tilde{E}^{\sigma\tau}$ now satisfy the following commutation relations:

$$[\tilde{E}_{ij}, \tilde{E}_{kl}] = \delta_{jk}\,\tilde{E}_{il} - \delta_{li}\,\tilde{E}_{kj} \tag{13a}$$

$$[\tilde{E}^{\sigma\tau}, \tilde{E}^{\varrho\varepsilon}] = \delta_{\tau\varrho}\,\tilde{E}^{\sigma\varepsilon} - \delta_{\varepsilon\sigma}\,\tilde{E}^{\varrho\tau} \tag{13b}$$

$$[\tilde{E}_{ij}, \tilde{E}^{\varrho\varepsilon}] = 0 \tag{13c}$$

and with conditions (12b), (12d) and (13c) show that they are generators of the chain of groups:

$$GL(2n) \supset GL(n) \otimes U(2) \tag{14}$$

Hence the spin-free hamiltonian in Eq. (7) may be written as:

$$\hat{H} = \sum_{ij} \langle \tilde{i}|\hat{h}|j\rangle \tilde{E}_{ij} + \frac{1}{2} \sum_{ijkl} (\tilde{i}\tilde{j} \mid \tilde{k}l)(\tilde{E}_{ij}\tilde{E}_{kl} - \delta_{kj}\tilde{E}_{il}) \tag{15}$$

in complete analogy with the case for orthogonal orbitals, except that the $U(n)$ generators have been replaced with $GL(n)$ generators.

These ideas are not new. Following the original work of Moshinsky and Seligman [18], Cantu et al. [21] discussed the use of this type of formalism in the VB context using a Rümer–Weyl basis of states expressed in terms of Bose creation operators [22, 23]. Payne [24] has also discussed the use of dual bases in configuration interaction (CI) calculations, paying special attention to the formulation of a variational principle for biorthogonal basis sets. However, apart from the initial investigation of this formalism with the H_3 surface by Moshinsky and Seligman [18], the only applications to molecules appear to be those of Norbeck and McWeeny [25]. The main disadvantage of using the hamiltonian in Eq. (15) with many-electron bra vectors built from $\{\bar{\Phi}\}$ and the ket vectors built from

$\{\Phi\}$ is that it leads to an unsymmetric eigenvalue problem with no variational bound. The variational property can be restored by permitting full CI, in which case the space spanned by the many-electron functions built from the dual basis is equivalent to that spanned by those built from the primary basis [25]. Since full CI is not a realistic goal for general problems, the course chosen was to take a small number of configurations or just one (perfect-pairing approximation) and optimize the orbitals. Given a suitable choice of reference configurations it was assumed that optimization of the orbitals should lead to a sufficiently good wavefunction such that the lack of a variational bound would be of little consequence. The technicalities of the orbital optimization process are outlined in the next section.

3. Implementation

The choice of structures to include in a VB calculation is a central consideration. The interest here centres on a suitable representation of the so-called 'covalent' structures whose spin factors couple electron pairs into singlets and in general are taken to correspond to chemical bonds between atoms. These are usually represented by the Rümer–Weyl basis and [26] contains a thorough discussion of a number of schemes for obtaining this type of basis. More recently, Paldus [27] has extended his Clifford algebra unitary group approach (CAUGA) to facilitate the evaluation of matrix elements between Rümer–Weyl states. In evaluating matrix elements over the hamiltonian in Eq. (15), the bra vectors will be taken to be Rümer–Weyl states built from the dual basis $\{\tilde{\Phi}\}$ defined in Eq. (3), while the ket vectors will be built from the primary orbital basis $\{\Phi\}$. Hence:

$$H_{\tilde{K}L} = \langle \tilde{\Psi}_K | \hat{H} | \Psi_L \rangle \tag{16a}$$

where

$$\Psi_L = \mathscr{A}[\phi_1^L(r_1)\phi_2^L(r_2) \ldots \phi_N^L(r_N)\Theta^L(\omega_1\omega_2 \ldots \omega_N)] \tag{16b}$$

$$\tilde{\Psi}_K = \mathscr{A}[\tilde{\phi}_1^K(r_1)\tilde{\phi}_2^K(r_2) \ldots \tilde{\phi}_N^K(r_N)\Theta^K(\omega_1\omega_2 \ldots \omega_N)] \tag{16c}$$

In Eq. (16b,c) $\mathscr{A}$ is the usual antisymmetrizer and Θ is an appropriate spin function. This procedure yields the tremendous simplification that the matrix elements, $H_{\tilde{K}L}$, can be evaluated as if they were between orthogonal orbitals, thus avoiding the familiar $N!$ problem. As has already been stated the price for doing this is that $H_{\tilde{K}L} \neq H_{\tilde{L}K}$ and consequently the eigenvalues of $\hat{H}$ are not variationally bound.

In implementing this procedure the techniques to be found in [27] may be used or alternatively the older schemes based on superposition diagrams [28–30]. The latter schemes appear to perform well compared with the newer approaches as the number of electrons becomes large. All matrix elements in the current investigation were obtained using superposition diagrams. Having obtained the matrix representation of the hamiltonian over suitable Rümer–Weyl states, the non-hermitian generalized eigenvalue problem:

$$HC = SCE \tag{17}$$

must be solved. This can be done using the procedure to be found in [31] or the EISPACK routine RGG. In general, only the lowest eigenvalue and eigenvector are required, these can be obtained using a modification of Nesbet's algorithm

[32] or a modified Davidson procedure [33]. The lowest right-eigenvector of Eq. (17) yields the VB wavefunction Ψ_0:

$$\Psi_0 = \sum_K C_K \Psi_K \tag{18}$$

To optimize the orbitals $\{\Phi\}$ from which Ψ_0 is built, it is useful to adopt a 'super-CI' (SCI) approach in the manner of Grein and Chang [34–36]. This type of procedure was first used in the VB context by van Lenthe and Balint-Kurti in their VBSCF method [37]. The great advantage of SCI methods is that they are very easy to implement and have a broad radius of convergence. However, they do not possess the rapid convergence associated with full Newton–Raphson type methods. Also the number of matrix elements can become very large making SCI a less attractive proposition. Van Lenthe et al. [38] have discussed these matters in some detail and have suggested hybrid optimization schemes which provide a balance between the number of iterative cycles and the cost of a cycle.

To motivate the SCI scheme, consider the transformation of an orbital ϕ_i:

$$\phi_i' = \phi_i + \sum_j a_{ij} \phi_j \tag{19}$$

this induces a transformation in Ψ_0 which to first order may be written [34]:

$$\Psi_0' = \Psi_0 + \sum_{ij} a_{ij} \Psi_{ij} \tag{20}$$

where Ψ_{ij} is a state generated from Ψ_0 by replacement of an electron in orbital i by an electron in orbital j. This type of single replacement gives rise to the SCI wavefunction:

$$\Psi_{\text{SCI}} = C_0 \Psi_0 + \sum_{ij} C_{ij} \Psi_{ij} \tag{21}$$

from which the orbital transformation:

$$\phi_i' = \phi_i + \sum_j \left(\frac{C_{ij}}{C_0} \right) \phi_j \tag{22}$$

can be obtained. After transformation, Ψ_{SCI} is formed again using the transformed orbitals $\{\Phi'\}$ by solving the appropriate secular problem, and the process is repeated until the C_{ij} in Eq. (21) vanish. Some care must be exercised in applying this type of procedure to the biorthogonal bases. Only the primary basis is transformed according to Eq. (22), since the dual basis is uniquely specified once the primary basis is known. At convergence:

$$\langle \tilde{\Psi}_{ij} | \hat{H} | \Psi_0 \rangle = 0 \tag{23a}$$

but

$$\langle \tilde{\Psi}_0 | \hat{H} | \Psi_{ij} \rangle \neq 0 \tag{23b}$$

By transforming the primary basis only, the projection of $\tilde{\Psi}_{ij}$ is removed from Ψ_0 (equivalently the dual basis could be transformed to eliminate the projection of Ψ_{ij} from $\tilde{\Psi}_0$). Denoting the space containing the reference VB configurations by $\{0\}$ and that of the SCI configurations by $\{Q\}$, at convergence the SCI secular

problem will take the form:

$$\begin{pmatrix} \langle \tilde{\Psi}_0 | \hat{H} | \Psi_0 \rangle & \langle \tilde{\Psi}_0 | \hat{H} | \Psi_Q \rangle \\ 0 & \langle \tilde{\Psi}_Q | \hat{H} | \Psi_Q \rangle \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = E \begin{pmatrix} \langle \tilde{\Psi}_0 | \Psi_0 \rangle & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad (24)$$

Clearly the left-eigenvector of Eq. (24) will not have a zero contribution in the Q space, but because of Eq. (23a) will still have zero contribution to E in Eq. (24).

The only other point that needs to be addressed is the transformation of the one- and two-electron integrals to the dual basis:

$$\langle \tilde{i} | \hat{h} | j \rangle = \sum_a T_{ai} \langle a | \hat{h} | j \rangle \qquad (25a)$$

$$(\tilde{ij} | \tilde{kl}) = \sum_{ab} T_{ai} T_{bk} (aj | bl) \qquad (25b)$$

it should be noted that the usual eight-fold symmetry associated with two-electron integrals (when evaluated over real orbitals) is lost. There is now only a two-fold symmetry since:

$$(\tilde{ij} | \tilde{kl}) \neq (\tilde{ji} | \tilde{kl})$$

$$\neq (\tilde{ij} | \tilde{lk})$$

$$\neq (\tilde{ji} | \tilde{lk})$$

$$\neq (\tilde{kl} | \tilde{ji})$$

$$\neq (\tilde{lk} | \tilde{ij})$$

$$\neq (\tilde{lk} | \tilde{ji})$$

$$= (\tilde{kl} | \tilde{ij}) \qquad (26)$$

4. Applications

The applications reported here were chosen to expose the properties of the biorthogonal VB (BOVB) wavefunctions by comparison with established methods rather than to present new data. All one- and two-electron integrals were evaluated using the standard procedures implemented in GAUSSIAN 90 [39] and passed to the BOVB program. The CASSCF calculations were also performed using GAUSSIAN 90.

4.1. Hydrogen fluoride

The wavefunction for hydrogen fluoride is taken to be:

$$\Psi_{H-F} = \mathscr{A}[\phi_1^2 \phi_2^2 \phi_3^2 \phi_4^2 (\alpha\beta\alpha\beta\alpha\beta\alpha\beta)\phi_5 \phi_6 (\alpha\beta - \beta\alpha)] \qquad (27)$$

where the orbitals $\phi_1-\phi_4$ correspond to a core of doubly occupied pairs on fluorine and orbitals ϕ_5 and ϕ_6 describe the H–F bond. Since the core orbitals are given a restricted description, i.e. the spatial parts of α and β spin orbitals are the same, there is no restriction imposed by requiring orbitals $\phi_1-\phi_4$ to be orthogonal to ϕ_5 and ϕ_6 [40]. In addition all virtual orbitals are chosen to be

Table 1. Total energies (au) obtained with the 6-31G* basis for H–F, $R_e = 0.9308$ Å

	E(CASSCF)	E(BOVB)	E(CASSCF) − E(BOVB)
R_e	−100.0272040	−100.0266037	0.0006003
$1.5R_e$	−99.9462886	−99.9459837	0.0003049
$2R_e$	−99.8851918	−99.8851608	0.0000310

orthogonal to all occupied orbitals. This is achieved by symmetrically orthogo-
nalizing the core and virtual orbitals within each set and then applying the
following projections: valence orbitals (t, u, v, w) are orthogonalized to the core
orbitals (i, j, k, l) according to:

$$|t'\rangle = |t\rangle - \sum_i^{\text{core}} |i\rangle S_{it} \tag{28a}$$

and virtual orbitals (a, b, c, d) are orthogonalized to the core and valence orbitals
by:

$$|a'\rangle = |a\rangle - \sum_i^{\text{core}} |i\rangle S_{ia} - \sum_{tu}^{\text{valence}} |t\rangle T_{tu} S_{ua} \tag{28b}$$

the occurrence of the inverse of the overlap matrix in the last term of Eq. (28b)
arises from the nonorthogonality of the valence orbitals [17]. With this core/
valence partitioning of the orbital space, H–F can be described by the single
covalent spin function (perfect-pairing approximation) shown in Eq. (27).

Table 1 shows the results obtained with the 6-31G* [41] basis at the
equilibrium bond length R_e (obtained from a CASSCF optimization using the
same core/valence partition as in Eq. (27), and also at $1.5R_e$ and $2R_e$. The BOVB
results were obtained by considering all possible rotations, i.e. core/valence,
core/virtual, valence/valence and valence/virtual replacements in the SCI expan-
sion. Two important results emerge from Table 1. First of all, the BOVB results,
with optimal orbitals, do not violate the variation principle and in addition the
difference between the CASSCF and BOVB energies is extremely small, indicat-
ing that some confidence may be put in the BOVB scheme outlined above.

4.2. Water molecule

The water molecule contains 10 electrons, 6 of which constitute lone pairs on
oxygen and are considered to provide the core, while the remaining 4 electrons
make up the two O–H bonds. Again the molecule was optimized at the CASSCF
level using the 6-31G* basis with the same partition of core/valence orbitals as
in the BOVB wavefunction:

$$\Psi_{H_2O} = \mathscr{A}[\phi_1^2 \phi_2^2 \phi_3^2 (\alpha\beta\alpha\beta\alpha\beta)\phi_4\phi_5\phi_6\phi_7(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)] \tag{29a}$$

It is also possible to introduce a second spin pairing,

$$\Psi'_{H_2O} = \mathscr{A}[\phi_1^2 \phi_2^2 \phi_3^2 (\alpha\beta\alpha\beta\alpha\beta)\phi_4\phi_6\phi_5\phi_7(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)] \tag{29b}$$

where the valence orbitals on oxygen are spin-coupled together and the valence
orbitals of the two hydrogen atoms are spin-coupled together. However, there is
much in favour of an interpretation based on a single spin-coupling [42–44] and

Table 2. Total energies (au) obtained with the 6-31G* basis for the symmetric stretch of H_2O, $R_e = 0.9707$ Å, $\theta = 102.807°$

	E(CASSCF)	E(BOVB)	E(CASSCF) − E(BOVB)
R_e	−75.0626070	−76.0555339	0.0070731
$1.5R_e$	−75.9145492	−75.9080342	0.0065150
$2R_e$	−75.8088049	−75.8005250	0.0082799

Table 3. Relative energies (kcal mol^{-1}) for the symmetric stretch of H_2O

	E($2R_e$) − E($1.5R_e$)	E($1.5R_e$) − E(R_e)	E($2R_e$) − E(R_e)
CASSCF	66.36	92.91	159.26
BOVB	67.46	92.56	160.02
ΔE	1.10	0.35	0.76

the BOVB calculations on the water molecule were performed with the function in Eq. (29a) only. The results are shown in Table 2.

The absolute difference between the BOVB and CASSCF energies is greater than for the previous example. The CASSCF wavefunction contains 20 configurations compared to the single BOVB configuration. The function in Eq. (29b) would be expected to have a greater contribution as the molecule dissociates since it corresponds to a 'long-bond' structure, but at least as far as $2R_e$ the *PP* approximation is quite valid. Since the total energies are only a guide to the behaviour of a computational model across a whole reaction surface, the relative energies of H_2O at different points are compared in Table 3. As can be seen, the BOVB model performs well when compared with the CASSCF method, given the same orbital partitioning.

4.3. Dioxygen difluoride

The final example was chosen to illustrate the chemically appealing insights that can be obtained from a VB description of bonding which does not contain any orthogonality constraints. Dioxygen difluoride (F_2O_2) has been discussed from the point of view of unrestricted Hartree–Fock (UHF), CASSCF and unrestricted natural orbital CAS (UNO-CAS) by Pulay [45]. The calculations reported here were carried out using the valence double-zeta Dunning–Huzinaga basis [46, 47]. The geometry used [48] is shown in Fig. 1. It should be noted that

1.575 Å

109.5°

1.217 Å
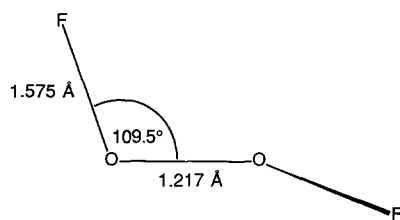
D(FOOF) = 87.5°

Fig. 1. Equilibrium geometry of F_2O_2 (see [45, 48])

a UHF natural orbital analysis shows an occupation of 0.414 for each of the O–F antibonding orbitals with all other virtual orbitals having an occupancy <0.003. However, the eigenvalue of $\hat{S}^2$ for this singlet species at the UHF level is 1.325, the application of a single spin annihilator produces an $\hat{S}^2$ eigenvalue of 2.376! Clearly the UHF description of this molecule is highly questionable. A natural orbital analysis based on CASSCF orbitals reduces the occupation of the antibonding orbitals to ~ 0.2. Taking the core/valence partition to be the same as in [45], the BOVB procedure was used with the function

$$\Psi_{F_2O_2} = \mathscr{A} \left[\left(\prod_{i=1}^{15} \phi_i^2 (\alpha\beta) \right) \phi_{16}\phi_{17}\phi_{18}\phi_{19}(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) \right] \qquad (30)$$

where $\phi_1 - \phi_{15}$ represent a doubly occupied core and $\phi_{16} - \phi_{19}$ describe the two O–F bonds. The BOVB energy obtained was -348.3529991 au compared with the CASSCF energy of -348.3562471 au ($\Delta E = 0.0032480$ au).

The structure of F_2O_2 is unusual from the point of view of the shortness of the O–O bond and the relatively long O–F bonds. One MO based explanation that has been suggested is that each singly occupied π^* orbital of O_2 interacts with a singly occupied fluorine σ orbital to form two O–F bonds in approximately perpendicular planes. The CASSCF valence orbitals are shown schematically in Fig. 2a and are notable for the fact that the contribution of each atom to each orbital is approximately the same and no simple picture of the bonding is obtained. In Fig. 2b the orbitals obtained with the BOVB procedure are depicted (again schematically). Given the function in Eq. (30), the bonding is clearly exposed to be brought about by the spin pairing of a fluorine valence electron with an O_2 valence electron. The overlap integral between ϕ_{16}/ϕ_{17} and ϕ_{18}/ϕ_{19} is 0.497 while that between the largest interpair interaction is only 0.012.

5. Conclusion

A simple scheme has been described which enables VB calculations using nonorthogonal orbitals to be performed, while avoiding the notorious $N!$ dependence of the matrix elements. The procedure has been illustrated with some model applications and appears to look promising. The current BOVB program is being improved to enable a wider range of systems to be studied. Given the
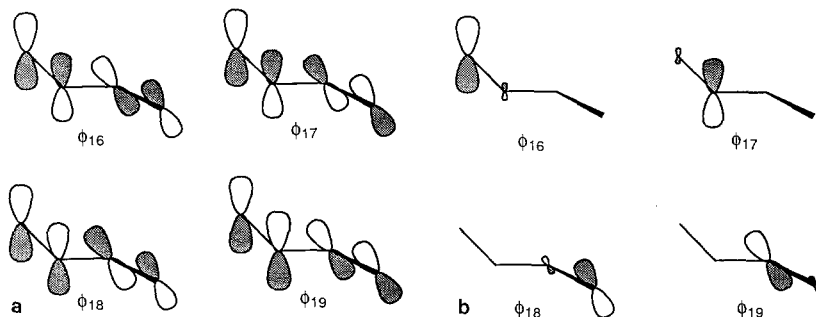

Fig. 2. a Schematic illustration of CASSCF valence orbitals of F_2O_2. b schematic illustration of BOVB valence orbitals of F_2O_2

simplicity of the matrix elements occurring in the energy calculation the whole process should be amenable to a 'direct' implementation along the lines of direct MCSCF codes which avoid the requirement of large amounts of disk space. Furthermore, it is entirely feasible that the pseudospectral methods of Friesner [49–54] could be adapted to the evaluation of the required matrix elements, leading to substantial simplification in computations.

Note added in proof

The BOVB description of F_2O_2 is similar to those obtained from localizing the orbitals of a CASSCF or FORS type wavefunction. However, it must be stressed that the BOVB orbitals arise uniquely from the orbital optimization, whereas the CASSCF/FORS descriptions exploit the invariance of the energy to mixing of orbitals in the valence space.

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