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Dynamic correlation for biorthogonal valence bond reference states

Joseph J. W. McDouall
Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

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Summary. The use of biorthogonal valence bond reference functions in evaluating the correlation energy is investigated. Since the method is not variationally bound some care must be taken in defining the reference state to ensure that the variational bound is not violated, some discussion is given to this matter. The procedure adopted here is a matrix element driven configuration interaction scheme. To reduce the computational labour involved, a configuration selection criterion is introduced. The method is tested through its application to the symmetric stretching of HF, H_2O, $(^2B_1)$ NH_2 and the singlet-triplet gap in CH_2. Comparison is made with other methods, including full CI. The results show that the current method is quite promising.

Key words: Valence bond theory – Biorthogonal representation – Dynamic correlation

1 Introduction

In a recent paper [1], a valence bond (VB) approach based on nonorthogonal orbitals in a biorthogonal representation was presented. While the scheme suffers from the lack of a variational bound, it was shown that with a suitable optimization of the orbitals reliable molecular wavefunctions could be obtained. The idea of using biorthogonal basis sets in molecular calculations was first proposed (and applied) by Moshinsky and Seligman [2]. The exploitation of this approach in VB calculations was considered by Cantu et al. [3] and Seligman [4], and applied to some model problems by Norbeck and McWeeny [5]. More recently, Li and Paldus [6] have discussed the use of such an approach but conclude that while being "*... very attractive theoretically, is very limited in its practical exploitation.*" Yet the conclusions of [1] contradict this suggestion. It is the purpose of this work to show that the biorthogonal valence bond (BOVB) method is capable of providing not only good quality zeroth-order wavefunctions (as in [1]) but also of yielding reliable estimates of the dynamic correlation energy.

In the following section a brief overview of the background theory is given emphasizing its origin in the "method of moments" and detailing some computational considerations. After this, some discussion is given to the choice of reference space and the method is illustrated by application to the stretching of HF and H_2O. To reduce the dimension of the secular problem, a configuration selection criterion is given and tested by application to the stretching in HF, H_2O, $(^2B_1)$ NH_2 and the singlet-triplet gap in CH_2. A comparison is made with other commonly used methods.

2 Theory

It is useful to begin by considering the wavefunction in the familiar expansion form:

$$\Psi = \sum_M C_M \psi_M \tag{1}$$

In the limit of a complete set, $\{\psi\}$, Ψ is exact and the Schrödinger equation may be written:

$$(\hat{H} - E)\Psi = \sum_M C_M (\hat{H} - E)\psi_M = 0 \tag{2}$$

Taking scalar products from the left with the members of an alternative complete set, $\{\tilde{\psi}\}$, yields the infinite system of equations:

$$\sum_N \langle \tilde{\psi}_M | H | \psi_N \rangle C_N = E \sum_N \langle \tilde{\psi}_M | \psi_N \rangle C_N \tag{3}$$

which can be used to determine the coefficients, C_N. The members of the set $\{\tilde{\psi}\}$, need not be specified yet, but will be chosen to simplify the calculation.

Since complete sets are used, Eq. (3) is formally exact. Approximations are obtained when a subset of $\{\psi\}$ are chosen as VB structures defined over nonorthogonal orbitals and the series is truncated. Equation (3) may then be written in matrix form as:

$$\tilde{H}C = \tilde{S}CE \tag{4}$$

where the matrix elements are:

$$\tilde{H}_{MN} = \langle \tilde{\psi}_M | H | \psi_N \rangle, \qquad \tilde{S}_{MN} = \langle \tilde{\psi}_M | \psi_N \rangle \tag{5}$$

In general Eq. (4) is not equivalent to the secular equations obtained from the variation method, and its eigenvalues are not variational upper bounds to the eigenvalues of $\hat{H}$.

This approach was first used in quantum chemistry by Boys and Handy [7, 8]. Boys [7] also provided a rigorous analysis of the error in the energy. By defining error vectors as the difference between the left and right eigenvectors $\tilde{C}$ and C of Eq. (4) and the hypothetical eigenvectors $\tilde{C}_\infty$ and C_∞ that would correspond to the solution of the Schrödinger equation in a complete basis:

$$\tilde{\Delta} = \tilde{C} - \tilde{C}_\infty \tag{6}$$

$$\Delta = C - C_\infty \tag{7}$$

Boys showed that the error in the energy is proportional to an error parameter ε that is defined as:

$$\varepsilon = (\tilde{\Delta} \cdot \tilde{\Delta})^{1/2} (\Delta \cdot \Delta)^{1/2} = |\tilde{\Delta}|\,|\Delta| \tag{8}$$

The significance of this is that the error contains no terms in $|\tilde{\Delta}|$ and $|\Delta|$ alone, but only in their product. Hence, if the set $\{\psi\}$ is a good set to fit the exact eigenfunction Ψ, then $|\Delta|$ will be small and an accurate energy will result since it will not depend too heavily on the set $\{\tilde{\psi}\}$. However, it is not possible to state that the errors will systematically decrease as the set $\{\psi\}$ is extended, although it may be expected that $|\tilde{\Delta}|\,|\Delta|$ will not increase and will most probably decrease such that a reasonable convergence will be obtained.

It now remains to specify the form of the set $\{\tilde{\psi}\}$. 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). In the BOVB approach, the function $\tilde{\psi}_M$ is chosen as a VB structure (exactly as is ψ_M), except that the orbitals used in its construction belong to a 'dual' set defined by [1]:

$$\tilde{\Phi} = \Phi T = \Phi S^{-1} \tag{9}$$

where S is the orbital overlap matrix. The two sets of orbitals $\{\Phi\}$ and $\{\tilde{\Phi}\}$ exhibit a biorthogonality property:

$$\langle \tilde{\phi}_i | \phi_j \rangle = \delta_{ij} \tag{10}$$

Hence, for every element $\langle \psi_M | H | \psi_N \rangle$ in a conventional VB calculation, which contains overlap integrals $\langle \phi_i | \phi_j \rangle$, the corresponding element $\langle \tilde{\psi}_M | H | \psi_N \rangle$ will contain the biorthogonal overlaps in Eq. (10) and may consequently be evaluated just as though the orbitals were orthonormal. The matrix elements in Eq. (4) now become:

$$\langle \tilde{\psi}_M | H | \psi_N \rangle = \sum_{ij} \langle \tilde{i} | \hat{h} | j \rangle \gamma_{ij}^{\tilde{M}N} + \sum_{ijkl} (\tilde{i}j | \tilde{k}l) \Gamma_{ijkl}^{\tilde{M}N} \tag{11}$$

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

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A}^{nuclei} \frac{Z_A}{r_{iA}} \tag{12}$$

and

$$\langle \tilde{i} | \hat{h} | j \rangle = \int \tilde{\phi}_i(1)^* \hat{h}\, \phi_j(1)\, dr_1 \tag{13}$$

$$(\tilde{i}j | \tilde{k}l) = \int \tilde{\phi}_i(1)^* \tilde{\phi}_k(2)^* \frac{1}{r_{12}} \phi_j(1) \phi_l(2)\, dr_1\, dr_2 \tag{14}$$

r denotes the spatial 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. The $\gamma_{ij}^{\tilde{M}N}$ and $\Gamma_{ijkl}^{\tilde{M}N}$ are the one- and two-electron vector coupling coefficients, respectively, and may be obtained by a variety of techniques [6, 9, 10]. All matrix elements in the current investigation were obtained over Rumer functions using superposition diagrams [11, 12, 13] and the non-hermitian generalized eigenvalue problem (Eq. (4)) was solved using the modified Davidson procedure of Rettrup [14].

When building the hamiltonian matrix elements it is useful to exploit the limited symmetry of the vector coupling coefficients [15]:

$$\gamma_{ji}^{\tilde{N}M} = \gamma_{ij}^{\tilde{M}N} \tag{15}$$

and

$$\Gamma_{jilk}^{\tilde{N}M} = \Gamma_{ijkl}^{\tilde{M}N} \tag{16}$$

Finally, in performing the transformation of the one- and two-electron integrals to the dual basis:

$$\langle\tilde{i}|\hat{h}|j\rangle = \sum_{a} T_{ai}\langle a|\hat{h}|j\rangle \tag{17}$$

$$(\tilde{i}j|\tilde{k}l) = \sum_{ab} T_{ai}T_{bk}(aj|bl) \tag{18}$$

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:

$$\begin{aligned}(\tilde{i}j|\tilde{k}l) &\neq (\tilde{j}i|\tilde{k}l)\\ &\neq (\tilde{i}j|\tilde{l}k)\\ &\neq (\tilde{j}i|\tilde{l}k)\\ &\neq (\tilde{k}l|\tilde{j}i)\\ &\neq (\tilde{l}k|\tilde{i}j)\\ &\neq (\tilde{l}k|\tilde{j}i)\\ (\tilde{i}j|\tilde{k}l) &= (\tilde{k}l|\tilde{i}j)\end{aligned} \tag{19}$$

3 Choice of reference space

In the BOVB approach, the orbital space is partitioned into three sets. The details of how this partitioning may be obtained have been given in [1]. Briefly, the first set comprises a core of doubly occupied orbitals which are chosen to be orthogonal amongst themselves and to all other orbitals. The second consists of the valence space in which the orbitals are nonorthogonal within the set but orthogonal to all other orbitals. The third set is the virtual space and is chosen to consist of those orbitals, orthogonal to the occupied orbitals, which remain.

As shown in [1], the perfect-pairing (PP) approximation (in which a single spin-coupling scheme is imposed on the electrons) is often very good and leads to relative energies which are very similar to those obtained by the CASSCF method. Yet the latter requires a full configuration interaction (CI) calculation to be performed in the valence space. While the PP approximation yields very good zeroth-order wavefunctions, it has been found to be a poor choice as a reference function for evaluating the dynamic correlation energy in the BOVB method. In some preliminary calculations using the present method, it was found that a wavefunction formed from all single and double replacements of the PP structure gave very good estimates of the correlation energy at long bond distances, but violated the variational bound at shorter distances. As shown by Norbeck and McWeeny [5], convergence of the BOVB wavefunction can be from below as well as above the limiting result.

At shorter distances the magnitude of the correlation energy is greater and excitations from the PP structure alone do not provide enough flexibility to describe the dynamic electron correlation. The solution to this problem is to expand the reference space. In the first instance this was done by including in the reference space all spin-couplings corresponding to the same spatial configuration as the initial PP structure. This spin-coupled wavefunction showed a marginal improvement, but still exhibited the same problem at short bond distances.

Goddard has shown [e.g. 16] that in defining correlation consistent wavefunctions based on strongly-orthogonal PP (SOPP) orbitals, the use of a reference expansion in which each spin-coupled pair in the PP structure is allowed to have all three possible occupations (for two electrons distributed among the given pair of orbitals) and the total expansion obtained by taking the direct product of all such structures, does provide a reliable reference set. This leads, for P pairs, to a total of 3^P configurations and is termed a restricted CI (RCI) by Goddard. The RCI allows interpair correlation (ionic configurations) in which the movement of charge in one bond pair is correlated with simultaneous movement of charge in adjacent pairs. The RCI energy will be identical to the BOVB energy for a single spin-coupled pair. When there is more than one pair, the RCI energy will be slightly lower than the BOVB energy. The reason for this is that by taking direct products of the single excitations within pairs, a subset of the double excitations is being included in the reference set. Accordingly, when single and double excitations are generated from the RCI set, a component of the triple and quadruple excitations (relative to the PP structure) is included. These serve to improve the estimate of the correlation energy and avoid the violation of the variational bound. A factor which makes this approach much more appealing than a CASSCF type expansion is that the RCI wavefunction grows much more slowly in size than does the CASSCF.

All calculations reported in this paper were performed with an RCI type reference function from which all single and double replacements were generated. As will be shown in the following section, this leads to a consistent and reliable dynamically correlated wavefunction at all geometries.

4 Application – Stretching of HF and H_2O

To begin, the method outlined above was applied to the stretching of HF and H_2O, the results were then compared with full Cl calculations in a double-zeta plus polarization (DZP) basis taken from the literature [17, 18]. All one- and two-electron integrals were evaluated using the standard procedures implemented in GAUSSIAN 90 [19] and passed to the BOVB program.

The wavefunction for hydrogen fluoride was taken to be:

$$\Psi_{\mathrm{HF}} = \mathscr{A}[\phi_1^2\phi_2^2\phi_3^2\phi_4^2(\alpha\beta\alpha\beta\alpha\beta\alpha\beta)\phi_5\phi_6(\alpha\beta - \beta\alpha)] \qquad (20)$$

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 ($\mathscr{A}$ is the usual antisymmetrizer). Table 1 shows the results obtained at the equilibrium bond length of 0.917 Å and also at $1.5R_e$ and $2R_e$. The BOVB orbitals were obtained by full optimization [1] of the function in Eq. (20). The BOVB + SD results correspond to single and double replacements from an RCI reference set built from ϕ_5 and ϕ_6. As in [17] the 1s orbital on F was kept frozen.

The water molecule contains 10 electrons, 6 of which constitute lone pairs on oxygen and are considered to provide the core, while the remaining

Table 1. Total and relative energies (au) obtained with DZP basis [17, 18] for HF and H_2O compared with full CI

		HF	
	R_e	$1.5R_e$	$2R_e$
BOVB + SD	−100.244604	−100.154136	−100.075653
Full Cl	−100.250969	−100.160393	−100.081108
		H_2O	
	R_e	$1.5R_e$	$2R_e$
BOVB + SD	−76.250961	−76.066210	−75.945164
BOVB + SD′	−76.251066	−76.066589	−75.948419
Full CI	−76.256624	−76.071405	−75.952269
	ΔE(BOVB + SD) − ΔE(Full CI)		
	$2R_e - 1.5R_e$	$2R_e - R_e$	$1.5R_e - R_e$
HF	−0.000802	−0.000910	−0.000107
H_2O	0.001910	0.001441	−0.000468
H_2O'	−0.000967	−0.001709	−0.000742

4 electrons make up the two O–H bonds. The BOVB wavefunction was chosen to be:

$$\Psi_{H_2O} = \mathscr{A}[\phi_1^2\phi_2^2\phi_3^2(\alpha\beta\alpha\beta\alpha\beta)\phi_4\phi_5\phi_6\phi_7(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)] \tag{21}$$

It is also possible to introduce a second spin pairing:

$$\Psi'_{\mathrm{H_2O}} = \mathscr{A}[\phi_1^2\phi_2^2\phi_3^2(\alpha\beta\alpha\beta\alpha\beta)\phi_4\phi_6\phi_5\phi_7(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)] \tag{22}$$

where the valence orbitals on oxygen are spin-coupled together and the valence orbitals of the two hydrogen atoms are spin-coupled together. The results are again shown in Table 1, the BOVB + SD entry corresponds to an RCI generated from (21) alone, while BOVB + SD′ refers to the same augmented with (22). As in [18] the 1*s* orbital on O was kept frozen and $R_e = 1.000$ Å, $\mathrm{H\hat{O}H} = 104.5°$.

In no case does the BOVB + SD energy violate the variational bound. With respect to total energies, the BOVB + SD results are no more than ≈ 6 mHartree above full CI. More importantly, in predicting relative energies the BOVB + SD results are no more than ≈ 2 mHartree away from the full Cl.

While these results are very encouraging, it must be borne in mind that the calculations presented so far are based on a matrix element driven CI procedure, and as such will not be applicable to large molecular systems since it is difficult to treat more than $O(10^4)$ configurations by such a process. It is possible to use a direct CI approach [15], but not for the choice of spin eigenfunctions used here. However, matrix element driven CI techniques have been successfully applied by the groups of Buenker [e.g. 20] and Davidson [e.g. 21]. These rely on the use of configuration selection and extrapolation. In adapting such techniques to the BOVB method, a number of Davidson-type corrections for higher excitations were tested and abandoned, since they were found to behave erratically in the present case. However, considerable success was achieved with configuration selected CI expansions.

5 Configuration selection

Let the configuration expansion be separated into two sets, the first corresponding to the reference function and the second to the single and double replacements obtained from the first. Denoting these as Ψ_0 and Ψ_1, respectively:

$$\Psi_0 = \sum_K C_K \psi_K \quad \{K \in \text{reference space}\} \tag{23}$$

$$\Psi_1 = \sum_S C_S \psi_S \quad \{S \in \text{secondary space}\} \tag{24}$$

The reference energy is given by:

$$E_0 = \frac{\langle \tilde{\Psi}_0 | H | \Psi_0 \rangle}{\langle \tilde{\Psi}_0 | \Psi_0 \rangle} \tag{25}$$

Applying perturbation theory, at second-order the contribution to the energy from a secondary space configuration, ψ_S, is:

$$\Delta E_S = \frac{(\langle \tilde{\Psi}_0 | H | \psi_S \rangle - E_0 \langle \tilde{\Psi}_0 | \psi_S \rangle)(\langle \tilde{\psi}_S | H | \Psi_0 \rangle - E_0 \langle \tilde{\psi}_S | \Psi_0 \rangle)}{E_0 - \langle \tilde{\psi}_S | H | \psi_S \rangle} \tag{26}$$

where Ψ_0 is given by Eq. (23). This type of criterion has been widely used for configuration selection [22]. If ΔE_S is found to be below a given threshold, ψ_S is removed from the configuration list. In the non-hermitian case, Eq. (26) does not always provide a sufficiently sensitive test of the contribution of ψ_S, unless very stringent thresholds are chosen. In the present work a more pessimistic selection criterion was adopted:

$$\Delta W_S = \frac{\sum_K (\langle \tilde{\psi}_K | H | \psi_S \rangle - E_0 \langle \tilde{\psi}_K | \psi_S \rangle)(\langle \tilde{\psi}_S | H | \psi_K \rangle - E_0 \langle \tilde{\psi}_S | \psi_K \rangle)}{E_0 - \langle \tilde{\psi}_S | H | \psi_S \rangle} \tag{27}$$

This proves to be a good test in reducing the dimension of the secular problem, while still giving reliable energies when thresholds of 10^{-5}–10^{-6} are used.

6 Application – Stretching of HF, H_2O, ($^2B_1$) NH_2 and the singlet-triplet gap in CH_2

To test the selection procedure outlined above, calculations were repeated for HF and H_2O using a selection threshold of 10^{-6} (all reference configurations and single excitations were retained). The same procedure was also applied to the symmetric stretching of ($^2B_1$) NH_2 and the singlet-triplet gap in CH_2.

The wavefunction for NH_2 ($R_e = 1.024$ Å, $\hat{HNH} = 103.4°$ [17]) was taken to be

$$\Psi_{NH_2} = \mathscr{A}[\phi_1^2 \phi_2^2 (\alpha\beta\alpha\beta) \phi_3 \phi_4 \phi_5 \phi_6 (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) \phi_7 (\alpha)] \tag{28}$$

where the core orbitals ϕ_1 and ϕ_2 correspond to the 1*s* orbital on N and the inplane lone pair, respectively. Orbitals ϕ_3–ϕ_6 describe the N–H bonds and ϕ_7 is the out-of-plane singly occupied orbital. ϕ_1 was kept doubly occupied as in [17]. The BOVB orbitals were obtained by full optimization of the function in Eq. (28) and the RCI was built from ϕ_3–ϕ_6. The results are shown in Table 2, the BOVB + SD entry corresponds to an RCI generated from (28) alone, while

Table 2. Total and relative energies (au) obtained with DZP basis[17, 18, 23] for HF, H_2O, ($^2B_1$) NH_2 and CH_2 using configuration selection with a threshold of 10^{-6} compared with full CI

		HF	
	R_e	$1.5R_e$	$2R_e$
BOVB + SD	−100.243343	−100.153558	−100.075085
Full CI	−100.250969	−100.160393	−100.081108
		H_2O	
	R_e	$1.5R_e$	$2R_e$
BOVB + SD	−76.250341	−76.065857	−75.944696
Full CI	−76.256624	−76.071405	−75.952269
		NH_2	
	R_e	$1.5R_e$	$2R_e$
BOVB + SD	−55.738194	−55.600292	−55.492491
BOVB + SD′	−55.738193	−55.601922	−55.503170
Full CI	−55.742620	−55.605209	−55.505524
		CH_2	
	$^2B_1$	$^1A_1$	$E(^1A_1) - E(^3B_1)$
BOVB + SD	−39.042491	−39.023353	0.019139
Full CI	−39.046260	−39.027183	0.019077
	ΔE(BOVB + SD) − ΔE(Full CI)		
	$2R_e - 1.5R_e$	$2R_e - R_e$	$1.5R_e - R_e$
HF	−0.000812	−0.001603	−0.000791
H_2O	0.002025	0.001290	−0.000735
NH_2	0.008116	0.008607	0.000491
NH_2'	−0.000933	−0.002074	−0.001140
	$E(^1A_1) - E(^3B_1)$		
CH_2	0.000062		

BOVB + SD′ refers to the same augmented with the four other spin-couplings possible using the valence orbitals ϕ_3–ϕ_7.

Finally, the wavefunctions for CH_2 ($^1A_1 : R_e = 1.116$ Å, $\widehat{HCH} = 102.4°$, $^3B_1 : R_e = 1.082$ Å, $\widehat{HCH} = 132.4°$ [23]) were taken as

$$^3\Psi_{CH_2} = \mathscr{A}[\phi_1^2(\alpha\beta)\phi_2\phi_3\phi_4\phi_5(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\phi_6\phi_7(\alpha\alpha)] \tag{29}$$

$$^1\Psi_{CH_2} = \mathscr{A}[\phi_1^2(\alpha\beta)\phi_2\phi_3\phi_4\phi_5\phi_6\phi_7(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)] \tag{30}$$

where ϕ_1 is the 1*s* orbital on C (kept doubly occupied). Orbitals ϕ_2–ϕ_5 describe the C–H bonds and ϕ_6–ϕ_7 contain the remaining two electrons. Table 2 shows the results for all systems.

As before, the BOVB + SD energy does not violate the variational bound in any of the cases studied. The discrepancy with the full CI results are little changed as a result of configuration selection. The NH_2 results show the importance of including other spin-couplings at long bond distances.

To put these results into perspective, it is useful to compare them with other 'popular' computational schemes, namely: SDCI, SDCI + Q, MRCI, MRCI + Q, MP2, MP4(SDQ), MP4(SDTQ), CCSD, CCSD + T, CCSDT − 1, QCISD, QCISD(T). Definitions of these models as well as results in the same basis set as that used here may be found in [17–18, 23–25]. The errors in the total BOVB + SD energies have already been stated and the errors in the methods above have been discussed in the literature cited. For chemical problems, the main interest lies in relative energies. Table 3 shows the mean absolute error in the relative energies compared with full CI for the stretching of HF, H_2O and ($^2B_1$) NH_2 (averaged over all bond distances considered). Finally, the results of the three molecules are averaged and the methods arranged in ascending order with respect to error. The BOVB + SD results perform well (it should be kept in mind that

Table 3. Mean absolute error in relative energies (au) compared with full CI (see text), averaged over $2R_e - R_e$, $2R_e - 1.5R_e$ and $1.5R_e - R_e$

Method	HF	H_2O	NH_2
SDCI	0.012130	0.041874	0.040102
SDCI + Q	0.001925	0.005291	0.005635
MRCI	0.000459	0.000846	0.001296
MRCI + Q	0.000683	0.000436	0.000517
MP2	0.010826	0.027134	0.030532
MP4(SDQ)	0.006508	0.019847	0.024776
MP4(SDTQ)	0.003402	0.009294	0.024886
CCSD	0.004782	0.011521	0.005396
CCSD + T	0.001373	0.005392	0.004532
CCSDT − 1	0.000213	0.003091	0.003985
QCISD	0.003885	0.011668	0.005266
QCISD(T)	0.000760	0.002050	0.004588
BOVB + SD	0.000606	0.001139	0.001382
Full CI	0.0	0.0	0.0

Mean error (au) averaged over HF, H_2O and ($^2B_1$) NH_2, in ascending order.

Method	$\overline{\Delta E}$
Full CI	0.0
MRCI + Q	0.000545
MRCI	0.000867
BOVB + SD	0.001042
CCSDT-1	0.002429
QCISD(T)	0.002466
CCSD + T	0.003765
SDCI + Q	0.004283
QCISD	0.006939
CCSD	0.007233
MP4(SDTQ)	0.012527
MP4(SDQ)	0.017043
MP2	0.022830
SDCI	0.031368

the MRCI expansions referred to in Table 3 use a CASSCF type reference and as such yield a much larger secular problem than the BOVB + SD calculations).

7 Conclusion

It has been the purpose of this study to show that the BOVB method provides a viable scheme for performing VB calculations in a nonorthogonal basis. The VB-CI procedure described here is made much less demanding by the elimination of configurations, as described above. The problem of an energy functional that is not bounded from below has been shown not to be troublesome. The current program is being developed to enable a wider range of systems to be studied and a number of perturbation schemes are being investigated to simplify the VB-CI procedure further.

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