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Optimization of virtual orbitals in the framework of a multiconfiguration spin-coupled wave function

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Abstract. A new method is introduced for the optimization of nonorthogonal virtual orbitals for use in general *multiconfiguration* spin-coupled wave functions. The use of a number of highly effective approximations greatly reduces the computational effort involved, the most important being the use of a second-order perturbation expression for the energy and an approximate expression for the elements of the Hessian. As a result, the overall scheme scales very favourably with respect to the numbers of active electrons and of basis functions, making it suitable for the accurate study of large systems. Benchmark calculations are presented for the dissociation of $\mathrm{LiH}(\mathrm{X}^1\Sigma^+)$ and $\mathrm{Li}_2(\mathrm{X}^1\Sigma_g^+)$ using a highly compact four-configuration wave function. Standard spin-coupled valence bond expansions in the same virtual space are required to be significantly larger before equivalent results are obtained. The results are shown to compare very favourably with full valence complete active space self-consistent field calculations using an identical basis, and binding energies are within 4% of the values obtained from full configuration interaction calculations in the same basis set.

Key words: Spin-coupled valence bond – Orbital optimization – Multiconfiguration – Virtuals

1 Introduction

The introduction of electron correlation into quantum chemical calculations frequently takes the form of configuration interaction (CI) expansions involving the replacement of one or more occupied orbitals from a (set of) reference configuration(s), with virtual orbitals chosen from a set that has been generated in some fashion. The amount of correlation introduced into a CI wave function, especially for heavily restricted expansions, is to some extent determined by how well the set of virtual orbitals reflects the physical nature of the system. The virtual orbitals generated from a Hartree-Fock calculation are eigenfunctions of an effective operator containing an averaged contribution to the potential from all N electrons. This is clearly not physically correct for the description of excited states [1], and results in orbitals which are too diffuse. Even though this need only be a consideration when using truncated expansions, full CI (FCI) calculations are still only feasible for very small systems using small basis sets, making the generation of optimal virtual orbitals of great importance. A good example is the amount of interest shown over many years in the so-called natural orbitals [2–5].

Considerable advances in the efficient implementation of, for example, complete active space self-consistent field (CASSCF) and multireference CI (MRCI) methods mean that there are many molecular orbital (MO) based methods well short of FCI that are still highly accurate. Such methods include direct optimization of orbitals which are unoccupied in the standard single-configuration Hartree-Fock description and thus, in the language of this article, involve optimization of virtual orbitals. The use of reference configurations evaluated at the CASSCF level in MRCI calculations is particularly successful. Unfortunately, these methods still scale severely with the size of the problem, so that the development of alternative virtual optimization methods, with better scaling properties, is still of considerable interest. Efficient virtual optimization allows one to restrict expansion sizes as far as possible, whilst retaining a high degree of accuracy. In this way the amount of direct chemical interpretation that can be extracted from the calculation is maximized. This has always been an integral part of the philosophy of modern developments of valence bond (VB) theory, such as the spin-coupled (SC) method.

In contrast to Hartree-Fock theory, each of the N occupied orbitals in a SC wave function is an eigen-

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function of a unique effective operator which involves potential energy contributions from only the remaining $(N-1)$ electrons [6]. Hence the N sets of virtual orbitals generated from diagonalizing each of these operators will be more representative of excited states of the system where one or more occupied orbitals has been replaced. Experience has indeed shown that the initial convergence characteristics of a spin-coupled valence bond (SCVB) nonorthogonal CI expansion is superior to that of a standard MO–CI treatment, thus allowing the use of considerably shorter expansion lengths [7–9]. The SCVB method has been applied to many diverse systems with great success and has proved especially valuable with regard to the interpretation of results in terms that are of use to the general chemical community.

Despite the excellent initial convergence, the SCVB expansion subsequently becomes much more slowly convergent, so that reasonably large numbers of structures still have to be used in many cases to achieve highly accurate results. Systems with a large enough number of electrons will no longer be adequately described by *compact* SCVB wave functions, and this is the motivation behind the development of the current method. Since a large number of single-point calculations need to be determined to generate a detailed picture of a full potential surface, any method that allows expansion sizes of wave functions to be greatly reduced without compromising accuracy could be of great value.

Thorsteinsson et al. have recently developed the complete active space valence bond (CASVB) method which uses CASSCF techniques, with all their inherent advantages, to perform fully variational optimizations of general types of modern VB wave functions [10–14]. These may be the single-configuration spin-coupled wave function, or multiconfiguration (MC) wave functions of the type considered in this paper, depending on the size and the type of the active space chosen. The nonorthogonal orbitals and structure coefficients are optimized simultaneously without approximation. This promises to be a very powerful technique of wide applicability and should serve to improve greatly our understanding of the connection between MO–CI and modern VB approaches.

As the number of active electrons in a system increases, however, the CASVB strategy will suffer the same scaling problems as experienced by CASSCF itself, meaning that alternative techniques for such systems are still necessary. The methodology described here, which utilizes a number of important approximations during the optimization procedure, has been developed precisely to address this need.

Raimondi et al. developed a scheme for optimizing SC virtual orbitals used in the description of intermolecular potentials for van der Waals complexes [15]. This involved the energy minimization of a SCVB wave function describing the complete "super-system", constructed using the N SC-occupied orbitals (fixed) determined in the usual fashion, and a set of N virtual orbitals (varied), each directly associated with a particular occupied orbital. The SCVB expansion included the SC configuration and all doubly excited configurations involving a single excitation local to each of the two molecular fragments. In this way, a description of the He...LiH system was achieved using an expansion length two orders of magnitude smaller than a standard SCVB calculation of equivalent accuracy. Whilst this is perfectly adequate for the study of long-range dispersion interactions, a generalized scheme for treating correlation in single molecules, as well as reactive collisions between fragments, requires the inclusion of a wider range of configurations and the use of a more robust optimization procedure. These generalizations are the subject of the current article and, since the previous scheme was presented strictly in the context of two distinct fragments using separate sets of basis functions (to avoid BSSE), we shall in the next section redevelop the basic theory for a single fragment, and then present in detail the new optimization scheme.

Section 3 provides a brief review of the Pyper–Gerratt (PG) MCSC wave function, which has many similarities to the work presented here [16]. However, there are certain important differences between the methods which are highlighted and discussed in Sect. 3, as are the recent advances of Penotti [17]. In Sect. 4 we present results for the LiH and Li_2 molecules, which demonstrate the high accuracy of these new extremely compact expansions. The results are compared with conventional SCVB calculations, and show the significant expansion size reduction possible with this new method. Comparison is also made with the results of Pyper and Gerratt (PG), with two-electron full valence CASSCF and FCI calculations, and with MRCI calculations using multiconfiguration self-consistent field (MCSCF) reference configurations.

2 Theory

The reference configuration from which we create our excited configuration is the SC wave function [6, 9], which can be written as follows:

$$\Psi_0 = \mathscr{A}\left(\phi_1^0\phi_2^0\ldots\phi_N^0\sum_{k=1}^{f_S^N} c_{Sk}^0\Theta_{SM;k}^N\right) \quad , \tag{1}$$

in which N is the total number of electrons, $\Theta_{SM;k}^N$ is the kth out of a total of f_S^N linearly independent spin eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$, $\mathscr{A}$ is the antisymmetrizing operator and the ^{0} superscript denotes an occupied orbital. As usual, each SC orbital is expanded in a basis set, in this case of M atomic orbitals $\{\chi_a\}$

$$\phi_i^0 = \sum_{a=1}^{M} c_{ia}^0\chi_a \quad . \tag{2}$$

The SC wave function is freely optimized simultaneously with respect both to the orbital coefficients c_{ia}^0 (Eq. 2) and to the spin-coupling coefficients c_{Sk}^0 (Eq. 1), without the imposition of any constraints that would change the total wave function. The N optimized ϕ_i^0 orbitals are nonorthogonal and they are each eigenfunctions of a different effective operator, built up from contributions from the other $N-1$ electrons:

$$\hat{\mathrm{F}}_i^{\mathrm{eff}}\phi_i^0 = \varepsilon_i\phi_i^0 \ . \tag{3}$$

The effective operators are of dimension M and so, in addition to the SC occupied orbital ϕ_i^0, diagonalization of this operator generates a further $M-1$ virtual orbital denoted as ϕ_i^j, where j signifies the position in the list. In this fashion, a "stack" of virtual orbitals is obtained for each electronic coordinate. The orbitals are mutually orthogonal within a given stack but they are not in general orthogonal to orbitals in the other stacks. Excited configurations can be constructed by replacing one or more occupied SC orbitals with a virtual orbital, frequently taken from the same stack as the occupied orbital, in which case it is referred to as a "vertical" excitation. If the occupied orbital is replaced with a virtual from a different stack, then this is referred to as a "cross" excitation. A linear combination of the reference SC configuration and the excited configurations described above constitutes a so-called SCVB wave function. Optimizing the expansion coefficients via resolution of the corresponding secular problem, which requires the evaluation of Hamiltonian and overlap matrices between nonorthogonal VB structures, gives the total energy of the system. Considering SCVB expansions which contain all possible double vertical excitations into M virtual orbitals for an N electron system of total spin S, we find that the expansion will include $\frac{1}{2}N(N-1)M^2 f_S^N$ excited structures. For a reasonably small system with $N=6$, $M=10$ and $S=0$, just double excitations result in 7,500 excited structures. Given that a large number of virtuals are often required [18] to achieve highly accurate results, calculations on systems containing a large number of electrons rapidly become untenable.

To overcome this severe size restriction, it is necessary to find ways to achieve equivalent, or almost equivalent, results with much smaller numbers of virtual orbitals. Considering that the standard SCVB virtuals already come from diagonalization of a physically reasonable operator, the next stage in improving virtuals must require a direct in situ optimization of these orbitals with respect to the energy of an SCVB wave function. If we have just one virtual orbital per stack, denoted ϕ_i^+, our N-electron all-double-excitation SCVB expansion can be written:

$$\Psi = c_0\Psi_0 + \sum_{i=1}^{N}\sum_{j>i}^{N} C_{ij}\Psi_{ij} \ , \tag{4}$$

where

$$\Psi_{ij} = \mathscr{A}\left(\phi_1^0\phi_2^0\ldots\phi_i^+\ldots\phi_j^+\ldots\phi_N^0\sum_{k=1}^{f_S^N} c_{Sk}^{ij}\Theta_{SM;k}^N\right) \ . \tag{5}$$

Our task is to find the set of virtual orbitals $\{\phi_i^+\}$ that minimizes the energy of the wave function in Eq. (4). Bearing in mind that our principal aim is to reduce the effort required to calculate each point on a potential surface, whilst retaining a high level of accuracy, it is important that we find a way to optimize these virtuals as economically as possible. To help achieve this we take advantage of the following approximations:

1. The spin-coupling coefficients c_{Sk}^{ij} for the excited configurations are fixed to the values for the SC reference configuration c_{Sk}^0.
2. The virtual orbitals for the expansion in Eq. (4) are optimized with respect to the energy of the overall wave function approximated by means of a perturbation expression up to second order [19, 20].

Once the orbitals are optimized, within these approximations, they can then be used in a standard nonorthogonal CI expansion in order to relax the spin-coupling coefficients and to find a variationally bound value for the energy. We shall refer to such an expansion as a SCVB* wave function. Optimizing the virtuals with respect to the second-order perturbation approximation to the energy introduces a major saving in that we need only to evaluate the diagonal and first-row elements of the Hamiltonian and overlap matrices. The energy expression is:

$$E^{(2)} = H_{00} + \sum_{i=1}^{N}\sum_{j>1}^{N}\frac{\left[H_{(0,ij)} - H_{00}S_{(0,ij)}\right]^2}{H_{00}S_{(ij,ij)} - H_{(ij,ij)}} \tag{6}$$

where $H_{00} = \langle\Psi_0|\hat{\mathrm{H}}|\Psi_0\rangle$, $H_{(0,ij)} = \langle\Psi_0|\hat{\mathrm{H}}|\Psi_{ij}\rangle$, $S_{(0,ij)} = \langle\Psi_0|\Psi_{ij}\rangle$, and so on.

The Hamiltonian matrix elements written in terms of density matrices correspond to those for the usual SC wave function except that now the bra and ket orbitals will in general be different. This has important consequences for the symmetry properties of the supercofactors [15, 21]. Taking the matrix element $H_{0,\mathrm{ij}}$ as a representative example we have

$$\begin{aligned}H_{(0,ij)} = &\sum_{rs}^{N}\langle\phi_r^0|\hat{h}(1)|\phi_s^{ij}\rangle D^{(0,ij)}(r|s)\\ &+\frac{1}{2}\sum_{rstu}^{N}\langle\phi_r^0\phi_t^{ij}\|\phi_s^0\phi_u^{ij}\rangle D^{(0,ij)}(rs|tu) \ ,\end{aligned} \tag{7}$$

where the integrals in the first and second terms are the one- and two-electron integrals, respectively (in charge-cloud notation). The $D^{(0,ij)}(r|s)$ and $D^{(0,ij)}(rs|tu)$ are the first- and second-order supercofactors in which the bra orbitals are all SC occupied orbitals, whilst for the ket orbitals, ϕ_i^0 and ϕ_j^0 are replaced by ϕ_i^+ and ϕ_j^+. To minimize the energy $E^{(2)}$ with respect to the virtual orbitals $\{\phi_j^+\}$ we use the stabilized Newton-Raphson procedure [22], as in some implementations of the SC method. This requires first and second derivatives of the energy with respect to an arbitrary virtual orbital, ϕ_j^+. The expression for the energy gradient with respect to ϕ_j^+ is

$$\begin{aligned}\frac{\partial E^{(2)}}{\partial\phi_j^+} = &\sum_{i\neq j}^{N}\left\{A^{ij}\left[\frac{\partial H_{(0,ij)}}{\partial\phi_j^+} - H_{00}\frac{\partial S_{(0,ij)}}{\partial\phi_j^+}\right]\right.\\ &\left.+\frac{1}{4}\left(A^{ij}\right)^2\left[\frac{\partial H_{(ij,ij)}}{\partial\phi_j^+} - H_{00}\frac{\partial S_{(ij,ij)}}{\partial\phi_j^+}\right]\right\}\end{aligned} \tag{8}$$

where

$$A^{ij} = 2\left(\frac{H_{(0,ij)} - H_{00}S_{(0,ij)}}{H_{00}S_{(ij,ij)} - H_{(ij,ij)}}\right) \ . \tag{9}$$

Performing the differentiations, having adopted the by now standard SC technique of applying Laplace's expansion of the supercofactor elements [21], and then expanding the ket orbitals in terms of the atomic orbital basis functions, we arrive at the following expression for the energy gradient with respect to the *a*th expansion coefficient of virtual orbital *j*:

$$\frac{\partial E^{(2)}}{\partial c_{ja}} = \varepsilon_{ja} + \sum_{i=1}^{N} \langle \phi_i^{+} | \hat{\mathrm{G}}_{ji} | \chi_a \rangle \ , \tag{10}$$

in which

$$\varepsilon_{ja} = \sum_{l=1}^{N} \langle \phi_l^0 | \hat{\mathrm{F}}_{jl}^{(0,ij)} | \chi_a \rangle + \sum_{i \neq j}^{N} \sum_{l \neq ij}^{N} \langle \phi_l^0 | \hat{\mathrm{F}}_{jl}^{(ij,ij)} | \chi_a \rangle \tag{11}$$

is independent of virtual orbital *j*, and

$$\hat{\mathrm{G}}_{ji} = \begin{cases} \hat{\mathrm{F}}_{ji}^{(ij,ij)} & \text{if } i \neq j \\ \sum\limits_{r \neq j}^{N} \hat{\mathrm{F}}_{jj}^{(rj,rj)} & \text{if } i = j \ . \end{cases} \tag{12}$$

The general expression for the operator $\hat{\mathrm{F}}$ is

$$\begin{aligned} \hat{\mathrm{F}}_{jl}^{(i'j',ij)} = \gamma^{(i'j',ij)} \Bigg\{ & (h(1) - H_{00}) D^{(i'j',ij)}(l|j). \\ & + \sum_{rs}^{N} \langle \phi_r^{i'j'} | h(1) | \phi_s^{ij} \rangle D^{(i'j',ij)}(rl|sj) \\ & + \frac{1}{2} \sum_{rstu}^{N} \langle \phi_r^{i'j'} \phi_t^{ij} \| \phi_s^{i'j'} \phi_u^{ij} \rangle D^{(i'j',ij)}(rsl|tuj) \\ & + \sum_{rt}^{N} S\left(\phi_r^{i'j'} | \phi_t^{ij} \right) D^{(i'j',ij)}(rl|jt) \Bigg\} \ , \end{aligned} \tag{13}$$

where

$$S(\phi_r^{i'j'} | \phi_t^{ij}) = \int \phi_r^{i'j'}(1) \frac{1}{r_{12}} | \phi_t^{ij}(1) d\tau_1$$

$$\gamma^{(i'j',ij)} = \begin{cases} A^{ij} & if\ \ i'j' = 0 \\ \frac{1}{2}(A^{ij})^2 & if\ \ i'j' = ij \ \ . \end{cases} \tag{14}$$

Starting from Eq. (10), we now consider a general element of the Hessian, $\partial^2 E^{(2)} / \partial c_{ja} \partial c_{lb}$. The gradient $\partial E^{(2)} / \partial c_{ja}$ depends on c_{lb} via the bra orbital ϕ_l^{+} and via the various $\hat{\mathrm{F}}$ operators. If we consider only the first of these dependencies, then it follows directly from Eq. (10) that we may write:

$$\frac{\partial^2 E^{(2)}}{\partial c_{ja} \partial c_{lb}} = \langle \chi_b | \hat{\mathrm{G}}_{jl} | \chi_a \rangle \ . \tag{15}$$

This approximate form for the Hessian does not require the computation of any individual terms not already evaluated for the gradient expression. The only overhead is the assembly of elements from precalculated quantities, making this a quick and highly efficient strategy. We have found this approximation to work extremely well for all of the systems studied.

Of course, the Hessian matrix must be Hermitian, which requires from Eq. (15) that

$$\langle \chi_b | \hat{\mathrm{G}}_{jl} | \chi_a \rangle = \langle \chi_a | \hat{\mathrm{G}}_{lj} | \chi_b \rangle \ . \tag{16}$$

In order to demonstrate that this relationship holds, we need to show, using Eqs. (12–14), that $\hat{\mathrm{F}}_{jl}^{(lj,lj)} = \hat{\mathrm{F}}_{lj}^{(lj,lj)}$, and that this operator is Hermitian. Using Eqs. (13) and (14) we see immediately that $\hat{\mathrm{F}}_{jl}^{(lj,lj)}$ is Hermitian, since for the matrix element $\langle \chi_a | \hat{\mathrm{F}}_{jl}^{(lj,lj)} | \chi_b \rangle$ the bra and ket orbitals appear only in the terms $\langle \chi_a | \hat{\mathrm{h}}(1) | \chi_b \rangle$, $\langle \chi_a | \chi_b \rangle$ and $\sum_{rt} \langle \phi_r^{(ij)} \phi_t^{(ij)} \| \chi_a \chi_b \rangle$, all of which are invariant to the exchange of labels *a* and *b*. Finally, to demonstrate that $\hat{\mathrm{F}}_{jl}^{(lj,lj)} = \hat{\mathrm{F}}_{lj}^{(lj,lj)}$, we note that the orbitals that correspond to the bra and ket labels in the supercofactors are identical, and so the general symmetry relation [21]

$$\begin{aligned} & D(\mu_1, \mu_2, \ldots, \mu_n | v_1, v_2, \ldots, v_n) \\ & \quad = D(v_1, v_2, \ldots, v_n | \mu_1, \mu_2, \ldots, \mu_n) \end{aligned} \tag{17}$$

must apply. From Eqs. (13) and (14) we can see by inspection that having swapped labels *j* and *l*, all other labels in the integrals and supercofactors correspond to identical summations over the same orbitals in both the bra and ket parts and so the equivalence is proven, as is the Hermitian nature of the approximate Hessian.

The combination of this approximate form for the Hessian with the use of the second-order perturbation expression for the energy, results in an overall orbital optimization strategy that scales extremely favourably with both the number of "active" electrons and the number of basis functions. Since the evaluation of any quantity does not require supercofactors beyond third order, the upper limit to the applicability of the method is currently fixed by the determination of the SC occupied orbitals, which require supercofactors up to fourth order. The number of active electrons that can be treated is therefore currently about 12–14. Obviously, the use of an alternative form for the reference configuration orbitals, e.g. GVB-SOPP, could in principle allow for a yet greater extension of the basic method to even larger systems. Test calculations on systems with larger numbers of electrons than those considered here have confirmed that the optimization procedure is sufficiently robust to deal with such cases.

We have found that our optimization procedure can be susceptible to the effects of linear dependence when using large basis sets. A natural and effective way to overcome this problem is to project out each of the *N* SC occupied orbitals from the *M* atomic basis functions and then Gram-Schmidt orthogonalize [23] the projected basis to extract $M - N$ linearly independent functions. Each of the *N* virtual orbitals is then expanded in a combined basis of the SC orbitals and the linearly independent projected functions. Problems with linear dependence can then easily be resolved by removing from each expansion the SC occupied orbital for that stack.

3 The MCSC wave function of Pyper and Gerratt

The present work has much in common with the MCSC wave function developed by Pyper and Gerratt [16], making it a very important reference point for these calculations. It is therefore worthwhile to review briefly the PG method, highlighting similarities and important differences to the present method. The basic form of the PG wave function for the LiH($X^1\Sigma^+$) ground state is:

$$\Psi_{PG}^{LiH} = C_\sigma\{\sigma_1\sigma_1'\sigma_2\sigma_2'\} + C_\pi \sum_{\alpha=x,y}\{\sigma_1\sigma_1'\pi_\alpha\pi_\alpha'\} \ . \tag{18}$$

This is, using the terminology of the present article, a three-configuration wave function, in which the lithium $1s1s'$ orbitals are constrained to be equivalent for each of the configurations. The two "valence" orbitals are constrained to be of purely σ symmetry in the first configuration and of one of the two π components in the other two. For each of the configurations, there is a restriction to just one mode of spin coupling, namely that in which the $\sigma_1\sigma_1'$ orbitals and the two valence orbitals and are singlet coupled. The energy of the wave function is minimized by optimizing simultaneously all of the orbitals and the C_σ/C_π weighting coefficients. The optimization procedure is completely equivalent to that used for the standard single-configuration SC wave function, using the full variational energy expression, analytic first and second derivatives, and the stabilized Newton-Raphson procedure. The PG wave function for $Li_2(X^1\Sigma_g^+)$ follows the same basic pattern:

$$\begin{aligned}\Psi_{PG}^{Li_2} = {} & C_\sigma\{\sigma_{1A}\sigma_{1A}'\sigma_{1B}\sigma_{1B}'\sigma_{2A}\sigma_{2B}\} \\ & + C_\pi \sum_{\alpha=x,y}\{\sigma_{1A}\sigma_{1A}'\sigma_{1B}\sigma_{1B}'\pi_{A\alpha}\pi_{B\alpha}'\}\end{aligned} \tag{19}$$

in which the A and B labels refer to each of the lithium centres.

As described in detail in Sect. 4, virtual orbitals of different symmetries are optimized in the current method in a completely independent fashion, using the *fixed* SC occupied orbitals as a reference configuration. In this way, for example, the π symmetry virtuals that introduce angular correlation are optimized without experiencing the influence of the σ symmetry virtuals, which in turn add significant additional radial correlation. On the other hand, the SC reference orbitals are not relaxed in any way to reflect the influence of the additional configurations, whereas in the PG method all of the valence orbitals are optimized in the presence of one another and of an optimizable $1s1s'$ "core". These differences are likely to have a noticeable effect on the final wave function and in particular on the nature of the individual optimized virtuals. The final significant difference between the two methods is in the treatment of the spin coupling. If the perfect-pairing spin function remains the overwhelmingly dominant mode of spin coupling, as is the case over all internuclear distances in both LiH and Li_2, then there is very little difference between the two methods. However, for systems containing more than two valence electrons, the description of the spin coupling can become much more complicated and the restriction of the PG method to the use of just the perfect-pairing spin function becomes much more severe, especially when following bond breaking and formation. Penotti [17] has recently developed a full generalization of the PG method in which the orbitals, all spin-coupling coefficients and basis function orbital exponents are freely optimized simultaneously. The computational demands of this method are very heavy and had previously limited applications to atomic states of He, B and B−. However, an extension to diatomic systems has been implemented and calculations are currently in progress; these will provide a very interesting comparison with the work presented here [24]. An attractive alternative strategy for calculating general types of multiconfiguration modern VB wave function is the CASVB approach [10–14].

4 Results and discussion

4.1 LiH

A basis set consisting of $(11s8p6d2f/9s7p5d)$ Cartesian GTOs contracted to $[6s5p3d1f/5s5p3d]$ was used for Li/H, and it is reported in Table 1 as a composite list of the basis functions used for LiH and Li_2. The LiH basis set constitutes a subset of the functions optimized by Roos and Sadlej for LiH [25]. In both the LiH and Li_2 calculations, the lithium $1s1s'$ electrons were considered to have very little effect on bond formation (see Refs. [16, 26]), so the only configurations that were included are those that correlate the nominally Li($2s$) and H($1s$) electrons, reducing the number of virtual orbitals to be determined to just two at each stage. Indeed, our own calculations treating Li_2 as a six-electron system have shown that correlating also the $1s1s'$ electrons results in a significant but uniform lowering of the energy over the whole potential curve, thus not affecting significantly the description of molecule formation. Since our main interest is to describe this process accurately using as few configurations as possible, we have concentrated on descriptions based on just two active electrons. Nevertheless, the six-electron calculations have provided, along with other tests, confirmation that our method is equally viable for a somewhat larger number of active electrons.

Because the electronic ground state of LiH is of $^1\Sigma^+$ symmetry, configurations containing both σ^2 and π^2 double excitations make a contribution, the first providing radial correlation and the second angular. Therefore two sets of virtual orbitals were optimized, the first being of pure σ symmetry whilst the second is expanded in basis functions of just a single π component. The virtuals representing the second π component were obtained via a rotation of the optimized π orbitals by an angle of $\pi/2$ about the internuclear axis. The final SCVB wave function (hereafter denoted SCVB*-4) constructed using these virtuals contained therefore just four configurations, namely the SC configuration, one double excitation into σ symmetry virtuals and two double excitations into π symmetry virtuals. Since $f_0^4 = 2$, the SCVB*-4 wave function contains eight valence bond structures. Further electron correlation could be introduced by optimizing virtuals of yet higher angular momentum (e.g. δ), but only at the expense of increasing the final expansion length.

Table 1. Exponents α_i and contraction coefficients k_i for the GTO basis set

Type	Lithium		Type	Hydrogen	
	k_i	α_i		k_i	α_i
s	0.000075	9497.9344	s	0.000044	1776.7756
	0.000584	1416.8112		0.000372	254.01771
	0.003062	321.45994		0.002094	54.698039
	0.012605	91.124163		0.008863	15.018344
	0.042356	29.999891	s	0.03054	4.915078
s	0.11478	11.017631		0.090342	1.794924
	0.239381	4.372801	s	1.0	0.710716
s	1.0	1.831256	s	1.0	0.304802
s	1.0	0.802261	s	1.0	0.138046
s	1.0	0.362648	p	0.0138	4.915078
s	1.0	0.113995		0.0684	1.794924
s^a	1.0	0.051237		0.2529	0.710716
s^a	1.0	0.022468	p	1.0	0.304802
p	0.034600	11.017631	p	1.0	0.138046
	0.114800	4.372801	p	1.0	0.062157
	0.264400	1.831256	p	1.0	0.027967
p	0.111700	0.802261	d	0.0503	1.794924
	0.147000	0.362648		0.3	0.710716
p	1.0	0.113995	d	0.1156	0.304802
p	1.0	0.051237		0.246	0.138046
p	1.0	0.022468	d	1.0	0.062157
d	0.0547	4.372801			
	0.1954	1.831256			
	0.3783	0.802261			
d	0.1816	0.113995			
	1.1978	0.051237			
d^b	1.0	0.022468			
f^b	0.5292	0.051237			
	0.8751	0.022468			

[a] Basis function used only in Li_2 calculation

[b] Basis function used only in LiH calculation

The LiH($X^1\Sigma^+$) dissociation energy curves for the SC wave function, a two-configuration wave function containing the SC and σ^2 configurations [SCVB*-2] (perturbation energy) and the SCVB*-4 wave function are presented in Fig. 1. Adding just the σ^2 configuration to the SC wave function makes a considerable difference to the potential energy curve (long dashed curve in Fig. 1). It is important to note that this curve is of the nonvariational second-order perturbation energy. It is perfectly smooth and continuous at each point, demonstrating that the virtual orbitals have been optimized in a consistent fashion and that the projection method used to overcome problems with linear dependence does not favour one region of the potential over another. Using these two configurations in a standard SCVB expansion to relax the spin-coupling coefficients and to obtain a variational result makes a minimal difference to the energy, typically less than 5×10^{-4} eV. This extra σ^2 configuration has so far increased only the amount of radial correlation in the wave function. The two π^2 configurations, which complete our wave function, introduce for the first time angular correlation, and the significant drop in energy between the two- and four-configuration wave functions demonstrate the relative importance of angular correlation in this system.

The fourth curve in Fig. 1 corresponds to full valence CASSCF (FVCAS) calculation using an identical basis. For LiH this involves distributing the two valence electrons in all symmetry allowed ways amongst the five valence orbitals, resulting in eight configuration state functions (CSFs). The lithium $1s^2$ core was relaxed during these calculations but it was not directly correlated. Since the SC calculation includes radial correlation for the Li core, the absolute FVCAS energies will be higher than those of the SC-based wave functions. However, the arguments given at the start of this section suggest that the two dissociation energies should be directly comparable. The FVCAS is a more realistic comparison to the current work than the MCSCF-4 results described below, the latter being included to highlight the advan-

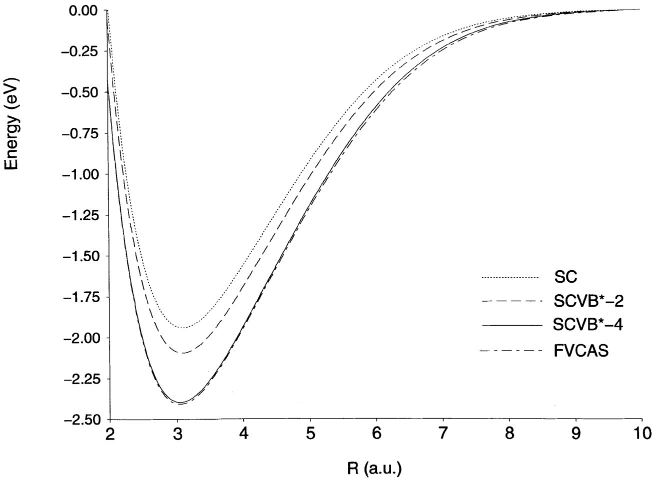

Fig. 1. Dissociation energy curves for the $X^1\Sigma^+$ state of LiH for the spin-coupled (SC), SCVB*-2, SCVB*-4 and full-valence complete active space self-consistent field (FVCAS) wave functions

tages of working with nonorthogonal orbials when including a very restricted configuration list. Since we are dealing with effectively a two-electron system, the FVCAS results can be expected to be very similar to the two-electron full CI (see Table 2 and later in this section). From Fig. 1 we can see that the SCVB*-4 and FVCAS curves are almost identical, with the FVCAS giving a marginally lower dissociation energy, suggesting that the SCVB*-4 wave function recovers a large amount of the correlation energy available with this basis set.

Table 2 presents a quantitative comparison between molecular properties calculated using the SVCB*-4 wave function of the current work and a range of other wave functions, along with experimental values [27–29]. We have considered the SC, PG (using a high quality STO basis set), the two-electron FVCAS and FCI wave functions, a four-configuration MCSCF [30], and finally two singles and doubles CI wave functions [30], using two and four reference configurations, respectively. (The PG is a SCVB*-3 type wave function using just the perfect-pairing spin function but with all orbitals simultaneously optimized). All values given refer to the equilibrium distance relevant for that wave function. We can see that the SC wave function overestimates the position of the minimum, R_e, by 2.4%, whilst the PG and SCVB*-4 wave functions overestimate it by 1.1% and 0.95%, respectively, a noticeable improvement in both cases. A much greater difference is seen, however, in the values of the dissociation energy, D_e. The SC wave function recovers 77% of the experimental value, whilst adding the two extra π^2 configurations in the PG wave function increases this to 89.5% . The four-configuration SCVB*-4 wave function represents a further significant improvement, raising this to 95% . It is clear that having the extra σ^2 configuration to augment the radial correlation is of considerable importance. The SCVB*-4 result is very satisfying indeed, considering the extremely small number of configurations used. The fact that we have improved so much on the already accurate PG wave function, for which orbitals were *rigorously* and *simultaneously* optimized, by the inclusion of just two extra σ virtuals, demonstrates that the use of the second-order perturbation energy during the optimization of the SCVB*-4 virtual orbitals is a viable strategy.

Table 2. Calculated and experimental molecular properties for the $X^1\Sigma^+$ state of LiH

	R_e/Å	D_e/eV	μ_e/D
SC	1.633	1.94	5.749
PG	1.612	2.26	5.762
SCVB*-4	1.610	2.39	5.736[a]
FVCAS	1.609	2.42	5.889
FCI	1.607	2.49	–
MCSCF-4	1.611	2.29	5.764
MCCI-2	1.602	2.47	5.775
MCCI-4	1.601	2.48	5.775
Experiment	1.595[b]	2.52[c]	5.882[d]

[a] Twelve configurations – see discussion
[b] Ref. [27]
[c] Ref. [28]
[d] Ref. [29]

The FVCAS results, using an identical basis, are very similar to SCVB*-4 whilst the1269-CSF FCI has only a very slight improvement in R_e and recovers 98.7% of D_e, i.e. SCVB*-4 is less than 4% (0.1 eV) short of the best possible valence-only result for this basis. It is instructive to contrast the relative sizes of the SCVB*-4 and FVCAS wave functions. In the former, we have just four configurations involving $2 \times \sigma$, $2 \times \pi_x$ and $2 \times \pi_y$ virtuals which, other than by symmetry, are mutually nonorthogonal. The $2 \times \sigma$ SC "occupied" orbitals are not optimized along with the virtuals and the σ and π symmetry orbitals are optimized separately. In the latter we have eight CSFs involving $3 \times \sigma$, $1 \times \pi_x$ and $1 \times \pi_y$ mutually orthogonal orbitals which are all fully optimized simultaneously in a strictly variational fashion. The FVCAS calculation has computational advantages linked to the many simplifications that arise from the use of orthogonal orbitals, but SCVB*-4 achieves practically equivalent result using just half the number of configurations. Clearly, each method has its attractions and it is not the purpose of the current article to detract from the enormous achievements of modern MO theory. The most attractive aspects of the SCVB* method, not fully brought out by these initial benchmark calculations, are the scaling properties which, due to the very compact nature of wave functions constructed from nonorthogonal orbitals, could make it very competitive with respect to standard FVCAS calculations.

The advantages of using nonorthogonal orbitals to maximize the accuracy of short expansions is admirably demonstrated by comparison with the MCSCF-4 wave function in Table 2. This also includes just four configurations involving σ, π_x, and π_y virtuals and uses a comparable $(7s5p3d/6s3p)$ GTO basis. MCSCF-4 recovers only 91% of D_e, and including all singles and doubles from both the $(1\sigma)^2(2\sigma)^2$ and $(1\sigma)^2(3\sigma)^2$ configurations (3728 CSF MCCI-2), or from all four reference configurations (6105 CSF MCCI-4), recovers only 98% and 98.5% of D_e, respectively, just a 0.09 eV improvement on SCVB*-4 for a 500-fold increase in the number of configurations.

One notable aspect of the LiH system is the behaviour of its dipole moment during dissociation. As the Li—H bond length R increases from its equilibrium value, the molecule initially tends to the form $Li^+ + H^-$, followed by a fairly abrupt change to covalent character in the region from ca. 5 to 7 a.u. This is reflected in the dipole moment, which extensive calculations have shown goes through a maximum at $R \sim 5$ a.u. [31, 32]. Reproducing the R-dependence of this dipole moment function is a severe test of the quality of a wave function, as it reflects directly the charge separation between the two centres. The single configuration SC wave function reproduces well the radial behaviour of the dipole, but it both underestimates and displaces the maximum to too short a distance [32]. We have found that SCVB*-4, despite the improvement in the energy, makes very little improvement to the dipole moment function (just 0.34% and 0.43% at R_e and at $R_{(\max\mu)}$ for the SC wave function, respectively). This appears to reflect the well-known fact that the perturbation energy will be accurate to order $(2k+1)$ for a wave function accurate to order k [33]. By comparison, the dipole moment from the PG wave function represents a considerable improvement over that of the SC. The difference in the behaviour of the dipole moment functions for the PG and SCVB*-4 wave functions is due, at least in part, to the fact that in the former, *all* of the σ and π symmetry orbitals are optimized simultaneously, and that different basis sets were used to describe the σ and π configurations.

Since it is clear that the SCVB*-4 wave function underestimates the degree of change separation in LiH, a simple way of improving the situation is to add at the final SCVB stage the eight ionic configurations in which one of the two valence and six virtual orbitals is doubly occupied. The additional cost is negligible since no more orbital optimization is required and, because the SCVB stage is fully variational, as much or as little ionic character may be naturally introduced as is necessary. The final wave function now has 12 configurations (SCVB*-12) and we find that adding the ionic configurations has a minimal effect on the energy ($\sim 5 \times 10^{-5}$ hartree at R_e) but a significant effect on the dipole moment, as expected. The SCVB*-12 dipole moment is still little changed from that for the SC wave function at its R_e ($\sim$0.38%) but the difference as R increases is marked. At $R_{(\max\mu)}$ for the SC wave function, the SCVB*-12 dipole moment is now 2.2% greater and the absolute maximum for the SCVB*-12 wave function is 6.927 D at 4.83 a.u., to be compared with 6.769 D at 4.72 a.u. for SC. Both the magnitude and the position of the maximum have been noticeably improved, although these remain inferior to those obtained from the PG wave function, for which STO exponents were reoptimized in this region of the potential curve. The accurate SCVB calculation of Cooper et al. [32], found a value of 7.63 D at 5 a.u., using a universal even-tempered STO basis set, whilst the CI calculation of Partridge et al. [31], employing a 22σ, 12π and 7δ STO basis, found a value of 7.57 D at the same distance. The SCVB*-12 dipole moment remains $\sim$9% lower than these values whilst the FVCAS calculations return a much better 7.60 D, confirming the adequacy of the GTO basis and reinforcing our suspicions that the absence of simultaneous σ and π virtual optimization causes SCVB* to underestimate the dipole. The dipole moment functions for the SC, SCVB*-4, SCVB*-12 and FVCAS wave functions are presented in Fig. 2. Note that the *apparent* superiority in the value of the dipole moment for the SC wave function over that of SCVB*-12 (see Table 2) occurs only because the former significantly overestimates R_e.

Finally, it is extremely instructive to compare the results of more conventional SCVB calculations using exactly the same basis set but now using the "standard" virtual orbitals obtained by diagonalizing the effective operators of the converged SC wave function. Two separate calculations were performed, one including all single and double replacements of the two valence SC orbitals (SCVB-SD) and the other including in addition all ionic configurations, in which the virtual orbitals are doubly occupied (SCVB-SDI). All configurations not of overall ${}^1\Sigma^+$ symmetry were discarded. The calculations were performed at R_e for the SCVB*-4 wave function and all the virtual orbitals were taken from a single stack. This is not exactly the standard SCVB technique, in which virtuals from *each* of the stack are used, and so the expansion will converge somewhat more slowly, possibly considerably so. We deviated from the standard approach specifically so as to allow us to go high up the chosen single stack and thus investigate more fully the virtual space, without the danger of introducing linear dependence which might otherwise occur when using a potentially *overcomplete* set of virtuals. It is important to bear in mind that the comparisons presented here are intended merely to demonstrate how the SCVB*-4 wave function spans the available virtual space and *not* to act as a direct comparison of the SCVB and SCVB* methods.

The dissociation energies of the wave functions are presented in Table 3 for different numbers of σ and π symmetry virtuals from a single stack – δ symmetry virtuals were not included, so as to keep the comparison consistent. The value in parenthesis after the energy is the number of structures in the SCVB expansion. A total of 18 σ and π virtual orbitals and 1046 VB structures, including an additional class of ionic structures, was required before this type of SCVB expansion matches

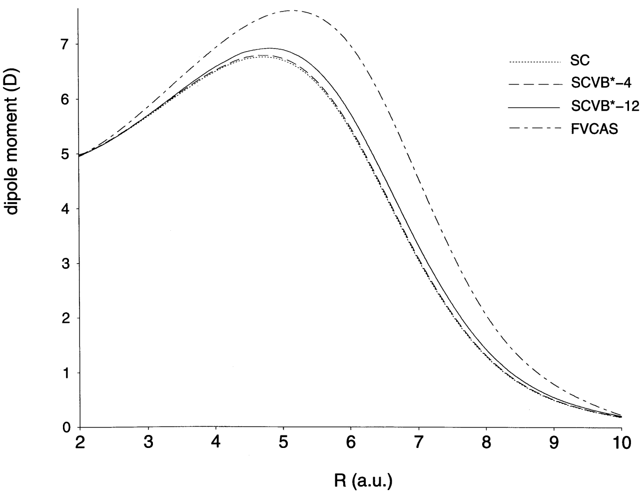

Fig. 2. Dipole moment functions for the $X^1\Sigma^+$ state of LiH for the SC, SCVB*-4, SCVB*-12 and FVCAS wave functions

Table 3. Calculated LiH($X^1\Sigma^+$) dissociation energies (eV) for spin-coupled valence bond (SCVB) wave functions using different numbers of σ and π symmetry virtual orbitals

n_σ/n_π	D_e(SCVB-SD)	(n_{struct})	D_e(SCVB-SDI)	(n_{struct})
2/2	−1.937	(16)	−1.951	(22)
4/4	−1.943	(54)	−1.958	(66)
6/6	−1.960	(116)	−2.001	(134)
8/8	−1.994	(202)	−2.020	(226)
10/10	−2.004	(312)	−2.033	(342)
12/12	−2.098	(446)	−2.164	(482)
14/14	−2.206	(604)	−2.302	(646)
16/16	−2.259	(786)	−2.372	(834)
18/18	−2.306	(992)	−2.423	(1046)
20/18	−2.314	(1074)	−2.432	(1130)
22/18	−2.323	(1164)	−2.443	(1222)
24/18	−2.334	(1262)	−2.458	(1322)

the accuracy of SCVB*-4. These 18 virtuals constitute a significant proportion of the virtual orbitals available, demonstrating that the SCVB*-4 optimized virtuals span a large proportion of the energetically useful available space. When 24 σ and 18 π virtuals are included in the wave function, generating 1322 structures (which is 165 times more than SCVB*-4), we obtain a value of 2.46 eV for D_e, marginally smaller than the values for the larger MCCI-2 and MCCI-4 wave functions.

The conventional SCVB calculations of Cooper et al. [32] show the dramatic improvement in convergence that is achieved when orbitals from *each* of the stacks of virtuals are included in the SCVB expansion. Using a universal even-tempered STO basis, a range of SCVB wave functions consisting of 78, 127, and 188 spatial configurations were investigated. These yielded D_e values of 2.35, 2.41, and 2.44 eV, respectively, clearly superior to the "single stack" SCVB results reported above. Nevertheless, the SCVB*-4 result still compares extremely favourably to these results.

4.2 Li$_2$

For Li$_2$ a basis set of (13*s*8*p*5*d*) Cartesian GTOs contracted to [8*s*5*p*2*d*] was used (see Table 1). The calculations were performed in a fashion entirely analogous to that described for LiH. Because $f_0^6 = 5$, the SCVB*-4 wave function now contains 20 VB structures. The Li$_2$($X^1\Sigma_g^+$) dissociation energies for the SC, SCVB*-2 (perturbation energy), SCVB*-4 and FVCAS wave functions are presented in Fig. 3. For Li$_2$, the 10-CSF FVCAS expansion distributes the two valence electrons amongst eight valence orbitals. It is immediately obvious when comparing Figs. 1 and 3 that the effect of introducing the extra configurations to the SC wave function has a markedly greater effect for Li$_2$ than for LiH. This reflects the fact that the single-configuration SC wave function provides a much poorer reference for Li$_2$. The SCVB*-4 and FVCAS curves are again very similar, although there is a marginally greater difference than for LiH, because the fully flexible CASSCF wave function is not hampered by a poor reference function. Table 4 puts all of this on a quantitative footing by comparing molecular properties calculated using the SC, PG, SCVB*-4, FVCAS, FCI, MCSCF-4, MCCI-2 and MCCI-4 [30] wave functions, and experimental values [27, 28].

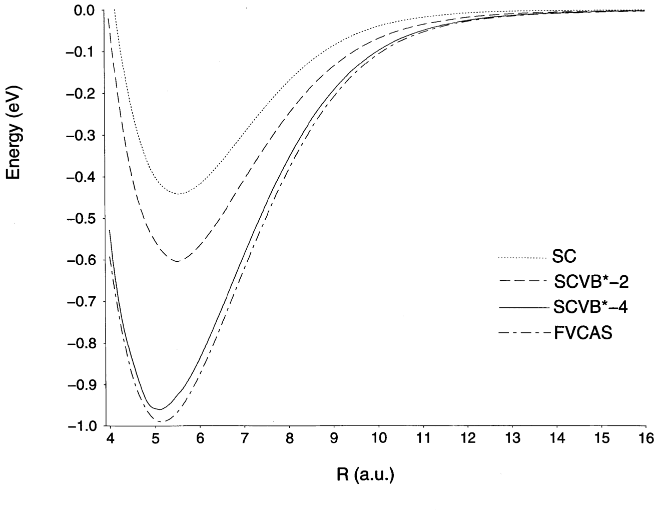

Fig. 3. Dissociation energy curves for the $X^1\Sigma_g^+$ state of Li$_2$ for the SC, SCVB*-2, SCVB*-4 and FVCAS wave functions

Table 4. Calculated and experimental molecular properties for the $X^1\Sigma_g^+$ state of Li$_2$

	R_e/Å	D_e/eV
SC	2.935	0.44
PG	2.728	0.83
SCVB*-4	2.693	0.96
FVCAS	2.714	0.99
FCI	2.714	0.99
MCSCF-4	2.695	0.88
MCCI-2	2.707	0.92
MCCI-4	2.676	1.00
Experiment	2.673[a]	1.05[b]

[a] Ref. [27]
[b] Ref. [28]

The SC wave function overestimates the value of R_e by 9.8% and it only recovers 42% of the experimental value of D_e. The PG wave function (a SCVB*-3 type function as for LiH) represents a considerable improvement on this, overestimating R_e by only 2% and recovering a highly creditable 79% of D_e, once again demonstrating the importance of including angular correlation. The SCVB*-4 wave function, however, represents a significant further leap in accuracy, overestimating R_e by only 0.7% and recovering 91.5% of D_e. When we take into consideration that the SC wave function is not an especially good zeroth-order wave function and that our method has no way of reoptimizing the SC orbitals, this is an excellent result. The FVCAS again marginally improves on SCVB*-4, whilst the two-electron FCI calculations produce a further energy lowering of less than 0.004 eV. The SCVB*-4 result is therefore an impressive 97% of the FCI value. MCSCF-4 recovers a relatively meagre 84% of D_e, 7.5% less than SCVB*-4. The 5480-CSF MCCI-2 recovers only 87.5% of D_e, whilst the 9640-CSF MCCI-4 is a considerable improvement, recovering 95% . However, this is still only a 0.04 eV improvement on SCVB*-4, despite the enormous differences in the size of these various calculations. Based on these benchmarks, the quality of the SCVB* wave functions, relative to FVCAS and FCI, is both extremely high and, just as importantly, extremely consistent. It seems that the performance of the final SCVB*-4 wave function is essentially unaffected by whether or not the SC wave function constitutes a good reference function.

The results of "single stack" SCVB calculations performed in exactly the same fashion as for LiH are presented in Table 5. This SCVB expansion is more rapidly convergent, compared to SCVB*-4, than was the case for LiH. A total of 8 σ and π virtuals, giving 553 VB structures (again included an additional class of ionic structures), were required to match the accuracy of SCVB*-4. By the time that 12 σ and π virtuals are included, the 1187-structure wave function has a value of 0.98 eV for D_e which, in spite of now being based on 60

Table 5. Calculated $Li_2(X^1\Sigma^+_g)$ dissociation energies (a.u.) for SCVB wave functions using different numbers of σ and π symmetry virtual orbitals

n_σ/n_π	D_e(SCVB-SD)	(n_{struct})	D_e(SCVB-SDI)	(n_{struct})
2/2	−0.519	(40)	−0.824	(52)
3/3	−0.560	(80)	−0.846	(98)
4/4	−0.601	(135)	−0.896	(159)
5/5	−0.604	(205)	−0.908	(235)
6/6	−0.644	(290)	−0.928	(326)
7/7	−0.668	(390)	−0.946	(432)
8/8	−0.676	(505)	−0.960	(553)
9/9	−0.680	(635)	−0.968	(689)
10/10	−0.694	(780)	−0.970	(840)
11/11	−0.699	(940)	−0.975	(1006)
12/12	−0.707	(1115)	−0.981	(1187)

times more structures than SCVB*-4, represents an improvement of only 0.02 eV. As was also seen for LiH, the SCVB*-4 optimized virtuals again span a significant proportion of the energetically useful virtual space.

5 Conclusions

We have introduced a new method for optimizing virtual orbitals for use in highly compact MCSC wave functions. Some approximations have been utilized in order to simplify the optimization process, which uses the stabilized Newton-Raphson procedure. This has resulted in a very cost-effective procedure which is capable of calculating rapidly a dense grid of points over a full potential surface.

Benchmark calculations for LiH and Li_2 show that a four-configuration SC wave function is a significant improvement over the standard single-configuration SC wave function. The difference is particularly dramatic for Li_2, where the quality of the final SCVB* wave function is not restricted by the relatively poor SC reference function. The accuracy has been shown to be comparable to that from standard SCVB procedures based on much greater numbers of structures. For both systems, the new method proved to be superior to the MCSC method of Pyper and Gerratt, in which all orbitals were fully optimized without approximation but with one less configuration, and to be comparable to a full valence CASSCF (an orthogonal orbital equivalent) using an identical basis. MCSCF calculations using the same number of configurations as the SCVB* method were, as expected, noticeably less successful. Large-scale CI expansions, using these MCSCF configurations as reference, lead to only very modest improvements to the results obtained by the four-configuration SCVB* wave function.

The various approximations implicit in our approach make the scaling of effort with numbers of electrons and of basis functions somewhat less severe than is the case for other MCSC methods, such as CASVB and that of Penotti, making possible calculations on larger systems. This scaling is noticeably better than that experienced with standard CASSCF methods. The results presented in this article demonstrate clearly that the various approximations made to improve computational efficiency do not prevent the method from obtaining highly accurate results. Indeed, the benchmarks show that the SCVB* method is capable of producing results of at least comparable accuracy to more traditional approaches. Calculations on Li_2 as a six-electron system, along with other larger test calculations, have confirmed that the method can treat such systems equally well as the smaller ones considered here. Developments in the technology used to determine the SC wave function will clearly increase further the potential of the SCVB* method. The calculation of the full reactive potential surface for H…Li…H has been recently completed and work on considerably larger systems is now in progress.

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