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Expansion of the spin-coupled wavefunction in Slater determinants

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Summary. The expansion of the spin-coupled wavefunction in Slater determinants constructed from nonorthogonal spin-orbitals is discussed. It proves possible to generate from cofactors of the appropriate overlap matrix all the density matrices, up to fourth order, required for the variational optimization of the wavefunction. The computational effort inherent in this 'super-cofactor' strategy scales in a very acceptable manner with the number of electrons.

Key words: Spin-coupled wavefunction – Slater determinants – Nonorthogonal spin-orbitals

1 Introduction

Recent years have seen a considerable revival of interest in proper modern generalizations of the ideas of Heitler and London [1], and of Coulson and Fischer [2] to many-electron molecular systems, without the imposition of orthogonality constraints or restrictions on the pairing of the electron spins. It is not appropriate here to review all of this work: representative recent accounts of efficient algorithms include Refs. [3–8]. A significant role in the resurgence of interest in modern valence bond descriptions of electronic structure has been played by spin-coupled valence bond or SCVB theory. The SCVB approach has now been applied successfully to a very wide range of chemical problems, and numerous recent reviews are available [4, 9, 10]. The purpose of this paper is to describe the expansion of the spin-coupled wavefunction in Slater determinants constructed from nonorthogonal spin-orbitals and to present a new strategy for obtaining the required density matrices using the Löwdin formula [11]. The algorithm described here evolved from an earlier scheme developed by Sironi [16].

The spin-coupled wavefunction, which is based on the antisymmetrized product of a single spatial configuration and the full spin space, provides a clear-cut chemically appealing picture of correlated electronic structure. This wavefunction constitutes an excellent starting point for more sophisticated multiconfiguration SCVB calculations. In general, the spin-coupled configuration dominates the final SCVB wavefunction and so it is possible to claim that this further quantitative refinement does not significantly modify the essential physical picture.

The single-configuration spin-coupled wavefunction for an N-electron system with total spin S (and projection M) takes the form:

$$\Psi_{SM} = (N!)^{1/2} \sum_{k}^{f_S^N} c_{Sk} \mathscr{A}[\phi_1 \phi_2 \cdots \phi_N \Theta_{SM;k}^N] \tag{1.1}$$

in which the singly-occupied orbitals $\phi_1 - \phi_N$ are nonorthogonal. The $\Theta_{SM;k}^N$ form a complete set of N-electron spin eigenfunctions of $\hat{S}^2$ and of $\hat{S}_z$. The c_{Sk}, which are termed spin-coupling coefficients, indicate the relative importance of the different modes of spin coupling, denoted by the index k. The dimension of the spin space is given by:

$$f_S^N = \frac{(2S+1)N!}{(\frac{1}{2}N+S+1)!(\frac{1}{2}N-S)!} \tag{1.2}$$

There are, of course, many different ways of constructing the $\Theta_{SM;k}^N$, with the most appropriate choice being dictated to a large extent by computational convenience as well as by the nature of the problem being studied. A useful account of different spin bases and of the relationships between them has been presented by Pauncz [12]. It is often instructive to transform the converged spin-coupling coefficients between the Kotani, Serber and Rumer bases [13].

In the case of the Kotani ('branching diagram') basis, the $\Theta_{SM;k}^N$ form a basis for orthogonal irreducible representations of $\mathscr{S}_N$, the symmetric group of degree N. In one strategy for calculating spin-coupled wavefunctions, all of the various orders of density matrix required for optimizing the spin-coupled orbitals $(\phi_1 - \phi_N)$ and the spin-coupling coefficients (c_{Sk}) are constructed from the corresponding representation matrices of the symmetric group. This algorithm, which may be termed 'the symmetric group approach', has been reviewed many times [4, 14, 15] and so it will not be described again here. However, it is important to notice that the current implementation of this approach utilizes all $N!$ representation matrices, each of which is of dimension f_S^N. The total number of matrix elements which must be processed increases very rapidly with increasing N, as indicated in Table 1, and so it seems very worthwhile to develop alternative schemes.

The structure of the paper is as follows. We identify in Sect. 2 the various orders of density matrices required for optimizing the spin-coupled wavefunction. The computation of density matrices from cofactors is discussed in Sect. 3

Table 1. Number of elements ($\tilde{N}$) of representation matrices processed in the 'symmetric group approach'

N	S	f_S^N	$\tilde{N}$
6	0	5	1.1×10^4
7	$\frac{1}{2}$	14	5.0×10^5
8	0	14	4.2×10^6
9	$\frac{1}{2}$	42	3.3×10^8
10	0	42	3.3×10^9
11	$\frac{1}{2}$	132	3.5×10^{11}
12	0	132	4.2×10^{12}

and our new strategy, which we term the 'super-cofactor approach', is described in Sect. 4. Some observations and final comments are presented in Sect. 5.

2 Density matrices required in spin-coupled theory

The spin-coupled wavefunction described in the previous Section can be recast in the form:

$$\Psi_{SM} = \sum_{k}^{f_S^N} c_{Sk} \Psi_k \tag{2.1}$$

in which each of the 'structures':

$$\Psi_k = (N!)^{1/2} \mathscr{A}[\phi_1(r_1)\phi_2(r_2) \cdots \phi_N(r_N)\Theta_{SM;k}^N] \tag{2.2}$$

is constructed from the same orbital product. The expectation value of the energy of the spin-coupled wavefunction is given by:

$$E = \frac{1}{\Delta} \sum_k \sum_l c_{Sk} c_{Sl} H_{kl} \tag{2.3}$$

in which H_{kl} is a matrix element of the usual spin-independent clamped nucleus hamiltonian between structures Ψ_k and Ψ_l, and Δ is the normalization integral. These hamiltonian matrix elements can be written:

$$H_{kl} = \sum_{\mu,\nu} D_{kl}(\mu \mid \nu) \langle \phi_\mu | \hat{H}_1 | \phi_\nu \rangle + \tfrac{1}{2} \sum_{\mu,\nu,\sigma,\tau} D_{kl}(\mu\nu \mid \sigma\tau) \langle \phi_\mu \phi_\nu | \hat{H}_2 | \phi_\sigma \phi_\tau \rangle \tag{2.4}$$

where $\langle \phi_\mu | \hat{H}_1 | \phi_\nu \rangle$ and $\langle \phi_\mu \phi_\nu | \hat{H}_2 | \phi_\sigma \phi_\tau \rangle$ are the usual one- and two-electron integrals in the orbital basis. The $D_{kl}(\mu \mid \nu)$ and the $D_{kl}(\mu\nu \mid \sigma\tau)$ are, respectively, elements of the one-electron and two-electron density matrices, and contain all of the effects of the nonorthogonality of the orbitals.

The different orders of density matrices are related to one another by a hierarchy of equations reminiscent of the Laplace expansion of a determinant:

$$D_{kl}(\mu_1 \cdots \mu_{n-1} \mid \nu_1 \cdots \nu_{n-1}) = \sum_{\nu_n} D_{kl}(\mu_1 \cdots \mu_{n-1}\mu_n \mid \nu_1 \cdots \nu_{n-1}\nu_n) \langle \phi_{\mu_n} | \phi_{\nu_n} \rangle \tag{2.5}$$

for any μ_n different from $\mu_1, \ldots, \mu_{n-1}$. Each of the density matrices is invariant to any simultaneous permutation of the μ_i and of the ν_j, and obeys the further symmetry property:

$$D_{kl}(\mu_1 \cdots \mu_n \mid \nu_1 \cdots \nu_n) = D_{lk}(\nu_1 \cdots \nu_n \mid \mu_1 \cdots \mu_n) \tag{2.6}$$

As a consequence, it is possible to generate all of the $D_{kl}(\mu_1 \cdots \mu_{n-1} \mid \nu_1 \cdots \nu_{n-1})$ from a subset of the $D_{kl}(\mu_1 \cdots \mu_{n-1}\mu_n \mid \nu_1 \cdots \nu_{n-1}\nu_n)$ with $\mu_n = N$.

The normalization integral, Δ, can be written:

$$\Delta = \sum_k \sum_l c_{Sk} c_{Sl} \Delta_{kl} \tag{2.7}$$

where Δ_{kl}, the overlap between structures Ψ_k and Ψ_l, is related to the one-electron density matrix according to:

$$\Delta_{kl} = \sum_{\nu} D_{kl}(\mu \mid \nu) \langle \phi_\mu | \phi_\nu \rangle \tag{2.8}$$

The orbitals, $\phi_1 - \phi_N$, which are common to all of the spin-coupled structures in Eq. (2.2), are expressed as linear combinations of a set of m atomic basis functions, χ_p:

$$\phi_\mu = \sum_p^m c_{\mu p} \chi_p \tag{2.9}$$

All of the $c_{\mu p}$ are variationally optimized simultaneously with the spin-coupling coefficients (c_{Sk}) appearing in Eq. (2.1). In common with other electronic structure approaches, the strategy adopted is based on the Newton–Raphson scheme. This requires first and second derivatives of the total spin-coupled energy with respect to all the variational parameters ($c_{\mu p}$ and c_{Sk}).

For our present purposes, it is sufficient to examine which density matrices appear in the expressions for the first derivatives. It should be clear from the form of Eqs. (2.3) and (2.7) that the computation of $\partial E / \partial c_{Sk}$ does not require density matrices higher than $D_{kl}(\mu\nu \mid \sigma\tau)$, which is already used in the computation of the energy. In the case of $\partial E / \partial c_{\mu p}$, we require:

$$\begin{aligned}\frac{\partial}{\partial c_{\mu p}} D_{kl}(\mu_1 \mu_2 \mid \nu_1 \nu_2) &= \frac{\partial}{\partial c_{\mu p}} \left[\sum_\nu^N D_{kl}(\mu_1 \mu_2 \mu \mid \nu_1 \nu_2 \nu) \langle \phi_\mu | \phi_\nu \rangle \right] \\ &= \sum_\nu^N D_{kl}(\mu_1 \mu_2 \mu \mid \nu_1 \nu_2 \nu) \langle \chi_p | \phi_\nu \rangle \end{aligned} \tag{2.10}$$

where we have used the fact that the derivative of $D_{kl}(\mu_1 \cdots \mu_n \mid \nu_1 \cdots \nu_n)$ with respect to $c_{\mu p}$ must be zero if μ matches any of $\mu_1, \ldots, \mu_n$. Thus, in order to calculate $\partial E / \partial c_{\mu p}$ we require density matrices up to third order.

It is convenient to introduce simplified notation as follows:

$$\begin{aligned} &D^n_{kl} \quad \text{for } D_{kl}(\mu_1 \cdots \mu_n \mid \nu_1 \cdots \nu_n) && \text{(required up to } n = 2) \\ &D^n_k \quad \text{for} \sum_l c_{Sl}[D_{kl}(\mu_1 \cdots \mu_n \mid \nu_1 \cdots \nu_n) + D_{kl}(\nu_1 \cdots \nu_n \mid \mu_1 \cdots \mu_n)] \\ & && \text{(required up to } n = 3) \\ &D^n \quad \text{for} \sum_k \sum_l c_{Sk} c_{Sl} D_{kl}(\mu_1 \cdots \mu_n \mid \nu_1 \cdots \nu_n) && \text{(required up to } n = 4) \end{aligned} \tag{2.11}$$

The *highest-order* density matrices of each of these three types are used as follows: D^4 to compute $\partial^2 E / \partial c_{\mu p} \, \partial c_{\nu q}$, D^3_k to compute $\partial^2 E / \partial c_{\mu p} \, \partial c_{Sk}$, and D^2_{kl} to compute $\partial^2 E / \partial c_{Sk} \, \partial c_{Sl}$. However, in the case of the spin/spin block of the second-derivative matrix (or Hessian), it turns out that it is more efficient to use directly Eqs. (2.3) and (2.7) to derive:

$$\begin{aligned} \tfrac{1}{2} \Delta \frac{\partial^2 E}{\partial c_{Sk} \, \partial c_{Sl}} = H_{kl} - E\Delta_{kl} &- \left[\sum_k c_{Sk} \; \Delta_{kl} \right] \frac{\partial E}{\partial c_{Sk}} \\ &- \left[\sum_l c_{Sl} \; \Delta_{kl} \right] \frac{\partial E}{\partial c_{Sl}} \end{aligned} \tag{2.12}$$

Explicit formulae for the first and second derivatives of the spin-coupled energy with respect to the variational parameters ($c_{\mu p}$ and c_{Sk}) have been given by Pyper and Gerratt [15].

From the definitions of the density matrices, and the various symmetry properties, it follows that the numbers of unique elements are as follows:

$$\begin{aligned}\tilde{N}(D^n) &= \tfrac{1}{2}\mathscr{C}(\mathscr{C}+1)n! \\ \tilde{N}(D^n_k) &= \tilde{N}(D^n)f^N_S \\ \tilde{N}(D^n_{kl}) &= \tilde{N}(D^n)\tfrac{1}{2}f^N_S(f^N_S+1)\end{aligned} \tag{2.13}$$

in which

$$\mathscr{C} = \begin{bmatrix} N \\ n \end{bmatrix} \tag{2.14}$$

The numbers of unique elements are listed in Table 2 for a few representative values of N (for the case with lowest spin). For these examples, the largest value of $\tilde{N}$ for a density matrix essential for the calculations is $\tilde{N}(D^3_k) = 1.9 \times 10^7$ for $N = 12$, $S = 0$, $f^N_S = 132$. These D^3_k quantities are used to construct the mixed orbital/spin-coupling block of the Hessian. For this system, we also require $\approx 1.0 \times 10^7$ elements of D^4 to build the orbital/orbital block of the Hessian. The value of $\tilde{N}(D^4_{kl})$ rapidly becomes particularly large and so it is very fortunate that these quantities are not required.

Table 2. The numbers of unique density matrix elements for a few representative values of N (for the case with lowest spin)

N	S	f^N_S	n	D^n	D^n_k	D^n_{kl}
6	0	5	1	21	105	315
			2	240	1200	3600
			3	1260	6300	18900
			4	2880	14400	43200
7	$\frac{1}{2}$	14	1	28	392	2940
			2	462	6468	48510
			3	3780	52920	396900
			4	15120	211680	1587600
8	0	14	1	36	504	3780
			2	812	11368	85260
			3	9576	134064	1005480
			4	59640	834960	6262200
9	$\frac{1}{2}$	42	1	45	1890	40635
			2	1332	55944	1202796
			3	21420	899640	19342260
			4	192024	8065008	173397672
10	0	42	1	55	2310	49665
			2	2070	86940	1869210
			3	43560	1829520	39334680
			4	531720	22332240	480143160
11	$\frac{1}{2}$	132	1	66	8712	579348
			2	3080	406560	27036240
			3	82170	10846440	721288260
			4	1310760	173020320	$\approx 1.15 \times 10^{10}$
12	0	132	1	78	10296	684684
			2	4422	583704	38816316
			3	145860	19253520	$\approx 1.28 \times 10^{9}$
			4	10256400	$\approx 1.35 \times 10^{10}$	$\approx 9.00 \times 10^{10}$

3 Evaluation of density matrices from cofactors

Each of the spin functions $\Theta^N_{SM;k}$ in Eq. (2.2) can be expanded in the following fashion:

$$\Theta^N_{SM;k} = \sum_I^{N_d} b_{Ik} \Omega_I \tag{3.1}$$

in which the symbol Ω_I denotes a string of N_α α's and N_β β's ($N = N_\alpha + N_\beta$), and the limit of the summation is given by:

$$N_d = \begin{bmatrix} N \\ N_\alpha \end{bmatrix} \tag{3.2}$$

In this way, each spin-coupled structure can be rewritten as a linear combinations of Slater determinants, U_I, constructed from N nonorthogonal spin-orbitals:

$$\Psi_k = \sum_I^{N_d} b_{Ik} U_I \tag{3.3}$$

where the index I corresponds to that used in Ω_I. In the particular case of the Rumer basis, all of the b_{Ik} are zero or ± 1. It is also straightforward to generate the values of b_{Ik} appropriate to the Kotani basis.

For each pair of Slater determinants, U_I and U_J, we can define S_{IJ}, the matrix of overlap integrals between the *spin-orbitals* appearing in the two determinants. Cofactors of various order, such as $S_{IJ}(\mu_1\mu_2 \mid \nu_1\nu_2)$, can then be generated by striking out appropriate rows and columns. It is useful to define the symbol $\delta_{IJ}(\mu\nu)$ to be unity if the spin of the μth spin-orbital in U_I matches the spin of the νth spin-orbital in U_J, but to be zero otherwise. With these definitions, the Löwdin expression [11] for the matrix elements of the hamiltonian between Slater determinants constructed from nonorthogonal spin-orbitals can be written:

$$\begin{aligned}\langle U_I|\hat{H}|U_J\rangle &= \sum_{\mu,\nu} S_{IJ}(\mu \mid \nu)\langle\phi_\mu|\hat{H}_1|\phi_\nu\rangle\delta_{IJ}(\mu\nu) \\ &\quad + \tfrac{1}{2} \sum_{\mu,\nu,\sigma,\tau} S_{IJ}(\mu\nu \mid \sigma\tau)\langle\phi_\mu\phi_\nu|\hat{H}_2|\phi_\sigma\phi_\tau\rangle\delta_{IJ}(\mu\sigma)\delta_{IJ}(\nu\tau)\end{aligned} \tag{3.4}$$

Comparing Eqs. (2.4), (3.3) and (3.4), we can identify:

$$\begin{aligned} D_{kl}(\mu \mid \nu) &= \sum_I^{N_d} \sum_J^{N_d} b_{Ik} b_{Jl}\, \delta_{IJ}(\mu\nu) S_{IJ}(\mu \mid \nu) \\ D_{kl}(\mu\nu \mid \sigma\tau) &= \sum_I^{N_d} \sum_J^{N_d} b_{Ik} b_{Jl}\, \delta_{IJ}(\mu\sigma)\delta_{IJ}(\nu\tau) S_{IJ}(\mu\nu \mid \sigma\tau) \end{aligned} \tag{3.5}$$

and in the general case [16]:

$$D_{kl}(\mu_1 \cdots \mu_n \mid \nu_1 \cdots \nu_n) = \sum_I^{N_d} \sum_J^{N_d} b_{Ik} b_{Jl} \delta_{IJ}(\mu_1\nu_1) \cdots \delta_{IJ}(\mu_n\nu_n) S_{IJ}(\mu_1 \cdots \mu_n \mid \nu_1 \cdots \nu_n) \tag{3.6}$$

Because of the orthogonality of the α and β spin functions, the $S_{IJ}(\mu_1 \cdots \mu_n \mid \nu_1 \cdots \nu_n)$, which are cofactors of the overlap matrix between spin-orbitals, assume block diagonal form. This reduces to $N_\alpha - n_\alpha$ and $N_\beta - n_\beta$ ($n = n_\alpha + n_\beta$) the dimensions of the minors which must be evaluated in order to

Table 3. Total numbers of sub-determinants of dimension n required for the computation of all the density matrices for the cases considered in Table 2

N	S	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$
6	0	21	120	–	–	–	–
7	$\frac{1}{2}$	28	231	630	–	–	–
8	0	36	406	1596	2485	–	–
9	$\frac{1}{2}$	45	666	3570	8001	8001	–
10	0	55	1035	7260	22155	31878	–
11	$\frac{1}{2}$	66	1540	13695	54615	106953	106953
12	0	–	2211	24310	122760	314028	427350

construct the density matrices. In Table 3, we list the total numbers of minors of each dimension required for the computation of all the density matrices (for the cases considered in Table 2). The computation of all the required minors is very fast but, in any case, all of them are already available in our program from the most recent energy evaluation.

4 The super-cofactor strategy

A suitable precursor for both D^4 and D^3_k is D^4_k but, as indicated in Sect. 2, only the subset of the D^4_k with $\mu_4 = N$ is actually required for the step $D^4_k \rightarrow D^3_k$. It is convenient to refer to sets of 'unique' indices $\mu_1 < \mu_2 < \mu_3 < \mu_4$ as ibra and $\nu_1 < \nu_2 < \nu_3 < \nu_4$ as jket, with ibra $\geqslant$ jket. It is necessary to generate the $4! = 24$ elements of D^4 or D^4_k which correspond to the different permutations of the ν's for a given set of μ's. However, it is not necessary to permute also the μ's, because of the symmetry property embodied in Eq. (2.6) – analogous considerations apply to the other quantities listed in Eq. (2.11). Because of the manner in which the elements of D^4 and D^4_k are utilized, it is appropriate to loop over ibra, generating in each pass only those portions of these density matrices which correspond to a given set of μ's. The relevant elements can be discarded once they have been used. In the description which follows, we refer to the corresponding arrays for a single value of ibra as D4 and D4k.

The form of Eq. (3.6) suggests that the construction of each unique density matrix element from cofactors of the overlap matrix between spin-orbitals (S_{IJ}) involves N_d^2 terms. However, the occurrence in this equation of the spin integration factors, $\delta_{IJ}(\mu_1\nu_1) \cdots \delta_{IJ}(\mu_n\nu_n)$, reduces significantly the computational effort. Although it is necessary to consider different arrangements of the α's and β's, in order to permute the ν's for a given set of μ's, non-zero contributions can only arise when n_α and n_β, the number of α's and β's, is the same for ibra and jket.

It is useful to classify the N_d terms in each summation for an element of D4 or D4k according to n_β, the number of β's, and to recognize:

$$N_d = \sum_{n_\beta} \begin{bmatrix} N-4 \\ N_\beta - n_\beta \end{bmatrix} \begin{bmatrix} 4 \\ n_\beta \end{bmatrix} \tag{4.1}$$

For a given value of n_β, the number of different arrangements of the α's and β's (or 'types') is given by:

$$\text{ntype}(n_\beta) = \begin{bmatrix} 4 \\ n_\beta \end{bmatrix} \tag{4.2}$$

and the number of determinants of order $N-4$ and of each type is:

$$\text{ndet}(n_\beta) = \begin{bmatrix} N-4 \\ N_\beta - n_\beta \end{bmatrix} \tag{4.3}$$

Processing the terms in Eq. (3.6) in order of increasing n_β, and according to 'types', reduces the number of contributions from N_d^2 to:

$$N_t = \sum_{n_\beta} \begin{bmatrix} N-4 \\ N_\beta - n_\beta \end{bmatrix}^2 \begin{bmatrix} 4 \\ n_\beta \end{bmatrix}^2 \tag{4.4}$$

Values of N_d and N_t are listed in Table 4 for the cases considered in Table 2. A further advantage of processing the terms in this way is that the list of 'allowed' permutations (i.e. α with α, β with β) depends only on n_β and on the types (itype and jtype) of the determinants (idet and jdet).

In that each cofactor $S_{IJ}(\mu_1 \cdots \mu_4 \mid \nu_1 \cdots \nu_4)$ is used only once, it is most practical to assemble them *in situ* as products of the precomputed minors. We denote the relevant product of (unsigned) minors as s(jket, ibra, jdet, idet) and the corresponding phase factor is P(ibra, idet) × P(jket, jdet). The array C contains the spin-coupling coefficients in the determinantal basis and the array b contains the values of b_{Ik} (Eq. (3.1)).

The strategy currently employed for the computation of the required density matrices is outlined in Scheme I: we have adopted the convention that when variables appear in parentheses to the *left* of an equality, then the notation signifies that all allowed values are processed together in a fully-vectorized DO loop nest. Thus for, example, the phrase 'Construct AIJ(jket, jdet, idet)' (if $\mu_4 \neq N$) means that jket runs from 1 to ibra, and that jdet and idet each take ndet(n_β) values, with the loops processed in the usual 'column major' or 'subscript progression' order.

In actual practice, greater efficiency has been achieved, for example, by combining jket and jdet, whenever they occur, into a single index and, of course, by accumulating various intermediate quantities. A further saving arises if $N_\alpha = N_\beta$: the upper limit on the loop over n_β is reset to $\min(2, N_\beta)$, and contributions from terms with $n_\beta < 2$ are included twice. A further, more modest

Table 4. Number of distinct cases which survive the spin integration factors in the construction of D^4 and D_k^4 from cofactors

N	S	N_d	N_d^2	N_t
6	0	20	400	160
7	$\frac{1}{2}$	35	1225	485
8	0	70	4900	1553
9	$\frac{1}{2}$	126	15876	5626
10	0	252	63504	18036
11	$\frac{1}{2}$	462	213444	71246
12	0	924	853776	227360

improvement might be achieved by exploiting the fact that different cofactors, $S_{IJ}(\mu_1 \cdots \mu_4 \mid \nu_1 \cdots \nu_4)$, can take the same value, mostly because of the symmetry of the spin integration factors. This feature has not yet been exploited in our codes.

The relative costs of the different parts of the scheme vary somewhat with the number of electrons and with the dimension of the spin space, so that it is difficult to present meaningful operation counts. However, the construction of AIJ (if $\mu_4 \neq N$) or of BIJ (if $\mu_4 = N$) always remains a key step. For given values of ibra and jket, the number of products of minors processed is N_t (Eq. (4.4)). The assembly from precomputed minors of a given s(jket, ibra, jdet, idet) requires one multiply.

In addition to (part of) the orbital/orbital block of the Hessian, the scheme generates both D^3 and D^3_k: it is straightforward to generate from these all of the other density matrices required. The largest memory requirement of the current implementation of the super-cofactor approach arises from D^3_k: it should prove

SCHEME I The basic strategy used in the super-cofactor approach

```
Do ibra = 1, nbra
  Do $n_\beta = \max(0,4-N_\alpha), \min(4,N_\beta)$
    Do itype = 1, ntype($n_\beta$)
      Do jtype = 1, ntype($n_\beta$)
        If ($\mu_4 \neq$ N) then
            Construct  AIJ(jket,jdet,idet) = s(jket,ibra,jdet,idet) × P(jket,jdet) × C(jdet)
            Construct  AI(jket,idet) = $\sum_{\mathrm{jdet}}$ AIJ(jket,jdet,idet)
            Construct  A(jket) = $\sum_{\mathrm{idet}}$ AI(jket,idet) × P(ibra,idet) × C(idet)
            Perform 'allowed' permutations of the $\nu$'s, i.e. use A(jket) to update D4(jket,1:4!)
        Else If ($\mu_4$ = N) then
            Construct  BIJ(jket,jdet,idet) = s(jket,ibra,jdet,idet) × P(jket,jdet) × P(ibra,idet)
            Construct  BI(jket,idet) = $\sum_{\mathrm{jdet}}$ BIJ(jket,jdet,idet) × C(jdet)
              and      BJ(jket, jdet) = $\sum_{\mathrm{idet}}$ BIJ(jket,jdet,idet) × C(idet)
            Construct  Bk(k,jket) = $\sum_{\mathrm{idet}}$ BI(jket,idet) × b(k,idet)
                                  + $\sum_{\mathrm{jdet}}$ BJ(jket,jdet) × b(k,jdet)
            Perform 'allowed' permutations of the $\nu$'s, i.e. use Bk(k,jket) to update
            D4k(k,jket, 1:4!)
        End if
      End Do (jtype)
    End Do (itype)
  End Do ($n_\beta$)
  If ($\mu_4$ = N) Contract D4k to D4, D4k to $D^3_k$, and D4 to $D^3$
  Use D4 to update the orbital/orbital block of the Hessian
  Discard D4, D4k, AIJ, AI, A, BIJ, BI, BJ and Bk
End DO (ibra)
```

possible to generate efficiently (and to process efficiently) this density matrix in sections, in much the same way as D^4 and D^4_k. When required, the matrix elements of the hamiltonian, H_{kl}, and the overlap integrals between spin-coupled structures, Δ_{kl}, are computed directly from minors, obviating the need to store any D^n_{kl} density matrices. The spin/spin block of the Hessian is assembled by means of Eq. (2.12), using matrix elements still available from the most recent energy evaluation.

5 Conclusions

The expansion of the spin-coupled wavefunction in Slater determinants constructed from nonorthogonal spin-orbitals makes it possible to calculate from cofactors of the appropriate overlap matrix all of the density matrices required for the simultaneous optimization of the orbitals and the spin-coupling coefficients. From a comparison of the entries in Tables 1, 3 and 4, it is clear that the computational effort associated with the new strategy, which we term the 'super-cofactor approach', scales in a much more acceptable way with increasing N than the earlier 'symmetric group approach'. This has been borne out by a number of applications to systems such as naphthalene [17], the reaction of singlet methylene with H_2 [18], the process of breaking the triple bond in HCN [19], clusters of lithium atoms [20], and the nature of the bonding in B_2H_6 [21], and by a number of studies in progress.

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