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Spin-coupled calculations based on projected spin eigenfunctions

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Abstract. It is outlined how the utilization of a basis of projected spin eigenfunctions can lead to increased computational efficiency in the evaluation of matrix elements and density matrices in spin-coupled valence bond calculations.

Key words: Spin-coupled – Projected spin eigenfunctions – Symmetric group

1 Introduction

Recently there has been a significant revival of interest in valence bond theory, with particular emphasis on approaches that involve full optimization of the orbitals. Modern valence bond theory in its spin-coupled form [1] has provided important insights into a wide range of chemical systems. The active electrons in spin-coupled calculations are described in terms of a product of N singly occupied nonorthogonal orbitals φ_μ, $\mu = 1, 2, \ldots, N$:

$$\Psi^N_{SM} = \sum_{k=1}^{f^N_S} C_{Sk}\hat{A}(\varphi_1\varphi_2\ldots\varphi_N\Theta^N_{SM;k}) \tag{1}$$

in which $\Theta^N_{SM;k}$ is an N-electron spin eigenfunction of $\hat{S}^2$ and $\hat{S}_z$, with eigenvalues $S(S+1)\hbar^2$ and $M\hbar$, respectively, and f^N_S is the dimension of the spin space:

$$f^N_S = \frac{(2S+1)N!}{(1/2N+S+1)!(1/2N-S)!} \quad . \tag{2}$$

$\hat{A}$ is the antisymmetrizer. The orbitals φ_μ are expanded in a basis set of atomic functions

$$\varphi_\mu = \sum_{p=1}^{m} c_{\mu p}x_p \quad , \tag{3}$$

and all the orbital expansion coefficients ($c_{\mu p}$) and the spin-coupling coefficients (C_{Sk}) are optimized simultaneously using a second-order procedure that involves the second derivatives of the energy with respect to the variational parameters (all of which are real).

There are, of course, many useful ways in which the spin eigenfunctions $\Theta^N_{SM;k}$ in Eq. (1) can be chosen [2], and a highly efficient code is available for transforming spin-coupling coefficients between different bases [3]. The present paper is concerned with the particular computational advantages associated with choosing a basis of projected spin eigenfunctions. The considerations discussed here apply equally well to a variety of valence bond approaches.

The structure of this paper is as follows. In Sect. 2 we introduce the projected spin eigenfunctions and express them in a form suited to implementation in the spin-coupled program "sk1" [4]. Utilizing some useful characteristics of the projected functions, a very compact form of the spin-coupled matrix elements is found in Sect. 3, and we outline the procedure used for evaluating the energy. We indicate in Sect. 4 how the use of projected spin eigenfunctions leads to significant computational improvements in the evaluation of the density matrices required for optimizing the energy. Finally, we present our conclusions in Sect. 5.

2 Projected spin eigenfunctions

For a system of N electrons with total spin quantum number S and its projection $M = S$, the first projected spin eigenfunction $\Theta^N_{SS;1}$ may be defined according to [2, 5, 6]:

$$\Theta^N_{SS;1} = K^N_S\hat{X}^{[\lambda]}_\sigma\theta_1 \tag{4}$$

in which θ_1 is the primitive spin string

$$\theta_1 = \alpha(1)\alpha(2)\ldots\alpha(n_\alpha)\beta(n_\alpha+1)\ldots\beta(n_\alpha+n_\beta) \tag{5}$$

and K^N_S is a normalization constant. $\hat{X}^{[\lambda]}_\sigma$ is the character projection operator for the irreducible representation $[\lambda] \equiv [n_\alpha, n_\beta] = [1/2N+S, 1/2N-S]$ of the symmetric group S_N:

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$$\hat{X}_\sigma^{[\lambda]} = \frac{f_S^N}{N!} \sum_{P \in S_N} X_\sigma^{[\lambda]}(P) \hat{P}^\sigma \ , \tag{6}$$

where the σ labels indicate that the various operators act only on spin variables. Kramer [7] has shown that $\hat{X}_\sigma^{[\lambda]}$ is equivalent to Löwdin's projection operator [8].

The complete linearly independent set of projected spin eigenfunctions is generated from the first function according to

$$\Theta_{SS;k}^N = \hat{P}_k^\sigma \ \Theta_{SS;1}^N, \qquad k = 1, 2, \ldots, f_S^N \ . \tag{7}$$

Assuming that the standard Young tableaux are ordered according to last letter sequence (see Ref. [9]), $\hat{P}_k$ is defined as the permutation which converts the first tableaux T_1 into the kth tableaux T_k

$$T_k = \hat{P}_k T_1 \ . \tag{8}$$

In the following, these permutations will be called standard Young tableaux permutations. The spin eigenfunctions $\Theta_{SS;k}^N$, which are nonorthogonal, are each normalized to unity provided

$$\left[K_S^N\right]^2 = \frac{1/2N + S + 1}{2S + 1} \ , \tag{9}$$

as was proved in Ref. [6].

The first projected spin eigenfunction may be rewritten in the form

$$\Theta_{SS;1}^N = \sum_{I=1}^{N_d} b_{I1} \theta_I \ , \tag{10}$$

in which there are $N_d = N!/(n_\alpha! n_\beta!)$ unique primitive spin functions θ_I with the given values of n_α and n_β. An explicit expression for the b_{I1} coefficients is given in Ref. [6]. However, the strategy used here for generating the character projected spin eigenfunctions relies on the observation that the first genealogical spin eigenfunction coincides with the first projected spin function [2], so that the values of b_{I1} in Eq. (10) are already known in the spin-coupled codes. The kth projected spin eigenfunction,

$$\Theta_{SS;k}^N = \sum_{I=1}^{N_d} b_{Ik} \theta_I \ , \tag{11}$$

is obtained by permuting the first spin eigenfunction according to Eq. (7):

$$\Theta_{SS;k}^N = \sum_{I=1}^{N_d} b_{I1} \ \hat{P}_k^\sigma \theta_I \ . \tag{12}$$

This means that all the character projected spin eigenfunctions for the given values N and S contain identical expansion coefficients, which are simply permuted according to the standard Young tableaux permutations.

3 Matrix elements

The expectation value of the energy for the spin-coupled wave function in Eq. (1) is independent of M and takes the form

$$E = \frac{\sum_{k,\ell}^{f_S^N} C_{Sk} C_{S\ell} H_{k\ell}}{\sum_{k,\ell}^{f_S^N} C_{Sk} C_{S\ell} \Delta_{k\ell}} \tag{13}$$

in which

$$H_{k\ell} = \langle \hat{A}(\varphi_1 \ldots \varphi_N \Theta_{SM;k}^N) | \hat{H} | \hat{A}(\varphi_1 \ldots \varphi_N \Theta_{SM;\ell}^N) \rangle \tag{14}$$

and

$$\Delta_{k\ell} = \langle \hat{A}(\varphi_1 \ldots \varphi_N \Theta_{SM;k}^N) | \hat{A}(\varphi_1 \ldots \varphi_N \Theta_{SM;\ell}^N) \rangle \ , \tag{15}$$

where $\hat{H}$ is the usual spin-independent clamped-nucleus Hamiltonian, with the inclusion of an effective core potential for any inactive electrons. Using Eq. (11), We may rewrite a spin-coupled wave function in the form

$$\Psi_{SS}^N = \sum_{k=1}^{f_S^N} \sum_{I=1}^{N_d} C_{Sk} b_{Ik} U_I \tag{16}$$

in which U_I denotes the Slater determinant

$$U_I = \hat{A}(\varphi_1 \varphi_2 \ldots \varphi_N \theta_I) \ , \tag{17}$$

so that, for example,

$$H_{k\ell} = \sum_{I,J}^{N_d} b_{Ik} b_{J\ell} \langle U_I | \hat{H} | U_J \rangle \ , \tag{18}$$

The particular advantage of choosing projected spin functions is that it becomes possible to reduce the number of summations over N_d terms. Note that the left-right symmetry in the $\langle U_1 | \hat{H} | U_J \rangle$ means that there are $1/2N_d \times (N_d + 1)$ unique elements in Eq. (18).

We write a matrix element of an arbitrary symmetric spin-independent operator $\hat{O}$ in the form

$$O_{k\ell} = \left[K_S^N\right]^2 \langle \hat{A}(\varphi_1 \ldots \varphi_N \hat{P}_k^\sigma \hat{X}_\sigma^{[\lambda]} \theta_1) | \hat{O} | \hat{A}(\varphi_1 \ldots \varphi_N \hat{P}_\ell \hat{X}_\sigma^{[\lambda]} \theta_1) \rangle \tag{19}$$

and recognize that since $\hat{X}_\sigma^{[\lambda]}$ belongs to the centrum of the group algebra of S_N [10] it must commute with any permutation of S_N and with $\hat{O}$. It follows that the character operator in the ket can be replaced by the Hermitian conjugate operator in the bra. The character operator is self conjugate and idempotent, so that we end up with an unchanged expression in the bra whereas in the ket we now have the Slater determinant corresponding to the ℓth standard Young tableau permutation:

$$O_{k\ell} = \left[K_S^N\right]^2 \langle \hat{A}(\varphi_1 \ldots \varphi_N \hat{P}_k^\sigma \hat{X}_\sigma^{[\lambda]} \theta_1) | \hat{O} | \hat{A}(\varphi_1 \ldots \varphi_N \hat{P}_\ell^\sigma \theta_1) \rangle \tag{20}$$

Denoting the determinant in the ket as U_ℓ, we have

$$O_{k\ell} = K_S^N \sum_I^{N_d} b_{Ik} \langle U_I | \hat{O} | U_\ell \rangle \, , \tag{21}$$

which now involves only one summation over N_d terms (compare Eq. 18). Here there is only left-right symmetry when U_I is a Slater determinant corresponding to a standard Young tableau permutation and so the number of unique matrix elements is $N_d \times f_S^N - 1/2 f_S^N (f_S^N - 1)$. This symmetry is not exploited in our code, which evaluates all $N_d \times f_S^N$ elements.

We may get a very crude estimate of the likely improvement in performance of a full calculation by assuming that the computer time depends only on the total numbers of matrix elements between determinants. Comparison of Eqs. (18) and (21) suggests a ratio of $1/2(N_d + 1)/f_S^N$. If, at the other extreme, the computer time depends on the number of summations over N_d terms, we might expect an improvement in performance as large as N_d. As indicated later, the actual speed-ups are closer to the lower prediction.

$$M^{I\ell,n_\alpha-1}(I_\mu|\ell_v) = (-1)^{\mu+v} \begin{vmatrix} \langle\varphi_{I_1}|\varphi_{\ell_1}\rangle & \cdots & \langle\varphi_{I_1}|\varphi_{\ell_{v-1}}\rangle & \langle\varphi_{I_1}|\varphi_{\ell_{v+1}}\rangle & \cdots & \langle\varphi_{I_1}|\varphi_{\ell_{n_\alpha}}\rangle \\ \vdots & & \vdots & \vdots & & \vdots \\ \langle\varphi_{I_{\mu-1}}|\varphi_{\ell_1}\rangle & \cdots & \langle\varphi_{I_{\mu-1}}|\varphi_{\ell_{v-1}}\rangle & \langle\varphi_{I_{\mu-1}}|\varphi_{\ell_{v+1}}\rangle & \cdots & \langle\varphi_{I_{\mu-1}}|\varphi_{\ell_{n_\alpha}}\rangle \\ \langle\varphi_{I_{\mu+1}}|\varphi_{\ell_1}\rangle & \cdots & \langle\varphi_{I_{\mu+1}}|\varphi_{\ell_{v-1}}\rangle & \langle\varphi_{I_{\mu+1}}|\varphi_{\ell_{v+1}}\rangle & \cdots & \langle\varphi_{I_{\mu+1}}|\varphi_{\ell_{n_\alpha}}\rangle \\ \vdots & & \vdots & \vdots & & \vdots \\ \langle\varphi_{I_{n_\alpha}}|\varphi_{\ell_1}\rangle & \cdots & \langle\varphi_{I_{n_\alpha}}|\varphi_{\ell_{v-1}}\rangle & \langle\varphi_{I_{n_\alpha}}|\varphi_{\ell_{v+1}}\rangle & \cdots & \langle\varphi_{I_{n_\alpha}}|\varphi_{\ell_{n_\alpha}}\rangle \end{vmatrix} . \tag{29}$$

In order to obtain explicit expressions for the usual overlap, one-electron and two-electron integrals it is more convenient to write the Slater determinant U_I in Eq. (17) in an alternative way. Firstly, we note that the spin product θ_I can be written as

$$\theta_I = \hat{R}_I^\sigma \theta_1 \tag{22}$$

where R_I is a permutation of S_N. Utilizing the operator identity (see for example Ref. [5])

$$\hat{A}\hat{R}_I^\sigma = \varepsilon_{R_I} \hat{A} \hat{R}_I^{-1,r} \tag{23}$$

where the label r indicates that the inverse acts on spatial variables, we rewrite U_I as

$$\begin{aligned} U_I &= \varepsilon_{R_I} \hat{A}(\hat{R}_I^{-1,r} \varphi_1 \varphi_2 \dots \varphi_N \theta_1) \\ &\equiv \varepsilon_{R_I} \hat{A}(\varphi_{I_1} \varphi_{I_2} \dots \varphi_{I_N} \theta_1) \ . \end{aligned} \tag{24}$$

An analogous expression can be found for the Slater determinant U_ℓ

$$\begin{aligned} U_\ell &= \varepsilon_{P_\ell} \hat{A}(\hat{P}_\ell^{-1,r} \varphi_1 \varphi_2 \dots \varphi_N \theta_1) \\ &\equiv \varepsilon_{P_\ell} \hat{A}(\varphi_{\ell_1} \varphi_{\ell_2} \dots \varphi_{\ell_N} \theta_1) \ . \end{aligned} \tag{25}$$

Integrating over spin variables, as in Ref. [5], we obtain for the overlap integral:

$$\langle U_I | U_\ell \rangle = \varepsilon_{R_I} \varepsilon_{P_\ell} M^{I\ell,n_\alpha} M^{I\ell,n_\beta} \tag{26}$$

where

$$M^{I\ell,n_\alpha} = \begin{vmatrix} \langle\varphi_{I_1}|\varphi_{\ell_1}\rangle & \langle\varphi_{I_1}|\varphi_{\ell_2}\rangle & \cdots & \langle\varphi_{I_1}|\varphi_{\ell_{n_\alpha}}\rangle \\ \langle\varphi_{I_2}|\varphi_{\ell_1}\rangle & \langle\varphi_{I_2}|\varphi_{\ell_2}\rangle & \cdots & \langle\varphi_{I_2}|\varphi_{\ell_{n_\alpha}}\rangle \\ \vdots & \vdots & & \vdots \\ \langle\varphi_{I_{n_\alpha}}|\varphi_{\ell_1}\rangle & \langle\varphi_{I_{n_\alpha}}|\varphi_{\ell_2}\rangle & \cdots & \langle\varphi_{I_{n_\alpha}}|\varphi_{\ell_{n_\alpha}}\rangle \end{vmatrix} \tag{27}$$

with an analogous definition for $M^{I\ell,n_\beta}$. Similarly, the one-electron matrix element becomes

$$\begin{aligned} \langle U_I|\hat{H}_1|U_\ell\rangle &= \varepsilon_{R_I}\varepsilon_{P_\ell} \\ &\times \Bigg\{ M^{I\ell,n_\beta} \sum_{\mu,v=1}^{n_\alpha} M^{I\ell,n_\alpha-1}(I_\mu|\ell_v)\langle\varphi_{I_\mu}|\hat{h}|\varphi_{\ell_v}\rangle \\ &+ M^{I\ell,n_\alpha} \sum_{\mu,v=n_\alpha^{+1}}^{N} M^{I\ell,n_\beta-1}(I_\mu|\ell_v)\langle\varphi_{I_\mu}|\hat{h}|\varphi_{\ell_v}\rangle \Bigg\} \end{aligned} \tag{28}$$

where

For the two-electron matrix element we find:

$$\begin{aligned} \langle U_I|\hat{H}_2|U_\ell\rangle &= \varepsilon_{R_I}\varepsilon_{P_\ell} \\ &\times \Bigg\{ M^{I\ell,n_\beta} \sum_{\mu<v}^{n_\alpha} \sum_{\sigma<\tau}^{n_\alpha} M^{I\ell,n_\alpha-2}(I_\mu I_v|\ell_\sigma\ell_\tau)(\langle\varphi_{I_\mu}\varphi_{I_v}|\hat{g}|\varphi_{\ell_\sigma}\varphi_{\ell_\tau}\rangle \\ &- \langle\varphi_{I_\mu}\varphi_{I_v}|\hat{g}|\varphi_{\ell_\tau}\varphi_{\ell_\sigma}\rangle) + M^{I\ell,n_\alpha} \sum_{n_\alpha<\mu<v}^{N} \sum_{n_\alpha<\sigma<\tau}^{N} M^{I\ell,n_\beta-2}(I_\mu I_v|\ell_\sigma\ell_\tau) \\ &\times (\langle\varphi_{I_\mu}\varphi_{I_v}|\hat{g}|\varphi_{\ell_\sigma}\varphi_{\ell_\tau}\rangle - \langle\varphi_{I_\mu}\varphi_{I_v}|\hat{g}|\varphi_{\ell_\tau}\varphi_{\ell_\sigma}\rangle) \\ &+ \sum_{\mu,v=1}^{n_\alpha} \sum_{\sigma,\tau=n_\alpha+1}^{N} M^{I\ell,n_\alpha-1}(I_\mu|\ell_v) M^{I\ell,n_\beta-1}(I_\sigma|\ell_\tau) \\ &\times \langle\varphi_{I_\mu}\varphi_{\ell_\sigma}|\hat{g}|\varphi_{I_v}\varphi_{\ell_\tau}\rangle \Bigg\} \ . \end{aligned} \tag{30}$$

These various expansions have been used to write a new routine for evaluating the total energy (Eq. 13) when using projected spin eigenfunctions. We find that the new procedure is significantly faster than our existing approach [4].

In practice, we first run a loop over all U_ℓ, recording indexes for the strings which arise from the deletion of up two αs or βs (as is required for indexing mirrors) and the identities of which particular orbitals have been deleted (as is required for accessing integrals in the orbital basis). The main code then consists of an outer loop over all U_I: for the given U_I, we first store in temporary arrays the indexes for strings which arise from the deletion of up to two αs or βs and the identities of which particular orbitals have been deleted; a fast inner loop over U_ℓ is then performed to assemble the required $\langle U_I|\hat{O}|U_\ell\rangle$ from precomputed minors and from integrals in the spin-coupled orbital basis. The various $O_{k\ell}$ matrix elements are then obtained in a separate stage, using Eq. (21).

A key consideration in the efficiency of the new routine is the availability of fast graphical indexing routines for the various orbital strings and for the minors [4, 11], as in our existing code.

4 Density matrices

Computation of the second derivatives of the energy with respect to the variational parameters requires density matrices up to fourth order. For larger values of N, the generation of these density matrices accounts for a very high proportion of the total computer time. An efficient strategy for evaluating all of the required density matrix elements is described in detail in Ref. [4], in which summations over $(N_d)^2$ terms are significantly reduced. Because of the dimensions of the various density matrices,[1] it is important to be able to generate them in a prearranged order that avoids excessive storage [4].

It is straightforward, if a little tedious, to generalize Eq. (30) for an arbitrary symmetric spin-independent four-electron operator, and then to recognize the elements of the fourth-order density matrices as the multipliers of the relevant four-electron integrals. The basic problem with adopting such an approach is that it does not generate the elements of the density matrices in a convenient order, as in our existing procedures. Instead, we recognize (cf. Eqs. 18 and 21) that we may make the replacement

$$\sum_{J}^{N_d} b_{J\ell}|U_J\rangle \rightarrow K_S^N|U_\ell\rangle \qquad (31)$$

in our existing strategy. The required changes to Scheme I in Ref. [4] are surprisingly modest. In essence, the contribution from a particular determinant in the ket is not considered unless that determinant corresponds to a standard Young tableau permutation. Of course, the numerical factors in front of the surviving terms must be modified according to the recipe shown in Eq. (31).

We indicated earlier that one very crude estimate of the expected improvement in performance is provided by the ratio $1/2(N_d+1)/f_S^N$. The actual speed-ups achieved in the evaluation of the fourth-order density matrix are shown in Table 1. Greater improvements in performance are observed with increasing N, and for low values of S. The symmetry properties of the various expressions are such that $S=0$ is no longer a special case for which some terms need not be computed, as in our existing strategy [4], so that the speed-up can be less than $1/2(N_d+1)/f_S^N$ for zero total spin.

Table 1. Relative performance of the evaluation of fourth-order density matrices when using projected spin functions

N	S	f_S^N	N_d	$1/2(N_d+1)/f_S^N$	Actual speed-up
9	$\frac{1}{2}$	42	126	1.51	1.64
9	$1\frac{1}{2}$	48	84	0.89	1.17
9	$2\frac{1}{2}$	27	36	0.69	1.05
10	0	42	252	3.01	2.73
10	1	90	210	1.17	1.66
10	2	75	120	0.81	1.31
10	3	35	45	0.66	1.04
12	0	132	924	3.50	3.49

5 Conclusions

In general, projected spin eigenfunctions contain the longest possible expansion in primitive spin products and they offer no straightforward physical interpretation. Their advantage is of the computational kind and arises from the idempotency of the projection operator. In essence, one sum over the full spin space in the matrix element evaluation may be replaced by one primitive spin product (cf. Eq. 31, in which the spatial product is also included). The consequence of this is that spin-coupled calculations performed with a projected spin basis, using the strategy outlined here, are significantly faster than the corresponding calculations using the schemes described in Ref. [4]. More importantly, most is gained (see Table 1) for larger values of N and low S, for which the calculations are most time consuming.

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[1] A transcription error occurred in the last line of Table 2 in Ref. [4]. The correct entries are $\tilde{N}(D^n) = 2946240, \tilde{N}(D^n_k) = 388903680$ and $\tilde{N}(D^n_{k\ell}) = \approx 2.59 \times 10^{10}$