

AN EFFICIENT METHOD FOR THE EVALUATION OF COUPLING COEFFICIENTS IN CONFIGURATION INTERACTION CALCULATIONS

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A new method for evaluating one-particle coupling coefficients in a general configuration interaction calculation is presented. Through repeated application and use of resolutions of the identity, two-, three- and four-body coupling coefficients and density matrices may be built in a simple and efficient way. The method is therefore of use in both multiconfiguration SCF (MC SCF) and multireference configuration interaction (MRCI) calculations. Examples show that the approach is efficient for both these applications.

1. Introduction

In recent years, there have been many significant advances in the methodology for performing direct configuration interaction (CI) calculations [1–11]. In particular for the case of a multiconfiguration reference CI (MRCI) configuration basis consisting of single and double excitations into a large orbital set out of a reference function built from a small orbital set, efficient methods are now available, which run at very high execution rates on vector computers. This is because in direct MRCI(SD) calculations, most quantities can be obtained in terms of multiplications of large integral and coefficient matrices.

Distinct from this is the case of a CI calculation in a small (less than 20) orbital space. This situation arises in MC SCF calculations, and the reference function for MRCI calculations is also of this form. The configuration basis may be complete within the orbital space, but frequently it is desirable that it is not; in MRCI calculations, the effort often depends quite strongly on the number of reference configurations. However, even in incomplete configuration expansions, if all the chemically important orbitals are included, the size of the basis often lies in the range 10^3 – 10^5 , and so efficient methods for calculating Hamiltonian matrix elements are required.

For these calculations, the techniques of single and double excitation CI, involving multiplication of matrices whose dimension is the orbital basis size, are not of use. Their application to cases involving more than double excitations is very complicated, and often there may be only three or four internal orbitals of each symmetry anyway, making matrix multiplications over these dimensions rather inefficient. Additional complication is introduced by the fact that we wish to compute three-particle density matrices and other special quantities for use in internally contracted MRCI calculations [6–9].

“Conventional” methods for performing CI calculations in a small orbital space involve a single computation of the one- and two-particle coupling coefficients in essentially random order. These coupling coefficients are then read from disc each time the Hamiltonian or density matrices are required. This approach has enabled

MC SCF calculations involving up to about 10^4 configurations to be carried out. However, the file of coupling coefficients gets extremely large for bases of this size, and with advances in computer hardware, it becomes more and more the case that the cost of storing and eventually reading these coupling coefficients dominates an entire calculation. Furthermore, we cannot possibly contemplate storing the much larger numbers of coupling coefficients which are required in MRCI calculations, where there are often also very many internal $N-1$ and $N-2$ electron states, for which coupling coefficients are also required [9]. In addition it is often the case that one wants the coupling coefficients in some specific order, necessitating an expensive sort of the formula file. All this means that "direct" methods, which recompute all coupling coefficients when needed, are highly desirable.

The first large-scale direct CI calculation in a small orbital space was that of Handy [12], which involved a basis of 2.5×10^5 configurations, the calculations actually being performed in a basis of 5×10^5 determinants. The key to this calculation was the use of Slater determinants, for which the coupling coefficients are very simple, and a special addressing scheme for complete configuration bases, similar to the graphical schemes in common use for unitary group [13] and symmetric group [14] bases.

Later, Siegbahn [10] presented a method whereby the two-body interactions are computed from the one-particle coupling coefficients through introduction of a resolution of the identity. This has the advantage that, for larger orbital spaces at least, the computation cost is dominated by large matrix multiplications, leading to efficient execution on a vector computer. However, it is still necessary to sort and store the one-particle coupling coefficients on disc.

Knowles and Handy [11] combined the Siegbahn approach with the simplifications that arise from using Slater determinants to give a method for full CI calculations in which no external storage is needed, and all coupling coefficients are computed as needed. This algorithm has been used in full CI calculations exceeding 10^7 in dimension [15].

Because of the special addressing scheme for the configuration basis, it is hard to generalise the method of ref. [11] to the case of a restricted CI expansion. Furthermore its use of Slater determinants, whilst efficient for full CI, is inconvenient for the MRCI reference space, where we wish to minimise the number of configurations, i.e. it is essential to work in a basis of pure spin eigenfunctions. The aim of this Letter is to show how it is possible to generate one-particle coupling coefficients in a spin eigenfunction basis directly in a simple and efficient way, in any desired order; this then allows us to use the Siegbahn approach [10] for diagonalising the Hamiltonian without any formula file. Similar techniques [8,9] allow efficient calculation of three-body and other terms needed in MRCI.

2. Method

We define the N -electron orthonormal basis for the calculation as the set of functions

$$|I_\lambda\rangle = \mathcal{A}(|I\rangle \Theta_{S_\lambda}^{(M)}), \quad (1)$$

where $|I\rangle$, an *orbital configuration*, is a simple product of L doubly occupied and $M=N-2L$ singly occupied orbitals,

$$|I\rangle = \phi_{j_1}(1) \phi_{j_1}(2) \phi_{j_2}(3) \phi_{j_2}(4) \dots \phi_{j_L}(2L-1) \phi_{j_L}(2L) \phi_{i_1}(2L+1) \phi_{i_2}(2L+2) \dots \phi_{i_M}(N). \quad (2)$$

The *spin function* $\Theta_{S_\lambda}^{(M)}$ is a function of the spin of particles $2L+1, 2L+2, \dots, N$, and we use the set of functions which form a basis for the appropriate representation of the symmetric group S_M , such that the total spin is S . These are the genealogical functions [16], which arise from successive coupling of electron spins in order of increasing orbitals. The index λ labels the component of the representation, and throughout we assume that for each of the orbital configurations $|I\rangle$ we include all spin couplings, i.e. we have the complete spin basis $\{\Theta_{S_\lambda}^{(M)}\}$. The configurations $\{|I_\lambda\rangle\}$ may be conveniently arranged into a standard order, such that all spin cou-

plings λ for a given orbital configuration $|I\rangle$ are contiguous. The orbital configurations may be classified by spatial symmetry and *shell number* $K = \frac{1}{2}M - S + 1$, where M is the number of singly occupied orbitals.

The one-particle coupling coefficients are the matrix elements, in this basis, of the orbital excitation operators \hat{E}_{ij} , which make the single orbital excitation $\phi_j \rightarrow \phi_i$ when acting on N -electron wavefunctions. Given a function $|J_\mu\rangle$ and excitation operator \hat{E}_{ij} , there is at most one orbital configuration $|I\rangle$, obtained by replacing orbital ϕ_j by ϕ_i in $|J\rangle$, for which the coupling coefficients

$$A_{\lambda\mu}^{I,ij} = \langle I_\lambda | \hat{E}_{ij} | J_\mu \rangle \quad (3)$$

are not zero. Therefore, by grouping all configurations with the same orbital part together, we deal naturally with matrices $\mathbf{A}^{I,ij}$ of coupling coefficients, whose dimensions, the ranges of λ and μ in (3), are the numbers of spin functions

$$f_S^{(M)} = \binom{M}{\frac{1}{2}M - S} - \binom{M}{\frac{1}{2}M - S - 1} \quad (4)$$

for bra and ket.

Explicit formulae for the matrix elements (3) in the symmetric group basis are now well known. Simple considerations show that there are four distinct cases for the evaluation of (3), depending on the occupancies of orbitals ϕ_i , ϕ_j in $|I\rangle$ and $|J\rangle$, and these are summarised as follows [17,18]:

(a) ϕ_i singly occupied, ϕ_j unoccupied in $|I\rangle$,

$$\langle I_\lambda | \hat{E}_{ij} | J_\mu \rangle = (-1)^{p(I,i) - p(J,j)} \langle \Theta_\lambda | \hat{C}(p(I,i), p(J,j)) | \Theta_\mu \rangle; \quad (5a)$$

(b) ϕ_i doubly occupied, ϕ_j unoccupied in $|I\rangle$

$$\langle I_\lambda | \hat{E}_{ij} | J_\mu \rangle = \sqrt{\frac{1}{2}} (-1)^{p(J,i) - p(J,j)} \langle \Theta_\lambda | \hat{C}(1, p(J, \min(i,j))) \hat{C}(1, p(J, \max(i,j))) | \Theta_\mu \rangle; \quad (5b)$$

(c) ϕ_i singly occupied, ϕ_j singly occupied in $|I\rangle$ (Hermitean conjugate of (5b))

$$\langle I_\lambda | \hat{E}_{ij} | J_\mu \rangle = \sqrt{\frac{1}{2}} (-1)^{p(I,i) - p(I,j)} \langle \Theta_\lambda | \hat{C}(p(I, \max(i,j)), 1) \hat{C}(p(I, \min(i,j)), 1) | \Theta_\mu \rangle; \quad (5c)$$

(d) ϕ_i doubly occupied, ϕ_j singly occupied in $|I\rangle$

$$\langle I_\lambda | \hat{E}_{ij} | J_\mu \rangle = \frac{1}{2} (-1)^{p(I,j) - p(J,i) + 1} \langle \Theta_\lambda | \hat{C}(p(I,j), p(J,i)) | \Theta_\mu \rangle. \quad (5d)$$

In the above, $p(I, i)$ is the position of orbital ϕ_i amongst the ordered set of singly occupied orbitals appearing in $|I\rangle$, and $\hat{C}(p, q)$ is a cyclic permutation operator acting on the labels of the coordinates which are the arguments of the spin function Θ_μ .

Straightforward application of these formulae involves two significant stages: first, the orbital positions $p(I, i)$, $p(J, j)$ must be computed; this is the problem of finding the "line-up" permutation. Secondly, the representation matrix for the cyclic permutation must be calculated. Most algorithms currently used [14] construct the representation matrices directly when needed, since the $\frac{1}{2}M(M+1)$ possible matrices for each of the four cases (5a)–(5d) usually exceed storage capacity available. For example, for a triplet state with up to 10 open shell orbitals, there are up to 90 spin functions, giving a total of the order of 10^9 matrix elements which would have to be stored.

The problem of determining line-up permutations can be solved with a graphical representation of the basis (analogous to the graphical unitary group approach to the equivalent problem in a unitary group basis of configurations [13]), and this approach also allows relatively simple evaluation of the two-particle coupling coefficients. But the applicability of the graphical scheme is limited to certain special types of configuration expansion, for example full CI, or a limited general excitation level from one reference. More general expansions must be mapped onto a graphical basis using an index vector, and this can be extremely wasteful. Therefore, we seek a method which avoids the use of special addressing schemes, using simply a list of orbital configurations which may be completely arbitrary. We wish to minimise the cost of calculating the line-up permutations, and cal-

culating the representation matrices. More importantly, perhaps, we require a method whereby we can calculate the coupling coefficients (3) in any desired order, for example all $\mathbf{A}^{IJ; ij}$ for fixed I, J , of fixed J, j , etc. These considerations are vital for multireference CI calculations in particular [8,9].

We propose to fulfill these requirements by making use of the identity

$$\hat{E}_{ij} = \hat{E}_{ia} \hat{E}_{aj}, \quad (6)$$

which holds for any orbital ϕ_a which is always unoccupied in any function on which the operator \hat{E}_{ij} acts. We take ϕ_a to be a hypothetical orbital of higher sequence number than all occupied orbitals. Then, inserting the identity, (3) becomes

$$A_{\lambda\mu}^{IJ; ij} = \sum_{\nu} \langle I_{\lambda} | \hat{E}_{ia} | S_{\nu}^a \rangle \langle S_{\nu}^a | \hat{E}_{aj} | J_{\mu} \rangle, \quad (7)$$

where $|S^a\rangle$ is the single orbital configuration with $N-1$ electrons in the occupied orbital space, plus one electron in an orbital ϕ_a , the occupancy of $|S^a\rangle$ being such that the matrix element is non-zero. Notice that $\{|S_{\nu}^a\rangle\}$ is exactly the basis of functions appearing in a first-order CI calculation, where ϕ_a is an external orbital, except that we choose to couple the spin of ϕ_a last rather than first, since this leads to simplifications for matrix elements involving excitation of doubly occupied orbitals. Note also that (6) is no more than an expression of identities for cyclic permutations in the symmetric group S_M , for example for case (5a), (6) is equivalent to

$$\hat{C}(p, q) = \hat{C}(p, M) \hat{C}(M, q), \quad \text{where } 1 \leq p, q \leq M, \quad (8)$$

since the position of orbital ϕ_a is always last. The advantage of this formal step is that it can drastically reduce the number of possible cases, such that all required matrix elements and permutations can be stored. The four cases of (5) reduce to two, for which the matrix elements are given by

$$\langle I_{\mu} | \hat{E}_{ia} | S_{\nu}^a \rangle = X_{\mu\nu}^{iI, S} = W_{\mu\nu}^{p(i, I), n(i, I)}, \quad (9)$$

with

$$W_{\mu\nu}^{p, 1} = (-1)^{M-p} \langle \Theta_{\mu} | \hat{C}(p, M) | \Theta_{\nu} \rangle, \quad (10a)$$

$$W_{\mu\nu}^{p, 2} = \sqrt{\frac{1}{2}} (-1)^{M-p} \langle \Theta_{\mu} | \hat{C}(1, p) \hat{C}(1, M) | \Theta_{\nu} \rangle. \quad (10b)$$

In the above, $n(i, I)$ is the occupation number of orbital ϕ_i in configuration $|I\rangle$, i.e. (10a) and (10b) correspond to the cases of ϕ_i singly occupied and doubly occupied, respectively. The definition of $p(i, I)$ is also extended to mean, for the case that ϕ_i is doubly occupied, the position of orbital ϕ_i in the set of singly occupied orbitals in the $(N-1)$ -electron configuration $|S\rangle$. M is the number of singly occupied orbitals in $|S^a\rangle$ (including the fictitious orbital ϕ_a). Instead of considering all $\frac{1}{2}M(M+1)$ cyclic permutation operators $\hat{C}(p, q)$, (7) involves of the order of M operators and, for all reasonable cases, the representation matrices for these operations $\mathbf{W}^{p, n}$, can be computed once using standard techniques [16,19] and then held in high-speed memory. Additionally, we note that it is necessary to store the $\mathbf{W}^{p, n}$ matrices only for the highest shell of configurations (those with largest M); if the spin functions are arranged in reverse dictionary ordering [20], the matrices for lower shells are obtained as submatrices. Given the matrices \mathbf{X}^p and \mathbf{W}^p , the coupling coefficients are then given by

$$\mathbf{A}^{IJ; ij} = \mathbf{X}^{iI, S} \mathbf{X}^{jJ, S^{\dagger}}. \quad (11)$$

Although in principle (11) requires a full matrix multiplication, usually one processes the coupling coefficients in an expression of the form $\sum_{\mu} A_{\lambda\mu}^{IJ; ij} c_{J, \mu}$, and so it is sufficient to perform matrix vector multiplications of the form

$$\sum_{\mu} A_{\lambda\mu}^{Ij; \dot{u}} c_{J, \mu} = \sum_{\nu} X_{\lambda\nu}^{I, S} \left(\sum_{\mu} X_{\mu\nu}^{J, S} c_{J, \mu} \right). \quad (12)$$

The remaining problem is the determination of the orbital positions $p(I, i)$; additionally, in order to generate coupling coefficients in the correct order, we need to be able to rapidly find, given I, i, j , the orbital configurations $|S^a\rangle$ and thence $|J\rangle$ appearing in (7). In our computer program, we store the orbital configurations $\{|I\rangle\}$ (and also, in separate areas $\{|S\rangle\}$ and possibly $\{|J\rangle\}$) as single-word bit patterns. Then all of these functions can be achieved through simple logical operations and pattern matching. However, if, as is usually the case, one eventually uses each $p(I, i)$ more than once, it becomes much more efficient to precompute and store all information. Specifically, we set up two lists:

- (i) $Y(I, i)$ = canonical index of orbital configuration $|S\rangle$ in $\langle I | \hat{E}_{ia} | S^a \rangle$, or zero if ϕ_i is not occupied in $|I\rangle$.
- (ii) $Z(I, i)$ = address of matrix $\mathbf{X}^{I, S}$.

To complete the evaluation of (7), one needs also similar lists in order to map the space $\{|S^a\rangle\}$ to the space $\{|J\rangle\}$. The storage requirement for each set of lists is $2 \times \text{number of orbitals} \times \text{number of orbital configurations}$. Introduction of this approach speeds up the determination of the interacting orbital configuration, and the address of the representation matrix, to such an extent that on a CRAY-XMP, the computation time is dominated by the matrix algebra of (12).

For MRCI calculations, many other types of coupling coefficient are required between various combinations of N -, $(N-1)$ -, and $(N-2)$ -electron functions [8,9]. All of these may be computed directly in a similar way using exactly the same set of $\mathbf{W}^{p, n}$ matrices; this is possible because of the genealogical spin coupling scheme with external orbitals coupled last. Also one may use the same subroutines to construct the lists $Y(I, i)$ and $Z(I, i)$ for different configuration spaces, resulting in a simple, transparent and efficient implementation of formulae.

We note that our convention of coupling external orbitals last, rather than before all other singly occupied orbitals, differs from most other MRCI implementations. We have chosen this coupling order because, as noted above, it allows the simple use of the same set of basic coupling coefficients $\mathbf{W}^{p, n}$ for interactions involving configurations of any number of internal electrons and any shell number. For uncontracted MRCI calculations, this approach would have the disadvantage that external singlet and triplet pair functions would become mixed; but for internal and singly external CI bases, and for internally contracted doubly external functions, this is of no consequence [9].

Given the one-particle coupling coefficients, higher-particle quantities may be constructed through insertion of resolutions of the identity [10]. For example, construction of the action of the two-electron part of the Hamiltonian on a trial wavefunction

$$\sigma_{I, \lambda} = \frac{1}{2} \sum_{\substack{ijkl \\ J\mu}} (ij|kl) \langle I_{\lambda} | \hat{E}_{ij} \hat{E}_{kl} | J_{\mu} \rangle c_{J, \mu}, \quad (13)$$

the basic operation in diagonalising the Hamiltonian can be accomplished through the sequence [10,11]

$$D_{ij}^{K, \lambda} = \sum_{J\mu} A_{\lambda\mu}^{KJ; \dot{u}} c_{J, \mu}, \quad (14)$$

$$E_{ij}^{K, \lambda} = \frac{1}{2} \sum_{kl} (ij|kl) D_{kl}^{K, \lambda}, \quad (15)$$

$$\sigma_{I, \lambda} = \sum_{\substack{ij \\ K\mu}} A_{\lambda\mu}^{IK; \dot{u}} E_{ij}^{K, \mu}. \quad (16)$$

Note that in the summations in eqs. (14) and (16), the formal summations over J and K respectively run only over the number of spin couplings, since for fixed orbital labels and a given configuration appearing on the left-hand side, only one-orbital configuration at most interacts. Note also that the set of intermediate config-

urations $\{|K_\lambda\rangle\}$ may be larger than the set $\{|I_\mu\rangle\}$ which form the basis for the calculation, so they must be stored in different areas.

The three-particle density matrix is a crucial quantity in the calculation of the interaction of pair functions in the internally contracted MRCI method. Its construction in this context is described in detail in ref. [9], but here we sketch the important details as an illustration of how the techniques described in this section can be applied to the efficient evaluation of rather complicated quantities. The third-order density matrix is defined as

$$D_{kl, mn}^j = \langle 0 | \hat{E}_{ik, jl, mn} | 0 \rangle = \langle 0 | (\hat{E}_{ik} \hat{E}_{jl} - \delta_{jk} \hat{E}_{il}) \hat{E}_{mn} - \delta_{km} (\hat{E}_{in} \hat{E}_{jl} - \delta_{jn} \hat{E}_{il}) - \delta_{lm} (\hat{E}_{ik} \hat{E}_{jn} - \delta_{jk} \hat{E}_{in}) | 0 \rangle, \quad (17)$$

where $|0\rangle$ is a reference wavefunction defined as a linear combination of reference configurations

$$|0\rangle = \sum_{I, \lambda} a_{I, \lambda} |I_\lambda\rangle. \quad (18)$$

For the pair-pair interaction it is necessary to calculate this matrix in a specific order (since it is usually too large to hold in memory), namely all matrix elements for a given i, j together. To achieve this conveniently, (17) may be rearranged using the technique of (6) to give

$$D_{kl, mn}^j = \sum_{I, \lambda} \langle 0 | \hat{E}_{ik, jl} | I_\lambda \rangle \langle I_\lambda | \hat{E}_{mn} | 0 \rangle - \delta_{km} \langle 0 | \hat{E}_{in, jl} | 0 \rangle - \delta_{lm} \langle 0 | \hat{E}_{ik, jn} | 0 \rangle, \quad (19)$$

where

$$\hat{E}_{ik, jl} = \hat{E}_{ia} \hat{E}_{jb} \hat{E}_{ak} \hat{E}_{bl} \quad (20)$$

and we have introduced two fictitious orbitals ϕ_a, ϕ_b and we assume $a > b$. Our algorithm for the first and most significant term in (19) then proceeds as follows.

(i) Calculate and store all $\langle K_\sigma | \hat{E}_{mn} | 0 \rangle$.

(ii) For each i, j :

Loop over orbital configurations $|I\rangle$ which are occupied in $|0\rangle$.

Determine orbital configurations $|S\rangle, |P\rangle$ interacting with $|I\rangle$, and

$$v_\nu = \sum_\mu \langle P_\nu^{ab} | \hat{E}_{ai} | S_\mu^b \rangle \left(\sum_\lambda \langle S_\mu^b | \hat{E}_{bj} | I_\lambda \rangle a_{I, \lambda} \right). \quad (21)$$

Loop over k .

Determine orbital configuration $|T\rangle$ interacting with $|P\rangle$, and

$$w_\rho = \sum_\nu \langle T_\rho^a | \hat{E}_{kb} | P_\nu^{ab} \rangle v_\nu. \quad (22)$$

Loop over l .

Determine orbital configuration $|K\rangle$ interacting with $|T\rangle$, and

$$\langle 0 | \hat{E}_{ik, jl} | K_\sigma \rangle = \sum_\rho \langle K_\sigma | \hat{E}_{ia} | T_\rho^a \rangle w_\rho. \quad (23)$$

Assemble contributions to third-order density according to the matrix multiplication in (19).

The crucial computational stages are firstly the innermost loop (23) in the determination of the two-particle coupling coefficients $\langle 0 | \hat{E}_{ik, jl} | K_\sigma \rangle$, which is performed by direct matrix-vector multiplication with the matrices $\mathbf{W}^{p, n}$ using the addressing lists as described above, and secondly the final assembly (19) which can be performed most efficiently as a matrix multiplication with long vector lengths.

3. Examples

The techniques described in section 2 form part of our new internally contracted MRCI program. The full capabilities of this code are described in ref. [9], but here we give some demonstration of the efficiency of the coupling coefficient evaluation techniques.

As a first example, we have performed a full CI calculation for H₂O at the equilibrium geometry in a 6-21G basis set [21]. The number of orbital configurations is 8090, giving a total of 18385 spin eigenfunctions, or 61441 Slater determinants. Table 1 shows the total energy, and CPU time per iteration. Comparison is made with the determinant full CI approach of Knowles and Handy [11], which is probably the most efficient method for this problem. Although the determinant program is more than twice as fast, it should be remembered that the new method is completely general, and deliberately does not take advantage of the special structure of the full configuration space in the way that the determinant program does. This is demonstrated by the subsequent rows of table 1, which show timings for smaller calculations where the configurations are selected, either against a threshold according to their weight in the full CI wavefunction, or by excitation level with respect to the SCF wavefunction. These are the kinds of selection procedures commonly used in obtaining reference configurations for a MRCI calculation, and the configuration lists now possess no special structure which could be taken advantage of in some graphical addressing scheme. It is seen that the CPU times are rather favourable, scaling approximately linearly with the size of basis. The advantage of using spin eigenfunctions rather than Slater determinants is seen in the reduction by a factor of nearly three in the CPU time for the matrix multiplication (15) for the case of a full CI calculation, consistent with the reduction in the number of intermediate states $|K_2\rangle$ in (14)–(16).

Our second example consists of the construction of the three-particle density matrix according to (17)–(23) during the evaluation of the pair-pair interaction in a MRCI calculation for the ground state X ¹Σ⁺ of CN at its equilibrium bond length. The reference configurations for this calculation are those whose weight in a complete active space MC SCF calculation, with the orbitals 3σ–6σ and 1π–2π active, is greater than a given threshold. Table 2 shows the CPU time spent in each of eqs. (21)–(23) and (19) for various values of the selection threshold. We observe again that the effort is approximately linear in the size of the reference space, and that

Table 1
Full and restricted CI calculations for H₂O ^{a)}

Selection	Configuration ^{b)}	Energy	CPU ^{c)}
full CI	8090/18385	–76.018515	6.22 (7%)
full CI ^{d)}	8090/61441	–76.018515	2.61 (45%)
0.0001 ^{e)}	1791/4664	–76.018467	1.73 (15%)
0.001 ^{e)}	355/936	–76.016910	0.41 (22%)
6 ^{f)}	6540/15421	–76.018514	5.11 (9%)
4 ^{f)}	2076/4313	–76.018376	1.74 (13%)
3 ^{f)}	645/1105	–76.014172	0.57 (16%)
2 ^{f)}	133/177	–76.012837	0.12 (18%)

^{a)} Geometry: O: (0,0,0); H: (±1.4744323,0,1.0781534) au. Orbital basis set: 6-21G [21], with the SCF 1a₁ orbital doubly occupied in all configurations.

^{b)} Number of orbital configurations/Number of variational parameters.

^{c)} Single processor CRAY-XMP48 CPU time per iteration. The figure in parentheses shows the percentage of the iteration time spent in the matrix multiplication (15), the remainder being in evaluating and processing the coupling coefficients in eqs. (14) and (16).

^{d)} Determinant full CI program [11].

^{e)} Configuration selection threshold. All configurations in the full CI wavefunction with weight larger than this threshold are included. The weight is calculated as the root of the sum of squares of CI coefficients of all configurations having the same orbital occupancy, but different spin couplings.

^{f)} Excitation level with respect to SCF determinant.

Table 2
Third-order density evaluation for MRCI calculations on $CN(X^2\Sigma^+)$

Selection ^{a)}	Ref. ^{b)}	Γ ^{c)}	D ^{d)}	CPU(Γ) ^{e)}	CPU(D) ^{f)}	CPU ^{g)}
0.0	616	435 693	65814	1.631	0.202	1.884
0.001	455	316 705	65803	1.142	0.156	1.340
0.01	141	94 401	51 536	0.366	0.055	0.447
0.05	26	18 331	11 927	0.096	0.015	0.131

^{a)} Threshold for selection of reference configurations from MC SCF wavefunction, as in table 1. The active orbital space consists of the orbitals $3\sigma-6\sigma$, 1π , 2π .

^{b)} Number of reference CSFs.

^{c)} Number of non-zero two-particle transition density matrix elements $\langle 0|\hat{E}_{ik,jl}|K_\sigma\rangle$ from (23).

^{d)} Number of non-zero three-particle density matrix elements $D_{kl, mn}^j$ from (19).

^{e)} Single processor CRAY-XMP48 CPU time for evaluation of two-particle transition density matrix through (21)–(23).

^{f)} CPU time for assembly of three-particle density matrix in (19).

^{g)} Total CPU time for evaluation of complete third-order density matrix.

the introduction of the resolution of the identity [10] is an efficient procedure, in the sense that the computational effort expended in the central matrix multiplication of (19) is not excessive. It should be emphasized that, up until now, MRCI calculations with several hundred reference configurations have been considered too expensive for normal applications. The results of table 2 demonstrate that the evaluation of pair-pair coupling coefficients for such very large reference spaces can be performed in just a few seconds of CRAY-XMP time.

4. Conclusion

We have presented a technique for computing coupling coefficients in a completely general CI efficiently in any required order. Because of the simplicity of the formulae, it is easy to design algorithms to construct almost any type of CI matrix element arising within a small orbital space. This has enabled us to develop a powerful new program for internally contracted MRCI calculations [9].

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