The direct CI method. A detailed analysis

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A thorough analysis of the direct CI method as applied to the case of a general set of reference configurations coupled to all single and double substitutions is presented. It is pointed out that there is no single strategy which proves optimal under all circumstances. A variety of procedures are therefore presented together with rules to enable the selection of the most favourable under a given circumstance. Much emphasis has been placed on organizing the calculations via a series of matrix multiplications, which enables a vector or array processing computer to be used to best effect. Some consideration is given to using an atomic integral (rather than molecular integral) driven scheme for some interactions, thus removing the necessity for a complete transformation of the molecular integrals to a molecular orbital basis, and the advantages and disadvantages of so doing are discussed. Improved procedures for carrying out both full and partial transformations of the molecular integrals are described. A number of test case calculations involving configuration lists of the order of $10^4$ to $10^5$ have been analysed in detail, to give a clear picture of the cost of the various interaction types which arise, and indicating that integrals carrying two external molecular orbital indices account for approximately 60 per cent of the cost in typical cases. Typically, a calculation involving $10^5$ configurations requires approximately two minutes of CRAY-1 computer time, allowing for ten iterations of the diagonalization procedure. The cost of the calculations are found, somewhat surprisingly, to be approximately linear in the dimension of the configuration space, indicating that calculations involving $10^6$ configurations are now quite feasible.

1. Background

The direct configuration interaction (CI) method for the construction of correlated electronic wavefunctions was first introduced by Roos [1] for the important special case of a single closed shell reference function coupled to all states derived therefrom by single and double excitation into an external space of molecular orbitals (MOs). The method has seen a number of generalizations [2], within the past decade, culminating in the work of Siegbahn [3], who succeeded in formulating a procedure applicable to the case of an arbitrary set of reference functions coupled to singly and doubly excited configurations. In the direct CI method one avoids the explicit construction of the CI Hamiltonian matrix. Instead, the matrix-vector multiplication

$$Z = HC$$

where $C$ is a trial (column) vector of CI expansion coefficients, is accomplished directly from the list of transformed molecular integrals. It is thus also characteristic of the direct CI method that a complete transformation of the molecular integrals from an atomic orbital (AO) to a MO basis set is required.

The method of self consistent electron pairs (SCEP) was introduced by Meyer [4] for the case of one closed shell reference state, based in part on a technique [5] for the calculation of two-electron wavefunctions. The method suffered further generalizations [6], culminating in the work of Ahlrichs [7] who generalized the procedure to the level that had been achieved in the direct CI method [3]. The work of Werner and Reinsch [8] contains many technical advances over [7], because the methodology for exploiting an internally contracted reference function [3, 4] and the first order interacting space [4, 9] is explored. However, the formalism of [8] is less general than [7], since the former permits use of only one (albeit contracted) reference state. In general, techniques associated with such restrictions in the flexibility of the trial form of the wavefunction, including the process of external contraction [10], involve much methodological adaptation, but they are not the subject of the present work.

The SCEP method is akin to the direct CI method in that one avoids the explicit construction of the CI Hamiltonian matrix, but differs in that the complete transformation of the molecular integrals is avoided, to be replaced by a partial transformation. Of course, the
SCEP method may be applied in the case that a complete transformation of the molecular integrals has been carried out [11], with some advantage in the CI phase of the calculation, but at the cost of the complete transformation. In this case, the SCEP method becomes rather similar to the direct CI method [3], but not identical. The principal distinguishing feature is that the Z and C vectors are usually subjected to a renormalization in the SCEP method, with considerable advantage in the evaluation of equation (1).

The central purpose of the present work is to attempt a hybridization of ideas, taken both from the direct CI and SCEP methods, and to add to the blend some new proposals. The most important outcome of this analysis is the realization that there is no single optimal procedure for carrying out direct CI like calculations. For a given interaction there would appear to be usually three possible strategies, each of which may prove the best in appropriate circumstances, and that all possible circumstances may arise during the course of a single calculation. Hence it is necessary to produce a code embodying all the possible options and capable of selecting the best strategy.

It seems to the present authors that a cost/benefit comparison of procedures based on complete versus partial transformation of the molecular integrals is now overdue, so that as a secondary task we attempt to assess where the balance of advantage currently lies. Improvements in procedures for performing the integral transformations are described.

The procedures advocated in the present work have quite deliberately been formulated in such a way that the process of matrix multiplication comprises the all important step and considerable importance is attached to this feature. This is because we hope to be able to drive vector and array processing computers at somewhere near the maximum of their potential and the use of a matrix multiply dominated algorithm provides a convenient and, it is to be hoped, machine independent way of achieving this [12]. The integral transformation phase is also dominated by a sequence of matrix multiply operations and, since we have used the same matrix multiply routine in both the transformation and CI phases of the present implementation, one can obtain a fair relative costing of these two steps. A CRAY-1S vector processing computer with 1/2 Mword of memory was used in the implementation.

2. Configuration state functions

The N-electron antisymmetrized and spin adapted configuration state functions (CSFs) are constructed from an orthonormal set of MOs. The MOs are partitioned into two sub-sets, an internal set (members of which will be denoted by $i, j, k$ or $l$ and deemed to be of primary importance in the construction of a qualitatively correct wavefunction) and an external set (members of which will be denoted $a, b, c$ or $d$). In any given CSF a maximum of two electrons are allowed to occupy the external space. The external MOs are assigned higher indices than the internal MOs and the CSFs are constructed using the Yamanouchi–Kotani (YK) [13] spin functions, the coupling order being highest indexed MO first, lowest indexed MO last. This order of coupling was first suggested by Shavitt [14] and is beneficial for the reasons given in [3].

The CSFs may now be placed in four categories, which we label according to the occupation and spin pattern found in the external space. Vacuum states carry no electrons in the external space, doublet states carry one electron in the external space which is necessarily coupled to doublet spin, whilst singlet and triplet states carry two electrons in the external space, appropriately spin coupled. The CSFs (whose total spin is a matter of problem choice, independent of the partial spin carried by the external space) will be notated $\psi_S^a$, $\psi_S^b$, $\psi_S^{ba}$ and $\psi_S^{ab}$ for vacuum, doublet, singlet and triplet states respectively. S and $\sigma$ indicate the occupation and spin pattern respectively within the internal space (a bar over these superscripts indicates coupling to a triplet external pair function), whilst the subscripts indicate which external MOs are occupied. In the case of singlets or triplets the right-most subscript indicates which MO is to be coupled first and, if the state is in standard coupling order, we will have $b \leq a$ (singlets) or $b < a$ (triplets). It is to be noticed that our definition of the CSFs has not invoked the concept of excitation. However, in practice, the CSFs are generated by the action of creation/annihilation operators on a set of reference vacuum CSFs. The total wavefunction is written

$$\psi = \sum_{S_\sigma} C_{S_\sigma}^a \psi_S^a + \sum_{S_\sigma} C_{S_\sigma}^a \psi_S^a + \sum_{S_{ab}} \left( \sum_{\sigma} C_{S_{ab}}^a \psi_S^{ba} + \sum_{\sigma} C_{S_{ab}}^a \psi_S^{ab} \right).$$

We now introduce the term canonical block of CSFs. Such a block consists of all the CSFs arising from a given occupation pattern within the internal MOs. Thus, having fixed the internal occupation pattern, CSFs may be generated by considering all possible internal spin patterns coupled to all possible external spin and space functions which give rise to CSFs of the desired point group irreducible representation. It is convenient to consider together the interactions of all members of two such canonical blocks over the hamiltonian. Actually, in the present work the contributions to such interactions are further broken down according to molecular integral type, the integrals being classified
into five categories according to the number of external MO indices found therein. Table 1 gives an overall view of the classification scheme. Charge distribution, or Mulliken, notation is adopted for the two-electron integrals

\[ \int_1 \int_2 ... \int_5 \]

where the primes in equation (5) indicate that the summations cover only the permutationally distinct integrals. Siegbahn [3] has demonstrated that, given the restriction that the maximum number of electrons in the external space is two, the coupling coefficients may be written as a simple product of an internal part \( B \) and an external part \( D \)

\[ A_{pqrs}^{\mu \nu} = B_{pqrs}^{\mu \nu} D_{pqrs}^{\mu \nu}. \]

Siegahn [3] has presented formulae for the external coupling coefficients assuming a Gelfand–Tsetlin (GT) spin basis [17] and the segment level phase conventions of Shavitt [18]. We consider it desirable to avoid the use of quantities which are dependent on such technical details as the segment level phase conventions adopted by the coupling coefficient generator. To this end we introduce a model external space consisting of two MOs, which we label \( \alpha \) and \( \beta \). MO \( \alpha \) will be coupled first and is thus assumed to be of higher index than \( \beta \). Each internal occupation and spin pattern is then represented by one model CSF. Model doublet CSFs are constructed by assigning one electron to MO \( \alpha \), whilst model singlet and triplet CSFs are constructed by assigning one electron to each of the model space MOs, appropriately spin coupled. It may be shown that the internal coupling coefficient of equation (6) may be equated to an appropriate total coupling coefficient between model CSFs [7, 19, 20]. Total coupling coefficients are of course independent of the segment level phase conventions or indeed any other technical feature of the coupling coefficient generator. We notate the model space coupling coefficients \( B_{pqrs}^{\mu \nu} \), where subscripts denote MOs within the internal or model external spaces and superscripts designate a pair of interacting model CSFs.

Certain of our results depend on the phase conventions adopted for the CSFs and we have consistently used the standard YK set [13]. Our results stand unaltered if a GT set [17] is used. However, the spin functions defined by Paldus and Boyle (see equation (42) of reference [21]) introduce a further phase factor \((-1)^{N_2}\), where \( N_2 \) equals the number of doubly occupied MOs, into the definition of a YK basis and would require the use of the factor \(-1\), rather than \(1\), wherever the latter appears in our equations. The coupling coefficient generator used in the present work is based on the formalism of Paldus and Boyle [21], which is in turn based on straightforward angular momentum recoupling techniques. For a discussion of the reduction of the coupling coefficients so that they refer to the permutationally distinct list of integrals, see Shavitt [18]. It often turns out in practice that the coupling coefficients arising from different interaction blocks are equal. We have not made any attempt to keep track of these equivalences.
and still find that the time taken to evaluate the coupling coefficients to be very small. Some account of these equivalences could be taken by loop driving the algorithm [22] in the internal space, or probably even more effectively by using the techniques advocated by Buenker and Peyerimhoff [23] in the matrix element driven CI context. We simply stress here that, if one is attempting to save time in the coupling coefficient generation by these methods, the returns are likely to be extremely small. If, however, some more effective scheme for computing the Z vector, equation (1), could be devised by taking account of these equivalences then the rewards might be considerable.

The internal occupation patterns of the canonical blocks are held in store, as a representation of the CSF list, using a packed binary format. In contrast, Lischka et al. [24] use the distinct row table representation [25] of the internal states, pruned using an internal walk index vector.

3. Renormalization of the C and Z vectors

It will be found convenient to renormalize the Z vector for singlet states such that

\[ (Z_{ba}^\sigma)' = (\sqrt{2})^{\delta ab} Z_{ba}^\sigma. \] (7)

In all subsequent equations, the Z vector may be assumed to be in this renormalized state, so that we omit the prime in the interests of notational simplicity.

It turns out to be convenient to use two normalizations for the C vector, depending on the particular interaction under consideration. In the case of renormalization I the singlet C vector is subjected to the transformation

\[ (C_{ba}^\sigma)' = (\sqrt{2})^{\delta ab} C_{ba}^\sigma, \] (8)

whilst in renormalization II we use the transformation

\[ (C_{ba}^\sigma)'' = (1/\sqrt{2})^{\delta ab} C_{ba}^\sigma. \] (9)

We will note in the text which normalization is to be used in a given context, so that the prime and double prime will be omitted hereon. The renormalizations are introduced with the aim of eliminating the external coupling coefficients from the formulae for the Z vector, as in [7, 8], a possibility foreseen by Meyer [4] and intimately connected to the use of the Shavitt [14] coupling order, which gives rise to particularly simple formulae for the external coupling coefficients [3].

The combination of the renormalized Z vector and the C vector in renormalization I corresponds closely to that advocated by Ahlrichs [7]. Thus the Ahlrichs renormalization is

\[ (Z_{ba}^\sigma)' = (\sqrt{2})^{\delta ab} / \sqrt{2} Z_{ba}^\sigma, \] (10a)

\[ (C_{ba}^\sigma)' = (\sqrt{2})^{\delta ab} / \sqrt{2} C_{ba}^\sigma. \] (10b)

On the other hand, the combination of the renormalized Z vector and the C vector in renormalization II corresponds to a change in normalization of the CSFs, such that

\[ \langle \psi_{ba}^S | \psi_{ba}^S \rangle = 2^{\delta ab} \] (11)

and thus is closely related to that adopted by Meyer [4], whose convention is

\[ \langle \psi_{ba}^S | \psi_{ba}^S \rangle = (2)^{\delta ab} / 2. \] (12)

4. The construction of the Z vector

The formulae to be presented below for the various contributions to the Z vector are given without derivation. In general, the derivations are rather simple, depending on the following.


(ii) The singlet and triplet CSFs are symmetric and antisymmetric respectively with respect to a transposition of the order of coupling of the occupied external MOs. These symmetries may be used to relate coupling coefficients to model space coupling coefficients more easily.

In the case of many of the contributions, to facilitate cross comparison of different techniques, we have evaluated the number of floating point multiplication operations (FPMOs) requires to implement a given technique. This analysis retains only terms of the highest order in the number of external MOs \(N_E\), it being assumed that \(N_E\) is larger than such quantities as the number of spin couplings associated with a given occupation pattern. We have also ignored the effects of matrix sub-blocking due to point group symmetry and the fact that the coupling coefficient matrices are often sparse, particularly when a large number of spin couplings are associated with an occupation pattern. Nonetheless, the analysis is sufficiently quantitative to point to the best method.

Off-diagonal interactions are not considered twice; instead the total contribution of each distinct block is specifically allowed for in the formulae. Some effort has been expended in defining appropriate data structures for the storage of the spin coupling coefficients, molecular integrals and the C and Z vectors, so that the analysis may proceed very largely in matrix notation and be amenable to a successful implementation on an array or vector processing computer.
4.1. The all internal integrals \([ij][kl]\) and \([ij]\)

Our treatment of these integrals borrows extensively from the techniques adopted in matrix element driven procedures \([23, 26]\) in as much as we propose the partial construction of hamiltonian matrix elements. These integrals may give rise to a finite interaction only if the spin coupling and occupation pattern of the external levels are identical in the bra and the ket. This selection rule gives rise to the following cases.

4.1.1. Vacuum/vacuum interactions

We define

\[
H^{S\sigma T\tau} = \sum_{ijkl} B_{ijkl}^{S\sigma T\tau} [ij][kl] + \sum_{ij} B_{ij}^{S\sigma T\tau} [ij],
\]

where \(S\) and \(T\) here denote vacuum state occupation patterns. A given interaction block gives rise to the following contributions to the \(Z\) vector

\[
Z^{S\sigma} = \sum_{\tau} H^{S\sigma T\tau} C^{T\tau}, \tag{14}
\]

or in matrix notation

\[
Z^S = H^{ST} C^T, \tag{15}
\]

where \(Z^S\) and \(C^T\) are column vectors of \(\lambda(S)\) or \(\lambda(T)\) elements of \(Z\) or \(C\) respectively (\(\lambda(S)\) denotes the number of internal spin couplings associated with internal occupation pattern \(S\)), whilst \(H^{ST}\) is a \(\lambda(S)\) by \(\lambda(T)\) matrix of partial hamiltonian matrix elements. The procedure corresponds to that of the matrix element driven CI method \([23, 26]\). If \(S \neq T\), there is also a contribution to \(Z^T\) of the form

\[
Z^T = (H^{ST})^\dagger C^S. \tag{16}
\]

4.1.2. Doublet/doublet interactions

A given interaction block gives the following contribution to the \(Z\) vector

\[
Z^{S\sigma}_a = \sum_{\tau} H^{S\sigma T\tau} C^{T\tau}_a, \tag{17}
\]

where \(S\) and \(T\) denote doublet internal occupation patterns, \(H\) being defined in equation (13). In matrix notation

\[
Z^S = C^T (H^{ST})^\dagger, \tag{18}
\]

where \(H^{ST}\) is a \(\lambda(S)\) by \(\lambda(T)\) matrix of partial hamiltonian matrix elements, and

\[
Z^S_{a\sigma} = Z^S_a, \tag{19}
\]

\[
C^S_{a\sigma} = C^S_a. \tag{20}
\]

If \(S \neq T\), there is an update to \(Z^T\) of the form

\[
Z^T = C^S H^{ST}. \tag{21}
\]

4.1.3. Singlet/singlet and triplet/triplet interactions

These interactions are evaluated using the renormalized singlet \(Z\) vectors, equation (7), and the singlet \(C\) vectors in renormalization I, equation (8), although it is also possible to use the \(C\) and \(Z\) vectors in standard normalization. A given interaction block gives rise to the following contributions for the singlet–singlet case

\[
Z^{S\sigma}_{ba} = \sum_{\tau} H^{S\sigma T\tau} C^{T\tau}_{ba}, \tag{22}
\]

where \(S\) and \(T\) denote singlet internal occupation patterns, \(H\) being defined in equation (13). In matrix notation

\[
Z^S = C^T (H^{ST})^\dagger, \tag{23}
\]

where \(Z^S\) and \(C^T\) are \(\mu_1\) by \(\lambda(S)\) and \(\mu_1\) by \(\lambda(T)\) matrices respectively (\(\mu_1\) is the number of external singlet pair functions), whilst \(H^{ST}\) is a \(\lambda(S)\) by \(\lambda(T)\) matrix of partial hamiltonian matrix elements. The corresponding triplet–triplet interaction gives the result

\[
Z^T = C^S H^{ST}, \tag{24}
\]

where \(Z^T\) and \(C^S\) are \(\mu_3\) by \(\lambda(S)\) and \(\mu_3\) by \(\lambda(T)\) matrices respectively (\(\mu_3\) is the number of external triplet pair functions) and \(H^{ST}\) is a \(\lambda(S)\) by \(\lambda(T)\) matrix of partial hamiltonian matrix elements. If \(S \neq T\), there will be updates to \(Z^T\) and \(Z^S\) of the form

\[
Z^T = C^S H^{ST}, \tag{25}
\]

\[
Z^S = C^S H^{ST}. \tag{26}
\]

4.2. The integrals \([ij][ka]\) and \([ia]\)

All interactions over these integrals involve doublet states, giving rise to the following possibilities.

4.2.1. Doublet/vacuum interactions

A given interaction block gives rise to the following contributions to the \(Z\) vector (\(T\) and \(S\) denote vacuum and doublet states respectively)

\[
Z^{S\sigma}_a = \sum_{\tau} \left( \sum_{ijkl} B_{ijkl}^{S\sigma T\tau} [ij][ka] + \sum_{ij} B_{ij}^{S\sigma T\tau} [ij] \right) C^{T\tau}_a \tag{27}
\]

\[
Z^{T\tau}_a = \sum_{\sigma} \sum_{a} \left( \sum_{ijkl} B_{ijkl}^{S\sigma T\tau} [ij][ka] + \sum_{ij} B_{ij}^{S\sigma T\tau} [ij] \right) C^{S\sigma}_a. \tag{28}
\]

Consider first the case that the sum of the absolute values of differences in occupation numbers of internal MOs, the internal occupation number difference, is equal to three for \(S\) and \(T\). Let levels \(i\) and \(k\) be more occupied in \(T\), level \(j\) be more occupied in \(S\). Only two categories
of integrals may contribute, $[ij|ka]$ and $[kj|ia]$. Indeed if $i = k$, only one category contributes.

We consider first a partial hamiltonian matrix element driven scheme as favoured by Ahlrichs [7] and define

$$ H_a^{ST\tau} = B_{gka}^{ST\tau}[ij|ka] + B_{jka}^{ST\tau}[kj|id]. $$

We then have

$$ Z_a^{ST} = \sum_{\tau} H_a^{ST\tau} C^{\tau}, $$

$$ Z^{\tau} = \sum_{\sigma} \sum_{a} H_a^{ST\tau} C_a^{\sigma}. $$

We note that if we arrange the partial hamiltonian matrix elements into a matrix, $H^{ST}$, whose column dimension ranges over all possible combinations of external index and internal spin coupling of $S$, $N_e\lambda(S)$, and row dimension $\lambda(T)$, whilst $Z^S$ and $C^S$ denote appropriate column vectors consisting of all the elements of $Z^S$ and $C^S$ respectively, we may rewrite equations (30, 31) as

$$ Z^S = H^{ST} C^T, $$

$$ Z^T = (H^{ST})^T Z^S. $$

The number of FPMOs consumed by this partial matrix element driven scheme is given by $4N_e\lambda(S)\lambda(T)N_E$, of which half could be saved by pre-computing the partial hamiltonian matrix elements, a strategy not recommended for large scale calculations because of the backing store problems that would be presented.

Consider now the evaluation of equation (27) by first contracting over the internal spin index, internal spin driven, and equation (28) by first contracting over the external MO index, external index driven. We consider explicitly the $[ij|ka]$ contribution and define

$$ L = B_{gka}^{ST\tau}, $$

$$ M = (C^S)^T I_{jk}, $$

where $I_{jk}$ is a column vector of the $N_e$ integrals $[ij|ka]$. We then find the $[ij|ka]$ contribution to be

$$ Z^S = I_{jk} L^T, $$

$$ Z^T = (B_{gka}^{ST\tau})^T M $$

with similar results for the $[kj|ia]$ contribution. The number of FPMOs consumed by this alternative scheme is $4N_e\lambda(S)N_E$ when both sets of integrals are allowed for, which will prove superior to the partial matrix element driven scheme when $\lambda(T)$ is greater than unity.

Suppose now that the internal occupation difference of $S$ and $T$ is unity. Let internal MO $i$ carry one more electron in $T$. We first define a Fock operator for the doublet state which depends only on the occupation pattern of the internal MOs

$$ F^{S}_{pq} = \sum_{j} n^S_{j} J^{ij}_{pq} - \sum_{j} K^{ij}_{pq}, $$

where $n^S_{j}$ gives the occupation number of the $j$th internal MO in $S$ and where Coulomb and exchange operators have been defined thus

$$ J^{ij}_{pq} = [ij|pq], $$

$$ K^{ij}_{pq} = [ip|jq], $$

and where the second summation in equation (38) is restricted to cover only the doubly occupied MOs of $S$. The doublet state Fock operators are computed prior to entering the diagonalization phase and cause no storage problems. We will later find it convenient to define similar Fock operators for the $N$-2 states (the term $N$-2 states will be used whenever we wish to refer to a set of singlet and triplet states of the same internal occupation pattern). The formulae for the $Z$ vector may now be simplified to the form

$$ Z_a^{ST} = \sum_{\tau} \left( \sum_{j\neq i} \left( \sum_{j\neq l} B_{gka}^{ST\tau}[ji|ja] + B_{jka}^{ST\tau} F^{S}_{ia} \right) \right) C^{\tau}, $$

$$ Z^{\tau} = \sum_{\sigma} \sum_{a} \left( \sum_{j\neq l} B_{gka}^{ST\tau}[ji|ja] + B_{jka}^{ST\tau} F^{S}_{ia} \right) C_a^{\sigma}, $$

where it has been assumed that level $i$ is more occupied in $T$. Equations (41, 42) may be evaluated using either the partial matrix element driven or internal spin/external index driven schemes described above, with a cost of $(x_S + 2)\lambda(S)\lambda(T)N_E$ or $2x_S\lambda(S)N_E$ FPMOs respectively, where $x_S$ denotes the number of singly occupied MOs in $S$ and assuming (as is most probable) that level $i$ is singly occupied in $S$. The partial matrix element driven scheme is to be preferred, given a large number of singly occupied MOs coupled to high total spin, so making the number of spin couplings in $T$ low, and in this case may be improved by the pre-computation of the partial matrix elements (the above assumes that they are not pre-computed), for it then consumes only $2\lambda(S)\lambda(T)N_E$ FPMOs so that, if $\lambda(T) < x_S$, it would be the preferred method. The storage of the partial matrix elements would probably not cause excessive backing store problems in this case. Because we
estimate that the opportunities for the optimal use of partial matrix element driven scheme are not numerous given a typical case and also because the treatment of the doublet/vacuum \( ij|ka \) interaction rarely consumes more than 3 per cent of the computer time required to compute \( Z \), this scheme has not been implemented in the present work. We stress that use of the \( F^S \) operators is of some importance in the internal spin/external index driven schemes and represents a useful advance over a purely integral driven scheme [3], which can become very expensive, particularly if \( S \) has a large number of doubly occupied MOs.

The use of similar Fock operators for dealing with other interactions (see below) has an even greater practical impact.

It is important to appreciate just how rapidly the number of spin possibilities rises as a function of the number of singly occupied MOs, given by

\[
\lambda(T) = \frac{(2s + 1)x_T!}{(x_T/2 + s + 1)!(x_T/2 - s)!},
\]

where \( s \) denotes the total spin. Table 2 gives a clear numerical perspective on this aspect.

<table>
<thead>
<tr>
<th>Number of singly occupied MOs</th>
<th>Total spin degeneracy ((2s + 1))</th>
</tr>
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<tbody>
<tr>
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<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
</tr>
<tr>
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<td>14</td>
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<tr>
<td>10</td>
<td>42</td>
</tr>
<tr>
<td>12</td>
<td>132</td>
</tr>
</tbody>
</table>

\[(b) \text{ Number of singly occupied MOs odd.}\]

<table>
<thead>
<tr>
<th>Number of singly occupied MOs</th>
<th>Total spin degeneracy ((2s + 1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
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<tr>
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<td>9</td>
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<td>11</td>
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</tr>
<tr>
<td>13</td>
<td>429</td>
</tr>
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\[4.2.2. N - 2/\text{doublet interactions}\]

A given interaction block gives rise to the following contributions to the \( Z \) vector (\( T \) and \( S \) denote doublet and \( N - 2 \) states respectively)

\[
\hat{Z}^S_{ba} = \sum_{\tau} \left( \sum_{\bar{jk}}' \! B^S_{jk\beta\gamma}[ij|kb] + \sum_i B^S_{ij\beta\gamma}[ib] \right) \hat{C}^T_{a\tau} \tag{44}
\]

\[
+ P(a, b),
\]

\[
\hat{Z}^S_{ba} = \sum_{\tau} \left( \sum_{\bar{jk}}' \! B^S_{jk\beta\gamma}[ij|kb] + \sum_i B^S_{ij\beta\gamma}[ib] \right) \hat{C}^T_{a\tau} \tag{45}
\]

\[
- P(a, b),
\]

\[
Z^T_{a\tau} = \sum_{\sigma} \sum_b \left( \sum_{\bar{jk}}' \! B^S_{jk\beta\gamma}[ij|kb] + \sum_i B^S_{ij\beta\gamma}[ib] \right) \hat{C}^S_{ba} \tag{46}
\]

where \( P(a, b) \) means take that part of the equation written down explicitly and interchange \( a \) with \( b \) and where \( \hat{C}^S_{ba} \) is a symmetric matrix such that
\[ \hat{C}_{ba}^{S\tau} = \hat{C}_{ab}^{S\tau} = C_{ba}^{S\tau} \quad (b \leq a) \] (47)

and \( \hat{C}_{ba}^{S\tau} \) is a skew symmetric matrix such that
\[ \hat{C}_{ba}^{S\tau} = -\hat{C}_{ab}^{S\tau} = C_{ba}^{S\tau} \quad (b < a) \] (48)

with similar definitions for \( \hat{Z}^{S\sigma} \) and \( \hat{Z}^{S\sigma} \). Note that for equations (44–46) to be correct it is necessary to use a renormalized \( \hat{Z} \) vector, equation (7), and the \( \hat{C} \) vector in renormalization \( I \), equation (8). The \( P(a,b) \) terms of equations (44, 45) are an example of the use of the transpositional symmetry of the external pair functions to relate coupling coefficients to model space coupling coefficients.

Consider first the case that the internal occupation difference of \( S \) and \( T \) is three, and let MOs \( i \) and \( k \) be more occupied in \( T \) and level \( j \) be more occupied in \( S \). Only two categories of integral may contribute, \([ij|ka]\) and \([kj|ia]\). Indeed, if \( i = k \), only the \([ij|ia]\) integrals contribute. We consider first the partial matrix element driven scheme [7] and define
\[ H_{a}^{S\sigma T\tau} = B_{ijk}^{S\sigma T\tau} [ij|ka] + B_{ij}^{S\sigma T\tau} [kj|ia] \] (49)

and similarly for \( H_{a}^{S\sigma T\tau} \). We then find
\[ \hat{Z}_{ba}^{S\sigma} = \sum_{\tau} H_{S\sigma T\tau} (C_{T}^{\tau})^{\dagger} - \text{transpose}, \] (50)
\[ \hat{Z}_{ba}^{S\sigma} = \sum_{\tau} H_{S\sigma T\tau} (C_{T}^{\tau})^{\dagger} - \text{transpose}, \] (51)
\[ \hat{Z}_{ba}^{T\tau} = \sum_{\sigma} \hat{C}_{ba}^{S\sigma} H_{S\sigma T\tau} - \sum_{\sigma} \hat{C}_{ba}^{S\sigma} H_{S\sigma T\tau}, \] (52)

where \( \hat{Z}_{T}^{\tau} \) and \( \hat{C}_{T}^{\tau} \) are the \( \tau \)th columns of the matrices \( \hat{Z} \) and \( \hat{C} \) respectively, whilst \( H_{S\sigma T\tau} \) and \( H_{S\sigma T\tau} \) are column vectors of the \( N_{E} \) elements of \( \{H_{S\sigma T\tau}\} \) and \( \{H_{a}^{S\sigma T\tau}\} \) respectively. The total number of FPMOs consumed by the above partial matrix element scheme is given by \( 2\lambda(T)\lambda(S + \bar{S}) N_{E}^{2} \), where
\[ \lambda(S + \bar{S}) = \lambda(S) + \lambda(\bar{S}). \] (53)

The cost of computing the partial matrix elements is only linear in \( N_{E} \), so that their pre-computation does not seem worthwhile in the present context.

We now consider the evaluation of equations (44, 45) and equation (46) by means of internal spin and external index driven schemes respectively. The \([ij|ka]\) contribution will be considered explicitly and we define
\[ L^{S} = C^{T}(B^{ST})^{\dagger}, \] (54)
\[ L^{S} = C^{T}(B^{ST})^{\dagger}, \] (55)
\[ M^{S\sigma} = \hat{C}^{S\sigma} I_{jk}, \] (56)
\[ M^{S\sigma} = \hat{C}^{S\sigma} I_{jk}. \] (57)

The column vectors \( M^{S\sigma} \) and \( S^{S\sigma} \) of dimension \( N_{E} \) may be arranged into matrices \( M^{S} \) and \( M^{S} \), of dimension \( N_{E} \) by \( \lambda(S) \) and \( N_{E} \) by \( \lambda(\bar{S}) \) respectively, whilst individual columns of \( L^{S} \) and \( L^{S} \) will be denoted \( L^{S\sigma} \) and \( L^{S\sigma} \). The \([ij|ka]\) contribution to the \( Z \) vector may be written
\[ \hat{Z}_{ba}^{S\sigma} = \sum_{\tau} \left( \sum_{j \neq i} B_{ij}^{S\sigma T\tau} [ij|jb] + B_{ij}^{S\sigma T\tau} F_{ib}^{S} \right) C_{ba}^{\tau} \] (58)
\[ \hat{Z}_{ba}^{S\sigma} = \sum_{\tau} \left( \sum_{j \neq i} B_{ij}^{S\sigma T\tau} [ij|jb] + B_{ij}^{S\sigma T\tau} F_{ib}^{S} \right) C_{ba}^{\tau} \] (59)
\[ Z^{T} = M^{S} B^{ST} - M^{S} B^{ST}. \] (60)

The cost of this external spin/internal index driven scheme is \( 4\lambda(S + \bar{S}) N_{E}^{2} \) FPMOs, when allowance is made for the \([kj|ia]\) integrals, and so will prove superior to the partial matrix element scheme whenever \( \lambda(T) \) is greater than 2.

Suppose now that the internal occupation difference of \( S \) and \( T \) is unity and let internal MO \( i \) carry one more electron in \( T \). It is convenient to define a Fock operator for the \( N - 2 \) states similar to that defined for the doublet states, equation (38). The formulae for the \( Z \) vector contributions simplify to the form, noting that \( F^{S} = F^{S} \)
\[ \hat{Z}_{ba}^{S\sigma} = \sum_{\tau} \left( \sum_{j \neq i} B_{ij}^{S\sigma T\tau} [ij|jb] + B_{ij}^{S\sigma T\tau} F_{ib}^{S} \right) C_{ba}^{\tau} \] (61)
\[ \hat{Z}_{ba}^{S\sigma} = \sum_{\tau} \left( \sum_{j \neq i} B_{ij}^{S\sigma T\tau} [ij|jb] + B_{ij}^{S\sigma T\tau} F_{ib}^{S} \right) C_{ba}^{\tau} \] (62)
\[ Z^{T} = \sum_{\sigma} \left( \sum_{b} B_{ij}^{S\sigma T\tau} [ij|jb] + B_{ij}^{S\sigma T\tau} F_{ib}^{S} \right) C_{ba}^{\sigma} \] (63)

Equations (61–63) may be evaluated using either the partial matrix element driven or internal spin/external index driven schemes as described above, with a cost of \( 2\lambda(S + \bar{S})\lambda(T) N_{E}^{2} \) or \( 2\lambda(S + \bar{S}) x_{S} N_{E}^{2} \) respectively, assuming (as is most probable) that level \( i \) is singly occupied in \( S \). The partial matrix element scheme is to be preferred whenever \( \lambda(T) \) is less than \( x_{S} \), such as would occur given a large number of singly occupied orbitals coupled to high spin. To summarize, both the partial matrix element and internal spin/external index driven schemes prove useful in the treatment of the
N – 2 doublet \([ij]ka\) interactions, and both schemes have been implemented in the present work. The time consumed by this interaction often reaches 15 per cent of the total required to compute \(Z\) (see later, table 4), and is thus far from negligible.

4.3. The integrals \([ij]ab\), \([ia]jb\) and \([ab]\)

These categories of integrals give rise to a considerable number of different interactions (see table 1), so that their treatment requires a somewhat extended discussion. It has been found in the present work that the computer time required to process these integrals is often of the order of 60 per cent of the total (see later, table 4), a finding in broad agreement with the work of Siegbahn [3], so that a careful analysis is well justified.

4.3.1. Doublet/doublet interactions

A given interaction block gives rise to the following contribution to the \(Z\) vector

\[
Z^S_{a\tau} = \sum_b \left( \sum_y \left( B^S_{y\tau} [ij]ab + B^S_{y\tau} [ia]jb \right) \right) C^S_{\tau \beta} + \delta_{S\tau} \delta_{\tau \beta} \right] C^S_{\beta} \tag{64}
\]

where \(\delta_{S\tau} \delta_{\tau \beta}\) equals unity if \(S = T\) and \(\sigma = \tau\), zero otherwise.

We consider first the case that the internal occupation difference of \(S\) and \(T\) is two. Let MO \(i\) be more occupied in \(T\) and MO \(j\) be more occupied in \(S\). Equation (64) then simplifies to the form

\[
Z^S_{a\tau} = \sum_b \left( \sum_y \left( B^S_{y\tau} [ij]ab + B^S_{y\tau} [ia]jb \right) \right) C^S_{\tau \beta} \tag{65}
\]

A partial matrix element driven scheme may be generated by defining

\[
H^{S\tau}_{ab} = B^S_{y\tau} [ij]ab + B^S_{y\tau} [ia]jb \tag{66}
\]

when

\[
Z^S = \sum_{\tau} H^{S\tau} C^S \tag{67}
\]

There will also be a contribution to \(Z^T\) of the form

\[
Z^T_{\tau} = \sum_{\sigma} \left( H^{S\tau} \right)^{\sigma} C^S_{\sigma} \tag{68}
\]

The number of FPMOs required to compute \(Z^S\) by the external index or internal spin driven schemes (inclusive of the \([ij]ab\) contribution) is given by \(2\lambda(T)N_E^2\) and \(2\lambda(S)N_E^2\) respectively, so that the internal spin driven scheme is to be preferred if \(\lambda(S)\) is less than \(\lambda(T)\). There will also be a contribution to the \(Z^T\) vector, which may be derived by analogy with the above.

We note that if the internal spin driven scheme is chosen to evaluate \(Z^S\), the external index driven scheme will be chosen to evaluate \(Z^T\), and vice versa. Let \(\lambda_s\) denote the smaller of \(\lambda(S)\) and \(\lambda(T)\). Then the total number of FPMOs consumed by the internal spin/external index driven schemes to evaluate both \(Z\) vector contributions will be \(4\lambda_s N_E^2\), a factor \(\lambda_1 / \lambda_s\) (\(\lambda_1\) is the largest of \(\lambda(S)\) or \(\lambda(T)\)) less than the partial matrix element driven scheme, so that the latter is never to be preferred, even though it has been recommended by both Siegbahn [3] and Ahlrichs [7]. It is of interest to note that \(\lambda_1 / \lambda_s\) may not exceed 4 and is typically of the order 1 to 3 in practical cases.

Consider now the case that the internal occupation difference of \(S\) and \(T\) is zero (so that \(S = T\)). Equation (64) simplifies to the form

\[
Z^S_{a\tau} = \sum_b F^S_{ab} C^S_{b\tau} + \sum_{\sigma} \left( \sum_i B^S_{i\tau} [ia]jb \right) C^S_{\beta} \tag{69}
\]

where \(F^S\) has been defined in equation (38). Equation (74) may be evaluated by means of a partial matrix element scheme, with a cost of \(1/2\lambda(S)\lambda(S + 1)N_E^2\), or \(1/2(x_S + 1)\lambda(S)\lambda(S + 1)N_E^2\) FPMOs depending on whether the partial matrix elements are pre-computed or not. On the other hand, equation (74) may also be evaluated by an external index or internal spin driven scheme, at a cost of \((x_S + 1)\lambda(S)N_E^2\). Thus the partial matrix element driven scheme is to be preferred (assuming pre-computation of the partial matrix elements) given that \(1/2(\lambda(S) + 1)\) is less than \(x_S + 1\).

Given the low overall probability of the partial matrix element driven scheme being preferred, we have not implemented it in the treatment of the doublet/doublet \([ij]ab\) and \([ia]jb\) interactions.
4.3.2. $N - 2/N - 2$ interactions

It is convenient here to use the renormalized singlet Z vector (equation (7)) and the singlet C vector in renormalization I (equation (8)). A given interaction block gives rise to the following contribution to the Z vector, given that the internal occupation difference of $S$ and $T$ is two

\[ Z^\sigma = \sum_\tau (B_{ij;j}^\sigma \tau \hat{J}^\sigma \tau + B_{ij;j}^\sigma \tau \hat{K}^\sigma \tau) + \sum_\tau \hat{B}_{ij;j}^\sigma \tau \hat{K}^\sigma \tau + \text{transpose}, \tag{75} \]

\[ \hat{Z}^\sigma = \sum_\tau (B_{ij;j}^\sigma \tau \hat{J}^\sigma \tau + B_{ij;j}^\sigma \tau \hat{K}^\sigma \tau) + \sum_\tau \hat{B}_{ij;j}^\sigma \tau \hat{K}^\sigma \tau - \text{transpose}, \tag{76} \]

where MO $i$ is more occupied in $T$, MO $j$ more occupied in $S$. Naturally similar equations are used to update $\hat{Z}^Z$ and $\hat{Z}^S$. We first consider the external index driven scheme and consider the $K^\sigma$ contributions explicitly. We define

\[ \hat{L}^\tau = \hat{K}^\sigma \hat{C}^\tau, \tag{77} \]

\[ \hat{L}^\tau = \hat{K}^\sigma \hat{C}^\tau, \tag{78} \]

whence the exchange update to $Z^S$ and $Z^S$ may be evaluated by means of

\[ \hat{Z}^S = \sum_\tau \hat{B}_{ij;j}^\sigma \tau \hat{L}^\tau + \sum_\tau \hat{B}_{ij;j}^\sigma \tau \hat{L}^\tau - \text{transpose}, \tag{79} \]

\[ \hat{Z}^S = \sum_\tau \hat{B}_{ij;j}^\sigma \tau \hat{L}^\tau + \sum_\tau \hat{B}_{ij;j}^\sigma \tau \hat{L}^\tau - \text{transpose} \tag{80} \]

and will consume $\lambda(T + T)N_E^3$ FPMOs. We consider now the treatment of the exchange interaction by means of an internal spin driven method and define

\[ \hat{M}^\sigma = \sum_\tau \hat{C}^\tau + \sum_\tau \hat{C}^\tau, \tag{81} \]

\[ \hat{M}^\sigma = \sum_\tau \hat{C}^\tau + \sum_\tau \hat{C}^\tau, \tag{82} \]

when

\[ \hat{Z}^S = \hat{K}^\sigma \hat{M}^\sigma + \text{transpose}, \tag{83} \]

\[ \hat{Z}^S = \hat{K}^\sigma \hat{M}^\sigma - \text{transpose}, \tag{84} \]

which consumes $\lambda(S + S)N_E^3$ FPMOs, and hence is to be preferred if $\lambda(S + S) < \lambda(T + T)$. The Coulomb interactions in equations (75, 76) may also be dealt with by means of an external index or internal spin driven scheme, with costings of $\lambda(T + T)N_E^3$ or $\lambda(S + S)N_E^3$ FPMOs respectively, so that the internal spin driven scheme is preferred in circumstances identical to those found for the treatment of the exchange interaction. Of course, the contributions to $Z^Z$ and $Z^S$ may be evaluated by either the external index or internal spin driven schemes and, if the internal spin driven scheme is chosen to evaluate $Z^S$ and $Z^S$, the external index driven scheme will be chosen to evaluate $Z^Z$ and $Z^Z$, and vice versa. The total number of FPMOs consumed by the external index/internal spin driven schemes will be $4\lambda_N^3N_E$, where $\lambda_N$ is the smaller of $\lambda(S + S)$ and $\lambda(T + T)$, to be compared with $2\lambda(S + S)\lambda(T + T)N_E^3$ for the partial matrix element scheme which we have not felt worthy of detailed description or implementation, on the grounds that it is so rarely to be preferred.

We turn now to consider the case that the internal occupation difference of $S$ and $T$ is zero (so that $S = T$). The $Z$ vector contributions may now be shown to take the form

\[ \hat{Z}^S = F^S \hat{C}^S + \sum_{\sigma'} \sum_{\sigma'} \hat{B}_{ij;j}^\sigma \tau \hat{K}^\sigma \hat{C}^\tau + \text{transpose}, \tag{85} \]

\[ \hat{Z}^S = F^S \hat{C}^S + \sum_{\sigma'} \sum_{\sigma'} \hat{B}_{ij;j}^\sigma \tau \hat{K}^\sigma \hat{C}^\tau - \text{transpose}, \tag{86} \]

where the summation over $\sigma'$ includes both singlets and triplets. A partial matrix element scheme may be generated by defining

\[ H_{\sigma;\sigma'} = \delta_{\sigma;\sigma'}F^S + \sum_{\sigma'} \hat{B}_{ij;j}^\sigma \tau \hat{K}^\sigma \hat{C}^\tau + \text{transpose}, \tag{87} \]

so that

\[ \hat{Z}^S = \sum_{\sigma'} H_{\sigma;\sigma'} \hat{C}^\tau + \text{transpose} \tag{88} \]

and

\[ \hat{Z}^S = \sum_{\sigma'} H_{\sigma;\sigma'} \hat{C}^\tau - \text{transpose}, \tag{89} \]

where again the summations over $\sigma'$ include singlets and triplets. The number of FPMOs consumed by the above is given by $1/2\lambda(S + S)(\lambda(S + S) + 1)N_E^3$. Of course, equations (85, 86) may be evaluated by means of an external index or internal spin driven scheme, costing, in either case, $(S + 1)\lambda(S + S)N_E^3$ FPMOs. Thus the partial matrix element driven scheme is to be preferred given that $1/2\lambda(S + S) + 1$ is less than $xS + 1$.

4.3.3. $N - 2/\text{vacuum}$ interactions

It is convenient here to use the renormalized Z vector, equation (7), and the singlet C vector in renormalization II, equation (9). We define

\[ P^{(2)}_{ba} = \langle b|a \rangle + \langle a|b \rangle, \tag{90} \]

where $b \leq a$ and $i \leq j$, and

\[ Q^{(2)}_{ba} = \langle b|a \rangle - \langle a|b \rangle, \tag{91} \]
where \(i < j\) and \(b < a\). The superscript is used to indicate that the super-matrix elements carry two indices in the external space and is introduced in anticipation of further generalizations. It is convenient to denote all elements of \(P^{(2)}\) and \(Q^{(2)}\) of common \(ij\) index pair as column vectors \(P^j\) and \(Q^j\) respectively. A given interaction block gives rise to the following contribution to the \(Z\) vector, where \(S\) and \(T\) denote \(N\)-2 and vacuum states respectively

\[
Z^T = (B_{ST}^S)^\dagger (C^S)^\dagger P^j + (B_{ST}^S)^\dagger (C^S)^\dagger Q^j, \tag{92}
\]

\[
Z^S = P^j (C^T)^\dagger (B_{ST}^T)^\dagger , \tag{93}
\]

\[
Z^S = Q^j (C^T)^\dagger (B_{ST}^T)^\dagger , \tag{94}
\]

where MOs \(i\) and \(j\) each carry one more electron in \(T\) than in \(S\) (the internal occupation difference must equal two for a finite interaction). If \(i = j\), MO carries two more electrons in \(T\) and there is no triplet/vacuum interaction. The matrix elements of \(B_{ST}^S\) are given by

\[
B_{ST}^S = B_{ST}^S (\frac{1}{\Delta ij}). \tag{95}
\]

Note that we have adopted the convention that \(i \leq j\).

The evaluation of equation (92) is best carried out using an external index driven scheme, so that it is first necessary to contract \(C^S\) with \(P^j\) and \(C^S\) with \(Q^j\). However, equations (93, 94) are best evaluated by means of an internal spin driven method, involving first the contraction of \(C^T\) with spin coupling coefficients.

### 4.4. The integrals \([ia|bc]\)

These integrals only give rise to a finite interaction between \(N\)-2 and doublet states, which will be denoted \(S\) and \(T\) respectively. Again, we use the renormalized singlet \(Z\) vector, equation (7), and the singlet \(C\) vector in renormalization \(I\), equation (9). A given interaction block gives the following contributions to the \(Z\) vector

\[
Z^T = (P^j)^\dagger C^S B_{ST}^S (\frac{1}{\Delta ij}) C^S B_{ST}^S (\frac{1}{\Delta ij}) , \tag{96}
\]

\[
Z^S = P^j C^T (B_{ST}^T)^\dagger , \tag{97}
\]

\[
Z^S = Q^j C^T (B_{ST}^T)^\dagger , \tag{98}
\]

where MO \(i\) carries one more electron in \(T\) than in \(S\) (the internal occupation difference must equal unity for a finite interaction). The definition of the \(P\) and \(Q\) super-matrices (see equations (90, 91)) has been extended to include integrals with three external indices and \(P^j\), \(Q^j\) denote \(\mu_1\) by \(N_E\) and \(\mu_3\) by \(N_E\) sub blocks of \(P^{(3)}\) and \(Q^{(3)}\) respectively involving common internal MO \(i\). A slight simplification of the coupling coefficient evaluation is possible when one notes that the two body coefficients \(B_{ST}^S\) may be equated to one body coefficients \(B_{ST}^S\) and similarly for \(B_{ST}^S\).

Consider first the evaluation of equation (96) by means of an external index driven scheme, where one first the \(P^{(3)}\) and \(Q^{(3)}\) supermatrices with the \(N\)-2 CI coefficients vectors. This scheme consumes \(1/2\lambda(S)N^3_E\) and \(1/2\lambda(T)N^3_E\) FPMOs to handle the singlet/doublet and triplet/doublet interactions respectively. Equation (96) may also be evaluated by means of an internal spin driven scheme, with a cost of \(1/2\lambda(T)N^3_E\) FPMOs each for the singlet/doublet and triplet/doublet interaction. Now it is easy to show that \(\lambda(S)\) may be greater than \(\lambda(T)\) and vice versa, so that both schemes need to be implemented for the triplet/doublet interaction. We turn now to consider the evaluation of equations (97, 98) and consider the use of an internal spin driven and external index driven schemes, which will consume \(1/2\lambda(S)N^3_E\) and \(1/2\lambda(T)N^3_E\) FPMOs respectively for equation (97), so that one will always prefer the external spin driven scheme in this case, and \(1/2\lambda(S)N^3_E\) and \(1/2\lambda(T)N^3_E\) FPMOs respectively for equation (98), so that both schemes need to be implemented for this case.

### 4.5. The integrals \([ab|cd]\)

These integrals couple only singlet to singlet and triplet to triplet states. Again it is convenient to use the renormalized \(Z\) vector, equation (7), and the \(C\) vector in renormalization \(I\), equation (9). A given interaction block gives rise to the following contribution to the \(Z\) vector

\[
Z_{ba}^{S_s} = \sum_{d \leq c} P_{ba,dc}^{(4)} C_{dc}^{S_s} , \tag{99}
\]

\[
Z_{ba}^{S_a} = \sum_{d < c} P_{ba,dc}^{(4)} C_{dc}^{S_a} . \tag{100}
\]

If we arrange all the singlet \(C\) and \(Z\) vectors into matrices \(C^{(1)}\) and \(Z^{(1)}\), whose column dimensions are equal \(\mu_1\) and row dimension equal to the total number of internal spin couplings, and likewise arrange the triplet \(C\) and \(Z\) vectors into matrices \(C^{(3)}\) and \(Z^{(3)}\) (of column dimension \(\mu_3\), row dimension equal to the number of internal triplet couplings), we find that the \([ab|cd]\) contribution to the \(Z\) vector may be summarized as follows

\[
Z^{(1)} = P^{(4)} C^{(1)} , \tag{101}
\]

\[
Z^{(3)} = Q^{(4)} C^{(3)} . \tag{102}
\]

### 5. Atomic orbital integral driven procedure

Ahlrichs [7] and Werner and Reinsch [8] have shown that the contributions of the \([ia|bc]\) and \([ab|cd]\) integrals...
to the Z vector may be evaluated by means of an AO integral driven procedure, thus generalizing the method of SCEP [4, 6]. It turns out that this AO integral driven scheme requires the construction of a number of symmetric and skew symmetric exchange operators from sets of symmetric and skew symmetric matrices respectively. Therefore we first present a method for the construction of such exchange matrices which is based on the matrix multiply operation and so is exceptionally well oriented [12] to effective implementation on a vector or array processing computer.

The general exchange operator (real basis functions assumed) is defined as follows

\[
K_{p,q} = \sum_{rs} D_{r,s} [pr|qs],
\]

(103)

where D is a square matrix. Consider first the case that D and the resultant K are symmetric. We have

\[
K_{p,q} = \sum_{r \leq s} D_{r,s} (\frac{1}{2})^{|r-s|} ([pr|qs] + [ps|qr])
\]

(104)

so that if the N(N+1)/2 distinct elements of K are arranged into a column vector L

\[
L_{pq} = K_{p,q} \quad (p \leq q)
\]

(105)

and the distinct elements of D (with diagonal elements halved) are arranged into a similarly dimensioned column vector E

\[
E_{rs} = D_{r,s} (\frac{1}{2})^{|r-s|} \quad (r \leq s)
\]

(106)

then equation (104) may be rewritten

\[
L = PE,
\]

(107)

where the AO integral based P supermatrix is defined through

\[
P_{pq,rs} = [pr|qs] + [ps|qr] \quad (p \leq q, r \leq s)
\]

(108)

and is symmetric with respect to interchange of pq with rs. Notice that in the past it has been conventional to halve the diagonal elements (where pq = rs) of P and to store only those elements where pq ≤ rs. Each distinct element of P so stored then gives rise to the updating algorithm

\[
L_{pq} = L_{pq} + P_{pq,rs} E_{rs},
\]

\[
L_{rs} = L_{rs} + P_{pq,rs} E_{pq}.
\]

However, on the CRAY we find it better to use the P supermatrix exactly as defined by equation (108). The supermatrix is then stored on backing store as a sequence of \( \gamma \) by \( \gamma \) sub blocks (where \( \gamma \) is a multiple of 64, the natural vector length of the CRAY-1), the border blocks being exceptions. Only the upper triangle and diagonal of sub-blocks is stored. Denote a particular sub-block by \( P_{\mu\nu} \). Then the updating algorithm proceeds

\[
L_{\mu} = L_{\mu} + P_{\mu\nu} E_{\nu},
\]

(109 a)

\[
L_{\nu} = L_{\nu} + (P_{\mu\nu}) E_{\mu},
\]

(109 b)

for off-diagonal blocks and

\[
L_{\mu} = L_{\mu} + P_{\mu\nu} E_{\nu}
\]

(109 c)

for diagonal blocks, and where \( E_{\alpha} \) and \( L_{\mu} \) denote appropriate sub-sections of the \( E \) and \( L \) vectors.

Consider now the case that D and the resultant K matrix are skew symmetric. We then find

\[
K_{p,q} = \sum_{r<s} D_{r,s} [pr|qs] - [ps|qr]
\]

(110)

so that if we arrange the \( N(N-1)/2 \) distinct elements of K and D into column vectors L and E

\[
L_{pq} = K_{p,q} \quad (p < q),
\]

(111)

\[
E_{rs} = D_{r,s} \quad (r < s)
\]

(112)

then equation (110) may be rewritten

\[
L = QE,
\]

(113)

where the AO integral based Q supermatrix is defined through

\[
Q_{pq,rs} = [pr|qs] - [ps|qr] \quad (p < q, r < s)
\]

(114)

and is symmetric with respect to interchange of pq with rs. Thus one may process the Q supermatrix similarly to the P supermatrix.

It is now possible to recognize that the singlet and triplet Z vector contributions arising from the integrals \([ia|bc]\) and \([ab|cd]\) (equations (97–100)) amount to no more than the computation of symmetric or skew symmetric exchange matrices for singlet or triplet Z vector contributions, respectively, in an MO based \( P \) or \( Q \) supermatrix formalism. Thus we define MO based D matrices, or rather E vectors, for singlet and triplet states \( S \sigma \) and \( S^\sigma \) as follows

\[
E_{ij}^S = 0 \quad (i \leq j),
\]

(115)

\[
E_{ij}^{S^\sigma} = 0 \quad (i < j)
\]

(116)

and

\[
E_{ij}^{S^\sigma} = \sum_\tau C_{\sigma \tau}^S B_{\beta \lambda \alpha \tau},
\]

(117)

\[
E_{ij}^{S^\sigma} = \sum_\tau C_{\sigma \tau}^T B_{\beta \lambda \alpha \tau},
\]

(118)

where doublet state \( T \) carries one more electron than \( S \) in MO \( i \), and
\[ E_{ha}^{S^\sigma} = C_{ha}^{S^\sigma} \quad (b \leq a), \]  
\[ E_{ha}^{S^\sigma} = C_{ha}^{S^\sigma} \quad (b < a). \]  

We then have
\[ Z_{ia}^{S^\sigma} = K_{ia}^{S^\sigma} \quad (b \leq a), \]  
\[ Z_{ia}^{S^\sigma} = K_{ia}^{S^\sigma} \quad (b < a). \]

The doublet \( Z \) vector contributions from the\( [ia|bc] \) integrals, equation (96), may be found from
\[ Z_a^T = \sum_i \sum_{\sigma} K_{ia}^{S^\sigma} B_{iaa}^{S^\sigma T}, \]  
where the summation over \( \sigma \) should include both single- and triplets. However, for equation (123) to be correct it is necessary to cancel some spurious\([ij|ab]\) and\([ia|jb]\) contributions to the doublet \( Z \) vector which are introduced by the semi-internal matrix elements of the \( E \) vectors, equations (117, 118). This can be most neatly carried out by modifying the doublet–doublet Coulomb and exchange coupling coefficients of equation (64) as follows
\[ (B_{iaa}^{S^\sigma T})' = B_{iaa}^{S^\sigma T} - \sum_{\rho} B_{j\rho a}^{S^\sigma} B_{i\rho a}^{S^\sigma T} - \sum_{\rho} B_{j\rho a}^{S^\sigma} B_{i\rho a}^{S^\sigma T}, \]  
\[ (B_{iaa}^{S^\sigma T})' = B_{iaa}^{S^\sigma T} - \sum_{\rho} B_{j\rho a}^{S^\sigma} B_{i\rho a}^{S^\sigma T} + \sum_{\rho} B_{j\rho a}^{S^\sigma} B_{i\rho a}^{S^\sigma T}, \]  
where the occupation patterns of doublet states \( S \) and \( T \) are related as described in §4.3.1. above and where the \( N-2 \) state \( R \) carries\( n_i^T - 1 \) and\( n_j^T - 1 \) electrons in MOs \( i \) and \( j \) respectively, with all other internal occupation numbers being equal in \( S \), \( T \) and \( R \). The cancellations of equations (124, 125) should not, of course, be implemented if occupation pattern \( R \) has not been used in the construction of the CSF list.

Naturally, to implement the above (which is equivalent to the procedure of Ahlrichs [7]), it is necessary to compute the \( E \) vectors in MO form, transform to AO form and contract with the AO based \( P \) or \( Q \) supermatrices to give AO based exchange matrices, which are subsequently transformed back to MO basis for use in equations (121–123). The disadvantages of the AO based scheme are as follows:

(i) The MO based \( E \) vectors are sparse, so that we have \( E_{ij}^{S^\sigma} = 0 \) (always) and \( E_{ij}^{S^\sigma} = 0 \) if MO \( i \) is doubly occupied in \( S \). The AO based \( E \) vectors will not usually exhibit such sparsity.

(ii) The dimensionality of the MO space may be less than that of the AO space, if, for example, inner shells have been removed from the problem (equations (3, 4)) or if certain external MOs are excluded from the calculation, perhaps because they are of very high energy.

Against these disadvantages must be weighed the following advantages of the AO based scheme.

(i) For a spatially well extended system the AO integral list is very sparse. No equivalent sparsity exists in the transformed list of MO integrals, because the MOs are usually at least somewhat delocalized. For systems with relatively small numbers of electrons this consideration is likely to be of importance only for molecules composed of two or more sub-systems interacting at long range.

(ii) The complete transformation of the two-electron integrals is avoided in the AO based scheme, to be replaced by a partial transformation where integrals of the type \([ab|cd]\) and \([ia|bc]\) are not required. The cost of the complete transformation (see below) is \( 25N^3/24 \) FPMOs, assuming that the number of active MOs\( (N_A) \) is equal to the number of AOs\( (N) \). The partial transformation procedure (see below) will cost\( 3N_1N^3/8 + 35N_1^3N^3/12 - 23N_1^3N^3/12 + 7N_1^3N/12 \) FPMOs, where \( N_1 \) is the number of internal MOs (so that\( N_A = N_1 + N_E \), again assuming that\( N = N_A \).

To decide if the AO based scheme offers any advantage over the MO scheme, we make two assumptions, both favourable to the AO scheme:

(i) that \( N_A = N_1 \);  
(ii) a single closed shell reference functions is used.

We further assume that the AO list of integrals is non-sparse, this assumption being unfavourable to the AO scheme. The number of FPMOs consumed in the treatment of the\([ia|bc]\) and\([ab|cd]\) integrals in the CI phase will be approximately\( N_1N_1N_1N_1 \) (MO basis) and\( N_1^3N_1^3N_1^3 \) (AO basis), where \( N_1 \) denotes the number of diagonalization cycles. Under the assumption that\( N_1 = 6 \) (again favourable to the AO based scheme, since this corresponds to a rapidly convergent case), we may calculate the break-even point for the MO integral based scheme for various ratios \( r = N_1/N_1 \). We then find that the MO scheme is to be preferred if\( N \geq 11, 35 \) and\( 81 \) for\( r \) values of 6, 9 and 12 respectively. Thus the AO based scheme is only favoured for relatively small basis sets even in relatively high accuracy calculations\( (r = 12) \). Our conclusion is that unless the AO integral
list exhibits considerable sparsity (for example in the treatment of long range interactions or perhaps large systems) it has little to offer, except where very high accuracy calculations \( r = 12 \) are to be performed on closed shell systems, with a single reference state. In the case of open shell systems (or even multi-reference closed shell cases) the MO integral driven scheme is favoured because of the larger number of possible internal spin couplings.

6. Improved 4-index transformation method

Consider the case of a transformation of a two-electron integral list over \( N \) AOs to one over \( N_A \) MOs. The improved procedure is based on two simple ideas.

First, consider the orthodox loop structure for generating a complete non-redundant list of two-electron integrals, shown in figure 1, and compare with an improved structure, figure 2, due to Elbert [27]. The improvement arises because the third loop (whose dummy index is \( r \)) is of average length \( 2N/3 \) or \( N/3 \) in the orthodox or Elbert scheme respectively, a feature which is of little importance in say a gaussian integrals code, but may be turned to some advantage in the 4-index transformation process.

The second idea concerns a procedure for accomplishing the operations

\[
B = Q^\dagger A Q, \tag{126}
\]

where \( A \) and consequently \( B \) are symmetric and of order \( N \) by \( N \) and \( N_A \) by \( N_A \) respectively. \( Q \) is of dimension \( N \) by \( N_A \), and we assume that \( N \geq N_A \). The most straightforward procedure requires

\[
X = AQ \tag{127}
\]

at a cost of \( N_A N^2 \) FPMOs, followed by

\[
B = Q^\dagger X \tag{128}
\]

at a cost of \( N_A^2 N/2 \) FPMOs (only the distinct elements of \( B \) are computed), so that the total cost is \( N_A N^2 + N_A^2 N/2 \) FPMOs. Consider now the decomposition

\[
A = L + L^\dagger \tag{129}
\]

where

\[
L_{ij} = A_{ij}/2^{|i-j|} (i \geq j) = 0 (i < j). \tag{130}
\]

Equation (126) may be evaluated as follows

\[
Y = L Q \tag{131}
\]

at a cost of \( N_A N^2/2 \) FPMOs (allowing for the sparsity of \( L \)), followed by

\[
Z = Q^\dagger Y \tag{132}
\]

at a cost of \( N_A^2 N \) FPMOs, when \( B \) may now be evaluated using

\[
p = 1, N
\]

Executed \( N \) times

\[
q = 1, p
\]

Executed \( N^3/2 \) times

\[
r = 1, p
\]

Executed \( N^3/3 \) times

\[
s = 1, r \text{ or } 1, q \text{ if } p = r
\]

Executed \( N^4/8 \) times

Figure 1. Orthodox structure for the generation of a complete permutationally non-redundant list of two-electron integrals.

\[
p = 1, N
\]

Executed \( N \) times

\[
q = 1, p
\]

Executed \( N^3/2 \) times

\[
r = p, N
\]

Executed \( N^3/6 \) times

\[
s = 1, r \text{ or } q, r \text{ if } p = r
\]

Executed \( N^4/8 \) times

Figure 2. The structure of Elbert for the generation of a complete permutationally non-redundant list of two-electron integrals.

\[
B = Z + Z^\dagger \tag{133}
\]

at a total cost of \( N_A N^2/2 + N_A^2 N \) FPMOs, with obvious advantage if \( N > N_A \). This idea appears to have been first employed in the context of the transformation procedure by Bender [28], see also [26, 27], and in the context of the partial transformation (where an incomplete list of transformed integrals is required) by Werner and Meyer [29]. The application of equations (129–133) arises in three contexts. First consider the semi-transformation process

\[
V_{pq}^{\text{sp}} = Q^\dagger W_{pq}^{\text{sp}} Q, \tag{134}
\]

where \( Q \) is the array of MO expansion coefficients and \( W_{pq}^{\text{sp}} \) is a symmetric matrix with elements

\[
W_{pq}^{rs} = [pq][rs] \tag{135}
\]

and \( V_{pq}^{\text{sp}} \) is a matrix of semi-transformed integrals

\[
V_{ij}^{pq} = [pq][ij]. \tag{136}
\]

The utility of equations (129–133) for the evaluation of equation (134) is obvious given there are fewer MOs than AOs. A second application arises during the production of the fully transformed from the semi-transformed integrals. A third, and slightly more subtle application is possible because of the symmetry \([pq][rs] = [rs][pq]\), which we will refer to as the supermatrix symmetry, to distinguish it from the overlap distribution symmetry used in the evaluation of equation (134). Thus the transformation can be represented by
The direct CI method

\[ G = E^{1FE}, \]

(137)

where \( G \) and \( F \) are symmetric supermatrices of MO and AO integrals respectively, so that, for example

\[ F_{pq,rs} = [pq|rs](p \geq q, r \geq s) \]

(138)

and

\[ E_{pq,ij} = (Q_{pi}Q_{qj} + Q_{qi}Q_{pj})/2^{pq} \]

(139)

Equation (137) may be evaluated by means of equations (129–133), so that only the lower triangle of \( F \) will be required. Note that equations (137–139) are not used in practice, they merely serve to indicate the symmetry of the procedure. Our improved transformation procedure is shown in figure 3, where it is hoped that loop termination points may be deduced from the indentation. The loop triples enclosed in boxes in figure 3 may be implemented by means of the matrix multiply operation, although one should note that the matrices of integrals (or partially transformed integrals) are sparse because of indicial restrictions. We have adopted the convention that the innermost loop of these loop triples corresponds to the recommended direction of vectorization, allowing such sparsity to be taken advantage of. Notice that the AO integrals must be scaled

\[ G_{pqrs} = [pq|rs]/2^{pq} + \delta_{pq} + \delta_{rs}. \]

(140)

The total number of FPMOs consumed by our scheme is \( N_A N^2/8 + N_A^2 N^3/6 + N_A^2 N^2/4 + N_A^4 N/2 \), limiting to \( 25N^5/24 \) if \( N_A = N \). The best scheme previously available [27] has a cost of \( N_A N^4/2 + N_A^2 N^3/4 + N_A^3 N^2/6 + N_A^4 N/8 \) FPMOs, also limiting to \( 25N^5/24 \) if \( N_A = N \). The advantage of the present scheme is even more marked in comparison with older methods [31] still in widespread use, whose cost limits to \( 29N^5/24 \) FPMOs when \( N_A = N \). The problem of sorting the AO integral list is also somewhat reduced in the present method, as we deal only with the lower triangle of the integral supermatrix, whilst the full square is required by [27, 31]. The Bender method [28] also benefits from this feature but is unfortunately organized so that large amounts of main memory (\( \sim N^3 \)) are required, making it not viable for large cases.

The present proposals will probably prove most useful in the treatment of transition metal or second row atom containing molecules, where a large number of inner shells can be frozen, equations (3, 4), and perhaps also for very large systems where one will perform be required to omit many of the higher energy MOs on the grounds of cost.

7. Improved partial 4-index transformation method

We now consider the transformation of the two-electron integrals in the case that the \([ab|cd]\) and \([ia|bc]\) integrals are not required, because either \( N-2 \) states have been eliminated from the CI expansion, or because interactions involving these integrals have been dealt with by the AO integral driven scheme described above. We group the transformed integrals into two sub-sets.

(a) Exchange integrals, which are of the type \([bj|ai]\). The computation of these integrals takes advantage of supermatrix symmetry of the integrals.

(b) Coulomb integrals, which are of the type \([\mu\nu|jj]\), where \( \mu \) and \( \nu \) denote any active MO. Computation of these integrals takes advantage of overlap distribution symmetry of the integrals.

Our recommended scheme is shown in figures 4–6, where again loop triples enclosed in boxes are intended to be implemented through matrix multiplications, the central loop of such triples indicating the recommended direction of vectorization.

We show the first stage of the process in figure 4, which produces the quantities \( K \) and \( N \) useful for the computation of the exchange and Coulomb integrals respectively. Implementation of figure 4 requires that \( G_{pqrs} \) (equation (140)) are ordered so that for a given \( pq(p \geq q) \) all \( rs(r \geq s) \) are available. This represents an important difference from the full transformation case (figure 3) because we now need to have available the full square of the integral supermatrix, so that the problem of sorting the AO integral list is magnified. Figure 5 defines the algorithm for computing the exchange integrals.

Figure 6 defines the procedure for computing the Coulomb integrals, and requires that the \( N_{pqij} \) be ordered [32] so that for a given \( jj(j \leq i) \) all \( pq(p \geq q) \) are available.

The partial transformation algorithm defined by figures 4–6 is not optimal unless \( N_A > 3N_1 \). Under the assumption that \( N_A = N \), the cost is \( 3N_1 N^4/8 + 35N_1^2 N^3/12 - 23N_1^2 N^2/12 + 7N_1^4 N/12 \) FPMOs, which is identical to the method of Werner and Meyer [29]. However, the latter method requires that all the Coulomb and exchange operators (in the AO basis) be held in store and is thus not viable when large basis sets are used. The present algorithm may be viewed as a synthesis of the Werner and Meyer algorithm [29] with the ordering techniques of Yoshimine [32] to produce an optimal scheme useful for large basis sets.

We may note in passing that if only the exchange integrals are needed, as for example in second order many body perturbation theory [30], then the above scheme may be simplified in an obvious way so that the cost is \( N_1 N^4/4 + 5N_1^2 N^3/3 - 3N_1^2 N^2/2 + N_1^4 N/2 \) FPMOs, a considerable improvement on previously available schemes [30, 33], which cost at least \( N_1 N^4/2 \) FPMOs (leading term).
### 8. Applications

Our intention here is to present data taken from a few test calculations, to indicate:

(i) the relative cost of the 4-index transformation and diagonalization steps, with an indication of how the cost of the diagonalization step varies with the size of the configuration list;

(ii) an analysis of the relative cost of treating the various integral types within the diagonalization step, so that future attention may be focused on the more expensive of these.

<table>
<thead>
<tr>
<th>Loop structure</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p=1, N$ $q=1, p$ (See Note A)</td>
<td></td>
</tr>
<tr>
<td>$r=p, N$ $i=1, N_A$ $j=1, N_A$ $H_{pqrs} = \sum_r G_{pqrs} Q_{rj}$</td>
<td>$N_A N^3/8$</td>
</tr>
<tr>
<td>$i=1, N_A$ $j=1, i$ $I_{pqij} = I_{pqij} + I_{pqij}$</td>
<td></td>
</tr>
<tr>
<td>$i=1, N_A$ $j=1, i$ (See Note C)</td>
<td></td>
</tr>
<tr>
<td>$p=1, N$ $q=1, p$ $k=1, N_A$ $K_{pqkl} = \sum_q J_{pqkl} Q_{rj}$</td>
<td>$N_A^2 N^3/4$</td>
</tr>
<tr>
<td>$p=1, N$ $k=1, N_A$ $l=1, N_A$ $L_{ijkl} = \sum_p K_{pqkl} Q_{pi}$</td>
<td>$N_A^4 N/2$</td>
</tr>
<tr>
<td>$k=1, N_A$ $l=1, k$ $M_{ijkl} = L_{ijkl} + L_{klji}$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. Improved algorithm for the complete transformation procedure.

A. The $G_{pqrs}$ (equation (140)) are ordered [32] so that for a given $pq (p \geq q)$ all $rs$ ($r \geq s$, $rs \geq pq$) are available.

B. The average range of $r$ for which $H_{pqrs}$ is finite is $N/3$. If the orthodox looping structure for $r$ and $s$ had been chosen, see figure 1, the average range would be $2N/3$, causing degradation of the subsequent step.

C. $J_{pqij}$ are ordered [32] so that for a given $ji (j \leq i)$ all $pq (p \geq q)$ are available.

D. Implementation requires that $M_{ijkl}$ be ordered [32] so that for a given $ji$ all $lk$ ($lk \leq ji$) are available.
The details of the calculations were as follows

(i) The water dimer, \((\text{H}_2\text{O})_2\). The basis set was as described in [34], being \(\text{O}(11, 7, 1), \text{H}(6, 1)\) contracted to \(\text{O}(5, 4, 1), \text{H}(3, 1)\), cartesian \(d\) functions (6 component) being used. The molecular geometry was also as in [34], with parameters \(d(00) = 3\ \text{Å}, \ \theta = 0^\circ\), the symmetry being \(C_s\). The SCF ground state configuration was chosen as the reference function and all possible single and double excitations were included except those from 1s orbitals of the oxygen atoms and to two very high energy virtual molecular orbitals, leading to a total of 56 269 CSFs. Energy and timing data are shown in table 3, the energies being in essentially exact agreement with previous calculations [34]. Perhaps the most pertinent observation is that the AO integral driven scheme for the \([ab|cd]\) and \([ia|bc]\) integrals would have been clearly preferable in this case, since there were somewhat fewer finite integrals in the AO than the MO integral list, an outcome not surprising in view of the discussion in § 5 above. In table 4 is shown the cycle time for the diagonalizer (4.4 s) and a breakdown of the cost of treating the various integral types. The present cycle time is approximately 300 times smaller than that of the reference calculation.
Figure 5. Evaluation of the transformed exchange integrals.

A. The $K_{pqri}$ should be ordered [32] so that for a given $ri$ all $pq(p \geq q, p \geq r)$ are available.
B. The $C_{pqri}$ should be ordered [32] so that for a given $i$ and $j$ all $C_{pqri}$ and $C_{pqji}$ are available.

Table 3. Energy and timing data for the test calculations.

<table>
<thead>
<tr>
<th></th>
<th>(H$_2$O)$_2$</th>
<th>O$_3$(^1$A_1$)</th>
<th>O$_3$(^1$B_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_1$</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>$N_E$</td>
<td>58</td>
<td>54</td>
<td>53</td>
</tr>
<tr>
<td>$N_{CSF}$</td>
<td>56 269</td>
<td>31 440</td>
<td>123 393</td>
</tr>
<tr>
<td>No. of diag. cycles†</td>
<td>7</td>
<td>11</td>
<td>13</td>
</tr>
<tr>
<td>Transformation time/s</td>
<td>57</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td>Diagonalization time/s</td>
<td>31</td>
<td>26</td>
<td>144</td>
</tr>
<tr>
<td>$E_{SCF}/E_h$</td>
<td>$-152.111,66$</td>
<td>$-224.327,37$</td>
<td>$-224.396,23$</td>
</tr>
<tr>
<td>$E_{CI}/E_h$</td>
<td>$-152.521,18$</td>
<td>$-224.909,31$</td>
<td>$-224.901,17$</td>
</tr>
</tbody>
</table>

† For convergence of the CI vector to $\pm 10^{-5}$. 
(22.1 min on an IBM 360/91) [34], indicating the extreme importance of vector processing technology in this sort of calculation. Also noteworthy is the considerable expense of treatment of the $[ij]ab$ and $[ia]jb$ integrals (both integral types are included in the line marked $[ij]ab$ in table 4), nearly all of which is required for the treatment of the $N-2/N-2$ interactions. Surprising is the low cost of the treatment of the far more numerous $[ia]bc$ and $[ab]cd$ integrals. The time spent in organizing the Davidson [30, 35] diagonalization procedure is relatively high, see the line marked Other in table 4, but this is because we have not yet vectorized the calculation of the perturbation vectors. When the latter has been done, the time spent in this part of the calculation will decrease by approximately a factor of 7, thus reducing it to insignificance.

(ii) Ozone, O$_3$. The basis set was the O(10, 6) sp set of Dunning [36] contracted to [6, 4], supplemented by spherical harmonic (5 component) set of $d$ functions of exponent $1.28 a_0^{-2}$. The molecular geometry was $C_2v$, and taken from [37]. Calculations on the ground state ($^1A_1$) and first excited triplet state ($^3B_2$) were performed using single configurational Hartree–Fock reference states. In both cases the oxygen 1$s$ shells were uncorrelated and three very high energy virtual levels were omitted from the single and double excitation process, leading to a total of 31 440 and 123 393 CSFs for the $^1A_1$ and $^3B_2$ states respectively. Energy and timing data are collected in table 3, where it can be seen that the $^3B_2$ is actually the more stable at the SCF level and only marginally less stable at the CI level, indicating the inadequacy of a single reference state CI treatment of the $^1A_1$ state in particular. It is particularly noticeable that the time for the transformation step is considerably less than for the CI step for the $^3B_2$ state, in line with the discussion presented in § 5 above. We consider that the AO integral driven scheme would be clearly uncompetitive in this case. An analysis of the timing for the diagonalization step is presented in table 4, where again we note that the $[ij]ab$ and $[ia]jb$
integrals are by far the most expensive and that the $[ij]ka$ integrals assume greater importance in the $^3B_2$ case, a symptom quite characteristic of open shell cases or multi-reference treatments.

The data given in table 4 indicates that the time for a cycle of the diagonalization iteration process is very nearly linear in the size of the configuration space and indeed we have many other results which support this conclusion, at least for configuration spaces up to 200 000.

9. Conclusions and summary

We have shown that the direct CI method may be formulated so that it may be implemented through a series of matrix multiplication operations well suited to an array or vector processing computer, such that improvements in speed by more than two orders of magnitude over previous implementations on scalar computers are possible. It would appear that there is no single strategy for carrying out this type of calculation; therefore a number of techniques for handling each integral type have been presented, with rules which enable the optimal procedure to be selected. Test calculations indicate that the time required for the CI diagonalization step is linear in the size of the configuration space, indicating that spaces of the order of $10^6$ are now quite tractable. Of course, to achieve this goal it may be necessary to process the $C$ and $Z$ vectors from backing store, but given the structure herein this causes little difficulty. We have specifically excluded from consideration approximate methods within the direct CI approach, such as the use of internally [3, 4, 8] or externally [10] contracted CSFs or the first order interacting space concept [4, 8, 9].

Improved procedures for carrying out full and partial 4-index transformations of the two-electron integrals have been presented and the advantages and disadvantages of using an AO integral driven scheme for handling the $[ai]bc$ and $[ab]cd$ interactions have been discussed, with the conclusion that this method has most to offer in the treatment of long range forces, where the AO integral list may reasonably be supposed to be rather sparse.

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References


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