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Direct Formation of the CI Hamiltonian Matrix from an Expansion of Bonded Functions

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A method of forming the CI Hamiltonian matrix directly from a list of Bonded Functions and the MO-SCF wavefunction is proposed. For small expansions (circa 500 members) this method is definitely more efficient than the normal symbolic techniques and can be more efficient than iterative energy construction techniques.

Key words: Configuration interaction (CI) expansions

1. Introduction

Solution of the time independent Schrödinger equation by the expansion technique [1] has been the basis of most research in quantum chemistry for many years. The technical difficulties associated with complete sets of functions have, however, imposed quite severe restrictions on the magnitude of Configuration Interaction (CI) expansions. In most cases, the expansion has been restricted to include only single and double excitations from the ground state valence orbitals. The justification of this restriction has, itself, been the subject of much research [2] and it has been shown that a major part of the non-relativistic correlation energy [3] may be recovered by constructing, in a suitable basis, a CI expansion consisting of single and double excitations from the ground state.

The purpose of the present work is to construct small CI expansions based on MO-SCF orbitals for molecules where MO-SCF [4] wave functions are readily available. We confine ourselves to systems with a closed shell ground state, and consider an expansion containing only single and double substitutions in the ground-state function.

The Boys Bonded Function (BF) formalism [5, 6] was used to construct the expansion since Bonded Functions have the correct spin symmetry properties while retaining a certain visual simplicity. The closed shell ground state BF for an N electron system can be written [6] as:

$$B_0 = \mathscr{A}(11)\,(22)\,(33)\cdots\left(\frac{N}{2}\,\frac{N}{2}\right) \tag{1}$$

where $(kk) = \phi_k(i)\phi_k(j)(\alpha(i)\beta(j) - \alpha(j)\beta(i))/\sqrt{2}$

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$\mathscr{A}$ is the antisymmetriser and ϕ_i the set of orthonormal basis functions (e.g. MOs). It is possible to construct excited BF using the set of virtual orbitals from the SCF calculation. If the occupied MOs are denoted by a, b, c... and the virtual MOs by r, s, t...; a set of "excited" BF can be written down as:

$B_A = \mathscr{A}\ (aa)\ (bb)\ (rc)\ (dd)$...(single excitation)
$B_B = \mathscr{A}\ (aa)\ (bb)\ (rr)\ (dd)$...(pair replacement)
$B_C = \mathscr{A}\ (aa)\ (bb)\ (rs)\ (dd)$...(pair replacement)
$B_D = \mathscr{A}\ (aa)\ (bb)\ (rc)\ (sd)$...(inter pair replacement)

The BF type B_D has a partner function namely

$$B_E = \mathscr{A}\ (aa)\ (bb)\ (rd)\ (cs).$$

since there are two linearly independent functions with $S=0$ that may be constructed from the given orbital set. B_E and B_D are said to be members of the same canonical set of functions. Using BF, the total wavefunction Ψ can be written as

$$\Psi = \sum_K C_K B_K \tag{2}$$

the resulting secular problem becomes

$$\sum_K C_K (H_{KL} - E_K S_{KL}) = 0 \tag{3}$$

and the central problem of the method is the determination of the Hamiltonian ($\boldsymbol{H}$) and Overlap ($\boldsymbol{S}$) matrices, where

$$\begin{aligned} H_{KL} &= (B_K|\mathscr{H}|B_L) \\ S_{KL} &= (B_K|B_L) \end{aligned} \tag{4}$$

$\mathscr{H}$ is the N electron fixed nuclei spinless Hamiltonian operator.

Unfortunately, the BF do not form a completely orthonormal set of functions. It is found that overlap matrix elements between BF belonging to the same canonical set are non-zero. In the closed shell case this complication is quite trivial, involving only functions like B_D and B_E and the few non-zero off-diagonal overlap elements can be constructed easily (see Appendix 1).

The $\boldsymbol{H}$ matrix elements, H_{KL}, can be constructed from the general formula

$$H_{KL} = \Gamma_{KL} \sum_{pq} U_{KL}^{pq} (\Phi_p|h|\phi_q) + \sum_{pqrs} V_{KL}^{pqrs} (\phi_p \phi_q|1/r_{12}|\phi_r \Phi_s) \tag{5}$$

where the Projective Reduction Coefficients U_{KL}^{pq} and V_{KL}^{pqrs} and the integral prefactor Γ_{KL} are independent of the form of the operator (provided it is spinless). The method of deriving them is well established [6]. In the general case their determination is quite a time-consuming task. In the closed shell case, however, the small number of possible types of BF makes evaluation of the coefficients particularly straightforward (see Appendix 1). Once the $\boldsymbol{H}$ and $\boldsymbol{S}$ matrices have been computed, it only remains to solve the secular equations (3). The common Jacobi or Housholder [7] methods may be used to perform this task. However, since only a few of the roots of (3) are required, the methods of Nesbet and Shavitt [8] are more suitable.

2. Direct H Matrix Formation

There are, broadly speaking, two current methods of approaching the straightforward CI problem. The symbolic method [9], as the name suggests, constructs each element symbolically and then scans the list of MO integrals, satisfying each symbolic reference with the appropriate numerical value. The secular problem is then solved. In this approach it is the actual construction of $\boldsymbol{H}$ which is extremely time-consuming. In the iterative energy construction method [10] explicit reference to the $\boldsymbol{H}$ and $\boldsymbol{S}$ matrices is avoided by using an updating formula for the vector, expressed directly in terms of the MO integrals. Thus starting from a guess at the vector, this procedure ends up with the final vector and energy directly. However, in this case the whole integral list must be re-scanned for each iteration of the process. Each iteration of the process can be thought of as a step in an iterative procedure for solving the secular problem. For large CI problems, these methods undoubtedly offer advantages (different for each method) over the method proposed here. However, if the expansion length is restricted so that it is possible to hold an upper triangle element of the $\boldsymbol{H}$ matrix in the core storage of the computer, we believe the present method combines advantages from both the previous methods. The method outlined below directly constructs the matrix elements for the integrals, thus avoiding the need for a symbolic enumeration step, and since the matrix elements themselves are stored there is no need to re-process the integral list at every iteration in the solution of the secular problem.

The method can be summarized as follows:

1. Each BF in the expansion is categorized as belonging to one of the types B_A, B_B etc. and the substitution position and orbital number are saved.
2. A label from the list of integral labels is examined and all the matrix elements to which the associated integral will contribute are determined.
3. The prefactor by which to multiply the integral in each contribution to a matrix element is uniquely determined for a given matrix element and need not be evaluated. The multiplication is performed and the contribution to the appropriate elements accumulated.
4. Steps (2) and (3) are repeated until all the integral labels have been processed. At this stage all the elements of $\boldsymbol{H}$ will have been made up.

Some examples of precisely what is involved in steps (2) and (3) are given in Appendix 2. It will be seen from these examples that the prefactors in (3) are coded into the program at step (3) and it is this feature that makes the program really efficient.

It is assumed in the summary given above, that a complete triangle of $\boldsymbol{H}$ may be held in core, that is all elements including those that are zero. The programming at step (2) would become almost impossibly complex if a complete triangle of $\boldsymbol{H}$ were not to be stored, but it is not absolutely necessary that all of the triangle be simultaneously resident in core. However if the triangle is broken up into core-blocks, each block requires one scan of the MO-integral list and there is the additional check to see if the particular matrix element is in core or not. (Thus if there are N core blocks, the total time needed to form the $\boldsymbol{H}$ matrix is more than N times that needed if the $\boldsymbol{H}$ matrix was entirely resident in core). Table 1 shows

Table 1

Expansion Length	Triangle[a] size	Store[b] size	Number of[c] Scans at 800K
200	20,100	300K	1
400	80,200	772K	1
600	180,300	1,693K	3
800	320,400	2,645K	4
1,000	500,500	4,051K	6
2,000	2,001,000	15,617K	24

[a] Number of elements in upper triangle of H matrix

[b] Storage needed for one scan of MO integral list

[c] The number of scans is the next highest integer found by dividing the number of matrix elements available at 800K, into the total number in the triangle.

Table 2

Number of MO's in Basis set	Expansion Length	Number of two-electron integrals	CPU time[a] for H matrix (sec)
12	350	3,081	38.10
25	379	52,975	60.91
25	280	52,975	30.69
30	286	108,345	40.12

[a] IBM 360/195 computer

how the size of the BF expansion influences the amount of core storage needed (on an IBM 360/195) to form the upper-triangle of the H matrix. It also shows the number of integral scans that would be necessary for the given problem at a level of core fixed at 800K bytes.

Table 2 shows how the number of MOs and expansion length affect the time needed for H matrix formation. The first and last pairs of entries show that, as the number of two-electron integrals increases, (for a fixed expansion length) so does the time. The centre two entries show that as the expansion length increases, (for a fixed number of two electron integrals) so does the time.

It is useful to note, that paged environments do not suit this type of problem; there is no advantage in attempting to spread the H matrix over many pages of virtual memory, since the number of page changes would seriously degrade the whole machine performance. The optimum operating conditions can be obtained by making maximum use of the available core storage to hold a section of the H matrix and then rescanning the integral list as required to complete the H matrix.

The solution of the CI secular equations was found using a modified version

[11] of the Nesbet diagonalization procedure, taken from the original Polyatom CI program [12].

The resulting CI vector was then processed to produce the one particle spinless density matrix $\boldsymbol{P}_1$ according to

$$(\boldsymbol{P}_1)^{rs} = \sum_{KL} C_K C_L \Gamma_{KL}\, U_{KL}^{rs} \tag{6}$$

Where C_K and C_L are CI vector coefficients and Γ_{KL} and U_{KL}^{rs} are as in (5) and can be easily calculated (see Appendix 1).

The realization of (6) involves a sub-set of the code for construction of $\boldsymbol{H}$ and it may be made extremely efficient, since the CI vector coefficients and the resulting elements of $\boldsymbol{P}_1$ can all be held in core storage. $\boldsymbol{P}_1$ may then be processed to yield an approximate set of natural orbitals (NO's) [13] in terms of the MO's and these may then be represented in terms of the AO's by means of a simple transformation. It is therefore possible to retransform the one- and two-electron integrals over the AO's to integrals over the approximate NO's and to restart the CI calculation. This procedure is essentially the INO method [14]. Transformation of the integrals from the AO representation to the MO (or approximate NO) representation was performed using the N^5 algorithm method [15].

The complete program can be summarized thus:

1. Construct LCAO-MO-SCF wavefunction [16]
2. Transform integrals from AO to MO basis
3. Construct BF expansion
4. Evaluate upper triangle of $\boldsymbol{H}$ matrix and $\boldsymbol{S}$ matrix elements
5. Solve CI Secular equations to give coefficient vector
6. Form approximate spinless one-particle density matrix
7. Evaluate set of approximate NO's.
8. Transform NO's from BO basis to AO basis
9. If necessary, test convergence of NO's and return to step (3). The convergence test was the lowest energy solution [17].

3. Program Timings and Preliminary Results

Two small test calculations were performed using the CI program. The two molecules studied were Lithium Hydride (LiH) and Boron Hydride monomer (BH_3). The rationale behind this choice is in the small number of electrons, which permits construction of a reasonably small CI expansion.

3.1 LiH

This small molecule has been studied by many methods with varying degrees of accuracy [18]. For the present calculation, a basis set consisting of only *s*-type functions has been chosen and thus only the sigma correlation error could be studied. The basis set consisted of six functions centred on Lithium atom and three on Hydrogen [19]. The interatomic distance was chosen to be 3.00 a.u. (1 a.u. ≡ 0.0529 nm). The molecular properties are shown in Table 3.

Table 3. LiH Molecular Properties

E_{SCF}[a]	−7.9708
E_{CI}	−8.0033
E_{HF}[b]	−7.9873
E_{NR}[b]	−8.0705
$E_{HF}-E_{CI}$	0.0160
$E_{HF}-E_{NR_{tot}}$	0.0832
$E_{HF}-E_{NR_{sigma}}$	0.0541
Sigma corrln. energy	29.5%
Ionisation Potential	8.12 (6.5)[c]
Dipole moment (debye) SCF	6.22
CI	5.50
expt	5.83 (Ref. 21)

[a] Energies in a.u. (27.21 eV)

[b] Estimate of Hartree fock limit energy (HF) and non relativistic energy (E_{NR}) from Ref. 20 (a)

[c] Experimental Ionisation potential from Ref. 20 (b)

Table 4. Molecular Energy of BH_3[a]

E_{SCF}	−26.3621
E_{CI}	−26.4387
E_{HF}	−26.410
$E_{HF}-E_{CI}$	0.029
% correln. energy	20.7%

[a] Energy in a.u.

Table 5. Timings (CPU time in Sec. IBM 360/195)

	LiH	BH_3
No. of MOs	9	16
Expansion Length	113	351
Transformation Time	1.75	6.29
Expansion Generation	0.12	0.20
H matrix triangle	1.25	6.30
Secular Solution	1.18	1.90
Approx. NO formation	0.20	0.44

3.2 BH_3

There have recently been some accurate studies of the dimerization energy of this molecule [22]. The present study makes no attempt to better any previous energy result and has been presented merely for the purpose of a timing test. The uncontracted 7*s*,3*p* basis set on Boron has been contracted [23] to (4*s*,2*p*). A (2*s*) contraction is centred on each Hydrogen atom. A B–H bond length of

2.25 a.u. has been adopted. The Hydrogen atom co-ordinates have been taken as $(0, a, 0)$ $(\frac{3}{2}a, -\frac{1}{2}a, 0)$ and $(-\frac{3}{2}a, -\frac{1}{2}a, 0)$ where a is 2.25 a.u.

The energy results are shown in Table 4.

The program timings are shown in Table 5. It can be seen that the ***H*** matrix formation time is the dominant step in the calculation.

4. Summary

From the results presented in the tables, it can be seen that once the integral transformation has been performed, the time taken to construct ***H*** (in core) depends more on the expansion length rather than the basis set size. Assuming a fixed time to treat each transformed integral, it can be seen that the calculation time increases linearly with the number of integrals. However, since in the simplified case every member of the CI expansion must be examined with every other member in order to form the matrix elements, it can be expected that a square relationship between the time for the calculation and the expansion length would exist. Also, since every possible ***H*** matrix element is considered (and there is no *a priori* method of determining which are zero exactly) the time taken for the calculation is largely independent of the sparsity of the ***H*** matrix. The results show that because of this inherent problem, the method is unsuitable for molecules where many ***H*** matrix elements are zero by symmetry. In this type of molecule, considerable gains can be made using a symbolic technique, where the non-zero matrix elements may be discarded at their conception.

It can be seen that the timings are good for an expansion up to roughly 400 BF. However, beyond this number the program efficiency does fall off markedly.

The figures presented suggest that, given a reasonable transformation time, the method should be especially effective in dealing with short sub-sets of expansions chosen from a longer list, generated from a large orbital basis set. It is also clear that selecting a sub-set of BF by either perturbation theory or by the Shavitt B_K [23] method, can be efficiently handled by the present process, since the collection of matrix elements required for such calculations is easily specified and computed.

Apart from the method's intrinsic capability for small CI expansions, it is also therefore ideally suited to the formation of perturbation approximate NO's in a manner similar to that proposed by Hay [25], with perhaps a full CI performed in the last cycle of the process. This makes it an ideal method for obtaining a set of starting orbitals, relatively inexpensively, for a bigger CI calculation.

Even though it would seem extremely difficult to get the method to work anything like as efficiently for open-shell systems, because of the complexities of specifying the matrix elements required, it should still have considerable utility for a broad class of problems.

Appendix 1

The general formula for matrix elements between BF has been reported previously [6]. The closed shell restriction allows the introduction of several simplifying features.

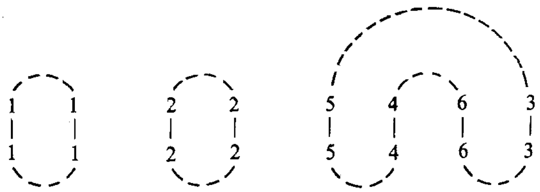
Consider the BF

$$B_K = \mathscr{A}(11)\,(22)\,53)\,(64) \tag{A1.1}$$

where the MO's (1–4) are doubly occupied and the MO's (5, 6) are virtual in the ground state. The canonical set partner to B_K is

$$B_L = \mathscr{A}(11)\,(22)\,(54)\,(36) \tag{A1.2}$$

Each BF can be represented by a sum of Slater Determinants. If there are x repetitions (i.e. identical spin-orbitals coupled) then B_K can be written as the sum of $2^{(N/2-x)}$ determinants (where N is the number of electrons). The number of determinant products which can be formed between the BF is therefore $2^{(N-(x+x'))}$. In order to find Γ, the diagrammatic method [5, 6] can be used. In the closed shell case, only cycles (i.e. closed loops) will appear, i.e.



(A1.3)

Since each cycle gives rise to two spin coupling schemes, the number of diagrams which can be constructed from $(m-x)$ cycles is $2^{(m-x)}$, where m is the total number of cycles and x the number of identical pairs in B_K which are linked to identical pairs in B_L (i.e. first two cycles in (A1.3)).

Integrating over electron spin gives rise to a contributing factor of $1/\sqrt{2}$ from each non-identical spin coupled pair. The number of spin coupled pairs in an N electron BF is $N/2$. However, x of these are repetitions (i.e. in each diagram there will be $(N-2x)$ spin coupled pairs, each contributing a factor $1/\sqrt{2}$). Thus Γ is formed from two factors

1. Number of possible diagrams 2^{m-x}
2. Product of the $(N-2x)$ spin factors of $1/\sqrt{2}$ in each diagram.

therefore

$$\Gamma = 2^{(m-x)}(1/\sqrt{2})^{N-2x} = (1/2)^{(N/2-m)}$$

If a parity is assigned to each dotted line in (A1.3) (corresponding to a spin interchange), the sign of Γ is given by $(-1)^s$ where

$$s = \sum_{i=1}^{m} \frac{N_1}{2} - 1 = \left(\frac{N}{2} - m\right) \tag{A1.4}$$

therefore

$$\Gamma = (-1/2)^{(N/2-m)}$$

(A1.4) fails to hold in the case where the BF pair has an orbital mismatch e.g.

$$\begin{aligned} B_K &= \mathscr{A}(11)\,(22)\,(63)\,(44) \\ B_L &= \mathscr{A}(11)\,(22)\,(66)\,(44) \end{aligned} \tag{A1.5}$$

In (A1.5), B_L has an identical pair (66) which does not appear in B_K. In this case, one of the $1/\sqrt{2}$ factors arising from spin integration will disappear. Generally, if there are J of these mismatched pairs then $1/\sqrt{2}$ will appear J times too often. Thus

$$\Gamma = (-1/2)^{(N/2-m)}\sqrt{2^J} \tag{A1.6}$$

(A1.6) is the general formula in the closed shell case. Since Γ accounts for the spin integration effects, the evaluation of the BF matrix elements (4) can be reduced to dealing with the spinless one-particle functions and (5) reduces to[1]

$$H_{KL} = \Gamma[\sum_i Q_i \Gamma(C_i|\hbar|C_i) + \sum_{i>j} Q_{ij}(\langle C_iC_i'|C_jC_j'\rangle + q_{ij}\langle C_iC_j'|C_jC_i'\rangle)] \tag{A1.7}$$

where Γ is evaluated by (A1.6) and C_i is the orbital in B_L corresponding to C_i in B_K.

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[1] In (A1.7) charge density notation is used for two-electron integrals.

N = Number of electrons in BF pair
M = Number of cycles
J = Number of pairs where $C_i = C_j$ and $C_i' \neq C_j'$ or *vice versa.*

Q_i = 0 if there exists a vertical pair $C_r \neq C_r'$ where $r \neq j$
Q_{ij} = 0 if there exists a vertical pair $C_r \neq C_r'$ where $r \neq i$ or $r \neq j$
q_{ij} = a code which depends upon the position of the orbital pair C_i and C_j in the cycle, but is zero if $C_i = C_j$ *or* $C_i' = C_j'$

(A1.7) may be simplified depending upon the number of non-coincident (or mismatched) pairs e.g.

1. *More than two Non-Coincident Orbitals:* both H_{KL} and S_{KL} disappear.
2. *Two Non-Coincident Orbitals:*

$$H_{KL} = \Gamma Q_{ij}[\langle C_i C_i' | C_j C_j' \rangle + q_{ij} \langle C_i C_i' | C_j C_j' \rangle]$$
$$S_{KL} = 0$$

3. *One Non-Coincident Orbital:*

$$H_{KL} = \Gamma[\langle C_i | \hbar | C_i' \rangle + \sum_j Q_{ij} (\langle C_i C_i' | C_j C_j' \rangle + q_{ij} \langle C_i C_j' | C_j C_i' \rangle)]$$
$$S_{KL} = 0$$

4. *Zero Non-Coincident Orbitals:*

H_{KL} takes the form (A1.7)

$$S_{KL} = \Gamma$$

It is now possible to explain the overlap term between the canonical set pair (A1.1) and (A1.2). It can be seen that the cycle pattern (A1.3) gives $\Gamma = -0.5$ ($N = 8$, $M = 3$, $J = 0$). Also, it follows from (4) that there can only be a non zero overlap term when the orbitals composing the BF pair are identical. Thus, diagonal overlap elements have $S_{ii} = 1.0$ and the only occurrence of an off-diagonal S_{ij} is between canonical set members, where the value of S_{ij} must, by necessity, be -0.5, otherwise, the BF form an orthonormal set of functions.

The factor q_{ij} may assume one of three possible values, depending upon the cycle structure. A parity is associated with each vertical line in a cycle (by convention, the first has parity +1) and alternates. The values of q_{ij} are shown in Table 6.

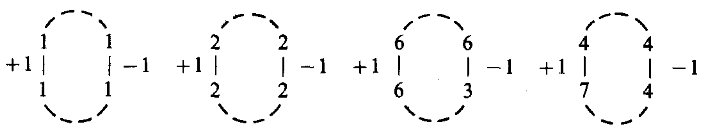
Table 6. q_{ij} values (closed shell only)

PARITY	CYCLE	q_{ij}
−1 +1	DIFFERENT	$-\frac{1}{2}$
−1 +1	SAME	+1 −2

Example 1

$$B_K = \mathscr{A}\,(11)\,(22)\,(66)\,(44)$$
$$B_L = \mathscr{A}\,(11)\,(22)\,(63)\,(74)$$

Linkage Pattern



Non-Coincident Orbitals are (6, 3) and (4, 7)

$$Q_1 = 0 \text{ (i.e. No one-electron contributions)}$$
$$\Gamma = 2 \quad (N=8,\ M=4,\ J=2)$$

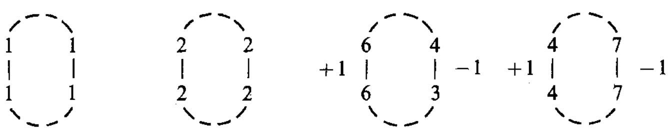
The non-coincidences are in different cycles, therefore q_{ij} can only be $-\frac{1}{2}$.

$$S_{KL} = 0$$
$$H_{KL} = 2\ [(74|63) - \tfrac{1}{2}(76|43)]$$

Example 2

$$B_K = A(11)\ (22)\ (67)\ (44)$$
$$B_L = A(11)\ (22)\ (63)\ (74)$$

Linkage pattern



One Non-coincidence (4, 3)

$$\Gamma = -\sqrt{2}/2\ (N=8,\ M=3,\ J=1)$$

There may be only one one-electron integral, (4|3). Using Table 6, the q_{ij} values for the various integrals are:

$(41|31)$ and $(42|32)$; $q_{ij} = -\frac{1}{2}$ (different cycle)
$(64|63)$ $q_{ij} = +1$ (same cycle; Parity -1)
$(74|63)$ $= -2$ (same cycle; Parity $+1$)

N.B. (44|43) has no contribution from q_{ij} since $C_i = C_j$ and hence q_{ij} is zero.

Appendix 2

Since the number of BF types has been restricted to B_A, B_B, B_C, B_D and B_E, it is possible to enumerate all the possible matrix element types which may receive a contribution from a particular type of MO integral.

In this appendix, only two of the cases will be mentioned; however, every integral type may be similarly treated.

Considering, initially, the one-electron integral type (II) (i.e. both indices the same), this integral type can be further classified according to whether *I* is one of the occupied MOs or virtual MOs in the ground state.

(*a*) *I is an occupied* MO *label*

This integral type may only contribute to BF matrix elements where there are no noncoincidences. If the root function is $B_0 = A(11)\ (22)\ (33)\ (44)$, then the matrix element $(B_0|H|B_0)$ has contributions from the one-electron integrals (11), (22) etc. up to (44), since $\Gamma = 1.0$ the contribution to the matrix element from each of these integrals is 2.0 times the value of the integral. Other candidates for contributions are:

$$(B_A|\mathscr{H}|B_A) \qquad \mathscr{A}(11)\ (62)\ (33)\ (44) \qquad \text{(A2.1)}$$
$$\mathscr{A}(11)\ (62)\ (33)\ (44)$$

Since Γ is 1.0, and if *I* is the position of the substituted orbital then the contribution factor of the integral is 1.0, otherwise it is 2.0.

(In the program, the integral (22), when found is directed into a section of the programme where the list of single excitation BF are scanned. If the excited orbital has replaced the orbital in position "2", then the integral value times 1.0 is added into the diagonal H matrix element (N.B. no-noncoincidences) belonging to the BF; otherwise, the integral value times 2.0 is added to the H matrix element).

Another candidate for a contribution is the diagonal element between two B type BF *viz.*:

$$(B_B|\mathcal{H}|B_B) \qquad \begin{matrix} \mathscr{A}\,(11)\,(22)\,(66)\,(44) \\ \mathscr{A}\,(11)\,(22)\,(66)\,(44) \end{matrix} \tag{A2.2}$$

If I is the position of the substituted orbitals, then the integral (II) does not contribute to the matrix element; otherwise, the contribution factor is 2.0

(*b*) *I an excited orbital*

The pattern closely resembles (a). Considering (A2.1), it can be seen that the integral (66) will make a contribution of 1.0 to the matrix element, all others will not contribute. Also, in (A2.2), the only integral of this type to contribute is (66) with a multiplying factor of 2.0.

Considering the two-electron integrals, the simplest case is when all the indices are identical, i.e. $(IIII)$. It can be seen that the integral can also be further classified according to the nature of the orbital I. When I is an excited orbital label, only one BF type pair may receive a contribution. (A2.2) is an example of this type; the integral (6666) makes a contribution, with a factor 1.0, to this matrix element. It is found that the contribution patterns of some of the more complicated integral types (e.g. $(IJKL)$, where I and K are excited and J and L root function orbitals) are considerably more involved than these simple examples.

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