Theoret. Chim. Acta (Berl.) 43, 197-205 (1976)

THEORETICA CHIMICA ACTA

On the Configuration Interaction Method for Singlet States

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The direct CI method, which avoids explicit calculation of the Hamiltonian matrix, is presented in a new form. The method is linked with Davidson's algorithm for "iterative evaluation" of the ground state eigenvector. The viability of the method is indicated by the test calculations on water which are described.

Key words: Singlet states, CI method for ~

1. Introduction

A major difficulty encountered in large-scale configuration interaction (CI) calculations has been the construction and storage of the Hamiltonian matrix. An approach which bypasses this problem has been proposed and implemented by Roos [1]. The method is applicable to a singlet CI expansion which is a closed shell determinant together with all single and double excitations to a chosen set of virtual orbitals. In essence the method involves the direct computation, from one- and two-electron integrals, of the vector $\boldsymbol{Hc}$, where $\boldsymbol{H}$ is the CI matrix and $\boldsymbol{c}$ some approximation to an eigenfunction of $\boldsymbol{H}$. This quantity $\boldsymbol{Hc}$ which is required at some stage in the iterative methods currently used to obtain eigenfunction of very large matrices [2, 3] is evaluated using $\boldsymbol{c}$, the one- and two-electron integrals, and various coupling constants. The coupling constants, which are the elements of a set of 5 by 5 matrices, may be derived by consideration of the different types of matrix element which can occur. They are tedious to calculate [4] and some errors are present in those published by Roos [1]. Roos divides the excitation functions into six classes, namely

$$\{\psi_i^m\};\ \{\psi_{ii}^{mm}\},\ \{\psi_{ii}^{mn}\},\ \{\psi_{ij}^{mm}\},\ \{\psi_{ij}^{mn}\} \text{ and } \{\psi_{ij}'^{mn}\}.$$

Where for example $\{\psi_i^m\}$ denotes the set of singlet functions obtained by promoting an electron from an occupied orbital - denoted by i - to a virtual orbital denoted by m. For double excitations, in the spin coupling scheme used by Roos, we have singlet functions constructed from determinants in which two electrons with different spins are excited - leading to sets two to five, and singlet functions which also include determinants where two electrons of the same spin are excited, which gives the last set $\{\psi_{ij}'^{mn}\}$. It is the occurrence of these five different classes of double excitation functions which leads to the five by five matrices. It is the purpose of this paper to show

how the first type of double excitation function, sets two to five, may be treated as a single set, so that the problem then reduces to a consideration of only three sets of functions with corresponding simplifications in the implementation of the method. The direct CI method is attractive and likely to be widely used because in addition to making very large calculations feasible the computational effort involved is not much larger than that required for an SCF calculation.

2. The CI Expansion and Energy Expression

Let ψ_0 be a single determinant of doubly occupied orbitals. Let the set of orbitals occupied in ψ_0 be S_0 and individual members of S_0 be denoted by letters i, j, k, and l. Further let S_v be a set of virtual orbitals to which excitations can be made. We shall denote particular members of S_v by m, n, p and q. It is assumed that the composite set of orbitals is orthonormal. We define our singly and doubly excited functions using the particle hole formalism of second quantization [5]. The operators refer to ψ_0 as a vacuum state. Thus $b_i^\dagger$ is the creation operator for a hole in orbital i (annihilation of electron in orbital i). We shall use the operators which refer to spin orbital occupations, thus $b_{\bar{i}}^\dagger$ creates a hole in orbital i with β spin; $b_i^\dagger$ the same but with α spin, $b_n^\dagger$ creates an electron in orbital n with α spin; $n \in S_v$.

The single and double excitation functions are defined as

$$\psi_i^m = (1/\sqrt{2})(b_m^\dagger b_i^\dagger + b_{\bar{m}}^\dagger b_{\bar{i}}^\dagger)\psi_0 \tag{1}$$

$$\psi_{ij}^{mn} = (\tfrac{1}{4})(b_n^\dagger b_j^\dagger b_{\bar{m}}^\dagger b_{\bar{i}}^\dagger + b_{\bar{n}}^\dagger b_{\bar{j}}^\dagger b_m^\dagger b_i^\dagger + b_m^\dagger b_j^\dagger b_{\bar{n}}^\dagger b_{\bar{i}}^\dagger + b_{\bar{m}}^\dagger b_{\bar{j}}^\dagger b_n^\dagger b_i^\dagger)\psi_0 \tag{2}$$

$$\begin{aligned}\chi_{ij}^{mn} = (\tfrac{1}{2}\sqrt{12})(2b_n^\dagger b_j^\dagger b_m^\dagger b_i^\dagger + 2b_{\bar{n}}^\dagger b_{\bar{j}}^\dagger b_{\bar{m}}^\dagger b_{\bar{i}}^\dagger + b_n^\dagger b_j^\dagger b_{\bar{m}}^\dagger b_{\bar{i}}^\dagger \\ + b_{\bar{n}}^\dagger b_{\bar{j}}^\dagger b_m^\dagger b_i^\dagger - b_m^\dagger b_j^\dagger b_{\bar{n}}^\dagger b_{\bar{i}}^\dagger - b_{\bar{m}}^\dagger b_{\bar{j}}^\dagger b_n^\dagger b_i^\dagger)\psi_0\end{aligned} \tag{3}$$

and the CI expansion as

$$\psi = c_0\psi_0 + c_i^m\psi_i^m + c_{ij}^{mn}\psi_{ij}^{mn} + d_{ij}^{mn}\chi_{ij}^{mn}, \tag{4}$$

where a repeated index implies a summation. Thus

$$c_i^m\psi_i^m \equiv \sum_{\substack{i\in S_0\\ m\in S_v}} c_i^m\psi_i^m.$$

The c's and d's are the CI expansion coefficients. From the definitions (2) and (3) it is apparent that the c_{ij}^{mn} and d_{ij}^{mn} are not uniquely defined because

$$\psi_{ij}^{mn} = \psi_{ji}^{mn} = \psi_{ij}^{nm} = \psi_{ji}^{nm} \tag{5}$$

and

$$\chi_{ij}^{mn} = -\chi_{ji}^{mn} = -\chi_{ij}^{nm} = \chi_{ji}^{nm} \tag{6}$$

The expansion (4) is not in terms of a linearly independent set. In a conventional expansion only one of the forms in (5) (or (6)) would be used in the expansion and it would occur with a coefficient equivalent to $(c_{ij}^{mn} + c_{ij}^{nm} + c_{ji}^{mn} + c_{ji}^{nm})(i \neq j; m \neq n)$ etc. It is this quantity which is uniquely determined when the secular equations are solved. The expansion (4) is more convenient for our purpose because the summations are unrestricted The overlap term $\langle \psi | \psi \rangle$ is readily evaluated.

$$\begin{aligned}\langle \psi | \psi \rangle = c_0^2 + c_i^m c_i^m + (\tfrac{1}{4}) c_{ij}^{mn}(c_{ij}^{mn} + c_{ji}^{mn} + c_{ij}^{nm} + c_{ji}^{nm}) \\ + (\tfrac{1}{4}) d_{ij}^{mn}(d_{ij}^{mn} - d_{ji}^{mn} - d_{ij}^{nm} + d_{ji}^{nm})\end{aligned} \tag{7}$$

Returning to the definitions (2) and (3) we note that if $i \neq j$ and $m \neq n$ then:

$$\langle \psi_{ii}^{mm} | \psi_{ii}^{mm} \rangle = 1, \tag{8}$$

$$\langle \psi_{ii}^{mn} | \psi_{ii}^{mn} \rangle = \langle \psi_{ij}^{mm} | \psi_{ij}^{mm} \rangle = \tfrac{1}{2}, \tag{9}$$

$$\langle \psi_{ij}^{mn} | \psi_{ij}^{mn} \rangle = \langle \chi_{ij}^{mn} | \chi_{ij}^{mn} \rangle = \tfrac{1}{4} \tag{10}$$

so that the functions $\psi_{ii}^{mm}, \sqrt{2}\psi_{ii}^{mn}; \sqrt{2}\psi_{ij}^{mm}; 2\psi_{ij}^{mn}$ and $2\chi_{ij}^{mn}$ are normalized to unity.

It is seen that the expression (7) correctly includes the terms when $i = j$ or $m = n$.

Finally we note that (6) implies

$$\chi_{ii}^{mn} = \chi_{ij}^{mm} = \chi_{ii}^{mm} = 0 \tag{11}$$

and that (7) correctly excludes terms arising from the coefficients of such functions.

The usual method for solving an equation of the form

$$\mathscr{H}\Psi = E\Psi \tag{12}$$

using an expansion in an orthonormal basis $\Phi = (\phi_1 \ldots \phi_n)$ leads, via the variation principle, to the secular equation

$$\boldsymbol{Ha} = E\boldsymbol{a} \tag{13}$$

where the matrix $\boldsymbol{H}$ and the column vector $\boldsymbol{a}$ are representations of $\mathscr{H}$ and Ψ in the basis Φ. (13) is derived via the relation

$$\langle \Psi | \Psi \rangle = \boldsymbol{a}^\dagger \boldsymbol{a} \tag{14}$$

which results from the orthonormality of the basis Φ.

As indicated earlier our expansion (4) contains linearly dependent terms which lead to cross terms appearing in the overlap expression which is our equivalent of (14). However it is only the quantities $c_0, c_i^m, (c_{ij}^{mn} + c_{ij}^{nm} + c_{ji}^{mn} + c_{ji}^{nm})$ and $(d_{ij}^{mn} - d_{ji}^{mn} - d_{ij}^{nm} + d_{ji}^{mn})$ which we seek to obtain. We are therefore free to impose relationships between the c_{ij}^{mn} (and d_{ij}^{mn}) belonging to the same i, j, m and n.

A natural choice is

$$c_{ij}^{mn} = c_{ji}^{mn} = c_{ij}^{nm} = c_{ji}^{nm} \tag{15}$$

$$d_{ij}^{mn} = -d_{ji}^{mn} = -d_{ij}^{nm} = d_{ji}^{nm} \tag{16}$$

in that (7) reduces to

$$\langle\psi|\psi\rangle = c_0^2 + c_i^m c_i^m + c_{ij}^{mn} c_{ij}^{mn} + d_{ij}^{mn} d_{ij}^{mn} \tag{17}$$

which is of the same form as (14). Further (16) supports the condition (11).

The CI problem using the expansion (4) and conditions (15) and (16) is thus equivalent to solving (13) where H is now the matrix of $\mathscr{H}$ over *all* the functions in (4) and a is the vector containing *all* the coefficients occurring in (4). For the remainder of the paper we take $\boldsymbol{H}$ and $\boldsymbol{a}$ to be these quantities. We now wish to indicate expressions for the matrix elements of H and to indicate how the quantities Ha can be evaluated directly and conveniently from the integral lists.

The energy expectation value $\langle\psi|\mathscr{H}|\psi\rangle$ is most conveniently evaluated using the methods of second quantization. In particular the operator $(\mathscr{H} - E_0)$, where $E_0 = \langle\psi_0|\mathscr{H}|\psi_0\rangle$, can be represented in a normal product form [5] in which, along with the usual electron repulsion operator $g(i,j) = 1/r_{ij}$, there occurs the Fock-like one-electron operator h^{F} with matrix elements

$$\langle r|h^{\mathrm{F}}|s\rangle = \langle r|h|s\rangle + 2\sum_{i\in S_0} (\langle ri|g|si\rangle - \tfrac{1}{2}\langle ri|g|is\rangle) \tag{18}$$

The standard procedure is then to express the matrix element corresponding to the energy relative to E_0 as a sum of products of normal products and to use the generalized Wick Theorem to evaluate the matrix elements. The operations involved, though individually simple, are somewhat numerous and it was found expedient to program the technique. This had the added advantage that the resulting expressions, which involve a large number of terms, could be automatically sorted and classified.

As is to be expected from (7) the expression for $(E - E_0)$ involves coefficients occurring as sums of the possible permutations of the indices. These may be simplified using Eqs. (15) and (16). We have also included the condition that the coefficients and orbitals be real. We obtain,

$$(E - E_0) = E_1 + E_2 \tag{19}$$

where

$$\begin{aligned}\tfrac{1}{2}E_1 = {} & \langle n|h^{\mathrm{F}}|m\rangle(\tfrac{1}{2}c_i^n c_i^m + c_{ji}^{np} c_{ji}^{mp} + d_{ji}^{np} d_{ji}^{mp})\\ & - \langle j|h^{\mathrm{F}}|i\rangle(\tfrac{1}{2}c_i^n c_j^n + c_{ik}^{nm} c_{jk}^{nm} + d_{ki}^{nm} d_{kj}^{nm})\\ & + \langle m|h^{\mathrm{F}}|i\rangle(\sqrt{2}c_0 c_i^m + \sqrt{2}c_{ji}^{nm} c_j^n + \sqrt{6}d_{ji}^{nm} c_j^n)\end{aligned} \tag{20}$$

and

$$\begin{aligned}E_2 = {} & \langle qp|g|nm\rangle(c_{ji}^{qp} c_{ji}^{nm} + d_{ji}^{qp} d_{ji}^{nm}) + \langle ji|g|lk\rangle(c_{ji}^{nm} c_{lk}^{nm} + d_{ji}^{nm} d_{lk}^{nm})\\ & + \langle nj|g|im\rangle(2c_i^n c_j^m + 2c_{ik}^{np} c_{jk}^{mp} + 6d_{ik}^{np} d_{jk}^{mp} - 4\sqrt{3}c_{ki}^{np} d_{kj}^{mp}\\ & + 2c_0 c_{ji}^{mn} + \sqrt{12}c_0 d_{ji}^{mn})\\ & - \langle jn|g|im\rangle(c_i^n c_j^m + 4c_{ik}^{np} c_{jk}^{mp} + 4d_{ik}^{np} d_{jk}^{mp}) + \langle pn|g|mi\rangle\\ & \times(2\sqrt{2}c_{ji}^{pn} c_j^m + 2\sqrt{6}d_{ji}^{pn} c_j^m) + \langle mk|g|ji\rangle(-2\sqrt{2}c_{ji}^{nm} c_k^n + 2\sqrt{6}d_{ji}^{nm} c_k^n)\end{aligned} \tag{21}$$

Eqs. (20) and (21) are not unique expressions, E_1 and E_2 may be written in many different ways using (15) and (16). Because the energy may be written in the form

$$(E - E_0) = a^{\dagger}Ha - E_0 \tag{22}$$

(20) and (21) lead directly to the elements of H. A particular element of H being the factor associated with the pair of appropriate CI coefficients. This is not strictly correct, for example from E_1 the factor associated with $c_{ji}^{np}c_{ji}^{np}$ is $2\{\langle n|h^{\mathrm{F}}|n\rangle - \langle j|h^{\mathrm{F}}|j\rangle\}$, so that apparently $\langle \psi_{ji}^{np}|\mathscr{H}|\psi_{ji}^{np}\rangle \neq \langle \psi_{ij}^{pn}|\mathscr{H}|\psi_{ij}^{pn}\rangle$.

This lack of correct symmetry stems from the way in which the energy expression has been simplified. This defect can be remedied in two ways. Either the expressions (20) and (21) can be expanded using (15) and (16) until they have the correct symmetry, or, matrix elements can be taken as being equal to the appropriate average of the matrix element values obtained from (20) and (21) for those matrix elements which are related as a consequence of (5) and (6). The former method is more elegant, the latter more convenient computationally. In the next section we consider the solution of the secular equations.

3. Solving the Secular Problem

The lowest eigenvalue and eigenfunction of large CI matrices have most frequently been obtained using Nesbet's method or one of its modifications [2]. These methods require the rows of the Hamiltonian matrix to be used one at a time in order to successively improve one by one the components of the approximate eigenfunction. If an attempt is made to simultaneously update all components the methods frequently fail to converge and often diverge [3]. The matrix element expressions contained in (20) and (21) are most suitable for the computation of contributions to the matrix elements in the order generated by considering each two-electron integral in turn. The two-electron integrals themselves are kept in backing store. We therefore require a method of solving the secular equations which does not depend upon access to the matrix elements in some particular order. Roos [1] presented a method, based upon higher orders of perturbation theory, and indicates that convergence can usually be obtained in 10 iterations.

More recent calculations by Roos and co-workers have used a "nonlinear variation-perturbation" method developed by Brädas and Goscinsky [9]. In this method the successive perturbation expansion functions are evaluated, and are then used variationally to obtain the eigenfunction for the CI problem by solution of a small-order secular problem. This variation-perturbation method gives faster convergence than the original scheme used by Roos. More recently Davidson [3] has given another algorithm which has some similarities to the method of Brädas and Goscinsky. The method involves a compromise between repeated evaluation of a first-order correction to a trial eigenfunction and a Lanczos method. Thus, like the method of Brädas and Goscinsky, the method is variational in that a small-order secular equation in the correction functions is solved. Unlike the Brädas and Goscinsky method the successive correction functions are determined as a first-order perturbation term, rather than using the higher order terms of the Rayleigh-Schrödinger perturbation theory. The Davidson method allows the evaluation of higher roots without necessarily determining the lower root first. We have used the Davidson method in order to solve the CI secular problem. The Davidson method involves as a basic step the evaluation of vectors $\boldsymbol{Hb}^i$ where b^i is a vector obtained during the ith iteration. Since evaluating $\boldsymbol{Hb}^i$ does not depend upon access to the elements of $\boldsymbol{H}$ in any particular order if the vector $\boldsymbol{b}^i$ can be accessed randomly the method is ideal for our purpose. In order to aid discussion of our implementation of the CI calculation we now indicate briefly the steps in the Davidson algorithm when used for the lowest root.

(1) Select a normalized vector $\boldsymbol{b}^1$ as an approximation to the desired eigenfunction. Form $\boldsymbol{Hb}^1$ and $\lambda = \boldsymbol{b}^1 \cdot \boldsymbol{Hb}^1$; Store $\boldsymbol{b}^1$ and $\boldsymbol{Hb}^1$ (on disk); set $\alpha_1 = 1.0, M = 1$ and $A_{11} = \lambda$.

(2) Form $\boldsymbol{q} = \Sigma_{i=1}^{\mathrm{M}} (\alpha_i \boldsymbol{Hb}^i - \lambda\alpha_i \boldsymbol{b}^i)$.

(3) Form $\|\boldsymbol{q}\|$. If $\|\boldsymbol{q}\|$ is sufficiently small the method has converged. We found $\|\boldsymbol{q}\| \simeq 10^{-4}$ indicated the correlation energy converged to about 8 significant places.

(4) Form $\boldsymbol{p}$ with elements $p_i = q_i/(\lambda - H_{ii})$.

(5) Orthogonalize $\boldsymbol{p}$ to the vectors $b^i (i = 1, M)$ by application of the Schmidt process

$$p \to p - b^i(b^i \cdot p), \quad i = 1 \ldots M.$$

(6) Normalize the resulting $\boldsymbol{p}$ vector which is to be $\boldsymbol{b}^{M+1}$. Form $\boldsymbol{Hb}^{M+1}$, store $\boldsymbol{b}^{M+1}$ and $\boldsymbol{Hb}^{M+1}$, set M to $M + 1$. Form a new border to the matrix A

$$A_{iM} = A_{Mi} = b^i \cdot (Hb^M), \quad i = 1 \text{ to } M.$$

(7) Diagonalize the M by M matrix A, set λ to the lowest root; set α_i $(i = 1, M)$ equal to the components of the lowest eigenvector. (When required, i.e. at convergence, the eigenvector of $\boldsymbol{H}$ is $\Sigma_{i=1}^{M} \alpha_i b^i$, λ is the eigenvalue.) Go to step (2).

The problem is to calculate $\boldsymbol{Hb}^i$, where $\boldsymbol{b}^i$ represents a set of values for the coefficients c_0, c_i^m, c_{ij}^{mn} and d_{ij}^{mn}. The vector $\boldsymbol{b}^i$ and matrix $\boldsymbol{h}^{\mathrm{F}}$ are kept in core. Space is also allocated in core to accumulate the vector $\boldsymbol{Hb}^i$ as it is formed. The two-electron integrals, which if ψ_0 is the SCF determinant are integrals in the SCF-MO basis, are kept on backing store sorted into the six classes which occur in (21), each class being processed separately.

If a term $b_\alpha^i y b_\beta^i$ occurs in the energy expression it may be regarded as representing the two contributions $\frac{1}{2} b_\alpha^i y b_\beta^i$, $\frac{1}{2} b_\beta^i y b_\alpha^i$ to the energy $\boldsymbol{b}^i \boldsymbol{Hb}^i$. The corresponding contributions to $(\boldsymbol{Hb}^i)_\alpha$ and $(\boldsymbol{Hb}^i)_\beta$ are then respectively $\frac{1}{2} y b_\beta^i$ and $\frac{1}{2} y b_\alpha^i$. The method of building up $\boldsymbol{Hb}^i$ is thus to consider each element of $\boldsymbol{h}^{\mathrm{F}}$ and each two-electron integral in turn and to obtain the contributions to $\boldsymbol{Hb}^i$ by multiplication by the appropriate constants and b_α^i, proper regard being paid to implicit summations and to the permutation symmetry of the two-electron integrals. The final vector $\boldsymbol{Hb}^i$ will not possess the correct symmetry, and this is corrected by averaging, e.g. if $\boldsymbol{b}^i$ does not fulfil conditions (15) and (16) then replace each

$$c_{ij}^{mn} \quad \text{by } (\tfrac{1}{4})(c_{ij}^{mn} + c_{ji}^{mn} + c_{ij}^{nm} + c_{ji}^{nm})$$

and each

$$d_{ij}^{mn} \quad \text{by } (\tfrac{1}{4})(d_{ij}^{mn} - d_{ji}^{mn} - d_{ij}^{nm} + d_{ji}^{nm}).$$

Hb^i can be similarly dealt with. The diagonal elements of H, required in step (4) of Davidson's algorithm may be calculated in a manner similar to that outlined above.

The core requirements, for both the Davidson algorithm and the calculation of the Hb^i, are limited to twice the core storage needed for the vector b^i. In this implementation of the method we store all the coefficients, although in principle it is only necessary to keep a unique set. Thus in our trial calculation on H_2O with five occupied and fifteen virtual orbitals a total of 190 K bytes was required for storage of the vectors. If unique coefficients alone were stored only some 50 K would be required.

4. Trial Calculations

In order to assess the viability of the approach we have carried out a number of small calculations on the water molecule using a basis set of 20 contracted Gaussian orbitals [6]. The standard geometry $R_{OH} = 1.811$ Bohr and $\theta = 104.45°$ was used.

Results were obtained, using 10, 13 and 15 of the virtual SCF-MO's, in order to assess how the iteration time and speed of convergence varied with the number of configurations.

In Table 1 we give details of timings whilst in Table 2 we indicate the performance of the Davidson algorithm. The CI iteration time is seen to be comparable with the total SCF time, and to increase in an approximately linear manner with respect to the number of configurations. The iteration times are particularly encouraging as no serious attempt has yet been made to optimize the program. The number of configurations quoted exaggerates slightly the size of the problem in that configurations which were not of A_1 symmetry were not excluded. In fact for 15 virtual orbitals and our basis set there are 2345 functions of A_1 symmetry. For the Roos method [1] as

Table 1. Details of water calculations using [11*s*, 3*p*] basis

AO Integral Calculation[b] Time (sec)[a]		7.9	
SCF Calculation Time[b] (sec)		6.1	
MO Integral Transformation[b] Time (sec)		9.1	
Number of Virtual Orbitals Used	10	13	15
Number of Distinct Configurations[c]	1276	2211	2926
Number of Coefficients	5051	8516	11326
Time per Iteration (sec)	3	5	8
Number of Iterations for Convergence of $(E - E_0)$ to Six Significant Figures	5	5	5

[a] Times refer to cpu time on 360/195.

[b] Using the ATMOL series of programs as implemented by the Atlas Computer Laboratory, Chilton, Didcot, U.K.

[c] Spacial symmetry has not been used in order to reduce the number of configurations considered.

implemented in the program Molecule the times per iteration are quoted by Diercksen [7] as 30 sec (CPU 360/91) for a 1917 configuration problem.

Table 2 shows the excellent convergence properties of the Davidson method. Between 3 and 5 iterations will suffice depending upon the accuracy the final energy and eigenvector are required to have. On this limited evidence it would appear that the algorithm is superior to the Roos perturbation scheme. In Table 3 the energies obtained in the three calculations are given. These are not of particular interest in themselves as many more extensive calculations have been made [8], but they may be of use as reference data for other implementations of the method.

Table 2. Performance of the Davidson method for the calculation with 15 virtual orbitals

Iteration	$(E - E_0)$ Hartree	$\| q \|$
1	−0.152116456	0.14×10^{1}
2	−0.158570082	0.37×10^{0}
3	−0.158828614	0.34×10^{-1}
4	−0.158850097	0.15×10^{-1}
5	−0.158851113	0.21×10^{-2}
6	−0.158851151	0.67×10^{-3}
7	−0.158851153	0.10×10^{-3}

Table 3. Energies obtained in the different calculations (in Hartrees)

SCF Energy E_0 (Electronic + Nuclear Repulsion)	−76.020250		
Number of Virtual Orbitals Used	10	13	15
Correlation Energy $(E - E_0)$	−0.123043	−0.146534	−0.158851

The program, and hence by implication Eqs. (21) and (22), has been extensively checked against a "brute force" small CI program which sets up the CI matrix using Slater's Rules. The quantity $b^i \cdot (Hb^i)$ from one program being compared with $(E - E_0)$ as obtained from the second, the b^i being constructed so that only 60 or fewer configurations were represented. Agreement between the two programs was obtained (eventually) to 11 significant figures, for b^i's which represented all the different classes of interaction between determinants. Finally we should indicate that the initial choice of b^i for step (1) was initially made somewhat arbitrarily by using an eigenvector from the small CI package when the first sixty configurations were considered. However, the Davidson algorithm worked just as well if we began with $c_0 = 1.0$ and all other coefficients zero. (It is then necessary to set $\lambda \neq H_{11}$ for iteration 1 to avoid the singularity in step (4). We found $\lambda \rightarrow \lambda - 0.1$ satisfactory.)

5. Conclusion

The new variant of the direct CI approach described here is seen to be simpler in formulation than that originally proposed by Roos, and to be computationally feasible when linked with the Davidson algorithm. The Davidson method is seen to be a very effective way of obtaining the eigenvectors and eigenvalues of large matrices. Finally we note that the advantages of the direct (Roos) approach to the CI problem are twofold, the ability to handle very large matrices, and the rapidity with which the calculations can be carried out.

Acknowledgements. The author wishes to thank the S.R.C. for the grant of computer time on the Rutherford 360/195. The author also wishes to acknowledge the use of the ATMOL programs provided for use on the 360/195 by the Atlas Computer Laboratory.

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Received April 22, 1976/July 29, 1976