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Short Communication

A New Program for CI Calculations in Molecules

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Based on the formalism developed in a recent note, we have worked out a program for CI calculations in molecules. In the present note, the details of the program are discussed. The usefulness of the program has been illustrated using some calculations.

Key words: Configuration interaction calculations

1. Introduction

In a recent note the authors [1] have suggested an efficient method for the implementation of CI calculations for molecules. Basically the method utilises the permutation and unitary group algebras to arrive at explicit algebraic expressions for the matrix elements of the spin-free Hamiltonian over projected spatial configurations. Choosing the projections to transform as the standard basis for the first row of the irrep $[2^{1/2N-S}\,1^{2S}]$ of the permutation group S_N, the problem is to evaluate the interconfiguration matrix elements,

$$\langle[\Phi_{i'_{p'}}]^{\lambda}_{1\rho'}|H|[\Phi_{i_p}]^{\lambda}_{1\rho}\rangle=\langle\Phi_{i'_{p'}}|H|\omega^{\lambda}_{\rho'\rho}\Phi_{i_p}\rangle, \tag{1}$$

where $\lambda=[2^{1/2N-S}\,1^{2S}]$ and [1, 2, 3],

$$\omega^{\lambda}_{\rho'\rho}=\left(\frac{f^{\lambda}_{N}}{N!}\right)^{1/2}\sum_{P\in S_N}[P]^{\lambda}_{\rho'\rho}P \tag{2}$$

is the Young idempotent for S_N.

Using the fact that H is quadratic in the generators, $\{C_{lm}\,|\,l, m=1,\dots, M\}$, of the unitary group U_M on the orbitals, we found in the earlier note [1] that 14 distinct categories of matrix elements of Eq. (1) result. These describe all possible

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interconfigurational matrix elements. The forms of these matrix elements have been listed in the Appendix of [1].

In the present note we give a brief outline of the program we have developed based on this method. As a check on the program, and to determine its efficiency, we have carried out a CI calculation on the manganate ion. The details of the program are presented in Sect. 2, and Sect. 3 contains the results obtained and a brief discussion.

2. The Programming Procedure

Consider an N electron system in a spin state S for which an ordered set of M orthonormal one electron orbitals are available for occupancy. A reducible basis for the irrep[1] $\Gamma\{2^{1/2N-S}\,1^{2S}\}$ of the unitary group U_M then consists of monomial products of these orbitals, such that no orbital in a monomial has an occupancy index greater than 2. As part of the program these configurations were generated by changing orbital occupancies successively, starting from a reference configuration. The program was made flexible enough to pick out all or specific excitations from this reference configuration. The adaptation of the configurations to the non-degenerate irreps of the molecular point group, D_{2h}, was done using standard procedures.

The matching of the configurations in Eq. (1) was done by treating Φ_{i_p} occurring on the right as the reference configuration and noting the changes in occupancies of the orbitals in going over to $\Phi_{i'_{p'}}$. The difference of the orbital occupancies in the two configurations indicates the type (A-1–A-14 of [1]) of matrix element to be considered. The matching permutations could also be determined in the same step. In determining the standard irreps corresponding to these permutations two distinct procedures were used. Expressions A-1–A-4 of [1] involve determination of these matrices over a number of general transpositions within each type of expression. A rapid method for handling such transpositions has been developed by one of us [4] and is used in the present program. The expressions A-2–A-14 of [1] involve, in addition, a determination of matching permutations which are not necessarily transpositions. The irreps corresponding to these permutations were handled by generating, first, the corresponding Rumer basis followed by evaluation of the matrix elements over the matching permutations [5–7]. These matrices were then transformed using the Schmidt procedure in order to generate the standard real orthogonal representation of S_N. To minimize the number of times the transformation matrix had to be constructed, it was found suitable to order the configurations in blocks of distinct pairing index values (the number of double occupied orbitals).

The matching of the energy expressions with the integral tape and the subsequent diagonalisation of the CI matrix was carried out by adapting the present program to the program system ALCHEMY [8].

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[1] irreducible representation.

Table 1. Computing times for energy expressions for some many-electron systems in definite spin states

	Number of configurations	Number of projected functions	Number of non-zero elements	Average number of determinants per projected function	A Present program (CPU sec.)	B[a] CONGEN SPEEDY (CPU sec.)	A/B (%)
$N=4, S=0$	19	20	183	2.00	1.15	2.23	51.6
$N=5, S=\frac{1}{2}$	51	75	1967	2.20	5.14	8.03	64.0
$N=6, S=0$	141	175	7833	3.26	18.65	37.30	50.0
$N=6, S=1$	121	189	9950	2.35	24.55	36.29	67.6
$N=7, S=\frac{1}{2}$[b]	1	14	99	21.00	0.66	24.96	2.6
$N=8, S=0$[b]	1	14	99	42.00	0.71	165.25	0.4

[a] ALCHEMY [8].

[b] Only the configuration with N singly occupied orbitals is included.

Table 2. Total computation times for CI calculations on MnO_4^{--} in the spin state $S=\frac{1}{2}$ including diagonalization of the energy matrix

Number of configurations	Number of projected functions	Average number of determinants per projected function	A Present program (CPU min.)	B[a] CONGEN SPEEDY (CPU min.)	A/B (%)	C Total time present program +ALCHEMY [8] (CPU min.)	D Total time CONGEN SPEEDY +ALCHEMY [8] (CPU min.)	C/D (%)
101	178	2.30	0.59	6.84	8.63	1.43	7.51	19.04
80	177	4.47	0.53	39.04	1.36	1.33	39.61	3.36

[a] ALCHEMY [8].

3. Results and Discussion

The programming of the above procedure was done on an IBM 370/165 computer. The grafting of the ALCHEMY CI package [8] to our program did not present any difficulties. The efficiency in generating configurations and the corresponding symbolic energy expressions was first investigated using the following test examples: $N=4$, $S=0$; $N=5$, $S=\frac{1}{2}$; $N=6$, $S=0, 1$; $N=7$, $S=\frac{1}{2}$; $N=8$, $S=0$. In these systems all possible configurations were included, except for the last two examples where only the configurations having N singly occupied orbitals were considered. The CPU time taken by the present program was compared with the equivalent CONGEN and SPEEDY programs of ALCHEMY [8] in Table 1. The last column of this table clearly indicates that the present program is more efficient than the corresponding parts of ALCHEMY. This is more marked in the last two cases considered in Table 1, where ALCHEMY uses a relatively large number of determinants per projected function.

In order to check the present program on a real molecular system we carried out two CI calculations on the manganate ion. The results are summarized in Table 2. In column 6 of Table 2 we compare the CPU time for our program with that for CONGEN and SPEEDY. In addition, column 7 gives the total time for the complete CI calculation including matching with the integral tape and diagonalization of the CI matrix using the present program. Column 9 of Table 2 is a comparison of these timings with the similar ones obtained from ALCHEMY. The results indicate that the present method compares favourably with ALCHEMY [8] and is suitable for fairly large CI calculations. Due to computer storage requirements we have for the present incorporated a maximum of 8 singly occupied orbitals. However, the program can be readily adapted to handle a larger number of open shells.

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