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**A note on a program to reduce the number of
molecular integrals to be computed for a molecule
with symmetry elements. Application to the CH_5^+ ion**

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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica fisica. — *A note on a program to reduce the number of molecular integrals to be computed for a molecule with symmetry elements. Application to the CH_5^+ ion* (*). Nota di STEFANIN POLEZZO, MASSIMO SIMONETTA e MARIA PAOLA STABILINI, presentata (**) dal Corrisp. M. SIMONETTA.

RIASSUNTO. — Viene descritto un procedimento generale che permette di ridurre il numero degli integrali molecolari da calcolare esplicitamente sfruttando la simmetria complessiva o anche solo parziale della molecola. Si è scritto un programma di calcolo che realizza il procedimento e lo si è inserito in un programma generale di calcolo autoconsistente per l'energia e alcune proprietà molecolari. Viene infine presentato un calcolo di prova per tre configurazioni dello ione CH_5^+ .

INTRODUCTION

Recent fast growing of ab initio calculations on molecules is due both to the employing of big computers and to the improvement of available molecular programs. Surely, in the evaluation of molecular properties the calculation of electronic repulsion integrals is one which requires a large computer time. It is therefore appropriate whenever possible to make use of all devices which make the calculation as short as possible. In particular when a molecule, or a part of it, has symmetry elements there are identities or, in general, relations among the integrals on atomic orbitals of equivalent atoms, which, if conveniently exploited, afford a remarkable reduction in the number of molecular integrals which must be calculated explicitly [1]. Hence the usefulness of inserting in a general SCF computation program a section in which the symmetry of the molecule is fully exploited in order to derive all molecular integrals from the knowledge of a restricted number of explicitly computed integrals.

A brief description of the method and of its application to the CH_5^+ ion are given in the following sections.

DESCRIPTION OF THE PROGRAM

Let us assume that all the atomic orbitals belonging to the different atoms of the molecule be referred to the same frame of reference and that each atom have the complete set of atomic orbitals corresponding to a given

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value of the azimuthal quantum number l (e.g. the three p orbitals). If a set of atoms A, B, C, \dots of the molecule under a symmetry operation R is transformed into the set A', B', C', \dots the integrals which involve orbitals on the second set need not be calculated explicitly but can be obtained by transforming with the same symmetry operation R the integrals involving the first set of atoms. This can be seen from the following arguments. For the sake of concreteness it is convenient to consider the case of fig. 1, in which

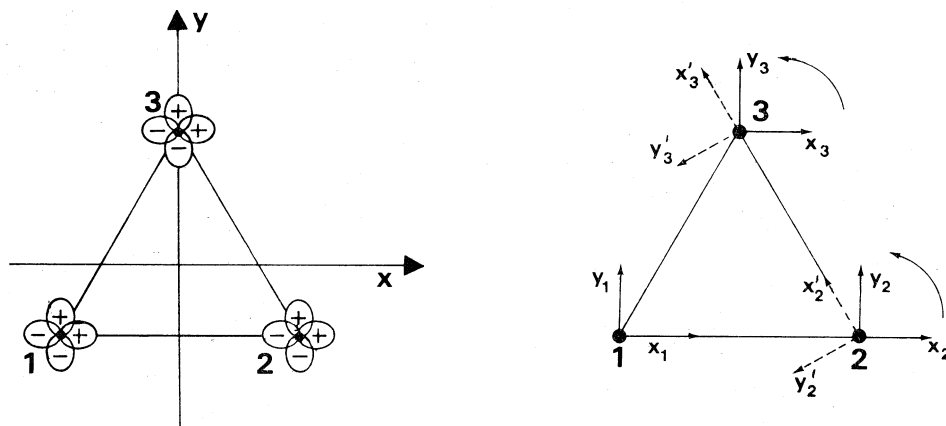


Fig. 1. – For the definition of the symmetry operation \bar{C}_3 .

an hypothetical molecule is made up of three equivalent atoms called 1, 2, 3 and placed at the vertices of an equilateral triangle (point group C_{3v}), each of which has its own set of three $2p$ atomic orbitals, which for brevity we shall denote by x_i, y_i, z_i ($i = 1, 2, 3$); their orientation is according the frame of reference shown in the fig. 1, and obviously coincides with the local frames of reference centered on the atoms. A certain symmetry operation must then be thought of as a whole inducing both a permutation of the atoms and a simultaneous transformation of the axes of the frame of reference with origin on the atoms. For instance, the symmetry operation \bar{C}_3 so defined consists in the mapping of atoms 1, 2, 3 into 2, 3, 1 and in the simultaneous rotation by 120° of each of the local frames. This last operation can be represented by the matrices ($c = -1/2$, $s = \sqrt{3}/2$)

	x_i	y_i	z_i	
x'_i	c	$-s$	0	$(i = 1, 2, 3)$
y'_i	s	c	0	
z'_i	0	0	1	

where the prime denotes the axes of the rotated frame. Let us assume e.g. that the overlap integrals $(x_1 | x_2)$, $(y_1 | y_2)$ and $(z_1 | z_2)$ have been calculated: starting from these we now want to generate by symmetry all the other overlap

integrals of the molecule. For instance, $(x_2 | x_3)$ can be obtained by the rotation operation \bar{C}_3 defined above and we have

$$(x_2 | x_3) \equiv \bar{C}_3(x_1 | x_2) = c^2(x'_2 | x'_3) + s^2(y'_2 | y'_3),$$

but $(x'_2 | x'_3) = (x_1 | x_2)$ and $(y'_2 | y'_3) = (y_1 | y_2)$ and therefore the required integral is readily obtained. Obviously the choice of the pair of integrals to be taken as parent is arbitrary.

Of course, when d orbitals are involved the transformation matrix has dimension 5×5 : it may be derived from the previous one and is explicitly reported in [2].

Let us assume that the matrices which represent the symmetry operations of the molecule and the permutations among equivalent atoms induced by them are known. Consider a set of four atoms A, B, C, D which is transformed into the set A', B', C', D' under a symmetry operation (of course, the method is equally valid also for a minor number of atoms). Once the integrals belonging to different sets of four atoms (or different pair of atoms if we are considering one-electron integrals) are labelled in a given way, it will be possible to generate by symmetry a set of integrals from another. By set of integrals we mean here all those integrals which involve orbitals on the same set of four atoms (or orbitals on the same pair of atoms for one-electron integrals). An advantage of this procedure is that account can be

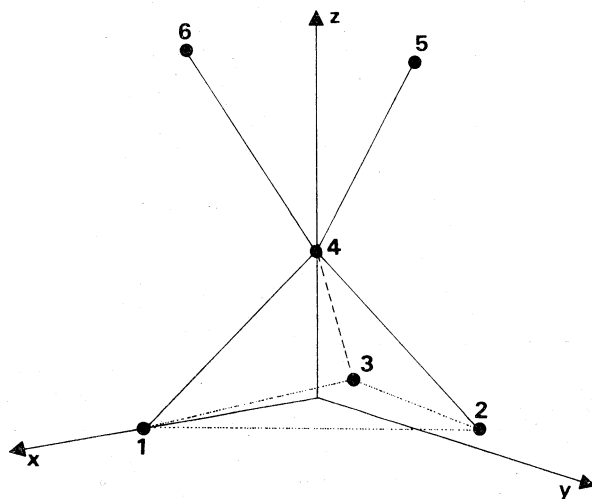


Fig. 2. — CH_5^+ in the configuration of C_s symmetry (atoms 5 and 6 are in the yz plane).

taken not only of the symmetry of the molecule as a whole but also of the local symmetry of its different parts. An example will clarify this point. Let us consider the ion CH_5^+ in the geometric configuration of fig. 2. It belongs to the point group C_s and its only symmetry element is the $\sigma(xz)$ plane. But if we momentarily disregard the hydrogen atoms denoted by 5 and 6, the

set of remaining atoms belongs to the point group C_{3v} and has therefore, besides the symmetry plane $\sigma(zx) = \sigma_1$, other two symmetry planes σ_2 and σ_3 and a ternary rotation axis C_3 . Let us then build up a matrix placing in each row the sequence of atoms into which the initial sequence 1, 2, 3, 4, 5, 6 is mapped under the various symmetry operations. If an atom is not brought into a position previously occupied by another atom, the corresponding matrix element will be 0. The operations associated with the symmetry elements of the CH_3 part of CH_5^+ are the counterclockwise rotation of 120° around the z axis C_3 , the rotation C_3^2 , the reflections σ_1 , σ_2 and σ_3 . The matrix which gives the correspondence between the various atoms under the different operations has five rows and is given by the permutations

	1	2	3	4	5	6
C_3	2	3	1	4	0	0
C_3^2	3	1	2	4	0	0
σ_1	1	3	2	4	6	5
σ_2	3	2	1	4	0	0
σ_3	2	1	3	4	0	0

This matrix immediately gives all the sets of four atoms which can originate by symmetry from another set. For instance the integrals on orbitals belonging to atoms 2 and 5, i.e. the integrals of the type $(22 | 55)$, generate by σ_1 reflection the integrals $(33 | 66)$. The integrals of the type $(11 | 34)$ generate: $(22 | 14)$ by the rotation C_3 , $(33 | 24)$ by the rotation C_3^2 , $(11 | 24)$ by the reflection σ_1 , $(33 | 14)$ by the reflection σ_2 , $(22 | 34)$ by the reflection σ_3 . So here from one set of integrals five other sets are generated by symmetry, hence from 5 explicitly calculated integrals (assuming a base of 1 s orbitals on H atoms and 1 s , 2 s and 2 p on C atom) 25 integrals can be derived. Another advantage of this procedure is that of providing a computer program with the minimum expenditure of memory since at any stage it is necessary to have in storage only the integrals relative to the set of four atoms being treated. Each set of four atoms of the molecule is progressively numbered and an array of integer numbers with a length equal to the number of sets of four atoms of the molecule is initially prepared with all its elements equal to zero; as soon as a set of integrals has been calculated or generated by symmetry, the ordinal number of the set of four atoms whose integrals have been just completed is placed at the position corresponding to this set. This array in practice indicates at any stage which sets of integrals have been completed. Considering in turn each set of four atoms a check is made if it has been already considered. If the check is positive the next set is introduced otherwise the relevant integrals are calculated and memorized. From the matrix of the permutations one sees which set of four atoms is generated by the set considered and by suitable transformations the relevant integrals are generated

from the original ones. The array specifying which integrals have been made is then brought up to date. The integrals are then recorded either on tape or on cards and supplied with labels which fully identify them.

A NUMERICAL CALCULATION

The method just outlined is inserted in a general SCF computation program. This program can be divided logically in three parts: the first part calculates the necessary one and two electron integrals along the lines of the method described in the previous section; the second part performs the transformation to integrals over symmetry adapted orbitals, from which the well known supermatrix is built; the final part is the SCF procedure where the Fock matrix is built up and diagonalized. The process of course is repeated up to a prescribed accuracy in the energy.

In order to test the efficiency of the program a calculation on three configurations of the CH_5^+ ion was performed. Some results are given here. The optimum geometry obtained in [3] and a minimum basis set of Slater type orbitals have been used: geometry and orbitals exponents are collected in Table I (same notation as in [3]). With this basis the total number of two electron molecular integrals is 1540 and the effectively computed integrals are 448, 409, 753 respectively for the D_{3h} , C_{4v} and C_s configurations.

TABLE I
Geometry and orbital exponents.

			D_{3h}	C_{4v}	C_s
Distance CH_1 (Å)			1.14	1.16	1.14
Distance CH_4 			1.16	1.13	1.21
$\text{H}_1\hat{\text{C}}\text{H}_2$ (degrees)			—	80	110
$\text{H}_4\hat{\text{C}}\text{H}_5$			—	—	50
Exponents:	H	1.2			
	$1s_{\text{C}}$	5.6727			
	$2s_{\text{C}}$	1.6083			
	$2p_{\text{C}}$	1.5679			

The order of the energies of the three configurations that we have obtained is given in the Table II, together with the charge distribution on atoms (total Mulliken overlap distribution), and confirms the already known stability of the C_s configuration, though the relative stability of this configuration is overestimated as compared with the results found in other recent works

TABLE II
Energies and charge distributions.

	D_{3h}	C_{4v}	C_s
Energy (A.U.)	36.6692	39.1603	40.2670
q_C	5.8067	6.3032	6.7743
q_{H_1}	1.1182	0.8763	0.6868
q_{H_2}	1.1182	0.8763	0.6453
q_{H_3}	0.4194	0.1918	0.6242

more complete than the present one ([4] and the references therein). We have not optimized neither the orbital exponent nor the geometry because our aim was only to perform a test computation on a significant molecular systems.

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