CALCULATION OF SOME FIRST-ORDER PERTURBATIVE TERMS IN THE INTERACTION BETWEEN MOLECULES

V. Beltrán-López[†]

Centro Nuclear de México. C. N. E. N.

and

O. Novaro[*]

Instituto Mexicano del Petróleo

ABSTRACT: A method is presented for the calculation of some first-order perturbative terms in the interaction between molecules, by means of the POLYATOM computing program for the calculation of LCAO-MO-SCF wave functions.

The first order perturbation intermolecular energy can in general be written out[1,2,3] as an expansion of terms in powers of the intermolecular potential U and the overlap integral S. A direct evaluation of these terms is in general difficult to do with reasonable wave functions such as Hartree-Fock orbitals centered about the individual atoms.

We present a method which allows us to evaluate the more important terms in the first-order perturbation energy by using the LCAO–MO–SCF Polyatom computing program and data obtained from it. We shall discuss in particular the case of two He atoms and evaluate its first-order intermolecular energy to within terms of the order of S^2.

If we take as zero-order wave function the antisymmetrized product $\Phi_0 = \mathcal{Q}A_0 B_0$ of the individual atomic wave functions, the first-order perturbation energy to within terms of order S^2 is given by the expressions,[4]

$$H = 4(1 - S^2)\{(A|h|A) - S(A|h|B)\}$$

$$1/2\ G = 2(1 - S^2)^2\{(AA|g|AA) + 2(AB|g|AB) - (AB|g|BA)\} -$$

$$- 8S(1 - S^2)^2(AB|g|AA) \tag{1}$$

where H is the one-electron and $1/2\ G$ the two-electron contributions to the energy.

In the Polyatom program each orbital is expanded over a gaussian basis set. Overlap, hamiltonian and density matrices are formed with the dimensions of the basis set. The energy values at each iteration are calculated by taking the traces of the products of the hamiltonian matrices by the density matrix of that iteration. Suppose now that we start the SCF procedure with the coefficients obtained from a calculation with the atoms at an infinite distance[5,7]. It can then be seen that at iteration zero, the density matrix elements are zero in all places corresponding to exchange terms, i.e., this matrix would split into two matrices referring to gaussians centered in each atom. The energy values computed at this iteration are then the un-normalized values of the one and two electron energies,

$$H^1 = 4(A|h|A)$$

$$1/2\ G^1 = 2\{(AA|g|AA) + 2(AB|g|AB) - (AB|g|BA)\}$$

the contributions arising from $S^2(A|h|A)$, $S(A|h|B)$ and $(AB|g|AA)$ are then completely missed.

We can obtain the missing terms by complementing the procedure as follows. With the coefficients C_A and C_B of the atomic orbitals we form C_{AA}, C_{AB} and C_{BB} matrices of half the dimension of the density matrix. We also split the

hamiltonian matrices at iteration zero into the matrices $\mathcal{H}_{AA}$, $\mathcal{H}_{BB}$ and $\mathcal{H}_{AB}$. Two of these referring to the isolated atom, the other to the interaction terms. By taking the traces of the products of the C and $\mathcal{H}$ matrices it can be seen that we obtain the following results:

$$\operatorname{tr} C_{AB} H_{AB} = (A|b|B)$$

$$\operatorname{tr} C_{AB} G_{AB} = 2(AB|g|AA)$$

$$\operatorname{tr} C_{AB} S_{AB} = 1 + S$$

where S_{AB} is the overlap matrix similarly split.

We have applied this method to the system formed by two helium atoms at a distance of 4 a.u., taking for our zero-order wave functions the two-gaussians basis set of Huzinaga[6] and we have obtained the following results,

$$S = 9.7798 \times 10^{-3}, \qquad\qquad (1 - S^2)^2 = 0.9998087,$$

$$\operatorname{tr} C_{AA} H_{AA} = -2.3881562, \qquad \operatorname{tr} C_{AA} G_{AA} = 1.5291598,$$

$$\operatorname{tr} C_{AA} H_{AB} = -0.0346586, \qquad \operatorname{tr} C_{AB} G_{AB} = 0.0095542$$

With these values, the energies of equations (1) are,

$$H = -9.552185$$

$$1/2\,G = 3.058530$$

The total first-order perturbation energy value to within terms in S^2 is then,

$$E^1 = -6.493655.$$

This is to be compared with the value obtained by the full SCF procedure which is

$$E_{SCF} = -6.493784.$$

REFERENCES

1. J.N. Murrell, M. Randic, and D.R. Williams, Proc. Roy. Soc. (London) A284 (65) 566.
2. J.N. Murrell and G. Shaw, J. Chem. Phys. 46 (1967) 1768.
3. D.R. Williams, L.J. Schaad and J.N. Murrell, J. Chem. Phys. Vol. 47 Nº 12 4916 (1967) pp. 4916–4922.
4. See for instance H. Margenau and N.R. Kestner "Theory of Intermolecular Forces" Academic Press, (1969) p. 49.
5. This part of the procedure was independently suggested by Van Dijneveldt in his Ph.D. Thesis. We thank Mme. Pullman for bringing this point to our attention in the course of a conversation during her visit to México.
6. S. Huzinaga, J. Chem. Phys. 42 (1965) 1293.
7. M. Dreyfus and A. Pullman, (to be published). We thank Mme. Pullman for sending us a preprint in advance of publication.

RESUMEN

Se presenta un método para calcular algunos términos perturbativos de primer orden en la interacción entre moléculas, utilizando el programa POLYATOM para el cálculo de funciones de onda tipo LCAO–MO–SCF.