Revista Mexicana de Física 22 (1973) 343-348

SOME COMMENTS ON OPEN SHELL HARTREE-FOCK METHODS FOR MOLECULES: THE HYDROGEN MOLECULE ANION

D. W. Davies and G. del Conde

Department of Chemistry, University of Birmingham,
P. O. Box 363, Birmingham, B15 2TT, England

(Recibido: noviembre 29, 1973)

ABSTRACT: Expressions for the one and two Fock operators for the H_2^- molecule are derived in Hartree-Fock methods for open shell molecules. Furthermore the values of the Lagrange multipliers for H_2^- are shown, and also the molecular orbital coefficients, by using two different sets of gaussians as basis functions.

The difficulties involved in open shell Hartree-Fock calculations have been recognised for a long time[1-3]. Recently there has been much interest in finding satisfactory methods for molecules[4-10].

Hillier and Saunders[7] have stressed the arbitrary nature of the molecular orbitals obtained, and referred the doubly occupied, singly occupied and virtual molecular orbitals to different Fock operators. The molecular orbitals that form a diagonal representation of the Fock operator they call canonical. Dodds and McWeeny[9] have given a similar discussion in density matrix terms. Hunt, Dunning and Goddard[6] have described a method in which the singly occupied orbitals are expanded in terms of the virtual orbitals associated with the doubly occupied orbitals. These authors have all made use of their methods in practical calculations by the ***ab initio*** Gaussian expansion technique for the integrals. There does not, however, seem to be a detailed comparison of results obtained by these methods available in the literature. The object of this note is to present some results for the hydrogen molecule anion, H_2^-.

The two basic methods were discussed by Roothaan[2], Method I using one Fock operator, and Method II using two Fock operators. In Method I the basic equations defining the molecular orbitals ψ_i^C for a closed shell and ψ_i^0 for an open shell are:

$$\hat{F}\psi_i^C = \psi_i^C \eta_i^C \tag{1}$$

$$\hat{F}\psi_i^0 = \psi_i^0 \eta_i^0 \quad , \tag{2}$$

where $\hat{F}$ may be written in terms of a one electron operator $\hat{h}$ and a two electron operator $\hat{G}$, thus,

$$\hat{F} = \hat{h} + \hat{G} \tag{3}$$

In Method II the equations are,

$$\hat{F}^C\psi_i^C = \psi_i^C \epsilon_i^C \tag{4}$$

$$\hat{F}^0\psi_i^0 = \psi_i^0 \epsilon_i^0 \tag{5}$$

where $\hat{F}^C$, $\hat{F}^0$ may be written as in equation (3). General expressions are given by Roothaan[2]. The precise form of the operators depends on the state, and involves three constants a, b, and f.

For H_2^- with one doubly filled ***gerade*** orbital ψ_1 and one singly filled ***ungerade*** orbital ψ_2, the diagonal elements of the Fock matrices are, Method I, with $a = 1$, $b = 2$, $f = \frac{1}{2}$

$$\eta_1 \equiv F_{11} = h_{11} + J_{11} + J_{21} + \tfrac{1}{2}K_{21} \tag{6}$$

$$\eta_2 \equiv F_{22} = h_{22} + 2J_{21} - K_{21} + \tfrac{1}{2} J_{22} \tag{7}$$

and Method II,

$$\epsilon_1^C \equiv F_{11}^C = h_{11} + J_{11} + \tfrac{1}{2}(2J_{12} - K_{12}) \tag{8}$$

$$\epsilon_2^0 \equiv F_{22}^0 = h_{22} + 2J_{12} - K_{12} \quad . \tag{9}$$

In Method I the incorrect term J_{22} appears in η_2, and η_1 has a rather surprising form. In Method II the terms have a clear physical meaning. The total energy W is the same for both methods,

$$W = 2h_{11} + h_{22} + J_{11} + 2J_{12} - K_{12} \quad . \tag{10}$$

The matrix elements h_{ij}, J_{ij} and K_{ij} are defined by,

$$h_{ij} = \int \psi_i^*(1)\, \hat{h}(1)\, \psi_j(1)\, d\tau_1 \tag{11}$$

$$J_{ij} = \int \psi_i^*(1)\, \psi_j^*(2) (1/r_{12})\, \psi_i(1)\, \psi_j(2)\, d\tau \tag{12}$$

$$K_{ij} = \int \psi_i^*(1)\, \psi_j^*(2) (1/r_{12})\, \psi_i(2)\, \psi_j(1)\, d\tau \ . \tag{13}$$

For the virtual orbitals ψ_3 .... ,

$$\eta_3 \equiv F_{33} = h_{33} + 2J_{31} - K_{31} + \tfrac{1}{2}(2J_{32} - K_{32}) - K_{32} \tag{14}$$

$$\epsilon_3 \equiv F_{33}^C = h_{33} + 2J_{31} - K_{31} + \tfrac{1}{2}(2J_{32} - K_{32}) \quad . \tag{15}$$

Calculations of these quantities were made using a modified version of POLYATOM (QCPE 47.1) on the KDF9 computer at the University of

Birmingham, and ATMOL 2,[10] on the IBM 370/195 computer linked to the SRC Atlas Computer Laboratory, Chilton. One s-type Gaussian orbital (exponent 0.3) and two s-type Gaussian orbitals (exponents 0.8, 0.2) per atom were used in the two sets of calculations. The internuclear distance was taken as 1.4 a.u. The results are shown in the tables. The lack of physical meaning of the η values is well shown[5], and care is needed in using the aufbau principle with Method I. Dodds and McWeeny have stressed this for Method II.[9]

The method used by the ATMOL programme[10] was developed by Hillier and Saunders[7] on the basis of conditions given by McWeeny[4]. The orbitals obtained by the method can be transformed to a set canonical for a given operator. For the Fock operator corresponding to ionization to the

TABLE 1

Lagrangian parameter

values for H_2^- (a.u.)

Symmetry		1 GTO	2 GTO
g	η_1	-0.07484	-0.07616
	ϵ_1^C	-0.09363	-0.1691
u	η_2	0.6158	0.4908
	ϵ_2^0	0.3785	0.2805
g	η_3	–	1.2069
	ϵ_3	–	1.2381
u	η_4	–	1.717
	ϵ_4	–	1.3583
Total energy		-0.581947	-0.787732

TABLE 2

Molecular orbitals in terms of normalised Gaussian functions

Symmetry	Orbital	1 GTO	2 GTO	
			ϕ_1, ϕ_3	ϕ_2, ϕ_4
g	1	0.5352	0.2330	0.3477
u	2	1.4010†	0.09296*	1.5706*
g	3	–	0.8712	-0.7275
u	4	–	1.2182*	- 1.4458*
Exponents	ϕ_1, ϕ_2	0.3	ϕ_1, ϕ_3 0.8; ϕ_2, ϕ_4 0.2	

† The coefficient of ϕ_2 is negative

* The coefficients of ϕ_3, ϕ_4 are opposite in sign to ϕ_1, ϕ_2

triplet state, with matrix H_3 in Hillier and Saunders' notation,

$$\epsilon_1^3 = h_{11} + J_{11} + J_{22} \tag{16}$$

which has the value -0.036021 in the one Gaussian per atom basis, and -0.12262 in the two Gaussian per atom basis. The corresponding Koopmans theorem ionization potentials are 0.98 eV and 3.34 eV.

ACKNOWLEDGEMENTS

The authors are indebted to the Deutsches Rechenzentrum, Darmstadt for the cards of QCPE 47.1, to Dr. V. R. Saunders for discussion, and to the staff of the SRC Atlas Computer Laboratory, Chilton for running the ATMOL computations. The National University of Mexico and the British Council are thanked for financial support (to G. del C.).

REFERENCES

1. D. R. Hartree, *The Calculation of Atomic Structures* (Chapman and Hall, Ltd., London, 1957) ch. 6.
2. C. C. J. Roothaan, Rev. Mod. Phys. 32 (1960) 179.
3. S. Huzinaga, Phys. Rev. 120 (1960) 866; 122 (1961) 131.
4. R. McWeeny, *Molecular Orbitals in Chemistry, Physics and Biology*, Ed. P.O. Löwdin and B. Pullman, (Academic Press 1964) p. 309.
5. R. L. Flurry, *Molecular Orbital Theories of Bonding in Organic Molecules*, (Edward Arnold, Ltd., 1968) p. 237.
6. W. J. Hunt, T. H. Dunning, and W. A. Goddard, Chem. Phys. Letters, 3 (1969) 606.
7. I. H. Hillier, and V. R. Saunders, Int. J. Quant. Chem. 4 (1970) 503.
8. T. E. H. Walker, Chem. Phys. Letters, 9 (1971) 174; Theor. Chim. Acta (Berlin) 25 (1972) 1.
9. J. L. Dodds, and R. McWeeny, Chem. Phys. Letters, 13 (1972) 9.
10. M. F. Chiu, M. F. Guest, and V. R. Saunders, S. R. C. Atlas Computer Laboratory, ATMOL 2, User Notice 5, March 1973).

RESUMEN

Se obtienen expresiones para casos de uno y dos operadores de Fock para la molécula de H_2^-, en métodos de Hartree-Fock para moléculas de capas abiertas; así mismo se muestran valores de los multiplicadores de Lagrange para H_2^-, al igual que los coeficientes de los orbitales moleculares, utilizando dos diferentes conjuntos de funciones gaussianas como funciones de la base.