

AN INVARIANT FORMULATION OF AN APPROXIMATE SCF LCAO-MO THEORY FOR MOLECULES WITH ONE OPEN ELECTRONIC SHELL IN THE GROUND STATE

By K. GUSTAV

Department of Chemistry, Ernst-Moritz-Arndt-University Greifswald*

(Received June 24, 1969)

An invariant approximate model with complete neglect of differential overlap (CNDO) in the SCF LCAO-MO theory for molecules with one open electronic shell is derived. The expressions for the Hartree-Fock-Roothaan matrix and the proof of the transformation behaviour to orthogonal transformations of the basis set of the atomic basis wavefunctions are given.

1. Introduction

Many compounds in chemistry are molecules or molecular systems with one or more open electronic shells representing systems with a rather large number of atomic centers and electrons. In such cases quantum chemical approximate (semi-empirical) methods become suitable and useful in the determination of the electronic structure and other interesting molecular properties. Unfortunately such important physical criteria like the correct transformation behaviour of the matrix elements and the invariance condition of the secular equations and the energy with respect to orthogonal (unitary) transformations have not always been proved for approximate procedures.

Some years ago an invariant approximate model for closed-shell electronic systems has been published [12, 13] and one on the basis of different molecular orbitals for different spins for open-shell electronic systems [13]. Several modifications of the mentioned model do exist in the sense of applicability of useful empirical approximations for some matrix elements sometimes failing the invariance concept. The developed model and its modifications have been applied with encouraging success [1, 2, 4, 5, 8, 11, 13].

Also Roothaan's theory for systems with one open electronic shell [15] has successfully been used in an approximate procedure for the investigation of the electronic structure of π -radicals and co-ordination compounds [3, 6, 7, 9, 10] but without any treatment of the invariance concept and the transformation behaviour of the matrix elements. It is the aim of this paper to formulate an invariant approximate model.

* Address: Ernst-Moritz-Arndt Universität, Sektion Chemie, 22 Greifswald, Soldtmanstrasse 16, D.D.R.

2. Foundations

The matrix elements of the Hartree-Fock-Roothaan operator and the formula for the total electronic energy described in the LCAO formalism by Roothaan's pseudo-eigenvalue equations are expressed as follows [15]:

$$F_{pq} = H_{pq} + P_{pq} - Q_{pq} + R_{pq}, \quad (1)$$

$$E_{el} = \frac{1}{2} \left[\sum_{p,q} D_{T,pq}^\dagger (H_{pq} + F_{pq}) - \sum_{p,q} (D_{C,pq}^\dagger + f D_{O,pq}^\dagger) Q_{pq} \right]. \quad (2)$$

All matrix elements and f possess the meaning as cited in [15]. The only difference in the explicit formulation arises due to the deviation in the normalization procedure for the open-shell molecular orbitals — normalized to unity in this paper — and due to the other definition of the density matrices as seen:

$$H_{pq} = \langle p|H|q \rangle, \quad (3a)$$

$$P_{pq} = \sum_{r,s} \left[\langle pq|rs \rangle - \frac{1}{2} \langle ps|rq \rangle \right] \cdot D_{T,rs}, \quad (3b)$$

$$Q_{pq} = \sum_{r,s} \left[\alpha \langle pq|rs \rangle - \frac{1}{2} \beta \langle ps|rq \rangle \right] \cdot D_{O,rs}, \quad (3c)$$

$$R_{pq} = \frac{1}{2} \sum_{r,s} [S_{pr} D_{T,rs} Q_{sq} + Q_{pr} D_{T,rs} S_{sq}], \quad (3d)$$

$$S_{pq} = \langle p|q \rangle \quad (3f)$$

and

$$D_{T,pq} = D_{C,pq} + D_{O,pq} = 2 \sum_{k \text{ c l. sh}} c_{pk} c_{kq}^\dagger + 2f \sum_{m \text{ c op. sh}} c_{pm} c_{mq}^\dagger. \quad (3g)$$

In his paper Roothaan [15] established the invariance of all operators of the Coulomb, exchange, Coulomb coupling and exchange coupling type with respect to a suitable unitary (or orthogonal) transformation of the molecular closed-shell and open-shell wavefunction among them. If the molecular wavefunction shows transformation invariance between the atomic basis functions it is possible to derive the transformation behaviour of the expressions (1) and (2) by introduction of a new set of basis functions X'_μ related to the original set X_p by the equation (4):

$$X'_\mu = \sum_p O_{\mu p} X_p. \quad (4)$$

It follows for the single matrix elements:

$$H'_{\mu\nu} = \sum_{p,q} O_{\mu p} H_{pq} O_{q\nu}^{-1}, \quad (5a)$$

$$P'_{\mu\nu} = \sum_{p,q} O_{\mu p} P_{pq} O_{q\nu}^{-1}, \quad (5b)$$

$$Q'_{\mu\nu} = \sum_{p,q} O_{\mu p} Q_{pq} O_{qv}^{-1}, \quad (5c)$$

$$R'_{\mu\nu} = \sum_{p,q} O_{\mu p} R_{pq} O_{qv}^{-1}, \quad (5d)$$

$$D'_{T,\mu\nu} = \sum_{p,q} O_{\mu p} D_{T,pq} O_{qv}^{-1}, \quad (5e)$$

$$S'_{\mu\nu} = \sum_{p,q} O_{\mu p} S_{pq} O_{qv}^{-1}. \quad (5f)$$

Analogous expressions are obtained for the matrices $D'_{C,\mu\nu}$ and $D'_{O,\mu\nu}$. By means of the relations (5) it can be verified the Hartree-Fock-Roothaan equations as well as the formula for the total electronic energy (2) satisfy the invariance condition in the following way:

$$\sum_{\nu} (F'_{\mu\nu} - \varepsilon_i S'_{\mu\nu}) c'_{\nu i} = \sum_q (F_{pq} - \varepsilon_i S_{pq}) c_{qi} = 0 \quad (6)$$

$$\begin{aligned} E &= \frac{1}{2} \left[\sum_{\mu,\nu} D_{T,\mu\nu}^{\dagger'} (H'_{\mu\nu} + F'_{\mu\nu}) - \sum_{\mu,\nu} (D_{C,\mu\nu}^{\dagger'} + fD_{O,\mu\nu}^{\dagger'}) Q'_{\mu\nu} \right] \\ &= \frac{1}{2} \left[\sum_{\substack{\mu,\nu \\ p,q}} O_{\mu p} D_{T,pq}^{\dagger} O_{qv}^{-1} O_{\mu p} (H_{pq} + F_{pq}) O_{qv}^{-1} - \sum_{\substack{\mu,\nu \\ p,q}} O_{\mu p} (D_{C,pq}^{\dagger} + fD_{O,pq}^{\dagger}) O_{qv}^{-1} \cdot O_{\mu p} Q_{pq} O_{qv}^{-1} \right] \\ &= \frac{1}{2} \left[\sum_{p,q} D_{T,pq}^{\dagger} (H_{pq} + F_{pq}) - \sum_{p,q} (D_{C,pq}^{\dagger} + fD_{O,pq}^{\dagger}) Q_{pq} \right]. \quad (7) \end{aligned}$$

Now we are able to develop the invariant approximate model.

3. The invariant approximate model

As mentioned in the first section of this paper each approximate step to be introduced in the theory of electronic structure of molecules in order to develop an approximate model should be in agreement with the correct transformation behaviour, *i.e.* with (5). The ideas to be used in the derivation of the invariant approximate model for molecular systems with one open electronic shell are analogous to those of the invariant approximate model (CNDO) for molecular systems with closed electronic shells [12, 13].

The following assumptions are made:

1. The assumption of zero overlap

$$S_{pq} = \langle p|q \rangle = \delta_{pq} = \begin{cases} 1 & \text{if } p = q \\ 0 & \text{if } p \neq q, \end{cases} \quad (8)$$

where δ_{pq} is the known Kronecker symbol. For X_p and X_q it holds in general $X_p \in A$ and $X_q \in B$ (A and B denote atomic centers).

2. The complete neglect of differential overlap (CNDO) for the electronic-repulsion integrals

$$\gamma_{pq} = \langle ps|rq \rangle \delta_{ps} \delta_{rq} = \gamma_{AB} \delta_{ps} \delta_{rq} \quad (9)$$

with $X_p, X_s \in A$ and $X_r, X_q \in B$. The special case $\gamma_{AB} = \gamma_{AA}$ is also contained in formula (9). As γ_{AA} as γ_{AB} are invariant quantities towards local orthogonal transformations of the basis set of atomic wavefunctions.

By means of these approximations one obtains the following expressions for the matrix elements P_{pq}^{AA} , P_{pq}^{AB} , Q_{pq}^{AA} , Q_{pq}^{AB} , R_{pq}^{AA} and R_{pq}^{AB} :

$$P_{pq}^{AA} = -\frac{1}{2} D_{T,pq} \gamma_{AA} + \left(D_{T,AA} \gamma_{AA} + \sum_{B \neq A} D_{T,BB} \gamma_{AB} \right) \delta_{pq} \quad \text{for } X_p, X_q \in A,$$

$$P_{pq}^{AB} = -\frac{1}{2} D_{T,pq} \gamma_{AB} \quad \text{for } X_p \in A \quad \text{and} \quad X_q \in B (A \neq B). \quad (10)$$

$$Q_{pq}^{AA} = -\frac{1}{2} \beta D_{O,pq} \gamma_{AA} + \alpha \left(D_{O,AA} \gamma_{AA} + \sum_{B \neq A} D_{O,BB} \gamma_{AB} \right) \delta_{pq} \quad \text{for } X_p, X_q \in A,$$

$$Q_{pq}^{AB} = -\frac{1}{2} \beta D_{O,pq} \gamma_{AB} \quad \text{for } X_p \in A \quad \text{and} \quad X_q \in B (A \neq B). \quad (11)$$

$$R_{pq}^{AA} = \alpha D_{T,pq} \left(D_{O,AA} \gamma_{AA} + \sum_{B \neq A} D_{O,BB} \gamma_{AB} \right) - \frac{\beta}{4} \gamma_{AA} \left(\sum_r^A D_{O,pr} D_{T,rq} + \right.$$

$$\left. + \sum_r^A D_{T,pr} D_{O,rq} \right) - \frac{\beta}{4} \left(\sum_{B \neq A} \sum_r^B \gamma_{AB} D_{O,pr} D_{T,rq} + \right.$$

$$\left. + \sum_{B \neq A} \sum_r^B \gamma_{AB} D_{T,pr} D_{O,rq} \right) \quad \text{for } X_p, X_q \in A, \quad (12)$$

$$R_{pq}^{AB} = \frac{\alpha}{2} D_{T,pq} \left(D_{O,AA} \gamma_{AA} + \sum_{B \neq A} D_{O,BB} \gamma_{AB} + D_{O,BB} \gamma_{BB} + \sum_{A \neq B} D_{O,AA} \gamma_{AB} \right) -$$

$$- \frac{\beta}{4} \left(\sum_r^A D_{O,pr} D_{T,rq} \gamma_{AA} + \sum_r^B D_{T,pr} D_{O,rq} \gamma_{BB} \right) - \frac{\beta}{4} \left(\sum_{B \neq A} \sum_r^B \gamma_{AB} \times \right.$$

$$\left. \times D_{O,pr} D_{T,rq} + \sum_{A \neq B} \sum_r^A \gamma_{AB} \cdot D_{T,pr} D_{O,rq} \right) \quad \text{for } X_p \in A \quad \text{and} \quad X_q \in B (A \neq B).$$

The given relations (10), (11) and (12) are symmetric for a simultaneous interchange of the p -, q - and A -, B -indices satisfying one important property of the matrix of the Hartree-

-Fock-Roothaan operator. The proof of the transformation behaviour takes the form in the following way using abbreviations for the invariant terms of the expressions¹:

$$\begin{aligned}\zeta &= \gamma_{AA} D_{T,AA} + \sum_{B \neq A} \gamma_{AB} D_{T,BB}, \\ \xi_1 &= \gamma_{AA} D_{O,AA} + \sum_{B \neq A} \gamma_{AB} D_{O,BB},\end{aligned}\quad (13)$$

$$\xi_2 = \gamma_{BB} D_{O,BB} + \sum_{A \neq B} \gamma_{AB} D_{O,AA}.$$

$$\begin{aligned}P_{\mu\nu}^{AA} &= -\frac{1}{2} \gamma_{AA} D'_{T,\mu\nu} + \zeta \delta'_{\mu\nu} = -\frac{1}{2} \gamma_{AA} \sum_{p,q} O_{\mu p} D_{T,pq} O_{qv}^{-1} + \\ &+ \zeta \sum_{p,q} O_{\mu p} \delta_{pq} O_{qv}^{-1} = \sum_{p,q} O_{\mu p} P_{pq}^{AA} O_{qv}^{-1},\end{aligned}\quad (14)$$

$$P_{\mu\nu}^{AB} = -\frac{1}{2} \gamma_{AB} D'_{T,\mu\nu} = -\frac{1}{2} \gamma_{AB} \sum_p \sum_q O_{\mu p} D_{T,pq} O_{qv}^{-1} = \sum_p \sum_q O_{\mu p} P_{pq}^{AB} O_{qv}^{-1}.\quad (15)$$

$$\begin{aligned}Q_{\mu\nu}^{AA} &= -\frac{\beta}{2} \gamma_{AA} D'_{O,\mu\nu} + \alpha \xi_1 \delta'_{\mu\nu} = -\frac{\beta}{2} \gamma_{AA} \sum_{p,q} O_{\mu p} D_{O,pq} O_{qv}^{-1} + \alpha \xi_1 \times \\ &\times \sum_{p,q} O_{\mu p} \delta_{pq} O_{qv}^{-1} = \sum_{p,q} O_{\mu p} Q_{pq}^{AA} O_{qv}^{-1},\end{aligned}\quad (16)$$

$$Q_{\mu\nu}^{AB} = -\frac{\beta}{2} \gamma_{AB} D'_{O,\mu\nu} = -\frac{\beta}{2} \gamma_{AB} \sum_p \sum_q O_{\mu p} D_{O,pq} O_{qv}^{-1} = \sum_p \sum_q O_{\mu p} Q_{pq}^{AB} O_{qv}^{-1}.\quad (17)$$

$$\begin{aligned}R_{\mu\nu}^{AA} &= \alpha \xi_1 D'_{T,\mu\nu} - \frac{\beta}{4} \gamma_{AA} \left(\sum_q D'_{O,\mu q} D'_{T,q\nu} + \sum_q D'_{T,\mu q} D'_{O,q\nu} \right) - \\ &- \frac{\beta}{4} \left(\sum_{B \neq A} \sum_q \gamma_{AB} D'_{O,\mu q} D'_{T,q\nu} + \sum_{B \neq A} \sum_q \gamma_{AB} D'_{T,\mu q} D'_{O,q\nu} \right) \\ &= \alpha \xi_1 \sum_{p,q} O_{\mu p} D_{T,pq} O_{qv}^{-1} - \frac{\beta}{4} \gamma_{AA} \left(\sum_{p,q} O_{\mu p} D_{O,pr} O_{rq}^{-1} O_{qr} D_{T,rq} O_{qv}^{-1} + \right.\end{aligned}$$

¹ The quantity $D_{.,AA}$ is defined as follows: $D_{.,AA} = \sum_t^A D_{.,tt}$. It possesses the property of being invariant to local orthogonal transformations:

$$D_{.,AA} = \sum_{\tau}^A D'_{.,\tau\tau} = \sum_{\tau}^A \sum_{t,s}^A O_{\tau t} D_{.,ts} O_{s\tau}^{-1} = \sum_{t,s}^A \delta_{st} D_{.,ts} = \sum_t^A D_{.,tt} = D_{.,AA}$$

$$\begin{aligned}
& + \sum_{\substack{p,q \\ r,q}}^A O_{\mu p} D_{T,pr} O_{r\varrho}^{-1} O_{\varrho r} D_{O,rq} O_{qv}^{-1} \Big) - \frac{\beta}{4} \left(\sum_{B \neq A} \sum_{p,q}^A \sum_{r,q}^B \gamma_{AB} O_{\mu p} D_{O,pr} \times \right. \\
& \times O_{r\varrho}^{-1} O_{\varrho r} D_{T,rq} O_{qv}^{-1} + \sum_{B \neq A} \sum_{p,q}^A \sum_{r,q}^B \gamma_{AB} O_{\mu p} D_{T,pr} O_{r\varrho}^{-1} O_{\varrho r} D_{O,rq} O_{qv}^{-1} \Big) = \sum_{p,q}^A O_{\mu p} R_{pq}^{AA} O_{qv}^{-1}, \tag{18}
\end{aligned}$$

$$\begin{aligned}
R_{\mu\nu}^{AB} & = \frac{\alpha}{2} (\xi_1 + \xi_2) D'_{T,\mu\nu} - \frac{\beta}{4} \left(\sum_q^A D'_{O,\mu\varrho} D'_{T,\varrho\nu} \gamma'_{AA} + \sum_q^B D'_{T,\mu\varrho} D'_{O,\varrho\nu} \gamma_{BB} \right) - \\
& - \frac{\beta}{4} \left(\sum_{B \neq A} \sum_q^{B'} D'_{O,\mu\varrho} D'_{T,\varrho\nu} \gamma'_{AB} + \sum_{A \neq B} \sum_q^A D'_{T,\mu\varrho} D'_{O,\varrho\nu} \gamma'_{AB} \right) \\
& = \frac{\alpha}{2} (\xi_1 + \xi_2) \sum_p^A \sum_q^B O_{\mu p} D_{T,pq} O_{qv}^{-1} - \frac{\beta}{4} \left(\sum_{\substack{p,r \\ q}}^A \sum_q^B O_{\mu p} D_{O,pr} O_{r\varrho}^{-1} O_{\varrho r} D_{T,rq} \times \right. \\
& \times O_{qv}^{-1} \gamma_{AA} + \sum_p^A \sum_{\substack{e,r \\ q}}^B O_{\mu p} D_{T,pr} O_{r\varrho}^{-1} O_{\varrho r} D_{O,rq} O_{qv}^{-1} \gamma_{BB} \Big) - \\
& - \frac{\beta}{4} \left(\sum_{A \neq B} \sum_{\substack{e,r \\ p}}^A \sum_q^B O_{\mu p} D_{T,pr} O_{r\varrho}^{-1} O_{\varrho r} D_{O,rq} O_{qv}^{-1} \gamma_{AB} + \sum_{B \neq A} \sum_p^A \sum_{\substack{e,r \\ q}}^B O_{\mu p} D_{O,pr} \times \right. \\
& \times O_{r\varrho}^{-1} O_{\varrho r} D_{T,rq} O_{qv}^{-1} \gamma_{AB} \Big) = \sum_p^A \sum_q^B O_{\mu p} R_{pq}^{AB} O_{qv}^{-1}. \tag{19}
\end{aligned}$$

Employing the made approximations for the H_{pq} -matrix from [12, 13], and considering the obtained transformation behaviour of (14)–(19) we see that the total Hartree-Fock-Roothaan matrix of the proposed approximate model must show the desired transformation properties in the same way. Since also the validity of the invariance to orthogonal transformations can easily be verified for the expression of the total electronic energy the approximate model satisfies all the necessary conditions of being an invariant one.

REFERENCES

- [1] F. P. Billingsley, J. E. Bloor, *Theor. Chim. Acta* (Berlin), **11**, 325 (1968).
- [2] R. D. Brown, F. R. Burden, *Theor. Chim. Acta* (Berlin), **12**, 95 (1968).
- [3] C. Ciullo, C. Furlani, A. Sgamelotti, *Coordin. Chem. Rev.*, **2**, 15 (1967).
- [4] D. T. Clark, *Tetrahedron* **24**, 2567 (1968); *ibid.*, **24**, 2663 (1968); *ibid.*, **24**, 3285 (1968); *ibid.*, **24**, 4689 (1968).
- [5] J. Del Bene, H. Jaffé, *J. Chem., Phys.*, **48**, 1807 (1968), *ibid.*, **50**, 1126 (1969).
- [6] L. Di Sipio, G. De Michelis, E. Tondello, L. Oleari, *Gazz. Chim. Ital.*, **96**, 1775 (1966).

- [7] J. R. Hoyland, L. Goodman, *J. Chem. Phys.*, **36**, 12 (1962).
- [8] C. Leibovici, *Theor. Chim. Acta* (Berlin), **12**, 34 (1968).
- [9] D. A. Lowitz, *J. Chem. Phys.*, **46**, 4698 (1967).
- [10] H. J. Monkhorst, J. Kommandeur, *J. Chem. Phys.*, **47**, 391 (1967).
- [11] A. S. N. Murthy, R. E. Davis, C. N. Rao, *Theor. Chim. Acta* (Berlin), **13**, 81 (1969).
- [12] J. A. Pople, D. P. Santry, G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); *ibid.*, **43**, S136 (1965).
- [13] J. A. Pople, G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).
- [14] B. Roos, *Acta Chem. Scand.*, **20**, 1673 (1966).
- [15] C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960).