Theoret. chim. Acta (Berl.) 5, 398—400 (1966)

# Self-Consistent-Field Theory for One-Electron Properties*

SERAFIN FRAGA and FRASER W. BIRSS

Division of Theoretical Chemistry, Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada

Received June 6, 1966

The SCF-formalism is modified to include as constraints in the variational procedure physical quantities defined by one-electron operators. Introducing empirical values for the expectation values of these operators, pseudo-eigenvalue equations are obtained whose solution will lead to self-consistent orbitals which are constrained to achieve the chosen empirical values.

Die SCF Methode ist abgewandelt, um als Nebenbedingung in der Variationsmethode physikalische Eigenschaften einzuschließen, die durch Ein-Elektron-Operatoren definiert sind. Durch Einführung von empirischen Werten für die Erwartungswerte dieser Operatoren erhält man Pseudo-Eigenwert-Gleichungen, deren Lösung zu SCF-Orbitalen führt, die die gewählten empirischen Werte geben.

On a modifié le formalisme de champ auto-cohérent à fin de pouvoir introduire les valeurs de propriétés physiques comme conditions sécondaires dans la méthode de variation. La solution des équations à valeurs propres, qu'on y obtient, permet d'obtenir des orbitales qui donnent les valeurs empiriques choisies.

## Introduction

The evaluation of expectation values of operators corresponding to physical observables has, in general, occupied a subordinate position within the framework of quantum-mechanical calculations. Notable exceptions are the work of MUKHERJI and KARPLUS [5], and RASIEL and WHITMAN [6]. Such expectation values are usually calculated from wave functions determined on the basis of an energy criterion. This situation exists in particular in the self-consistent-field (SCF) method.

The SCF formalism [1, 2, 3, 7] can be modified, however, in order to include as constraints in the variational procedure any physical observables related to one-electron operators.

## General Theory

FRAGA and MALLI [4] have shown that it is possible to derive the SCF equations without introducing the orthonormality conditions of the occupied orbitals as constraints in the variational treatment. This situation opens the way for the inclusion of any other constraint.

The proposed additional constraint to be considered in this work is that the expectation value for a one-electron operator $\mathscr{P}$,

$$P = \langle \Phi \mid \mathscr{P} \mid \Phi \rangle / \langle \Phi \mid \Phi \rangle \tag{1}$$

* This work has been supported in part by the National Research Council of Canada.

shall have a certain desired value.

Restricting the discussion to electronic systems with closed-shell configurations, variation of $E$ and $P$ leads to

$$\delta E = 2 \sum_i \langle \delta\varphi_i \,|\, \{\mathscr{F} - [E - \sum_k (F_{kk} + H_{kk})]\}\varphi_i - \sum_j F_{ji}\varphi_j\rangle + \\ + \text{complex conjugate} = 0\,, \tag{2}$$

$$\delta P = 2 \sum_i \langle \delta\varphi_i \,|\, [\mathscr{P} - (P - 2\sum_k P_{kk})]\varphi_i - \sum_j P_{ji}\varphi_j\rangle + \text{complex conjugate} = 0\,, \tag{3}$$

where $\mathscr{F}$ is the Hartree-Fock operator, defined* by

$$\mathscr{F} = H + \sum_i (2J_i - K_i)\,,$$

where $H$ is the one-electron operator which includes the kinetic and nuclear attraction terms, and $J_i$, $K_i$ are the coulomb and exchange operators, respectively. The summations extend over all the occupied orbitals in the system. The integrals are defined by the expressions

$$H_{ij} = \langle \varphi_i \,|\, H \,|\, \varphi_j\rangle\,, \qquad F_{ij} = \langle \varphi_i \,|\, \mathscr{F} \,|\, \varphi_j\rangle\,, \qquad P_{ij} = \langle \varphi_i \,|\, \mathscr{P} \,|\, \varphi_j\rangle\,.$$

Associating the Lagrangian multiplier $\lambda_p$ with $\delta P$ and summing $\delta E$ and $\lambda_p\,\delta P$, one obtains

$$\{\mathscr{F} + \lambda_p\mathscr{P} - [E - \sum_k (F_{kk} + H_{kk})] - \lambda_p[P - 2\sum_k P_{kk}]\}\varphi_i - \\ - \sum_j (F_{ji} + \lambda_p P_{ji})\varphi_j\rangle = 0\,. \tag{4}$$

The quantity $E - \sum_k (F_{kk} + H_{kk})$ is identically zero since the summation is the expression of the total electronic energy, which is entirely determined by the orbitals. The term $\lambda_p[P - 2\sum_k P_{kk}]$ must necessarily be given a different treatment if the object of the present formulation is to be attained. If no value of $P$ is pre-chosen, implying the calculation of $P$ from the orbitals, the term is zero and the above equation reduces to that obtained when only the energy minimization is operative. Making the distinction that $P$ shall have a fixed empirical value, Eq. (4) can be written as

$$(\mathscr{T} - \lambda_p[P - 2\sum_k P_{kk}]\,|\,\varphi_i\rangle = \sum_j |\,\varphi_j\,\rangle\,\tau_{ji}\,, \tag{5}$$

with

$$\mathscr{T} = \mathscr{F} + \lambda_p\mathscr{P}\,,$$
$$\tau_{ji} = F_{ji} + \lambda_p P_{ji}\,.$$

The unitary transformation which diagonalizes the matrix of the $\tau_{ji}$ will leave $\mathscr{F}$, and hence $\mathscr{T}$, invariant so that there exists the pseudo-eigenvalue equation**

$$(\mathscr{T} - \lambda_p[P - 2\sum_k P_{kk}]\,|\,\varphi_i\rangle = |\,\varphi_i\rangle\,\tau_{ii}\,. \tag{6}$$

If more than one physical property (with corresponding one-electron operator) is to be considered, one would require $\sum_p \lambda_p\,\delta P$ to be added to $\delta E$. The equations

* For more details see any of the original references [*1, 2, 3, 7*].

** Although all the quantities in this expression should be affected by a prime, in order to indicate that a transformation has taken place, the prime is dropped for simplicity.

for this more general cases are completely analogous to the case of a single constraint.

## Discussion

Because of the presence of the Lagrangian multiplier, $\lambda_p$, the application of the present formalism will differ from the normal, unrestricted SCF application. For a given pre-set value of $P$ there exists a unique value of $\lambda_p$. Restricted self-consistent orbitals which will give this value of $P$ will not be attained until the proper value of $\lambda_p$ is being used. This implies a procedure of trial and error centered about the value of $\lambda_p$. For an arbitrarily chosen set of values of $\lambda_p$, one would perform the corresponding set of restricted SCF calculations, computing the expectation value of $\mathscr{P}$ for each set of vectors so obtained. From this information a new series of $\lambda_p$ can be chosen, and the process repeated until one has found that unique value of $\lambda_p$ which permits self-consistent orbitals giving rise to the chosen value of $P$.

When more than one physical property is being used as the source of a constraint the above procedure is generalized to include one Lagrangian multiplier associated with each operator $\mathscr{P}$. In this case another problem can arise: that of being unable to find a single set of orbitals which can give the empirically chosen values of the physical properties simultaneously. In practice, some compromise would be required, or the attempt must be abandoned.

## References

[1] BIRSS, F. W., and S. FRAGA: J. chem. Physics **38**, 2552 (1963); **40**, 3212 (1964).
[2] FRAGA, S., and F. W. BIRSS: J. chem. Physics **40**, 3202, 3207 (1964).
[3] — Theoret. chim. Acta (Berlin) **2**, 403 (1964).
[4] —, and G. MALLI: Theoret. chim. Acta (Berlin) **5**, 446 (1966).
[5] MUKHERJI, A., and M. KARPLUS: J. chem. Physics **38**, 44 (1963).
[6] RASIEL, Y., and D. R. WHITMAN: J. chem. Physics **42**, 2124 (1965).
[7] ROOTHAAN, C. C. J.: Rev. mod. Physics **21**, 69 (1951).

Prof. S. FRAGA
Division of Theoretical Chemistry
Department of Chemistry
University of Alberta
Edmonton, Alberta, Canada