Theoret. chim. Acta (Berl.) 2, 181—185 (1964)

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

Koopmans' Theorem and Virtual Orbital Energies in the General SCF Theory

By

W. G. **Laidlaw*** and F. W. **Birss**

The equality of the ionization potential and the orbital energy of the electron being removed is investigated using a general SCF theory for open-shell configurations. The significance of virtual orbital energies is investigated in the same context.

Die Gleichsetzung von Ionisierungsenergie und entsprechender Einelektronenenergie wird für Konfigurationen mit unabgeschlossenen Schalen mit Hilfe einer allgemeinen SCF-Theorie geprüft. In diesem Rahmen wird auch die Bedeutung von virtuellen Einelektronenenergien untersucht.

L'équation entre le potentiel d'ionisation et l'énergie orbitale de l'électron correspondant est examinée à l'aide d'une théorie générale SCF pour les configurations à couches ouvertes. Au cadre de cette théorie, la signification des énergies d'orbitales inoccupées est étudiée.

Introduction

The determination of the electronic energy by a variational calculation was formerly restricted to those systems that the available SCF formalisms were capable of handling, namely, closed-shell and some open-shell configurations [*2, 6, 7*]. As a result the energies of many open-shell systems have been approximated by calculations based upon the nearest tractable configuration. Thus, the ionization potential has been approximated by the energy of the pertinent occupied orbital in the parent closed-shell system; excited state functions have been formed using virtual orbitals.

Recently more general methods have been advanced, in particular, **Huzinaga**'s method [*3*], in which SCF improvement of one orbital at a time is carried out, and the general SCF theory of **Birss** and **Fraga** [*1*] which formulates the problem with a simultaneous variation of all the orbitals.

In this paper the statement of Koopmans' theorem in the context of the general SCF theory is investigated and the applicability of virtual orbital energies is discussed.

The SCF Formalisms

For closed-shell systems **Roothaan** [*6*] has given the Hartree-Fock equations for orbitals φ_i' as:

$$F \varphi_i' = \Sigma_j \varphi_j' \varepsilon_{ji}'$$

where F is the Hartree-Fock operator:

$$F = H + \Sigma_k (2 J_k - K_k)$$

---

* Present address: Mathematical Institute, 10 Parks Road, Oxford, England.

with H the one-electron operator composed of the kinetic energy operator and the operators expressing the attractive field of the nuclei of the system. J_k and K_k are the coulomb and exchange operators defined in terms of the k^{th} orbital. The j and k summations are over all occupied orbitals. The ε'_{ji} are the Lagrangian multipliers introduced to satisfy the orthonormality constraints imposed upon the orbitals. A suitable unitary matrix can be found which diagonalizes the matrix of Lagrangian multipliers and transforms the orbitals into a new set while leaving the operator F invariant. This is possible only for closed-shell orbital sets. The Hartree-Fock equations then become:

$$F \varphi_i = \varphi_i \varepsilon_i$$

with:

$$\varepsilon_i = \langle \varphi_i \mid F \mid \varphi_i \rangle$$

being defined as the orbital energy. The total electronic energy is [*7*]:

$$E(F) = \Sigma_i (\varepsilon_i + H_i) \ ,$$

the summation extending over all occupied orbitals, with:

$$H_i = \langle \varphi_i \mid H \mid \varphi_i \rangle \ .$$

In open-shell systems the unitary transformation technique cannot be used to solve the problem presented by the off-diagonal Lagrangian multipliers. Following lines similar to those indicated by Roothaan [*7*] and Huzinaga [*3*], Birss and Fraga [*1*] derive the Hartree-Fock equations:

$$F_i^{\mu\alpha} \varphi_i^{\mu\alpha} = \Sigma_j \varphi_j^{\mu\alpha} \theta_{ji}^{\mu\alpha}$$

where the summation extends over all occupied orbitals bearing the symmetry species designation μ and subspecies designation α. The Hartree-Fock operator is:

$$F_i^{\mu\alpha} = f_i^{\mu} (H + \Sigma_j f_j^{\mu} I_j^{\mu\alpha} + \Sigma_{m\nu\beta \neq \alpha} f_m^{\nu} I_m^{\nu\beta})$$

with*:

$$I_k^{\lambda\gamma} = 2\, a_{ik}^{\mu\alpha,\lambda\gamma} J_k^{\lambda\gamma} - b_{ik}^{\mu\alpha,\lambda\gamma} K_k^{\lambda\gamma} \ .$$

The f_i^{μ} are fractional occupancy parameters allowing for incomplete occupancy of a set of degenerate orbitals. The a and b parameters are functions of the state of the configuration. Due to these parameters the Hartree-Fock operators are defined with respect to a single orbital. The J_k and K_k operators are similar to those defined in the Roothaan formalism.

Recognizing that:

$$\theta_{ji}^{\mu\alpha} = \langle \varphi_j^{\mu\alpha} \mid F_i^{\mu\alpha} \mid \varphi_i^{\mu\alpha} \rangle$$

the Hartree-Fock equations are rewritten as:

$$F_i^{\mu\alpha} \varphi_i^{\mu\alpha} - \Sigma_j \mid \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} \mid F_i^{\mu\alpha} \mid \varphi_i^{\mu\alpha} \rangle + \mid \varphi_i^{\mu\alpha} \rangle \langle \varphi_i^{\mu\alpha} \mid F_i^{\mu\alpha} \mid \varphi_i^{\mu\alpha} \rangle = \varphi_i^{\mu\alpha} \theta_{ii}^{\mu\alpha} \ .$$

Birss and Fraga then define a general coupling operator $R^{\mu\alpha}$ such that:

$$R^{\mu\alpha} \varphi_i^{\mu\alpha} = \varphi_i^{\mu\alpha} \theta_{ii}^{\mu\alpha} \ .$$

This requires that:

$$R^{\mu\alpha} = \Sigma_j r_j^{\mu\alpha}$$

---

* This expression differs slightly from that given in [*1*]. See reference [*5*].

with:

$$\begin{aligned} r_j^{\mu\alpha} = {} & | \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} | F_j^{\mu\alpha}) - \Sigma_k | \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} | F_k^{\mu\alpha} | \varphi_k^{\mu\alpha} \rangle \langle \varphi_k^{\mu\alpha} | + \\ & + | \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} | F_j^{\mu\alpha} | \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} | - \\ & - \Sigma_k | \varphi_k^{\mu\alpha} \rangle \langle \varphi_k^{\mu\alpha} | F_k^{\mu\alpha} | \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} | + (F_j^{\mu\alpha} | \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} | \ , \end{aligned}$$

all summations being taken over occupied orbitals bearing symmetry designation $\mu\,\alpha$.

The orbital energies are defined by:

$$\eta_i^{\mu\alpha} = \theta_{ii}^{\mu\alpha} / f_i^{\mu} \ .$$

The expression for the total electronic energy is:

$$E\,(R) = \Sigma_{i\mu\alpha}\, f_i^{\mu}\, (\eta_i^{\mu\alpha} + H_i^{\mu\alpha}) \ .$$

The Ionization Potential

The ionization potential is defined as $E_t - E_g$, where E_t and E_g are the total energies of the ionized and ground states respectively. Koopmans' theorem [*4*] approximates this difference by the orbital energy of the electron removed, on the assumption that the orbitals are unchanged by the change in configuration. The expression of the theorem for a closed-shell system in the formalism of Birss and Fraga may be readily found by properly relating some of their formulae to those of Roothaan. From equation (24) of reference [*1*] one has for the closed-shell that:

$$R^{\mu\alpha}\, \varphi_i^{\mu\alpha} = F_i^{\mu\alpha}\, \varphi_i^{\mu\alpha} = \varepsilon_i^{\mu\alpha}\, \varphi_i^{\mu\alpha} \ .$$

But:

$$R^{\mu\alpha}\, \varphi_i^{\mu\alpha} = \theta_{ii}^{\mu\alpha}\, \varphi_i^{\mu\alpha}$$

so that $\varepsilon_i^{\mu\alpha} = \theta_{ii}^{\mu\alpha}$ for the closed-shell. The equation of Birss and Fraga for the total energy of a closed-shell then becomes:

$$E\,(R) = \Sigma_{i\mu\alpha}\, (\theta_{ii}^{\mu\alpha} + H_i^{\mu\alpha}) = \Sigma_{i\mu\alpha}\, (\varepsilon_i^{\mu\alpha} + H_i^{\mu\alpha}) \ .$$

One thus obtains $E(R) = E(F)$, as one must, an explicit statement that the total energies by the two methods are identical for the closed-shell.

When the orbitals of the ionized and ground states are identical Roothaan [*6*] has shown that, for ionization from orbital v:

$$E_g\,(F) - \varepsilon_v = E_t\,(F) \ .$$

Since $E_g\,(F) = E_g\,(R)$ and $\varepsilon_v = \theta_{vv}$ for a closed-shell, one has:

$$E_g\,(R) - \theta_{vv} = E_t\,(F) \ ;$$

but:

$$E_g\,(R) - \theta_{vv} = E_t\,(R)$$

and hence $E_t\,(R) = E_t\,(F)$. Thus:

$$E_g\,(F) - E_t\,(F) = \varepsilon_v$$

$$E_g\,(R) - E_t\,(R) = \theta_{vv}$$

are identical statements and the latter may be taken as the statement of Koopmans' theorem for a closed-shell configuration in the formalism of the R operator.

The expression of $E_g - E_t$ in terms of the ground state parameters when both states, or the ground state, are open-shell configurations cannot be shown in general without explicit reference to the spin-states involved. This can be readily seen, for if the energies are written in terms of integrals over the Hartree-Fock operators, terms such as:

$$f_{i,g}^{\mu} f_{m,g}^{\nu} I_{im,g}^{\mu\alpha,\nu\beta} - f_{i,t}^{\mu} f_{m,t}^{\nu} I_{im,t}^{\mu\alpha,\nu\beta}$$

will occur. Expanding the integrals gives:

$$\begin{aligned} & f_{i,g}^{\mu} f_{m,g}^{\nu} (2\, a_{im,g}^{\mu\alpha,\nu\beta} J_{im}^{\mu\alpha,\nu\beta} - b_{im,g}^{\mu\alpha,\nu\beta} K_{im}^{\mu\alpha,\nu\beta}) - \\ & - f_{i,t}^{\mu} f_{m,t}^{\nu} (2\, a_{im,t}^{\mu\alpha,\nu\beta} J_{im}^{\mu\alpha,\nu\beta} - b_{im,t}^{\mu\alpha,\nu\beta} K_{im}^{\mu\alpha,\nu\beta}) \;. \end{aligned}$$

In general, to express this difference in terms of the ground state parameters only, it would be necessary to relate the ionized state a, b and f parameters to those of the ground state. Such a general relation can be found for the f parameters since they are independent of spin-states and depend on occupancy only. On the other hand the relation of the sets of a and b parameters is highly dependent upon the spin character of both states. For example, compare the parameters required for the description of the $1\,s^2\,2\,p^3\;{}^4S$ and ${}^2P$ states of the ion arising from the common ${}^3P$ ground state of the carbon atom. The relation between the f parameters is identical whereas that between the sets of a and b parameters cannot be simply generalized. Hence it is suggested that a demonstration of Koopmans' theorem be undertaken in the context of the particular case considered.

One such case is that of *Li*-*Li*$^+$. Here:

$$E_g = 2\,H_1 + H_2 + I_{11} + I_{12}$$

$$E_t = 2\,H_1 + I_{11} \;,$$

(since $I_{22} = 0$), so that:

$$E_g - E_t = H_2 + I_{12} \;.$$

Since the orbital energy is:

$$\eta_2 = \theta_{22}/f_2 = H_2 + I_{12}$$

one obtains:

$$E_g - E_t = \eta_2 \;.$$

Virtual Orbital Energies

The virtual orbital energies from the closed-shell formalism of ROOTHAAN [6] could be used in the calculation of excitation energies assuming that all orbitals are the same in both ground and excited states. However, it can be shown that this application is possible only for certain cases in the formalism of the general SCF theory.

In the definitions of the $R^{\mu\alpha}$ and $r_k^{\mu\alpha}$ operators the subscripts refer to occupied orbitals and the summations extend over occupied orbitals only. In fact, the development makes no reference to unoccupied orbitals. However, in the LCAO context both occupied and unoccupied orbital coefficients are obtained and, whether occupied or not, all corresponding orbitals must be orthogonal.

Letting $\varphi_m^{\mu\alpha}$ be an unoccupied orbital, one has that:

$$\begin{aligned} & R^{\mu\alpha} \mid \varphi_m^{\mu\alpha} \rangle = \Sigma_j\, r_j^{\mu\alpha} \mid \varphi_m^{\mu\alpha} \rangle \\ & = \Sigma_j \mid \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} \mid F_j^{\mu\alpha} \mid \varphi_m^{\mu\alpha} \rangle - \Sigma_{jk} \mid \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} \mid F_k^{\mu\alpha} \mid \varphi_k^{\mu\alpha} \rangle \times \\ & \times \langle \varphi_k^{\mu\alpha} \mid \varphi_m^{\mu\alpha} \rangle + \Sigma_j \mid \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} \mid F_j^{\mu\alpha} \mid \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} \mid \varphi_m^{\mu\alpha} \rangle - \\ & - \Sigma_{jk} \mid \varphi_k^{\mu\alpha} \rangle \langle \varphi_k^{\mu\alpha} \mid F_k^{\mu\alpha} \mid \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} \mid \varphi_m^{\mu\alpha} \rangle + \\ & + \Sigma_j \mid F_j^{\mu\alpha} \mid \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} \mid \varphi_m^{\mu\alpha} \rangle \;. \end{aligned}$$

Because of the range of the summations, $j, k \neq m$, and by virtue of the orthogonality:

$$\langle \varphi_j^{\mu\alpha} | \varphi_m^{\mu\alpha} \rangle = \langle \varphi_k^{\mu\alpha} | \varphi_m^{\mu\alpha} \rangle = 0 \ ,$$

the equation reduces to:

$$R^{\mu\alpha} | \varphi_m^{\mu\alpha} \rangle = \Sigma_j | \varphi_j^{\mu\alpha} \rangle \langle \varphi_j^{\mu\alpha} | F_j^{\mu\alpha} | \varphi_m^{\mu\alpha} \rangle \ .$$

In an attempt to determine a quantity similar to that obtained for occupied orbitals, one forms:

$$\theta_{mm}^{\mu\alpha} = \langle \varphi_m^{\mu\alpha} | R^{\mu\alpha} | \varphi_m^{\mu\alpha} \rangle \ .$$

Again orthogonality causes the right hand side to vanish so that the $\theta_{mm}^{\mu\alpha}$ for unoccupied orbitals are all zero simply on the grounds of orthogonality; they cannot be considered as being related to proper orbital energies.

Virtual orbital energies, although not obtainable as the expectation value of the $R^{\mu\alpha}$ operator, may be found for some cases by the use of the $F_i^{\mu\alpha}$ operators which occur in the formulation of the $R^{\mu\alpha}$. For occupied orbitals one has:

$$\langle \varphi_i^{\mu\alpha} | R^{\mu\alpha} | \varphi_i^{\mu\alpha} \rangle = \langle \varphi_i^{\mu\alpha} | F_j^{\mu\alpha} | \varphi_j^{\mu\alpha} \rangle = \theta_{jj}^{\mu\alpha}$$

i.e., the $\theta_{ii}^{\mu\alpha}$ for the occupied orbital $\varphi_i^{\mu\alpha}$ can be obtained with equal validity as the expectation value of $R^{\mu\alpha}$ or $F_i^{\mu\alpha}$. From the definition of orbital energy one has:

$$\eta_i^{\mu\alpha} = \theta_{ii}^{\mu\alpha} / f_i^{\mu} = \langle \varphi_i^{\mu\alpha} | F_i^{\mu\alpha} / f_i^{\mu} | \varphi_i^{\mu\alpha} \rangle \ .$$

Taking the definition of virtual orbital energy to mean the expectation value of that operator which may be used to evaluate the occupied orbital energies, one can use exactly the same form to determine the virtual orbital energies. The problem is then to choose the $F_i^{\mu\alpha}/f_i^{\mu}$. In closed-shell configurations all such operators are identical and no uncertainty arises; even in some open-shell configurations the $F_i^{\mu\alpha}/f_i^{\mu}$ may be the same within a given symmetry species (e. g., the operators for the $1s$ and $2s$ orbitals in the configurations $1s^1 2s^1 2p^n$). However, in situations where the $F_i^{\mu\alpha}/f_i^{\mu}$ are different within a symmetry species, the selection of the proper operator cannot be made. Some further step must be taken, such as using an operator averaged within a symmetry species.

Acknowledgments. The authors wish to express their thanks to Dr. S. Fraga for helpful comments on this work. The financial assistance of the National Research Council of Canada is gratefully acknowledged.

References

[1] Birss, F. W., and S. Fraga: J. chem. Physics **38**, 2552 (1963).
[2] Huzinaga, S.: Physic. Rev. **120**, 866 (1960).
[3] — Physic. Rev. **122**, 131 (1961).
[4] Koopmans, T. A.: Physica **1**, 104 (1933).
[5] Laidlaw, W. G.: J. chem. Physics accepted publication, April 1964.
[6] Roothaan, C. C. J.: Revs. mod. Physics **23**, 69 (1951).
[7] — Revs. mod. Physics **32**, 179 (1960).

(Received February 6/27, 1964)