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Self-Consistent-Field Theory for Positive Ions*

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Investigation of the stability characteristics of Hartree-Fock functions leads to conclusions of interest in relation to the functions of positive ions. These considerations, in conjunction with an existing modified SCF formalism, make it possible to reformulate the SCF method in order to adapt it to the determination of Hartree-Fock functions for positive ions.

Die Untersuchung der Stabilitätseigenschaften von Hartree-Fock-Funktionen führt zu Schlußfolgerungen, die von Interesse sind im Zusammenhang mit Funktionen für positive Ionen. Diese Betrachtungen, in Verbindung mit einem veränderten SCF-Formalismus, machen es möglich, die SCF-Methode umzuformulieren, um sie der Bestimmung von Hartree-Fock-Funktionen für positive Ionen anzupassen.

L'étude de la stabilité des fonctions de Hartree-Fock mène à des conclusions présentant un intérêt par rapport aux fonctions des ions positifs. Ces considérations, liées à un formalisme SCF modifié, permettent de reformuler la méthode SCF en l'adaptant à la déterminantion des fonctions de Hartree-Fock des ions positifs.

Introduction

FRAGA [*2*] and PRIESTLEY and FRAGA [*8*] have reported the existence of certain numerical characteristics for Hartree-Fock functions. The numerical values found for neutral systems and negative ions show a very interesting behavior: they are almost constant, with oscillations within a very small range. On the other hand the discrepancies observed for positive ions increase with the number of positive charges.

It was therefore considered important to investigate the possible reasons for such difference, arriving at the conclusion that perhaps the functions for positive ions should be determined through a formalism different from that used for neutral systems and negative ions.

The development of this formalism involves a series of considerations. First of all, an examination of the stability conditions for Hartree-Fock functions shows that it is legitimate to have orbital energies that are identically zero. This fact opens the way to the new formulation, where one introduces as constraints the conditions that the orbital energies of the ionized electrons will be precisely zero. The mathematical apparatus makes use of the fact that there is no need of intro-

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ducing the orthonormality constraints in the variational treatment, as shown by FRAGA and MALLI [*6*], being able to use instead any other constraint, following the formulation of FRAGA and BIRSS [*5*].

General Theory

The Stability Conditions of Hartree-Fock Functions

In order to deal with a simpler mathematical formulation, an electronic system with a closed-shell configuration will be considered here. The corresponding electronic Hamiltonian is

$$\mathscr{H} = \sum_{\varrho} H^{\varrho} + \sum_{\varrho<\tau} (1/r^{\varrho\tau}) \,, \tag{1}$$

where the summations extend over all the electrons in the system. H^{ϱ} represents the one-electron part of the Hamiltonian, and contains the kinetic and nuclear attraction terms; the term $(1/r^{\varrho\tau})$ represents the electronic repulsion between electrons ϱ and τ. The (normalized) total electronic function is given, within the independent-particle approximation, by a single Slater determinant.

The total electronic energy can be written*, for orthonormal orbitals, as

$$E = 2 \sum_{i} H_{ii} + \sum_{i} \sum_{j} I_{ij} \,, \tag{2}$$

where the summations extend over all the occupied orbitals in the system. The integrals in this expression are defined by the relations

$$H_{ii} = \langle \phi_i \mid H \mid \phi_i \rangle \,, \tag{3a}$$

$$I_{ij} = \langle \phi_i \mid I_j \mid \phi_i \rangle = \langle \phi_j \mid I_i \mid \phi_j \rangle = I_{ji} \,, \tag{3b}$$

where ϕ_i represents any of the orbitals for the system under consideration; the subindices $i, j, \ldots$ label the occupied orbitals, and the subindices $m, n, \ldots$ correspond to unoccupied orbitals. I_j represents a two-electron operator, made up of coulomb and exchange operators, J_j and K_j, respectively.

The best orbitals, under an energy criterion, are determined by application of a variational treatment, in which one investigates the behavior of the energy variations corresponding to infinitesimal variations of the orbitals. It is customary, in such treatments, to impose the subsidiary condition that the varied orbitals remain orthonormalized.

Two facts must be pointed out in this connection. First of all it must be mentioned that, as proved by FRAGA and MALLI [*6*], there is no need whatsoever of introducing these subsidiary conditions in order to obtain the usual SCF equations (see below) for orthonormal orbitals. On the other hand, it must be emphasized that the orbitals can be varied one at a time, while insuring that they remain orthogonal to all the remaining occupied orbitals, and properly normalized.

In order to attain such a condition, as indicated by THOULESS [*11*], it is required that the varied orbital be expressed as

$$\phi_i' = \phi_i + \omega \phi_m \,, \tag{4}$$

where ω is an arbitrarily chosen infinitesimal and ϕ_m is an unoccupied orbital,

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* For more details, see the work of ROOTHAAN [*10*].

orthogonal to all the occupied orbitals. The orthonormality conditions for the varied orbital ϕ_i' are then given by

$$\langle \phi_i' \mid \phi_i' \rangle = \langle \phi_i \mid \phi_i \rangle + \omega \langle \phi_i \mid \phi_m \rangle + \omega \langle \phi_m \mid \phi_i \rangle + \omega^2 \langle \phi_m \mid \phi_m \rangle = 1 + \omega^2 \,, \quad \text{(5a)}$$

$$\langle \phi_i' \mid \phi_j \rangle = \langle \phi_i \mid \phi_j \rangle + \omega \langle \phi_m \mid \phi_j \rangle = 0 \,, \quad \text{(5b)}$$

which show that the varied orbital is certainly orthogonal to all the other occupied orbitals, and remains normalized (to first order in ω).

When the orbital ϕ_i is varied into ϕ_i', the resulting total electronic energy E', to second order in ω and for real orbitals, is given by

$$E' = [E(1 + 2\omega^2) + 2\omega(\delta E + \delta \bar{E}) + 2\omega^2 \, \delta^2 E]/(1 + 2\omega^2) \,, \quad \text{(6a)}$$

with

$$\delta E = \langle \phi_m \mid H + \sum_j I_j \mid \phi_i \rangle \,, \quad \text{(6b)}$$

$$\delta^2 E = \langle \phi_m \mid H + \sum_j I_j \mid \phi_m \rangle - \langle \phi_i \mid H + \sum_j I_j \mid \phi_i \rangle \,, \quad \text{(6c)}$$

where the summations extend over all the occupied orbitals. The composite operator $(H + \sum_j I_j)$ is the SCF operator, usually represented by F. The term $\delta \bar{E}$ represents the complex conjugate of δE.

In SCF theory it is stated that the necessary, though not sufficient condition for E to reach an absolute minimum is that $\delta E = 0$ (and, therefore, $\delta \bar{E} = 0$) for any infinitesimal, non-vanishing variation of ϕ_i, which satisfies, of course, the orthonormality requirements. The condition $\langle \phi_m \mid F \mid \phi_i \rangle = 0$ leads to the pseudo-eigenvalue equation*

$$(F \mid \phi_i \rangle = \sum_j \mid \phi_j \rangle \, \theta_{ji} \,. \quad \text{(7)}$$

It can then be seen, as mentioned by THOULESS [*11*], that the stability of Hartree-Fock functions, to first order, is satisfied whenever $\theta_{mi} = 0$, for any ϕ_i and ϕ_m. That is, the Lagrangian multipliers matrix θ must be factored into two blocks, one for the occupied and the other for the unoccupied orbitals. These two submatrices can be diagonalized by independent, unitary transformations of both sets of orbitals.

The stability of the Hartree-Fock functions can now be investigated to second order in ω. Taking into account that $(1 + 2\omega^2)$ must necessarily be positive, the necessary condition reduces to $\delta^2 E \geq 0$, which leads, taking into account Eq. (6), to

$$\theta_{mm} - \theta_{ii} \geq 0 \,. \quad \text{(8)}$$

The condition represented by this equation simply states that the orbital energy of any occupied orbital must be lower than, or equal to the orbital energy of any of the unoccupied orbitals**. This condition is usually satisfied as the orbital energies of occupied orbitals are negative and the orbital energies of unoccupied orbitals are positive.

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* It must be mentioned that this result confirms the independent proof given by FRAGA and MALLI [*6*].

** THOULESS [*11*] arrives at this result by considering the theoretical excitation energies, with neglect of some terms which do not affect the discussion. Similarly, a term $(3K_{im} - J_{im})$ has been neglected in Eqs. (6c) and (8) of this paper.

It can be seen, though, that it does not have to be necessarily so. That is, the orbital energies of unoccupied orbitals may be negative, as long as they will be greater than those of the occupied orbitals; as a matter of fact there are cases where at least the lowest θ_{mm} has been found to be negative; in this connection one can mention the results of RANSIL [*9*].

Because of the uncertainty in ascribing a meaning to the orbital energies corresponding to unoccupied orbitals, as pointed out by ROOTHAAN [*10*], one might conclude that the above condition does not offer any special importance, especially taking into account that it seems to be automatically satisfied in every case. There is, though, one case where it can be of special interest, namely in connection with positive ions.

General Considerations Regarding Positive Ions

Theoretical calculations for positive ions should be carried out in the same way as those for neutral systems and negative ions. The only difference will arise from the fact that the coordinates of the ionized electrons are removed from the Hamiltonian of the corresponding neutral system.

This procedure is based on the following considerations. If $\mathscr{H}^N$ and $\mathscr{H}^{N-1}$ are the N- and $(N–1)$-electron Hamiltonians for the system under consideration, and ψ^N and ψ^{N-1} the corresponding eigenfunctions, then the condition

$$(\mathscr{H}^N \mid \psi^{N-1}\,\psi^1\rangle = \mid \psi^{N-1}\,\psi^1\rangle\, E^{N-1} \tag{9}$$

must be satisfied, ψ^1 representing here an appropriate free-particle function*, as shown by KEMBLE [*7*]. In particular, when ψ^{N-1} represents the lowest eigenstate of H^{N-1} and ψ^1 corresponds to a free-electron at rest, E^{N-1} is the energy of the groundstate of the positive ion. Considering that in such a case ψ^1 is simply a constant, the part of the Hamiltonian dependent on the coordinates of this electron becomes inoperative, and Eq. (9) transforms into

$$(\mathscr{H}^{N-1} \mid \psi^{N-1}\rangle = \mid \psi^{N-1}\rangle\, E^{N-1}\,, \tag{10}$$

which can then be used to determine ψ^{N-1}. The difference $(E^{N-1} - E^N)$ defines then the first ionization potential for the system under consideration, that is, the energy required to remove a single electron to infinity, with zero kinetic energy.

The situation is different, though, when the problem is tackled within the independent-particle approximation, using the SCF variational techniques mentioned above.

Let us consider a hypothetical system where one would follow the removal of the electron, from the original bound situation to the ionized state. From the beginning to the end of this transition, the kinetic and the interaction (nuclear attraction and electronic repulsion) energy with the rest of the system will decrease asymptotically, reaching a value zero at complete ionization. The remaining electronic density distribution will adjust itself to the new situation at each stage of the removal of the electron during this process.

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* Similar expressions can be written for higher orders of ionization. The discussion will be restricted here to the case of singly charged positive ions, with the understanding that it can be extended to ions with any number of positive charges.

One could assume that the total state function for the complete system can be determined at each stage of this transition; in particular, one could determine it for the ionized state, under the condition that the ionized electron must be at rest. The transformation of the total state function, when going from the completely bound to the ionized situation, should be monotonous. This procedure, if mathematically feasible, would lead to the correct situation at the ionization limit and therefore the result thus obtained could be used to test the accuracy of the calculations carried out by any other method. In particular, if the calculation is carried within the framework of the SCF method, it will provide a test for the existing functions of positive ions. The indications, as summarized below, seem to point out a difference.

The procedure sketched above, and its implications, can be best understood through a concrete example. Let us consider the case of Li, with an electronic configuration $(1s)^2(ns)$, where n can take successively higher values. The corresponding functions can be determined by the SCF procedure developed by FRAGA and BIRSS [*4*] on the basis of a generalized variational procedure. The orbital energy of the orbital *ns* will increase with n, tending asymptotically to zero (which will correspond to the ionization limit).

Let us now consider the calculation of the function for the groundstate of the positive ion, applying the standard SCF techniques. No reference is made to the ionized electron, which is neglected. If one uses the same basis set (in order to standardize the comparison) one will find a curious situation regarding the orbital energies.

For each case of the series $(1s)^2(ns)$, there are two negative orbital energies. At high values of n the results will be such that the interaction of the electron in the *ns*-orbital with the rest of the system (i.e., the nucleus and the other two electrons) will be very small, and so will be its kinetic energy. This fact is reflected in the small (negative) orbital energy. But suddenly, when the calculation for the groundstate of the ion is carried out, there will be, in general, only one negative orbital energy, corresponding to the 1*s*-orbital; the second lowest orbital energy will already be positive, and there is nothing in the standard formulation which will impose any restriction on the actual value it can take. There is clearly a discontinuity and the function thus determined cannot be considered to constitute a proper representation of the groundstate of the positive ion. The functions of positive ions should be determined by a modified SCF procedure.

Let us consider the case of a singly-charged positive ion. The procedure consists then of solving the problem for the complete system with N electrons, but imposing the subsidiary condition that one of them will have zero kinetic energy, with no interaction with the rest of the system. Within the orbital approximation, the above conditions, when coupled together, lead to the composite condition that the orbital energy of the ionized electron must be identically zero, which, as shown in the preceeding section, is perfectly compatible with a stable system.

The corresponding mathematical formulation is now possible due to a recent development in SCF theory by FRAGA and MALLI [*6*] who have shown that there is no need of introducing the orthonormality conditions within the variational treatment. This fact makes it possible, as used by FRAGA and BIRSS [*5*], to introduce any other constraint one may find convenient.

Mathematical Formulation

One is then faced with the development of an SCF formalism in which the special conditions concerning the ionized electrons are used as secondary constraints.

Two problems require special consideration: the symmetry of the unoccupied orbitals and their occupancy. For the exact solution of the problem, as mentioned above, the orbitals "occupied" by the ionized electrons must be free-electron functions, without any symmetry designation and singly occupied. Within the framework of the orbital approximation, the natural solution seems to assume they posess the same symmetry and occupancy as in the groundstate of the corresponding neutral system*. In order to simplify the formulation to be presented in this paper, with the understanding of its possible generalization, the case of a doubly-charged positive ion, with a closed-shell electronic configuration, will be considered here. The corresponding neutral system is also considered to have a closed-shell configuration.

Before proceeding any further it is necessary to mention also the problem that may arise in connection with the basis set to be used in practical calculations, as this consideration is closely related to the distinction between "bound" and "ionized" orbitals. This problem has been discussed by **Fraga** [*3*] in connection with a similar problem, with the conclusion of using independent basis sets for the two sets of orbitals; difficulties in the practical execution would hinder the calculations, and therefore it seems advisable to compromise on the extent to which the subsidiary constraints will be satisfied, as discussed below.

The set of constraints to be considered are those corresponding to the energy interactions**. An accurate treatment would require the formulation of the separate conditions

$$\langle \phi_m \mid -\tfrac{1}{2}\nabla^2 \mid \phi_m \rangle = 0\,, \tag{11a}$$

$$\left\langle \phi_m \left| -\sum_a \frac{Z_a}{r_a} \right| \phi_m \right\rangle = 0\,, \tag{11b}$$

$$\langle \phi_m \mid \sum_i I_i \mid \phi_m \rangle = 0\,, \tag{11c}$$

where $-\frac{1}{2}\nabla^2$ represents the kinetic energy operator, $-\sum_a \frac{Z_a}{r_a}$ consists of the nuclear attraction terms (with the summation extending over all the nuclei present) of the Hamiltonian under consideration, and $\sum_i I_i$ gives the potential field due to the bound electrons.

A simpler formulation is obtained if one takes into account that the virtual orbital energies roughly represent the interaction of excess electrons with the nuclei and the bound electrons. Therefore one can consider, instead of the conditions represented by Eqs. (11) the single condition

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* A modification must be introduced, e.g., when dealing with those cases where there is a partial ionization of an electronic shell; this is the problem that will be encountered when dealing, e.g., with C^+, F^+, etc.

** In those cases where there are more than one ionized electron, it may also be necessary to consider their mutual interactions. In this case this condition is taken partially into account by the introduction of a composite constraint.

$$\theta_{mm} = \langle \phi_m \mid F \mid \phi_m \rangle = 0\,, \tag{12}$$

where F is the Hartree-Fock operator corresponding to the closed-shell orbitals.

Following the method of Fraga and Birss [5] one has really to consider the condition

$$\theta_{mm} = \langle \phi_m \mid F \mid \phi_m \rangle / \langle \phi_m \mid \phi_m \rangle\,. \tag{13}$$

When both the occupied and unoccupied orbitals are given an infinitesimal variation, the above condition transforms into

$$\begin{aligned} \delta\theta_{mm} \langle \phi_m \mid \phi_m \rangle + \theta_{mm} \{\langle \delta\phi_m \mid \phi_m \rangle + \langle \phi_m \mid \delta\phi_m \rangle\} \\ = \langle \delta\phi_m \mid F \mid \phi_m \rangle + \langle \phi_m \mid F \mid \delta\phi_m \rangle + \\ + \sum_j \{\langle \delta\phi_j \mid I_m \mid \phi_j \rangle + \langle \phi_j \mid I_m \mid \delta\phi_j \rangle\}\,, \end{aligned} \tag{14}$$

where the summations extend over all the occupied orbitals, including ϕ_m.

This condition can now be used as a constraint in the variational treatment of the energy. The necessary (though not sufficient) condition that E will reach an absolute minimum is that $\delta E = 0$, subject to the above constraint. Multiplying this constraint by the multiplier $2\lambda_m$, and adding it to δE, the new condition in order that E will reach an absolute minimum is that (for orthonormal orbitals)

$$\delta E' = \delta E - 2\lambda_m\, \delta\theta_{mm} = 0\,. \tag{15}$$

Proceeding in the standard fashion one obtains the SCF equations

$$(F - \lambda_m I_m \mid \phi_i \rangle = \sum_j \mid \phi_j \rangle\, \theta_{ji}\,, \tag{16a}$$

$$(F - \lambda_m (F + I_m) \mid \phi_m \rangle = \sum_{j \neq m} \mid \phi_j \rangle\, \theta_{jm} + \mid \phi_m \rangle\, \theta_{mm}(1 - \lambda_m)\,, \tag{16b}$$

with

$$\theta_{ji} = \langle \phi_j \mid F \mid \phi_i \rangle\,. \tag{17}$$

Let us now first consider the case when $\lambda_m = 0$. The constraint becomes inoperative and the above equations reduce to those corresponding to the neutral system. On the other hand, for $\lambda_m = 1$, Eq. (16a) reduces to that which is normally used for a positive ion, without any subsidiary constraint. Eq. (16b), on the other hand, leads to the condition

$$(I_m \mid \phi_m \rangle = 0\,, \tag{18}$$

which is in agreement with the original constraints, but that will only be satisfied if ϕ_m vanishes identically.

One should try, therefore, a different constraint. The one chosen is $\theta_{mm}^2 = 0$, in which case one obtains

$$\begin{aligned} \delta\theta_{mm}^2 [\langle \phi_m \mid \phi_m \rangle]^2 + 2\theta_{mm}^2 \{\langle \delta\phi_m \mid \phi_m \rangle + \langle \phi_m \mid \delta\phi_m \rangle\} \langle \phi_m \mid \phi_m \rangle \\ = 2 \langle \phi_m \mid F \mid \phi_m \rangle \{\langle \delta\phi_m \mid F \mid \phi_m \rangle + \langle \phi_m \mid F \mid \delta\phi_m \rangle + \\ + \sum_j [\langle \delta\phi_j \mid I_m \mid \phi_j \rangle + \langle \phi_j \mid I_m \mid \delta\phi_j \rangle]\}\,, \end{aligned} \tag{19}$$

which, for orthonormal orbitals, leads to the equations

$$(F - \lambda_m \langle \phi_m \mid F \mid \phi_m \rangle\, I_m \mid \phi_i \rangle = \sum_j \mid \phi_j \rangle\, \theta_{ji}\,. \tag{20a}$$

$$(F - \lambda_m \langle \phi_m \mid F \mid \phi_m \rangle\, (F + I_m) \mid \phi_m \rangle = \sum_{j \neq m} \mid \phi_j \rangle\, \theta_{jm} + \mid \phi_m \rangle\, \theta_{mm}(1 - \lambda_m \theta_{mm})\,. \tag{20b}$$

For $\lambda_m = 0$ the situation is identical to that described above. But for any other value of λ_m (and the discussion is independent of the value of λ_m, except for the extreme values, zero and infinity), the situation is now completely different.

For the practical solution there is only need to use Eq. (20a), as it will be evident from the discussion below. ROOTHAAN [*10*] showed that a unitary transformation of the occupied orbitals leaves F invariant; choosing the transformation so that all the off-diagonal Lagrangian multipliers θ_{ji} $(j \neq i)$ become zero, one can write*

$$(F - \lambda_m \langle \phi_m \mid F \mid \phi_m \rangle I_m \mid \phi_i \rangle = \mid \phi_i \rangle \theta_{ii} \,, \tag{21a}$$

$$(F - \lambda_m \langle \phi_m \mid F \mid \phi_m \rangle (F + I_m) \mid \phi_m \rangle = \mid \phi_m \rangle \theta_{mm}(1 - \lambda_m \theta_{mm}) \,. \tag{21b}$$

Eq. (21a) can now be solved by the usual procedure of trial and error, but the presence of the extra term in the operator introduces a difference. It is evident, taking into account the definition of θ_{ji}, that self-consistency will only be attained when that extra term is precisely zero. If one takes for the calculation $\lambda_m \neq 0$, say $\lambda_m = 1$, and if ϕ_m does not vanish identically, then $I_m \neq 0$. Therefore the only possibility which subsists is that $\langle \phi_m \mid F \mid \phi_m \rangle = 0$, which is precisely the constraint one wished to impose. In that case, furthermore, Eq. (20b) vanishes identically.

Discussion

First of all one has to mention that, at self-consistency, the formal definition of the Hartree-Fock operator has not changed as compared with the unrestricted formalism, except for the existence of the term I_m within it. The subsistence of this term is due to the fact that the composite constraint has been used instead of the original constraints, represented by Eq. (11). The actual difference is, of course, due to the orbitals involved in it.

This fact makes it impossible to predict how the orbital energies will change from the unrestricted to the restricted case. Given a fixed operator, not defined in terms of its own eigenfunctions, with one set of negative and another of positive eigenvalues, one would expect that a constraint similar to the one discussed here would raise the negative and/or the positive eigenvalues, in order that the trace of its matrix should remain unchanged.

The first possibility appears to be rather attractive, especially when considered in conjunction with the ratios reported by FRAGA [*2*] and PRIESTLEY and FRAGA [*8*]. A raising of the orbital energies of the occupied orbitals would certainly give a contribution in the right direction.

In any case, the present formulation insures a continuity in the transition from the high-lying excited states of a neutral system to the groundstate of the corresponding positive ion.

For those positive ions, where there is no conflict of partial ionization of a given shell, the set of orbital energies will be subdivided into three subsets of negative, zero, and positive values, corresponding to the occupied orbitals, orbitals housing the ionized electrons, and the unoccupied virtual orbitals, respectively. The meaning of the virtual orbital energies will still be effected by the same uncertainty as pointed out by ROOTHAAN [*10*] for unrestricted calculations.

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* The orbitals should be written now as ϕ_j' to indicate that a transformation has been effected. The prime is dropped for simplicity.

For those positive ions involving a partial ionization of an electronic shell, the corresponding formulation, to be carried out within the context of the general SCF theory of BIRSS and FRAGA [1], should offer no mathematical difficulty. The only question that remains to be solved is that concerning the symmetry and occupancy of the ionized orbitals. It is believed that it will be more appropriate to assume they belong to the same symmetry designation as the orbitals in the groundstate of the neutral system from which the electrons have been ionized. Regarding the occupation numbers it must be taken into account that single occupancy of the ionized orbitals finds itself in better agreement with the true situation.

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