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Non-Relativistic Self-Consistent-Field Theory. I.*

By

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A reformulation of the general self-consistent-field formalism is presented.

Es wird eine Umformulierung des allgemeinen „self-consistent-field"-Formalismus angegeben.

Le formalisme de la méthode du champ «auto-cohérent» est reformulé.

Introduction

Since the original formulation [3] of the self-consistent-field (SCF) formalism most of the efforts on this subject have been directed towards the development of new mathematical methods. General SCF formulations exist now for all electronic systems, in lowest [1] or excited [2] states, with any electronic configuration.

Unfortunately, all these formulations need the evaluation of interelectronic repulsion integrals which can, in general, be difficult to evaluate and, in any case, are time consuming. It is the purpose of this series of papers to develop a new, exact SCF formulation which obviates the need of evaluating such integrals.

The work presented in these papers consists of four main parts. First the general SCF formalism is reformulated, omitting the orthogonality constraints, in order to obtain a simpler matrix formulation. Using this reformulated SCF method the condition to be satisfied by SCF orbitals which minimize the orbital energies is then investigated. It is seen that the SCF orbitals cannot minimize the orbital energies, but this condition is then used to provide a link with the Thomas-Fermi approximation. Furthermore this condition can then be generalized, leading to the introduction of a single convergence parameter and to the development of a new SCF scheme, requiring only the evaluation of kinetic and nuclear attraction integrals. Finally, numerical results are presented for atomic systems and the practical method for the calculations outlined.

Mathematical Formulation

The general SCF procedure for lowest states can be summarized as follows**. The expression for the total electronic energy is determined (for orthonormal orbitals) by proper averaging over all the degenerate wave functions corresponding to the state under consideration, using a non-relativistic, time- and spin-independent Hamiltonian. The energy variation corresponding to an infinitesimal variation of the occupied orbitals of each symmetry designation (species and subspecies) is determined. Coupled with the adequate orthonormality conditions it

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** Only the general outline will be presented here. For more details, see Ref. [1].

leads to sets of SCF equations, one set for each symmetry designation. A general coupling operator reduces each set to a single SCF pseudo-eigenvalue equation; e. g., for symmetry designation $\lambda\,\alpha$,

$$R^{\lambda\alpha}\varphi_i^{\lambda\alpha} = \varphi_i^{\lambda\alpha}\,\theta_{ii}^{\lambda\alpha}\ , \tag{1}$$

with

$$\begin{aligned}
R^{\lambda\alpha} &= \sum_k r_k^{\lambda\alpha}\ ,\\
r_k^{\lambda\alpha} &= |\varphi_k^{\lambda\alpha}\rangle\langle\varphi_k^{\lambda\alpha}|F_k^{\lambda\alpha}| - \sum_l |\varphi_k^{\lambda\alpha}\rangle\langle\varphi_k^{\lambda\alpha}|F_l^{\lambda\alpha}|\varphi_l^{\lambda\alpha}\rangle\langle\varphi_l^{\lambda\alpha}|\\
&\quad + |\varphi_k^{\lambda\alpha}\rangle\langle\varphi_k^{\lambda\alpha}|F_k^{\lambda\alpha}|\varphi_k^{\lambda\alpha}\rangle\langle\varphi_k^{\lambda\alpha}|\\
&\quad - \sum_l |\varphi_l^{\lambda\alpha}\rangle\langle\varphi_l^{\lambda\alpha}|F_l^{\lambda\alpha}|\varphi_k^{\lambda\alpha}\rangle\langle\varphi_k^{\lambda\alpha}| + |F_k^{\lambda\alpha}|\varphi_k^{\lambda\alpha}\rangle\langle\varphi_k^{\lambda\alpha}|\,,\\
F_k^{\lambda\alpha} &= f_k^{\lambda}\Big\{H + \sum_m \sum_\mu \sum_\beta f_m^{\mu} I_{m(k)}^{\mu\beta(\lambda\alpha)}\Big\}\,,\\
I_{m(k)}^{\mu\beta(\lambda\alpha)} &= 2\,a_{km}^{\lambda\alpha,\,\mu\beta} J_m^{\mu\beta} - b_{km}^{\lambda\alpha,\,\mu\beta} K_m^{\mu\beta}\ .
\end{aligned}$$

$J_m^{\mu\beta}$ and $K_m^{\mu\beta}$ are the typical Coulomb and exchange operators of the first kind, and H is the one-electron operator; f_k^{λ}, $a_{km}^{\lambda\alpha,\,\mu\beta}$, and $b_{km}^{\lambda\alpha,\,\mu\beta}$ are constants of the problem under consideration.

These equations are solved by the usual procedure of trial and error (e. g., within the framework of the expansion method). The solution of all the SCF pseudo-eigenvalue equations is carried out simultaneously until self-consistency has been reached.

The preceding formulation can be simplified if only the normalization conditions

$$S_{mm}^{\mu\beta} = \langle\varphi_m^{\mu\beta}|\varphi_m^{\mu\beta}\rangle = 1 \tag{2}$$

are imposed as constraints. For independent, infinitesimal variations of the orbitals of any symmetry designation, e. g., $\lambda\alpha$, one obtains, proceeding in the standard fashion, the SCF equations

$$F_i^{\lambda\alpha}\varphi_i^{\lambda\alpha} = \varphi_i^{\lambda\alpha}\,\theta_{ii}^{\lambda\alpha}\ , \tag{3}$$

one for each occupied orbital of symmetry designation $\lambda\alpha$. Similar equations are obtained for all other symmetry designations. In these equations the operators $F_i^{\lambda\alpha}$ are defined as above.

Defining a coupling operator for symmetry designation $\lambda\alpha$ by

$$G^{\lambda\alpha} = \sum_k |\varphi_k^{\lambda\alpha}\rangle\langle\varphi_k^{\lambda\alpha}|F_k^{\lambda\alpha}|\varphi_k^{\lambda\alpha}\rangle\langle\varphi_k^{\lambda\alpha}|\ ,$$

with the summation extending over all the occupied orbitals of symmetry designation $\lambda\alpha$, one can write

$$G^{\lambda\alpha}\varphi_i^{\lambda\alpha} = \varphi_i^{\lambda\alpha}\,\theta_{ii}^{\lambda\alpha} \tag{4}$$

which is equivalent, but not identical, to Eq. (3). These two formulations are equivalent in the sense that

$$\langle\varphi_i^{\lambda\alpha}|G^{\lambda\alpha}|\varphi_i^{\lambda\alpha}\rangle = \langle\varphi_i^{\lambda\alpha}|F_i^{\lambda\alpha}|\varphi_i^{\lambda\alpha}\rangle = \theta_{ii}^{\lambda\alpha}\ , \tag{5}$$

under the condition that orthonormal orbitals will be used at all times. This condition must be imposed only at the beginning of the calculations, because if in any successive iteration the vectors obtained in the preceding iteration are used, being eigenfunctions of the same eigenvalue equation, they will be automatically orthogonal. The orthogonality constraints are really imposed when the coupling operator is defined.

It must be pointed out that at self-consistency the solutions will be eigenfunctions of both $G^{\lambda\alpha}$ and $R^{\lambda\alpha}$; at self-consistency only the central term of $R^{\lambda\alpha}$ subsists*.

Expending the individual orbitals in terms of a set of basis functions χ_p, i. e.,

$$\varphi_i^{\lambda\alpha} = \sum_p \chi_p^{\lambda\alpha} c_{pi}^{\lambda} = \boldsymbol{\chi}^{\lambda\alpha} \mathbf{c}_i^{\lambda} \ ,$$

where $\boldsymbol{\chi}^{\lambda\alpha}$ is a row vector and $\mathbf{c}_i^{\lambda}$ is a column vector, Eq. (4) can then be written as

$$\mathbf{G}^{\lambda\alpha} \mathbf{C}^{\lambda} = \mathbf{S}^{\lambda\alpha} \mathbf{C}^{\lambda} \theta^{\lambda\alpha} \ ,$$

where $\mathbf{C}^{\lambda}$ is the matrix formed by the column vectors $\mathbf{c}_i^{\lambda}$ and $\theta^{\lambda\alpha}$ is a diagonal matrix with elements $\theta_{ii}^{\lambda\alpha}$. The elements of the matrices $\mathbf{G}^{\lambda\alpha}$ and $\mathbf{S}^{\lambda\alpha}$ are defined by

$$G_{pq}^{\lambda\alpha} = \langle \chi_p^{\lambda\alpha} | G^{\lambda\alpha} | \chi_q^{\lambda\alpha} \rangle \ ,$$
$$S_{pq}^{\lambda\alpha} = \langle \chi_p^{\lambda\alpha} | \chi_q^{\lambda\alpha} \rangle \ .$$

The matrix $\mathbf{G}^{\lambda\alpha}$ will only be diagonalized by those vectors which also diagonalize the matrix $\mathbf{R}^{\lambda\alpha}$, constructed from the same basis functions. Let us assume that $\mathbf{R}^{\lambda\alpha}$ and $\mathbf{G}^{\lambda\alpha}$ have been constructed using a certain set of vectors $\mathbf{c}_i^{\lambda}$ (obtained in a preceding iteration), and that these same vectors are used in a new trial to diagonalize both matrices. In such conditions only the central term of $\mathbf{R}^{\lambda\alpha}$ will subsist. But this term is identical to $\mathbf{G}^{\lambda\alpha}$, and therefore if $\mathbf{G}^{\lambda\alpha}$ is diagonalized so will be $\mathbf{R}^{\lambda\alpha}$: that is, self-consistency has been reached.

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