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

By

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An exact self-consistent-field formalism, which obviates the need of evaluating interelectronic repulsion integrals, is developed. This formulation claims general applicability and can lead either to Hartree-Fock functions or to the exact solutions of a non-relativistic Hamiltonian, depending on the trial functions used.

Es wird ein exakter „self-consistent-field"-Formalismus entwickelt, der die Berechnung von Elektronenwechselwirkungsintegralen unnötig macht. Diese Formulierung beansprucht allgemeine Anwendbarkeit und kann, je nach Art der verwendeten Funktionen, entweder zu Hartree-Fock-Funktionen oder zu exakten Lösungen eines nichtrelativistischen Hamilton-operators führen.

On a développé un formalisme exact de champ «auto-cohérent», où il n'y en a pas besoin de calculer les intégrales concernant la répulsion interélectronique. Ce formalisme est complètement général et il peut être employé pour déterminer bien des fonctions de Hartree-Fock ou les fonctions propres d'un hamiltonien non-relativistique, dépendant des caractéristiques des fonctions employées.

Introduction

In the preceding papers of this series, hereafter designated as I and II, using a reformulated SCF scheme [1] a simple formula, relating the one- and two-electron contributions to the electronic energy, was developed [2] for special sets of orthonormal orbitals, to show an interesting relation to the Thomas-Fermi approximation.

That same relation is reintroduced here in a general way, by means of simple algebraic concepts, and used as the foundation of a simplified SCF scheme, i. e., simplified in the sense that the calculations are simple, as no interelectronic repulsion integrals have to be evaluated. Otherwise the method claims general applicability and can be used to determine, in both a priori and a posteriori calculations, exact Hartree-Fock functions and the exact solutions of the non-relativistic Hamiltonian used, depending on the trial functions.

Mathematical Formulation

The electronic energy of any system, corresponding to a normalized wave function Ψ, is given by

$$\boldsymbol{E} = \langle \Psi | \mathscr{H} | \Psi \rangle \ ,$$

where $\mathscr{H}$ is the non-relativistic, time- and spin-independent Hamiltonian for the system under consideration. The terms of this Hamiltonian can be grouped in two

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classes: the first one includes the kinetic energy and the nuclear attraction terms, while the second includes the interelectronic repulsion terms.

The same kind of grouping could then be applied to the energy expression, which could be written as

$$\boldsymbol{E} = \boldsymbol{H} + \boldsymbol{I} \ ,$$

but because it has been customary to write the energy expression as*

$$\boldsymbol{E} = 2\,\boldsymbol{H} + \boldsymbol{I} \ , \tag{1}$$

this last expression will be adopted in this paper: $\boldsymbol{H}$ then represents one half of the kinetic energy and nuclear attraction contribution to the total electronic energy of the system under consideration, while $\boldsymbol{I}$ constitutes the total interelectronic contribution.

It was seen in II that special sets of orthonormal orbitals satisfy the condition

$$\boldsymbol{H} + 2\,\boldsymbol{I} = 0 \ ,$$

and that exact SCF functions of neutral systems and negative ions almost satisfy it.

The above condition can be generalized by introduction of an arbitrary parameter g, such that the condition

$$\boldsymbol{H} + 2\,g\,\boldsymbol{I} = 0 \tag{2}$$

will now be satisfied by any function (in particular, the Hartree-Fock function and the exact wave function) for the system under consideration, with each function characterized by a different value of g.

The energy expression can then be written as

$$\boldsymbol{E} = \frac{4g-1}{2g}\,\boldsymbol{H} \ , \tag{3}$$

and if the virial theorem is satisfied by the wave functions under consideration, one can also write**

$$\boldsymbol{N} = \frac{8g-1}{2g}\,\boldsymbol{H} \ . \tag{4}$$

Equations (3) and (4) will only be simultaneously satisfied by the same value g if the virial theorem is satisfied; that is, when the wave function used is, e. g., the Hartree-Fock function or the eigenfunction of the Hamiltonian under consideration.

The parameter g offers certain special characteristics. First of all, taking into account that $\boldsymbol{H} < 0$ and $\boldsymbol{I} > 0$, g must be positive, in order that Eq. (2) will be satisfied. But for that same reason one can see from Eq. (1) that $2\,\boldsymbol{H} < \boldsymbol{E} < 0$, and coupling this condition with Eq. (3) it can be concluded that $g > 1/4$. For all the systems investigated** it has been seen that the value of g is actually very close to 1 (except for positive ions).

Furthermore, the dependence of g on the wave function presents a monotonous behavior. When the value of g is calculated from Eq. (3) for different wave func-

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* This is the expression already used in II.

** For more details see II.

tions, it can be seen that the series of values tends monotonically towards the value corresponding to the wave function which simultaneously satisfies the virial theorem. The table presents the values of g for different SCF functions for the ground state of He, determined by HUZINAGA [3] using from 1 to 10 Gaussian functions in the expansion of the $1s$ orbital. The value corresponding to the Hartree-Fock function is included for comparison.

On the basis of all these considerations it has been decided that Eqs. (3) and (4) can constitute the foundation of a new SCF scheme which obviates the need of evaluating interelectronic repulsion integrals, and in which the parameter g can be used as a criterion of convergence.

It is true that the virial theorem could be used alone in an a posteriori (that is, when the energy is known) calculation. But in such case it could not be claimed with certainty that the wave function obtained in such way, that is, a wave function with the only characteristic of giving a certain value for the total kinetic energy, is the Hartree-Fock function or the exact eigenfunction.

The present formulation, using Eqs. (3) and (4), can, on the other hand, lead to functions with the proper distribution, because the nuclear attraction terms are included. Furthermore the calculations can be carried out within the frame of a self-consistent scheme and the method can be used in a priori calculations.

Table. *Values of the parameter g for different* SCF *functions** *for the ground state of* He *(using Gaussian functions)*

Number of Gaussian functions	Energy	g
1	−2.30099	0.8321
2	−2.74707	0.9172
3	−2.83568	0.9393
4	−2.85516	0.9451
5	−2.85989	0.9468
6	−2.86112	0.9474
8	−2.86161	0.9474
10	−2.86166	0.9474
Hartree-Fock	−2.86168	0.9474

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* Determined by Prof. S. HUZINAGA (IBM Research Laboratory, San Jose, California, U. S. A.). The author is indebted to Prof. HUZINAGA for letting him use his results before publication.

SCF Formulation

The general formalism will be presented first and later its application to the determination of both Hartree-Fock functions and exact eigenfunctions in a priori and in a posteriori calculations will be discussed.

In order to simplify the following discussion the following conventions will be made:

$\boldsymbol{E}$ – energy value, either known or estimated;

g_n – value of the parameter g, used in the n-th iteration;

$\boldsymbol{H}_n$ – value of $\boldsymbol{H}$, calculated from Eq. (3), once $\boldsymbol{E}$ and g_n are known;

$\boldsymbol{H}'_n$ – one half of the expectation value of the one-electron terms (kinetic energy and nuclear attraction) of the Hamiltonian, calculated with the wave function used in the n-th iteration;

$\boldsymbol{N}'_n$ – expectation value of the nuclear attraction terms of the Hamiltonian, calculated with the wave function used in the n-th iteration, plus the nuclear repulsion energy if it exists for the system under consideration;

g'_n – value of the parameter g, calculated from Eq. (4), once $\boldsymbol{H}'_n$ and $\boldsymbol{N}'_n$ are known.

General Formalism

The energy value is chosen and a proper trial function is selected.

A test value g_0 is chosen (e. g., $g_0 = 1$ for neutral systems and negative ions) and the value $\boldsymbol{H}_0$ calculated. The trial function is properly varied until the evaluated value $\boldsymbol{H}'_0$ approximates $\boldsymbol{H}_0$ within the desired accuracy. Using the values $\boldsymbol{H}'_0$ and $\boldsymbol{N}'_0$ in Eq. (4), the new value g'_0 is evaluated. If g'_0 approximates g_0 within the desired accuracy, the process is finished and a self-consistent function, which satisfies the virial theorem, has been obtained. If not, a new value g_1 is chosen and used in repetition of the process.

Though not explicitly stated, it is clear that the evaluation of a value $\boldsymbol{H}'_n$ which approximates $\boldsymbol{H}_n$ within a certain accuracy involves also an iteration process.

1. Determination of Hartree-Fock Functions

a) A posteriori calculations. The Hartree-Fock energy is known. The general formalism is applied as indicated above. The wave function obtained will be a Hartree-Fock function within the precision chosen.

b) A priori calculations. It is necessary to distinguish two cases, depending on whether or not the exact energy is known.

If the exact energy is known the general process is repeated for different energy values, lying in a region above the exact value, until for one of them the desired self-consistency will be reached. This energy value can only be the Hartree-Fock energy if the trial function was so chosen that it could develop into the Hartree-Fock function by proper variation of the parameters.

If the exact energy is not known an estimate must be made and the process used when the exact energy was known repeated for energy values in a certain region around the originally estimated value.

2. Determination of Exact Eigenfunctions

a) A posteriori calculations. The exact energy is known. The general formalism is applied as indicated above. The wave function obtained will be the exact eigenfunction if the trial function was properly chosen.

b) A priori calculations. The exact energy is not known. An estimate is made and the general process is repeated for different values in the neighborhood of that value. The energy value for which self-consistency is obtained will be the exact eigenvalue.

Simplified Calculation of Close-to-Hartree-Fock Functions

In these calculations, for which an estimate of the energy must be available, a single value of g, equal to 1, is used.

The value of this method lies on the fact that the exact energies are known for many systems. The error committed when taking this energy instead of the Hartree-Fock energy (which is not known) can be expected to be cancelled or at least partially compensated by the error committed when taking the value 1 for g instead of the proper value, which in general is lower.

References

[1] FRAGA, S.: Theoret. chim. Acta (Berl.) **2**, 403 (1964).
[2] – Theoret. chim. Acta (Berl.) **2**, 406 (1964).
[3] HUZINAGA, S.: Unpublished results.

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