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

# Non-Relativistic Self-Consistent-Field Theory. IV.*

By

**R. E. D. McClung**** and **S. Fraga**

The general, exact self-consistent-field formalism developed in III of this series has been applied to the determination of the Hartree-Fock wave function for the ground state of Li. Practical details of the calculations are given.

Der allgemeine, exakte „self-consistent-field"-Formalismus, der in III dieser Serie entwickelt wurde, ist für die Bestimmung der Hartree-Fock-Funktion für den Grundzustand von Li verwendet worden. Praktische Einzelheiten dieser Berechnungen sind angeführt.

Le formalisme exact de champ «auto-cohérent», qui a été développé dans III de cette série, est employé pour déterminer la fonction de Hartree-Fock pour l'état fondamental de Li. On présente aussi les détails pratiques des calculs.

## Introduction

The new SCF procedure, developed in a preceding paper [2] of this series, hereafter designated as III, can be very easily applied to actual calculations, as only kinetic energy and nuclear attraction integrals are evaluated.

The purpose of this paper is, besides presenting the results obtained for the ground state of Lithium, to discuss some of the characteristics of this new type of calculation.

## Theory

The new scheme is based on the equations***

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

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

where: $\boldsymbol{E}$ is the total electronic energy; $\boldsymbol{H}$ is one half of the kinetic energy and nuclear attraction contribution to that energy; $\boldsymbol{N}$ is the total nuclear attraction energy (including the nuclear repulsion if it exists for the system under consideration); and $g$ is an appropriate parameter. Equation (2) represents a possible formulation of the virial theorem.

This scheme can be used in both a priori and a posteriori calculations. Self-consistency is obtained when both equations are satisfied by the same value of $g$.

In a general, a priori calculation within this scheme there are two distinct (though closely interrelated in practice) processes: first, the determination of the

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** Present address: Department of Chemistry, University of California, Los Angeles 24, California, U. S. A.

*** See III for more details.

value of $g$ for which self-consistency is obtained; second, the actual determination of the wave function for that value of $g$.

The search for the correct $g$ can be carried out in a straightforward and systematic manner, without any practical difficulty being foreseen at this moment, other than the amount of computer time involved, which in any case will be much smaller that that needed for the evaluation of integrals used in the classical SCF formulations. Though this investigation will be taken up in the future, it has been considered at this moment more convenient to emphasize the procedure which leads to the actual determination of wave functions.

For this reason the calculations reported in this paper have been carried out for a fixed value of $g$, assuming that the Hartree-Fock energy for the system under consideration is known. In order to clarify the following discussion a notation similar to that given in III will be adopted:

$\boldsymbol{E}_{HF}$ – Hartree-Fock energy for the system under consideration;

$\boldsymbol{H}$ – one half of the expectation value of the one-electron terms (kinetic energy and nuclear attraction) of the Hamiltonian, calculated for a certain wave function ($\boldsymbol{H}_{HF}$ and $\boldsymbol{H}_n$ correspond to the Hartree-Fock function and to that function constructed using the $n$-th set of trial vectors, respectively);

$\boldsymbol{N}$ – expectation value of the nuclear attraction terms of the Hamiltonian, calculated with a certain wave function ($\boldsymbol{N}_{HF}$ and $\boldsymbol{N}_n$ correspond to the Hartree-Fock function and to that function constructed using the $n$-th set of trial vectors, respectively), plus the nuclear repulsion (if existing);

$g_{HF}$ – value of $g$ which satisfies Eqs. (1) and (2) for the quantities $\boldsymbol{E}_{HF}$, $\boldsymbol{H}_{HF}$, and $\boldsymbol{N}_{HF}$;

$g_n$ – value of $g$ evaluated from Eq. (2), using $\boldsymbol{H}_n$ and $\boldsymbol{N}_n$.

The procedure can now be summarized in the following way. The values $\boldsymbol{E}_{HF}$ and $g_{HF}$ are known, and the value of $\boldsymbol{H}_{HF}$ is determined using Eq. (1). A set $n$ of trial vectors is chosen and properly varied (see below) until the evaluated $\boldsymbol{H}_n$ approximates $\boldsymbol{H}_{HF}$ within a fixed accuracy. $\boldsymbol{N}_n$ and $g_n$ are then evaluated, and $g_n$ compared with $g_{HF}$. If they agree to a fixed accuracy, the calculation is terminated and the wave function constructed using that set of trial vectors constitutes an approximation to the Hartree-Fock function within the accuracy chosen.

If such agreement is not obtained, the calculations are repeated for different sets of trial vectors, until the condition

$$g_i < g_{HF} < g_j$$

is obtained. Then the whole procedure is started all over again for trial vectors intermediate between the sets $i$ and $j$, carrying on the process until the desired self-consistency is obtained.

The trial vectors, not necessarily orthonormal, are identified by the value given to the first coefficients in the expansions that will approximate the lowest orbitals of each symmetry; the other coefficients in the trial vectors are given arbitrary values.

## Details of the Calculations

A program has been prepared for an IBM 1620 computer, which can be used for the determination of Hartree-Fock wave functions for atoms in both a priori and a posteriori calculations, in the way described in III.

Slater-type functions have been used for the expansion of the orbitals, with orbital exponents arbitrarily chosen. The results can be improved, if so desired, by proper optimization of the orbital exponents, but the aim of the present calculations is not so much an extremely good accuracy as the investigation of the feasibility of the new scheme, and for this reason the calculations have not been carried out beyond an accuracy which has been considered reasonable.

The program needs as input data not only the orbital exponents of the basis functions but also the trial values for the expansion coefficients, number and symmetry designation of the occupied orbitals and their occupancies, the energy value (as known or estimated) and the $g$ value (for a posteriori calculations), and the precision desired for $\boldsymbol{H}$ and $g$.

The program carries out the calculations in a straightforward manner, but it is worthwhile to mention the way in which the vectors are varied. This variation is given, in order to simplify the calculations, only to the first coefficients of those expansions that will approximate the lowest orbitals of each symmetry. It is expected that the effect of this variation will be properly transmitted over to the other coefficients during the orthonormalization process.

In connection with a priori calculations one special characteristic must be reported here. It was indicated in III that $g$ must be greater than 1/4, but this is not a sufficient condition when operating within the framework of the expansion method. There is a certain value of $\boldsymbol{H}$ which is the lowest possible value that can be obtained using a given basis set. That value can be best found by a typical diagonalization of the corresponding matrix.

The practical influence of this fact can be best described as follows*. The first iteration is carried out for an arbitrarily chosen value $g_0$ (usually $g_0 = 1$). The new value $g_0'$, found at the end of this iteration, is now used as the $g_1$ of the following iteration, and so on, until self-consistency has been reached. It can happen, especially at the beginning, that the new value of $g$ produces, when used in Eq. (1), such a value of $\boldsymbol{H}$ that cannot be reached with the basis set being used. For that reason the program must determine at the beginning which is the lowest possible value of $g$ which can be used in conjunction with the basis set chosen. This value is calculated by means of Eq. (1) using the energy given as input data and the lowest value (maximum absolute value) of $\boldsymbol{H}$, as determined above. Without this restriction the program can be misled into an infinite loop around a wrong value.

The output consists of the expansion coefficients of the occupied orbitals and the corresponding absolute and relative (to the highest absolute value) radial functions. The final value of $g$ is also given.

## Results

The calculations have been carried out for the ground state of Lithium, using as input data the Hartree-Fock values [*1*]

$\boldsymbol{E}_{HF} = -7.432730$ a. u., $\boldsymbol{H}_{HF} = -4.856815$ a. u., $g_{HF} = 1.064670$,

carrying on the iterations until the evaluated $\boldsymbol{H}$ approximates $\boldsymbol{H}_{HF}$ within an accuracy of 0.0001.

The orbital exponents have been chosen in such a way as to cover a certain region around the corresponding Slater exponents. Tab. 1 presents those orbital

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* The notation used here is that introduced in III.

Table 1. *Orbital exponents and coefficients of the* 1*s and* 2*s orbitals*

| $n$* | Exponents | Coefficients | |
|---|---|---|---|
| | | 1*s* | 2*s* |
| 1 | 3.00 | 0.020793 | 0.004442 |
| 1 | 2.70 | 0.935707 | −0.162529 |
| 1 | 2.40 | 0.048864 | −0.004396 |
| 1 | 2.10 | −0.004470 | 0.006373 |
| 1 | 1.80 | −0.000935 | 0.001273 |
| 2 | 0.80 | 0.000956 | −0.116479 |
| 2 | 0.65 | 0.000914 | 1.065450 |
| 2 | 0.50 | 0.000873 | 0.056775 |
| 2 | 0.35 | −0.004678 | 0.005870 |
| 2 | 0.20 | −0.000987 | −0.001017 |

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* Principal quantum number of the Slater-type basis functions.

Table 2. *Radial function of the* 1*s orbital*

| $r$ | Absolute | | Relative | |
|---|---|---|---|---|
| | This paper | Hartree-Fock* | This paper | Hartree-Fock* |
| 0.00 | 2.49663 | 2.61450 | 10000 | 10000 |
| 0.05 | 2.18166 | 2.25092 | 8737 | 8608 |
| 0.10 | 1.90645 | 1.94212 | 7635 | 7427 |
| 0.15 | 1.66598 | 1.67912 | 6672 | 6421 |
| 0.20 | 1.45585 | 1.45452 | 5830 | 5562 |
| 0.25 | 1.27224 | 1.26222 | 5095 | 4827 |
| 0.30 | 1.11180 | 1.09716 | 4452 | 4196 |
| 0.35 | 0.97161 | 0.95515 | 3891 | 3652 |
| 0.40 | 0.84910 | 0.83271 | 3400 | 3184 |
| 0.45 | 0.74205 | 0.72692 | 2971 | 2780 |
| 0.50 | 0.64851 | 0.63534 | 2597 | 2429 |
| 0.55 | 0.56676 | 0.55591 | 2269 | 2126 |
| 0.60 | 0.49532 | 0.48691 | 1983 | 1862 |
| 0.65 | 0.43290 | 0.42687 | 1733 | 1632 |
| 0.70 | 0.37834 | 0.37455 | 1515 | 1432 |
| 0.75 | 0.33067 | 0.32890 | 1324 | 1257 |
| 0.80 | 0.28901 | 0.28902 | 1157 | 1105 |
| 0.85 | 0.25260 | 0.25415 | 1011 | 971 |
| 0.90 | 0.22078 | 0.22361 | 884 | 855 |
| 0.95 | 0.19297 | 0.19685 | 772 | 752 |
| 1.00 | 0.16866 | 0.17338 | 675 | 663 |
| 1.10 | 0.12886 | 0.13469 | 516 | 515 |
| 1.20 | 0.09846 | 0.10479 | 394 | 400 |
| 1.30 | 0.07523 | 0.08164 | 301 | 312 |
| 1.40 | 0.05749 | 0.06367 | 230 | 243 |
| 1.50 | 0.04393 | 0.04971 | 175 | 190 |
| 1.60 | 0.03358 | 0.03885 | 134 | 148 |
| 1.70 | 0.02566 | 0.03038 | 106 | 116 |
| 1.80 | 0.01962 | 0.02378 | 78 | 90 |
| 1.90 | 0.01500 | 0.01863 | 60 | 71 |
| 2.00 | 0.01147 | 0.01460 | 45 | 55 |
| 2.50 | 0.00299 | 0.00437 | 12 | 16 |
| 3.00 | 0.00077 | 0.00134 | 3 | 5 |
| 3.50 | 0.00018 | 0.00042 | 0 | 1 |

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* Using the Hartree-Fock function (unpublished) determined by Dr. E. Clementi (IBM Research Laboratory, San Jose, California, U. S. A.).

Table 3. *Radial function of the 2s orbital*

| r | Absolute | | Relative | |
|---|---|---|---|---|
| | This paper | Hartree-Fock* | This paper | Hartree-Fock* |
| 0.00 | −0.39033 | −0.40925 | −10000 | −10000 |
| 0.05 | −0.33613 | −0.35145 | −8610 | −8587 |
| 0.10 | −0.28844 | −0.30161 | −7388 | −7369 |
| 0.15 | −0.24648 | −0.25846 | −6314 | −6314 |
| 0.20 | −0.20955 | −0.22095 | −5368 | −5398 |
| 0.25 | −0.17703 | −0.18823 | −4534 | −4599 |
| 0.30 | −0.14839 | −0.15959 | −3801 | −3899 |
| 0.35 | −0.12316 | −0.13444 | −3154 | −3284 |
| 0.40 | −0.10092 | −0.11230 | −2585 | −2743 |
| 0.45 | −0.08132 | −0.09274 | −2083 | −2265 |
| 0.50 | −0.06404 | −0.07542 | −1640 | −1842 |
| 0.55 | −0.04880 | −0.06005 | −1250 | −1467 |
| 0.60 | −0.03537 | −0.04639 | − 906 | −1133 |
| 0.65 | −0.02352 | −0.03423 | − 602 | − 836 |
| 0.70 | −0.01307 | −0.02338 | − 334 | − 571 |
| 0.75 | −0.00385 | −0.01369 | − 98 | − 334 |
| 0.80 | 0.00426 | −0.00503 | 109 | − 122 |
| 0.85 | 0.01141 | 0.00271 | 292 | 66 |
| 0.90 | 0.01771 | 0.00963 | 453 | 235 |
| 0.95 | 0.02325 | 0.01583 | 595 | 386 |
| 1.00 | 0.02812 | 0.02137 | 720 | 522 |
| 1.10 | 0.03615 | 0.03075 | 926 | 751 |
| 1.20 | 0.04229 | 0.03821 | 1083 | 933 |
| 1.30 | 0.04693 | 0.04409 | 1202 | 1077 |
| 1.40 | 0.05039 | 0.04868 | 1290 | 1189 |
| 1.50 | 0.05289 | 0.05219 | 1355 | 1275 |
| 1.60 | 0.05463 | 0.05480 | 1399 | 1339 |
| 1.70 | 0.05576 | 0.05667 | 1428 | 1384 |
| 1.80 | 0.05639 | 0.05791 | 1444 | 1414 |
| 1.90 | 0.05662 | 0.05862 | 1450 | 1432 |
| 2.00 | 0.05653 | 0.05890 | 1448 | 1439 |
| 2.50 | 0.05290 | 0.05587 | 1355 | 1365 |
| 3.00 | 0.04677 | 0.04911 | 1198 | 1200 |
| 3.50 | 0.04000 | 0.04139 | 1024 | 1011 |
| 4.00 | 0.03347 | 0.03396 | 857 | 829 |
| 4.50 | 0.02754 | 0.02735 | 705 | 668 |
| 5.00 | 0.02238 | 0.02174 | 573 | 531 |
| 6.00 | 0.01435 | 0.01336 | 367 | 326 |
| 7.00 | 0.00894 | 0.00799 | 229 | 195 |
| 8.00 | 0.00546 | 0.00469 | 140 | 114 |
| 9.00 | 0.00328 | 0.00272 | 84 | 66 |
| 10.00 | 0.00195 | 0.00156 | 50 | 38 |
| 11.00 | 0.00115 | 0.00088 | 29 | 21 |
| 12.00 | 0.00067 | 0.00050 | 17 | 12 |
| 13.00 | 0.00039 | 0.00028 | 10 | 6 |
| 14.00 | 0.00023 | 0.00015 | 5 | 3 |
| 15.00 | 0.00013 | 0.00008 | 3 | 2 |

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* Using the Hartree-Fock function (unpublished) determined by Dr. E. Clementi (IBM Research Laboratory, San Jose, California, U. S. A.).

exponents and the corresponding expansion coefficients. Tab. 2 and 3 present the absolute and relative radial functions of the 1*s* and 2*s* orbitals; for comparison purposes the radial functions obtained using the Hartree-Fock functions determined by CLEMENTI [*1*] in classical SCF calculations are also presented*.

Inspection of the results obviates all need of discussion. As it was pointed out before, these results could still be improved by an adequate optimization of the orbital exponents.

The final value of $g$ is 1.0715, which shows what a close approximation the present wave function is to the Hartree-Fock function. In this connection it must be pointed out that the present scheme does not involve more trial and error efforts than the classical procedures. While in the latter the energy is used as criterion of self-consistency, the parameter $g$ plays the same role in this method. It is true that normal SCF treatments offer the advantage of the diagonalization procedure, but an over all comparison of both methods will still show that the present treatment is simpler, mainly due to the fact that no complicated integrals are evaluated.

## Conclusions

First of all it must be emphasized that the scheme used in the present calculations, as developed in III, is an exact method, which offers the possibility of attaining any desired precision in a systematic manner.

The interest of this scheme lies in the fact that it can be carried out as easily for molecules as for atoms. Because there is no need of evaluating interelectronic repulsion integrals, the actual time involved in the calculations can be considered to be negligible when compared with the time needed for the schemes used at present. At the same time, the storage needs are so extraordinarily reduced that it is possible to undertake the calculation of SCF functions for molecules of any size even with small computers.

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[*1*] CLEMENTI, E.: Unpublished results.
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