ON THE NUMERICAL SOLUTION
OF HARTREE–FOCK EQUATIONS
INDEPENDENT OF COUPLING SCHEME*

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The solution of Hartree—Fock equations by a numerical method on computers, type BESM, is described. The minimization of the input information is reached by using the equations independent of coupling scheme and the universal potential field for obtaining the initial radial wave functions. The results obtained are compared with those evaluated from the solutions of conventional Hartree—Fock equations.

1. Introduction

A proper theoretical investigation of atomic properties is possible only when radial wave functions are available. These are obtained, in the main, from traditional Hartree—Fock equations. Sometimes improved methods, e.g. multi-configuration approximation, extended method of calculation, incomplete separation of variables, and other methods are used. However, these latter methods are applied only for rather simple cases. Consequently, the traditional Hartree—Fock radial wave functions remain the best available, especially as concerns many-electron atoms. For this reason they are very widely used at present and the solution of Hartree—Fock equations is the problem of to-day.

The method of numerical solution of Hartree—Fock equations have been elaborated mainly by FOCK, PETRASHEN [1] and HARTREE [2]. The development of modern computing techniques provides new possibilities for obtaining the corresponding solutions in an easy way. Various programmes by different authors for carrying out the corresponding calculations have been compiled, and the tabulation of numerical functions has gradually been given up. Therefore, efforts are made to draw up programmes suitable for any atom in any state in order to provide for any problem to be solved by the wave functions.

At the present time programmes for numerical solution of Hartree—Fock equations have been given by WORSLEY [3], RIDLEY [4], PIPER [5], IVANOVA et al. [6], BRATSEV [7], HERMAN and SKILLMAN [8], FROESE [9, 10], MAYERS and O'BRIEN [11] and by others. Besides this the method of analytical solution of Hartree—Fock equations [12] is widely used as well. As far as we

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* Dedicated to Prof. P. GOMBÁS on his 60th birthday.

are dealing with the methods of numerical solution we give no further references on this last very interesting approach in this paper.

The process of solution of Hartree—Fock equations is rather complicated even for powerful computing machines. For this reason simplifications are sometimes used to facilitate the numerical procedures. This is achieved by neglecting the non-diagonal Lagrange multipliers, as is done in [7], or by replacing the exchange terms by a more simple expression, as is done in [8], and so on.

In this paper we describe the method of solution of Hartree—Fock equations in which the simplification is achieved by solving the corresponding equations independent of coupling scheme instead of accurate Hartree—Fock equations and by the use of the universal potential for estimating the initial one-electron radial wave functions. Such an approach allows the "input" information to be minimized considerably.

In the next two Sections we describe the Hartree—Fock equations independent of the coupling scheme and the universal potential, correspondingly. In Section 4 we indicate the methods of numerical calculations and in Section 5 we present and discuss the results for NeII.

2. Hartree—Fock equations independent of the coupling scheme

The solutions of Hartree—Fock equations for each term of a given configuration is rarely done, because it requires a great number of operations. Therefore, it is usual to solve the equations either for the "centre of gravity" of the configuration or for one particular term of the configuration under consideration. The solutions so obtained are used to evaluate the physical quantities to be calculated.

The modification of Hartree—Fock equations we shall use are those equations which do not depend on particular coupling scheme, i.e., the equations are quite similar to those proposed by JUCYS and VIZBARAITE [13] and are obtained by making the functional stationary which is equal to the energy expression with all interactions depending on terms omitted. Such terms, besides magnetic interactions, are

I. The non-spherical part of the direct electrostatic interaction between electrons belonging to the same incomplete shell.

II. The non-spherical part of the direct electrostatic interaction between electrons belonging to different incomplete shells (when one or both shells are complete this part vanishes).

III. The non-spherical exchange electrostatic interaction between electrons belonging to different incomplete shells, under the concept of the shell being understood the group of electrons with the same set of quantum numbers nl.

Under these circumstances integrals $F_k(nl, nl)$ $(k > 0)$ and $G_k(nl, n'l')$ are partially neglected, integrals $F_k(nl, n'l')$ $(k > 0, n'l' \neq nl)$ are all omitted, nl and $n'l'$ belonging to the incomplete shells. Then we are left with the expression (in atomic units of HARTREE [2])

$$E = \sum_{nl} \left\{ N_{nl} I(nl) + \frac{N_{nl}(N_{nl}-1)}{2} F_0(nl, nl) - \right.$$

$$- \frac{N_{nl}}{4l+2} \sum_{k>0} (l\|C^{(k)}\|l)^2 F_k(nl, nl) +$$

$$+ N_{nl} \sum_{n'l'}{}' N_{n'l'} F_0(nl, n'l') -$$

$$\left. - \frac{N_{nl}}{4l+2} \sum_{n'l'}{}' \sum_{k} \frac{N_{n'l'}}{2l'+1} (l\|C^{(k)}\|l')^2 G_k(nl, n'l') \right\},$$

(1)

which is to be made stationary by FOCK's variation method [14].

N_{nl} in (1) denotes the number of electrons in the shell characterized by the quantum numbers nl. The prime to the summation symbol shows that $n'l' = nl$ is to be excluded from the summation. The radial integrals I, F_k and G_k are defined according to HARTREE [2]. $(l\|C^{(k)}\|l)$ is the reduced matrix element of the spherical harmonic as defined by RACAH [15]. Its numerical values can be found in Appendix 6 of [16].

The functional (1) coincides with the expression for the energy not involving magnetic interactions when only one electron is present outside the complete shells or one electron is missing as well as when the configuration contains the complete shells only. The deviation from the energy increases with increasing number of electrons in partially filled shells and increasing number of missing electrons in almost closed shells. This is true for the highest and lowest energy levels, because the functional under consideration is usually not far from the the "centre of gravity" of a given configuration. This last involves the radial integrals representing the dependence on the coupling scheme mostly with small coefficients and do not matter very much. Absence of these integrals in our functional makes it more convenient for calculation.

When applying the FOCK variation method [14] to (1) supplemented by Lagrange multipliers one obtains the equations

$$\left[\frac{d^2}{dr^2} - 2Y(nl|r) - \frac{l(l+1)}{r^2} - \varepsilon_{nlnl} \right] P(nl|r) -$$

$$X(nl|r) - \sum_{n'}{}' \varepsilon_{nln'l} P(n'l|r) = 0 ,$$

(2)

(for all nl)

where

$$Y(nl|r) = \frac{1}{r}\left\{ -Z + \sum_{n'l'} (N_{n'l'} - \delta_{nln'l'})\, Y_0\,(n'l', n'l'|r) - \right.$$
$$\left. - (2l+1)^{-1} \sum_{k=2}^{2l} (l\|C^{(k)}\|l)^2\, Y_k(nl, nl|r) \right\} \tag{3}$$

is the potential function and

$$X(nl|r) = -\frac{1}{r}\sum_{n'l'}\sum_{k} \frac{N_{n'l'}}{(2l'+1)(2l+1)} (l\|C^{(k)}\|l')^2 Y_k(nl, n'l'|r)\, P(n'l'|r) \tag{4}$$

represents the exchange terms, the $Y_k(nl, n'l'/r)$ being radial integral functions defined by the formula 3.5 (1) of [2].

Owing to the fact that (2) does not involve terms depending on the coupling scheme it is easier to make calculations fully automatic.

3. The universal potential

Besides the configuration, there must be put into the computer initial estimates of one-electron radial wave functions from which a process of successive approximation must be started. Generally, there the complementary procedure is programmed by which the estimates mentioned are obtained automatically. Such procedures used to be of several kinds. One of them consists of using analytic hydrogen-like one-electron radial wave functions and the other in making use of the interpolations or extrapolations from the wave functions of neighbouring atoms or ions already computed. The third consists of using the Thomas—Fermi statistical potential. The first procedure is applied mostly in the case of light atoms and the second in the case of heavy ones. The procedure we are going to describe is a modification of the third approach mentioned and used in [8]. It consists of using the universal potential field derived from the statistical theory of the atom with a correction fitting it to ions as well as to neutral atoms.

The statistical theory of the atom founded by THOMAS [17] and FERMI [18] and further developed by GOMBÁS [19] allowed GÁSPÁR [20, 21] to approximate the Hartree—Fock potential by the so-called universal potential field. This universality consists in scaling the radial variable in such a way that the potential field has an expression independent of the atomic number in the periodic system of elements.

The universal potential mentioned above, giving a good approximation for neutral atoms (c.f. GÁSPÁR [22]) has been adjusted to ions as well by the use of a simplified Fermi—Amaldi correction (c.f. GOMBÁS [19] p. 65 and [21]

p. 40). The resulting expression is given by equation (5) of [23]. As far as we are interested in the first estimates of radial wave functions we neglect the exchange part and the adjustable parameter α in this last equation. Such an approach leads us to this Schrödinger equation

$$\left[\frac{d^2}{dr^2} + \frac{2I}{r} + \frac{2}{r}(Z-I)\frac{e^{-\lambda_0 r}}{1+A_0 r} - \frac{l(l+1)}{r^2} - \varepsilon_{nln l}\right]P(nl|r) = 0, \quad (5)$$

where I is the degree of ionization and

$$\lambda_0 = 0{,}2075\, Z^{1/3}, \quad A_0 = 1{,}19\, Z^{1/3}. \quad (6)$$

Z is the nuclear charge number here as well as in the preceding Section.

For all one-electron wave functions equation (5) is the same, hence the solutions are spontaneously orthogonal. The programme for solving equation (5) was used as the complementary procedure mentioned above.

4. The process of numerical solution

The system of equations (2) was solved under well known boundary conditions [1, 2]

$$P(nl|0) = P(n, l|\infty) = 0 \quad (7)$$

numerically following, on the whole, the methods used by FROESE [9, 10] which conforms well to the specificity of the computer.

In order to keep the intervals between adjacent points constant in the entire range of r a logarithmic mesh [2] has been used. Then

$$\varrho = \ln Zr \quad (8)$$

s the independent variable instead of r. The last is then calculated by this simple formula

$$r_n = e^h r_{n-1}, \quad (9)$$

where h is the interval between adjacent points in the logarithmic mesh, subscript n showing the ordinal number of mesh points.

The solution of equations (2) was performed with NUMEROV's formula [24]. However, for small and large values of r, the solutions are unstable. In these regions the LOCKUCIEVSKY [25] method of factorization was used as is done by FROESE [9]. The main point of this last approach is the replacement of NUMEROV's formula by two stable ones of lower order.

The calculations have been carried out by outward and inward solutions. Both solutions are connected at a fixed point in the second half of the range of r. The difference between these solutions at this point allows the correction of the diagonal Lagrange multiplier to be determined. This procedure is applied mainly in solving the equations for radial wave functions of inner shells.

As FROESE has pointed out, the method of DETTMAR and SCHLÜTER [26] is more appropriate in the case of outer shells. They suggest the expansion of the function in power series of $\varepsilon - t$, ε and t being, correspondingly, the accurate and approximate values of the diagonal Lagrange multiplier. The coefficients of such an expansion are found step by step.

An important feature of radial wave functions is their orthogonality between the shells with the same l and different n. This orthogonality is secured by the non-diagonal Lagrange multipliers which must be used when incomplete shells are present. The functions are orthogonalized by Schmidt procedure and the estimates of non-diagonal Lagrange multipliers calculated by the method of FROESE [10]. Then the solution of equations (2) is carried out using the estimated values of non-diagonal Lagrange multipliers. Afterwards, those radial wave functions are improved for which self-consistency is poor.

The degree of self-consistency is measured by the value of

$$\Delta P = \max(r)|P^i - P^{i-1}|, \tag{10}$$

where i indicates the iteration number, max (r) denotes the maximum value over the entire range of r. Iterations are performed until

$$\max(nl)\, \Delta P(nl) \approx 10^{-5} \tag{11}$$

is attained, max(nl) denoting the maximum over all shells of electrons.

5. The results for NeII

The numerical procedures described in the preceding Section have been programmed for computers BESM—2 and BESM—4. The programme works entirely automatically and is suitable for each atom in the periodic system of elements in any state of excitation. What initially must be known is the atomic number and the configuration. After self-consistency is attained the radial integrals are calculated and automatically printed by the output mechanism.

We are presenting some results for the configuration $1s^2 2s^2 2p^4 3p$ of NeII in order to see how the solutions of Hartree—Fock equations independent of

Table I

The quantities of self-consistent field independent of coupling scheme in comparison with those of accurate Hartree—Fock method

quantity A	independent of coupling scheme	differences ΔA			
		$(^3P)^2P$	$(^1D)^2P$	$(^1S)^2P$	$(^3P)^4P$
ε_{2p2p}	4.16203	0.27711	0.16449	—0.01591	0.23861
ε_{3p3p}	0.69866	0.00288	0.01088	0.02008	0.05235
$\bar{r}(2p)$	0.8141	—0.0138	—0.0097	0.0038	—0.0153
$\bar{r}(3p)$	3.958	0.056	—0.002	—0.260	—0.331
$F_2(2p, 2p)$	0.51661	0.01095	0.00682	—0.00259	0.00485
$F_2(2p, 3p)$	0.03452	—0.00467	—0.00220	—	0.01358
$G_0(2p, 3p)$	0.00977	—0.00365	—0.00227	0.00541	0.00899
$G_2(2p, 3p)$	0.00986	—0.00320	—0.00287	0.00471	0.00812
$\lambda_{2p,3p}$	—0.20366	—0.22149	—0.06382	0.1697	—

Table II

Values* of the total energy (in atomic units)
for NeII $1s^22s^22p^43p$

	$(^3P)^2P$	$(^1D)^2P$	$(^1S)^2P$	$(^3P)^4P$	$(^3P)^4D$	$(^3P)^2D$	$(^3P)^2S$
E_t	—126.7163	—126.6001	—126.4200	—126.7474	—126.7364	—126.7290	—126.7215
E_{nr}	—126.7144	—126.6007	—126.4201	—126.7422	—126.7339	—126.7295	—126.7215

* E_t — from the accurate Hartree—Fock equations.
E_{nr} — from those independent of coupling scheme.

coupling scheme work as compared with the solutions of traditional Hartree—Fock equations as given by FROESE [10]. In Table I the values of Lagrange multipliers and some integrals widely used (the first two columns) and their deviations from the values as given by FROESE [10] (columns 3—6) are given. Table II contains the energy values evaluated by us (E_{nr}) and by FROESE (E_t).

The results show the well known fact that every modification of Hartree—Fock equations affects the individual quantities noticeably. However, the values of physical quantities are affected rather slightly. In our case, the non-diagonal Lagrange multipliers undergo the maximum changes. However, this deviation is less than the maximum difference between separate terms in accurate traditional Hartree—Fock equations, as is to be seen from the results of FROESE. The next quantity which is considerably affected is the radial integral G_2 and then G_0. For the term ^4P it reaches 90 per cent. Nevertheless, the difference in total energy does not exceed 0.004 per cent.

On account of the simplicity of handling and rather good final results the use of the Hartree—Fock self-consistent field equations independent of coupling scheme is justified, especially as the difference under consideration is considerably less than the difference between traditional Hartree—Fock equations and those accounting for the correlation effect. As an example we can take the method of a self-consistent field in multi-configurational approximation (cf. [27]).

The results of the theoretical calculations of the energy spectra of ZnIV isoelectronic sequence in the configuration d^8p [28] may serve as the additional confirmations of usefulness of the solutions of Hartree—Fock equations independent of coupling scheme.

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К ВОПРОСУ О РЕШЕНИИ УРАВНЕНИЙ ХАРТРИ—ФОКА, НЕ ЗАВИСЯЩИХ ОТ ТИПА СВЯЗИ, ЧИСЛЕННЫМ МЕТОДОМ

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Р е з ю м е

Рассматривается методика решения уравнений Хартри—Фока численным методом и её применение к электронным вычислительным машинам типа БЭСМ. Минимизация начальной информации достигается путём использования уравнений, не зависящих от типа связи (2)—(4) и универсального потенциала (5) для получения исходных радиальных волновых функций. Результаты для $NeII\ 1s^22s^22p^43p$ сравниваются с решениями уравнений Хартри—Фока для каждого терма. Обсуждается точность полученных функций и их пригодность в расчётах.