

New Method of the Approximation of Hartree-Fock Wave Functions

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Abstract

A new method of the approximation of the solution to the Hartree-Fock equation for many-electron atoms and ions is proposed. The method is based on the increase in the accuracy of the approximation of wave functions corresponding to different shells. This makes it possible to reach the accuracy that is close to the error of the numerical solution. More than 14000 wave functions of the ground and excited states of atoms and ions with the number of electrons ranging from 2 to 18 are obtained.

Keywords

Hartree-Fock Equation, Wave Function, Excited States of Ions

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1. Introduction

Hartree-Fock atomic wave functions are independent-particle-model approximations to the nonrelativistic Schrodinger equation for stationary states [1, 2]. The Pauli principle is imposed through the use of Slater determinants, and for an N -electron system, the Hartree-Fock equations yield N Hartree-Fock spin orbitals.

In the conventional Hartree-Fock approximation, the spin orbitals are expressed as products of a radial function times a spherical harmonic times a spin function. Radial functions are taken to depend only on the quantum numbers n and l , and the total wave function is required to be an eigenfunction of the total orbital and spin angular momentum; the form of the spin orbitals guarantees that L , S and parity are good quantum numbers.

Hartree-Fock wave functions for atoms may be computed numerically by standard methods [3]. Multi Configuration Hartree Fock (MCHF) program [4] allows obtaining the numerical solution of the nonrelativistic Hartree-Fock equation for ground and excited states of atoms and ions. MCHF program is very efficient for treating correlation in a

large variety of systems. MCHF calculation of total energy takes into account the hyperfine structure and relativistic effects. Progress in atomic transition probability calculations has been made offering the possibility of separate and independent optimization of the initial and final configuration spaces. The disadvantage of numerical wave functions is that nontrivial software is required for their using.

Roothaan-Hartree-Fock wave functions [5, 6] are approximations to conventional Hartree-Fock wave functions in which the radial atomic orbitals are expanded as a finite superposition of primitive radial functions. These wave functions offer some advantages over their numerical counterparts as they can be readily incorporated into a variety of codes for atomic calculations, and also for molecular and solid-state calculations by density-functional methods. The Roothaan-Hartree-Fock atomic wave functions are useful as starting points for relativistic calculations and in atomic structure calculations for atomic physics and quantum chemistry.

The method for analytically approximating the numerical solution of the Hartree-Fock equation by means of the combination of Slater orbitals was used for the wave functions of the ground states of negative ions with the

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nuclear charges $Z \leq 16$ [7] and atoms with the nuclear charges $Z \leq 54$ [8] and $Z = 55$ [9] and $55 \leq Z \leq 92$ [10] and $Z \leq 54$ [11] and ions with $Z \leq 18$ [8]. The paper [8] is cited more than 3000 times. However, using this method for approximating the wave functions of the excited states of atoms and ions leads to a significant increase in the estimation error.

The aim of this paper is to propose a new method for obtaining the wave functions in the Hartree-Fock approximation, which makes it possible to represent the wave functions of the excited states of atoms and ions in the analytical form and carry out the calculation for the lower excited states of atoms and ions with the nuclear charges $Z \leq 18$.

2. Traditional Approximation Method

We let the function $\varphi_{nl}(r)$, where n is the principal quantum number of the electron, l is its orbital number, and r is the radial variable, denote the numerical solution of the radial Hartree-Fock equation. The function $\varphi_{nl}(r)$ must satisfy the orthogonality conditions:

$$\langle \varphi_{nl}(r) \mid \varphi_{n'l}(r) \rangle = \delta_{nn'}. \quad (1)$$

Because of the error of the numerical solution to the Hartree-Fock equation, this equality holds only approximately:

$$\langle \varphi_{nl}(r) \mid \varphi_{n'l}(r) \rangle = \eta_{nn'}, \quad (2)$$

where $|\eta_{nn'}| \ll 1$ for $n' < n$ and $\eta_{nn'} = 1$ for $n' = n$.

The problem of the approximation of the function $\varphi_{nl}(r)$ consists in finding the function $\psi_{nl}(r)$ that is expressed in terms of the analytical functions with the least error Δ_{nl}

$$\Delta_{nl} = \int dr r^2 \mid \varphi_{nl}(r) - \psi_{nl}(r) \mid^2 \quad (3)$$

and satisfies the orthogonality conditions as well as possible:

$$\langle \psi_{nl}(r) \mid \psi_{n'l}(r) \rangle = \xi_{nn'}, \quad (4)$$

where $|\xi_{nn'}| \ll 1$ for $n' < n$ and $\xi_{nn'} = 1$ for $n' = n$.

To do this, it is possible to use the expansion $\psi_{nl}(r)$ in terms of the basis of Slater orbitals:

$$\psi_{nl}(r) = \sum_i C_i(nl) S_{n_i l}(\alpha_i, r), \quad (5)$$

where $S_{n_i l}(\alpha_i, r) = r^{n_i-1} \exp(-\alpha_i r)$ and $C_i(nl)$ are the expansion coefficients.

In what follows, as an example, we consider the approximation of the numerical solution to the Hartree-Fock equation for the M_1 shell of the atom or ion that has 10 electrons or more. We first find the parameters of the

function corresponding minimum energy for the given l :

$$\psi_{1s}(r) = \sum_i C_i(1s) S_{n_i l}(\alpha_i, r), \quad (6)$$

where the parameters $C_i(1s)$, n_i , and α_i are calculated from the minimum of functional (3) with the functions $\varphi_{1s}(r)$ and $\psi_{1s}(r)$. Then, as a test function for the approximation of $\varphi_{2s}(r)$, we chose

$$\begin{aligned} \psi_{2s}(r) &= \sum_j C_j(2s) S_{n_j l}(\alpha_j, r) - \\ &< \sum_j C_j(2s) S_{n_j l}(\alpha_j, r') \mid \psi_{1s}(r') \rangle \psi_{1s}(r), \end{aligned} \quad (7)$$

which, by construction, satisfies the orthogonality condition

$$\langle \psi_{2s}(r) \mid \psi_{1s}(r) \rangle = 0. \quad (8)$$

The parameters $C_j(2s)$, n_j , and α_j in (7) are determined from the minimum of functional (3) with the functions $\varphi_{2s}(r)$ and $\psi_{2s}(r)$. Now, as a test function for the approximation of $\varphi_{3s}(r)$, we chose the function

$$\begin{aligned} \psi_{3s}(r) &= \sum_k C_k(3s) S_{n_k l}(\alpha_k, r) - \\ &< \sum_k C_k(3s) S_{n_k l}(\alpha_k, r') \mid \psi_{1s}(r') \rangle \psi_{1s}(r) \\ &- < \sum_k C_k(3s) S_{n_k l}(\alpha_k, r') \mid \psi_{2s}(r') \rangle \psi_{2s}(r), \end{aligned} \quad (9)$$

which, by construction, satisfies the orthogonality conditions:

$$\begin{aligned} \langle \psi_{3s}(r) \mid \psi_{1s}(r) \rangle &= 0, \\ \langle \psi_{3s}(r) \mid \psi_{2s}(r) \rangle &= 0. \end{aligned} \quad (10)$$

The parameters $C_k(3s)$, n_k , and α_k in (9) are determined from the minimum of functional (3) with the functions $\varphi_{3s}(r)$ and $\psi_{3s}(r)$.

The advantage of this approximation method consists in that the set of orthonormalized functions is obtained. However, the rounding of the coefficients C_j in (7) and C_k in (9) leads to the fulfillment of (10) only with an error $\xi_{nn'} \neq 0$ (4). The drawback of this method is that the approximation error Δ_{nl} increases rapidly with increasing n . The increase in the number of shells in the atom or ion leads to an increase in the number of additional conditions imposed on the test function.

A strong correlation between the parameters $C_i(nl)$ and α_i exists in expansions (6), (7), (9). The variation in the value of one of the parameters in these expansions leads to a change in all $C_i(nl)$ and α_i , which makes it difficult to find the minimum of the multiparameter function. In addition, the overlap integrals in (7) and (9), which also depend on the varied parameters, become a strong perturbation. Such a

“feedback” also makes it difficult significantly to perform the variation of functional (3) and leads to an increase in the error Δ_{nl} . The variation of the parameters $C_k(3s)$ and α_k in (9) must not only decrease the deviation of the first term in (9) from $\varphi_{3s}(r)$, but also decrease overlap integrals (10) in order that they remains corrections to the first term in (9).

This approximation method was used previously [7-11] to describe the ground state of atoms and ions and was not applied to excited states of many-electron atoms and ions.

3. New Approximation Method

We propose to refuse to choose the test function with conditions (1) taken into account and thereby to decrease Δ_{nl} . If the errors Δ_{nl} are rather small, then orthogonality conditions (4) are satisfied with the error that is close to that of numerical solution (2):

$$|\xi_{n'}| \rightarrow |\eta_{n'}|. \quad (11)$$

For the case of the approximation of the wave function of the M_1 shell, the test function for the K shell has the same form (6), and for the states with higher energies in absolute value, the test functions were chosen in the forms

$$\begin{aligned} \psi_{2s}(r) &= \sum_j C_j(2s) S_{n_j}(\alpha_j, r); \\ \psi_{3s}(r) &= \sum_k C_k(3s) S_{n_k}(\alpha_k, r). \end{aligned} \quad (12)$$

Because any additional conditions are imposed on functions (12), then it is possible to obtain small Δ_{2s} and Δ_{3s} such that conditions are satisfied (11).

Based on the proposed method, we calculated the wave functions of atoms and ions with the nuclear charge $Z \leq Z_{\max}$, where $Z_{\max} = 18$, and the number of electrons N_e ($2 \leq N_e \leq 18$). In addition to the ground states, we also took into account the states with one excited valence electron in the case where there are no vacancies in the inner shells. We considered the following excited states: 2s for $Z=2$, 2p for $Z \leq 4$, 3s for $Z \leq 10$, and 3p for $Z \leq 12$, as well as the 3d, 4s, 4p, 4d, 5s, 5p, and 5d states for $Z \leq 18$. For atoms and ions with one valence electron ($N_e = 3, 11, 13$), the spin in the excited state remains the same as in the ground state. Two possible values of the spin for the excited states are taken into account in the other cases.

The approximation accuracy Δ_{nl} in the calculations was as follows: $\Delta_{1s} \leq 3 \times 10^{-10}$, $\Delta_{nl} \leq 10^{-9}$ for $n=2$ and $\Delta_{nl} \leq 3 \times 10^{-9}$ for $n \geq 3$. This accuracy Δ_{nl} is sufficient for condition (11) to be satisfied. In this case, the obtained value of $|\xi_{n'}|$ for atoms and ions in the ground state turns out to be less than that for the wave functions [8, 11]. As a result, more than 14000 wave functions were obtained:

$$N_{wf} = N_Z (N_{ex} N_{nl} + N_{nl} - 1), \quad (13)$$

where N_{wf} are the number of wave functions, N_Z is the number of atoms and positive ions ($N_Z = Z_{\max} - N_e + 1$), N_{nl} is the maximum number of shells, and N_{ex} is the number of considered excited states. The value of N_{nl} , N_{ex} , and N_{wf} are given in the table.

The results of calculations (the parameters of wave functions) are represented in free access [12]. These wave functions are useful for atomic calculations [13, 14].

4. Conclusions

We have proposed a new method for approximating the solution to the Hartree-Fock equation for many-electron atoms and ions. The method is based on the increase in the approximation accuracy for the wave functions of electrons of all shells. This makes it possible to obtain the accuracy for the wave functions that is close to that of the numerical solution. We were first to obtain more than 14000 wave functions of the excited states of atoms and ions with nuclear charge $Z \leq 18$ and with the number of electrons ranging from 2 to 18 in the form of the expansion in terms of analytical functions. For atoms and ions with one valence electron ($N_e = 3, 11, 13$), the spin in the excited state remains the same as in the ground state. Two possible values of the spin for the excited states are taken into account in the other cases.

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Dependence of the number of atoms and positive ions N_Z , the values of the parameters N_{nl} and N_{ex} , and the number of obtained wave functions N_{wf} on the number of electrons N_e

N_e	N_Z	N_{nl}	N_{ex}	N_{wf}
2	17	2	22	765
3	16	2	10	336
4	15	3	21	975
5	14	3	9	406
6	13	4	42	2223
7	12	4	42	2052
8	11	4	20	913
9	10	4	42	1710
10	9	4	42	1539
11	8	4	8	280
12	7	5	15	553
13	6	5	7	234
14	5	6	30	925
15	4	6	30	740
16	3	6	14	267
17	2	6	30	370
18	1	6	30	185

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