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Abstract

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ON EXTENDED HARTREE AND FOCK METHODS

In Fock' s self-consistent-field method [1], as the variational wave function of the whole atom one uses a function satisfying the requirements of symmetry. The Hamiltonian, in atomic units, has the form

$$H = -\sum_{i=1}^{N}\left[\frac{1}{2}\frac{1}{r_i^2}\frac{\partial}{\partial r_i}\left(r_i^2\frac{\partial}{\partial r_i}\right) - \frac{\Lambda}{2r_i^2} + \frac{Z}{r_i}\right] + \sum_{k>i=1}^{N}\frac{1}{r_{ik}}. \tag{1}$$

Here Λ is the Legendre operator, N is the number of electrons in the atom, and Z is the nuclear charge number.

It is easy to show that in the Hartree method [2], as the variational wave function there may be used the product of radial one-electron wave functions, if as the Hamiltonian one uses expression (1) with the Legendre operator replaced by $l_i(l_i+1)$, where l_i is the orbital quantum number of the i-th electron. All other calculations are carried out using the wave function of the whole atom, satisfying the same conditions as in the case of the Fock method.

By the extended Hartree and Fock methods we shall mean the corresponding self-consistent-field methods using different radial one-electron wave functions in one and the same shell. In the extended Fock method we take the wave function of the whole atom in the form

$$\Psi' = NK\Psi, \tag{2}$$

where Ψ is the wave function of the whole atom in the ordinary Fock method, N is a normalization factor, and K is the operator

$$K = \sum P_1 P_2 \dots P_k. \tag{3}$$

Here the operator P_i introduces a distinction into the radial wave functions of the i-th shell and performs permutations, while the summation sign denotes summation over these permutations. It should be emphasized that the permutation is performed only among radial wave functions. If the distinction between functions is introduced by means of primes over the orbital quantum numbers, then the primes are permuted.

It is not difficult to see that in the extended Hartree method the variational wave function is the expression

$$\Psi^+ = N\Phi_1^+\Phi_2^+ \ldots \Phi_k^+. \tag{4}$$

Here Φ_i^+ is the symmetrized product of the radial one-electron wave functions of the i-th shell, which are regarded as differing from one another; it is a determinant composed of radial one-electron functions in which the negative terms have been replaced by positive ones.

Variation of the mean energy value leads to the equations of the extended Hartree and Fock methods, respectively, using as vari-

of the variation function (4) and (2). In the case of the ground state of helium-type atoms, the equations of the extended Hartree and Fock methods coincide with one another. They are the same as in ([3]).

Calculations using the extended Fock method are very complicated. This is the reason why, in the 30 years since the proposal made by Eckart ([4]), the use of different radial functions in one and the same shell has not found practical application beyond helium-type atoms ([4],[3] ,[5]).

For the purpose of simplifying the calculations, the radial one-electron wave functions may be determined by the extended Hartree method (by solving the equations of the extended Hartree method or by determining the parameters of analytic one-electron wave functions), while all the remaining calculations are then carried out in accordance with the requirements of the theory of the extended Fock method.

Table 1

Energy values in Rydberg units for the $2p^2$ shell of the $1s^22p^2$ configuration of the beryllium atom

	^3P	^1D	^1S
a	-1.451	-1.393	-1.306
b	-1.421	-1.355	-1.253
v	-1.430	-1.364	-1.276
g	-1.480	-1.509	-1.372

As an example we carried out calculations for the $1s^22p^2$ configuration of the beryllium atom using hydrogen-like one-electron wave functions. The results obtained for the energy of the $2p^2$ shell are given in row a of Table 1. Row b gives the results obtained by the usual (non-extended) method of calculation.

The difference between rows a and b gives the effect of passing from the usual method of calculation to the extended method. Row v gives the results obtained with the aid of solutions of the ordinary Fock equations and taken from (6). Row g gives the experimental data, taken from (7).

The results of Table 1 show that the correction to the energy upon transition to the extended method of calculation increases from -0.030 Rydberg units for ^3P to -0.053 Rydberg units for ^1S. The crude analytic functions used, as is evident from the table, in the extended method of calculation gave results about 0.02–0.03 Rydberg units closer to experiment than the best functions of the ordinary method of calculation (solutions of the Fock equations).

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Note: Figure translations are in progress. See original paper for figures.