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Abstract

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ON GENERALIZED HARTREE AND FOCK METHODS

The multiconfiguration approximation is understood (^{1}) as a method of refining the quantum-mechanical calculation of an atom in which the wave function of the entire atom is expressed in the form:

$$\Psi = N \sum_i \lambda_i \Psi_i, \tag{1}$$

where Ψ_i is the wave function of the entire atom corresponding to the i-th configuration; λ_i is a factor determined by means of the variational principle, and N is a normalization factor.

If, in applying Fock' s variational method (variation of the expression for the energy with respect to one-electron wave functions (^{2})), (1) is used as the variational function, then one obtains the equations of the generalized self-consistent-field method of Fock (g.m.F.) (^{3}), or the Fock equations in the multiconfiguration approximation (^{1}).

The transition from solutions of the Hartree equations (^{4}) to solutions of the Fock equations (^{2}) represents a refinement of the calculation of atomic quantities, the method of calculation being understood as indicated in (^{5}). The transition from solutions of the ordinary Fock equations to solutions of the g.m.F. equations represents a further refinement of the calculation. In many cases this second refinement greatly exceeds the first.

As an example, let us take the total energy of the neutral beryllium atom, which has been rather well studied theoretically. The transition to solutions of the Fock equations gives a correction (^{6}) of -0.025 Rydberg units, while the transition to the g.m.F. gives (^{7}) -0.130 Rydberg units, if one restricts oneself to the three-configuration approximation. Therefore the question arises of the transition from solutions of the ordinary Hartree equations to solutions of the Hartree equations in the multiconfiguration approximation. In (^{8}) this was done by neglecting the exchange terms in the Fock equations and retaining the configuration terms. However, such an approach does not constitute the Hartree method in the sense in which it is presented in (^{5}), where the variational function consists of radial one-electron wave functions. For this reason it should be considered expedient to construct a generalized Hartree self-consistent-field method (g.m.H.), in which the radial one-electron wave functions are found by varying a wave function constructed with the aid only of radial one-electron wave functions.

On the basis of the experience of the works (^{9}), where it was found that the solutions of the g.m.F. equations are not sensitive to the coefficient in the configuration term, we shall arrive at the conclusion that the solutions of the Fock equations depend only weakly on the term of the given configuration, since the equations for different terms differ mainly in the coefficient in the configuration term. This indicates a weak dependence of the solutions of the g.m.F. equations on the type of coupling. To become more thoroughly convinced of this, multiconfigur-

···approximation

$$1s^2 - 2p^2 - 2s^2 - 3d^2 - 3p^2 \tag{2}$$

in LS-coupling, considered in (^{10}, ^{11}), we transformed to jj-coupling and determined the one-electron wave functions, as well as the correction to the energy. The results showed that both the one-electron wave functions and the correction to the energy practically coincide with their values in LS-coupling.

The property of independence of the type of coupling is possessed by the equations of both the ordinary and the extended Hartree methods, in deriving which the wave function of the whole atom is used as the variational function, constructed in the corresponding manner (^{5}) with the aid of radial one-electron wave functions. Thus, we arrive at the following way of constructing the G.H.M.

In (1), as Ψ_i one should use products of radial one-electron wave functions and apply Fock' s variational method in the same way as it is applied in the G.F.M.; this means that, in varying the radial one-electron wave functions, we also vary the constants λ_i. The solutions of the G.H.M. equations obtained in this way are used for calculating physical quantities in exactly the same way as the solutions of the corresponding G.F.M. equations are used. The use of solutions of the G.H.M. equations simplifies the process of obtaining one-electron wave functions in the multiconfiguration approximation, since they are much simpler than for the G.F.M. Moreover, only one system of equations is solved for all equations of one definite configuration. It goes without saying that, instead of solutions of the G.H.M. equations, one may use the corresponding analytic one-electron wave functions, whose constants are determined by using, as the variational function, the same function as in the G.H.M.

In the same way as was done in the case of the G.F.M. (^{7}), it can be shown that, instead of solutions of the G.H.M. equations in the multiconfiguration approximation, one may practically use solutions of the G.H.M. equations in the two-configuration approximation for the perturbing configurations, and solutions of the ordinary Hartree equations for the configuration under investigation (the configuration under investigation is the one whose calculation is being refined, while the perturbing configurations are those which enter as a correction to the wave function of the one-configuration approximation in order to obtain it in the multiconfiguration approximation). The same applies also to the case of using analytic one-electron wave functions (^{12}).

The relation of the G.H.M. constructed in the indicated way to the G.F.M. differs from the relation of the ordinary and extended Hartree methods to the ordinary and extended Fock methods (^{5}) in that neglecting the exchange terms in the G.F.M. equations leads to equations that differ from the G.H.M. equations. This natural difference consists in the configuration terms. In the G.F.M. they are expressed by functions Y_k ($k \geqslant 0$), while in the G.H.M. by functions Y_0, where

$$Y_k(nl,\ n'l'|r)_i = \frac{1}{r^k}\int_0^r R(nl|r_1)R(n'l'|r_1)\,r_1^{k+2}\,dr_1 + \\ + r^{k+1}\int_r^\infty R(nl|r_1)R(n'l'|r_1)\,r_1^{-k+1}\,dr_1. \tag{3}$$

In the G.H.M. $k=0$, independently of the quantum numbers nl and $n'l'$. This leads to the fact that, in the G.H.M. equations in the two-configuration approximation, only a single configuration term appears. This applies to those important cases in which the perturbing configurations differ from the one under investigation by two sets of one-electron quantum numbers nl.

As an example, we carried out calculations applying the multiconfiguration approximation (2) to the helium atom by the generalized Hartree method constructed above, using, instead of the solutions of the generalized Hartree equations, analytic one-electron wave functions for the correction configurations and the solution of the ordinary Hartree method equation (which in the present case coincides with the Fock equation) for the configuration under study (the ground configuration). The results proved to be practically the same as in the case of the generalized Fock method (^{11}), both for the one-electron wave functions and for the correction to the energy.

The extended Hartree and Fock methods proposed in (^{5}) can be generalized by extending them to the case of the multiconfiguration approximation, yielding extended generalized Hartree (e.g.m.H.) and Fock (e.g.m.F.) methods. The application of the e.g.m.F. method is a rather difficult problem; however, simplifying it by using the e.g.m.H. method makes the e.g.m.F. method practically applicable, since the determination of the one-electron wave functions is considerably simplified. To this end, when determining the one-electron wave functions, one should use (1) with the substitution (4) (^{5}) instead of Ψ_i as the variational function, and carry out all the remaining calculations with a wave function of the form (1), in which expressions of type (2) (^{5}) are substituted for Ψ_i.

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