New Self-Consistent-Field Method for Atoms

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The spin-optimized self-consistent-field procedure is generalized for atoms. This new method is flexible, can allow for the angular correlation, and is applicable to the lowest state of any given symmetry type.

In the spin-optimized self-consistent-field (SOSCF) procedure,[1-4] the wave function of an N-electron system is written in the form

$$\Psi = \alpha \, \Xi \, \Theta , \qquad (1)$$

where α is an antisymmetrizer, Ξ is a product of one-electron spatial functions

$$\Xi = \prod_{i=1}^{N} \chi_i(\vec{r}_i) , \qquad (2)$$

and Θ is a linear combination of all independent spin functions ω_k spanning the space of appropriate S and M_S,

$$\Theta = \sum_k t_k \Theta_k . \qquad (3)$$

The orbitals χ_i and the coefficients t_k are then optimized to make the energy expectation value $\langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ stationary.

It is evident that the SOSCF method can allow for the correlation of a certain type only (for small atoms the radial correlation[1]), and that, in general, restrictions have to be imposed on the orbitals to obtain wave functions of correct symmetry.[2,3] Furthermore, the form of the wave function (1) makes it impossible to apply the procedure to the states of a certain symmetry type (e.g., the lowest ^1S state of carbon).

The purpose of this comment is to suggest a method for atoms which is a generalization of the SOSCF procedure and is not subject to the mentioned limitations.

Let us start with the specification of the SOSCF wave function (1) for an atom. A one-electron spatial function $\chi_i(\vec{r})$ can be written in the form

$$\chi_i(\vec{r}) = R_i(r) \, r^{l_i} \, Y_{l_i m_i}(\hat{r}) , \qquad (4)$$

where $Y_{l_i m_i}(\hat{r})$ is a spherical harmonic. Evidently, the wave function (1) can be rewritten in the form

$$\Psi = \alpha \, R \, \Omega' , \qquad (5)$$

where

$$R = \prod_{i=1}^{N} R_i(r_i) , \qquad (6)$$

$$\Omega' = \sum_k t_k \Omega'_k , \qquad (7)$$

$$\Omega'_k = \left(\prod_{i=1}^{N} r_i^{l_i} \, Y_{l_i m_i}(\hat{r}_i) \right) \Theta_k . \qquad (8)$$

Let us inspect now the case when the radial parts R_i of all orbitals, from which the SOSCF function (1) is built up, are not restricted to form equivalent orbitals. Then the entities Ω'_k of (7) are independent simultaneous eigenvectors of the operators L^2, L_z, S^2, S_z, and the parity operator $\mathcal{P}$. Furthermore, in this case, the SOSCF wave function (1) could as well be obtained by optimizing the functions R_i and the parameters t_k appearing in the rearranged expression (5) of Ψ.

Let us further introduce a space formed by the fixed linear combinations

$$\Omega_k = \sum_\kappa a_{k\kappa} \varphi_\kappa , \qquad (9a)$$

where functions φ_κ are of the type

$$\prod_{p=1}^{N} \left(r_p^{l_p} \, Y_{l_p m_p}(\hat{r}_p) \begin{Bmatrix} \alpha(s_p) \\ \beta(s_p) \end{Bmatrix} \right) , \qquad (9b)$$

with the coefficients $a_{k\kappa}$ chosen in such a way that the elements Ω_k are eigenfunctions of the operators L^2, L_z, S^2, S_z, and $\mathcal{P}$ with eigenvalues $L(L+1)$, M_L, $S(S+1)$, M_S, and p, respectively. The space formed by *all* the elements Ω_k [Eq. (9a)] will be referred to as the $W(L, M_L, S, M_S, p)$ space.

As has been indicated above, only the elements of very limited type of the $W(L, M_L, S, M_S, p)$ space can occur in the expressions (5)–(7) of an SOSCF wave function.

The above considerations lead us to suggest a new method, which we call the LS-optimized SCF (LSOSCF) method. The main idea of this method is to approximate the wave function of an atom by

$$\Psi = \alpha \, R \, \Omega , \qquad (10a)$$

where R is a simple product (6) of one-particle *radial* functions, and the angular dependence is transferred to the Ω part, which is a linear combination of the independent elements Ω_k (when taken multiplied by R) of the appropriate space $W(L, M_L, S, M_S, p)$,

$$\Omega = \sum_k \omega_k \Omega_k . \qquad (10b)$$

No further specifications are given as to the num-

ber of elements Ω_k and their form.

Obviously, the form of the wave function (10a) removes all the limitations of the SOSCF approach to the atomic systems mentioned above.

The radial functions R_i of (6) and the linear parameters ω_k of (10b) are supposed to be optimized to make the energy expectation value stationary— by the procedure used in the SOSCF scheme.[1] The method of Ritter and Pauncz,[5] which has the advantage of being monotonically convergent, may serve as an alternative to the optimization of the radial functions. It should be noted that the coefficients ω_k of (10b) are obtained by solving the configuration-interaction-like characteristic problem, and each resulting set of coefficients ω_k is connected with a corresponding upper bound to the exact eigenvalue.[6] A systematic use of the appropriate set of ω_k during the optimization process makes it possible to obtain an LSOSCF approximation to the lowest state of the given symmetry.

We wish to note that we do not exclude the case when Ω [Eq. (10b)] reduces to one Ω_k from the scope of the scheme (cf. Ref. 7). Apparently, only radial functions then have to be optimized and in this special version, the method could be applied to relatively large atoms.

We want to point out that the potentiality of the scheme can be extended by the augmentation of the space $\mathcal{W}(L, M_L, S, M_S, p)$—allowing the functions of (9b) to take the form

$$\prod_{p=1}^{N} \left(f_p(r_p) \, r^{l_p} \, Y_{l_p m_p}(\hat{r}_p) \begin{Bmatrix} \alpha(s_p) \\ \beta(s_p) \end{Bmatrix} \right), \qquad (9b')$$

where the functions $f_p(r_p)$ are spherically symmetric and could be, for example, products of exponential and polynomial functions of r_p. Apparently, when such an augmented space $\mathcal{W}'(L, M_L, S, M_S, p)$ is extensively exhausted in forming (10b), the LSOSCF scheme could provide results comparable with the quite general version of the projected Hartree-Fock method.[8]

For the construction of the functions Ω_k, various techniques are available.[9] Of course, the question of the usefulness and effectiveness of a particular choice of the elements to be used in (10b) will have to be decided on physical grounds and by numerical experience (cf. second paper in Ref. 7).

In concluding this comment we wish to stress the fact that by writing the wave function of an atom in the form (10), the proper symmetry is ensured by the choice of the elements of $\mathcal{W}(L, M_L, S, M_S, p)$ only. Apparently, there is no difficulty in constructing spaces analogous to the $\mathcal{W}'(L, M_L, S, M_S, p)$ which would be eigenspaces of another set of the constants of motion of a many-fermion system possessing central symmetry. Consequently, the above approach can be used to approximate the eigenvectors of a spin-dependent Hamiltonian of an atom, and the main idea of the method might be fruitful in treating many-nucleon systems with central symmetry. Work on the applications of the method is in progress.

[1]U. Kaldor and F. E. Harris, Phys. Rev. 183, 1 (1969).

[2]U. Kaldor, Phys. Rev. A 1, 1586 (1970).

[3]U. Kaldor, Phys. Rev. A 2, 1267 (1970).

[4]R. C. Ladner and W. A. Goddard III, J. Chem. Phys. 51, 1073 (1969). See also S. Lunell, Phys. Rev. 173, 85 (1968); S. Hameed, S. Seung Hui, J. Musher, and J. R. Shulman, J. Chem. Phys. 51, 502 (1969).

[5]Z. W. Ritter and R. Pauncz, J. Chem. Phys. 32, 1820 (1960); S. Lunell, Phys. Rev. A 1, 360 (1970).

[6]E. A. Hylleraas and B. Undheim, Z. Physik 65, 759 (1930); J. K. L. MacDonald, Phys. Rev. 43, 830 (1933).

[7]W. A. Goddard III, Phys. Rev. 157, 81 (1967); 169, 120 (1968).

[8]P. O. Löwdin, Phys. Rev. 97, 1509 (1955); in Quantum Theory of Atoms, Molecules and Solids, edited by P. O. Löwdin (Academic, New York, 1966), p. 601.

[9]E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge U. P., Cambridge, England, 1967), Chap. III, Secs. 11 and 12; R. K. Nesbet, J. Math. Phys. 6, 701 (1961); H. F. Schaefer and F. E. Harris, J. Computational Phys. 3, 217 (1968).