Theoret. Chim. Acta (Berl.) 48, 257–261 (1978)

THEORETICA CHIMICA ACTA

Molecular Orbitals for Excited States of Atoms and Molecules

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A method is described for calculating SCF wavefunctions for excited electronic states of atoms and molecules. The orthogonality conditions with the ground state wavefunction and the underlying excited states wavefunctions are introduced in the SCF process in a simplified form.

Key words: Excited states – Orthogonality conditions

1. Introduction

Among the various known methods for the determination of the wavefunctions of the excited states of atoms and molecules [1–12], the generalization of the Hartree–Fock method (lowest number of determinants which shall assure a right spatial symmetry and spectral multiplicity) seems to be more advantageous for the following reasons: 1) the wavefunction is more easily interpretable; 2) the molecular orbitals can be determined by the solution of a monoelectronic problem in an effective field. It is, moreover, reasonable to think that these molecular orbitals provide an electronic charge density, which does not undergo modifications when the short range electronic correlation is introduced. Hence, a better determination of energy can be made for the second time by the introduction of the electronic correlation as a functional of the charge density.

Many authors have suggested iterative processes based on suitable coupling operators [13–26]. Although these methods are correct in principle, they generally involve great difficulties in attaining convergency. This handicap can be overcome by employing the method recently proposed by us [27], based on a number of diagonalizations of matrices representative of different operators at every iteration.

0040-5744/78/0048/0257/$01.00

Besides the difficulties related to the solution of open-shell problems, another obstacle is to impose the orthogonality constraints with the wavefunctions of the underlying states. The aim of the present paper is to present a method which resolves this difficulty. We shall develop the formulae for a series of electronic levels corresponding to monoexcited singlet and triplet states. The generalization to other similar cases (e.g. states corresponding to double excitations on the same symmetry of the ground one) is evident.

Let $\phi_1, \phi_2 \ldots \phi_m \ldots \phi_n$ be n molecular orbitals, built up as linear combinations of n basis functions $\sigma_1 \ldots \sigma_n$: $\boldsymbol{\phi} = \boldsymbol{\sigma C}$, with $\boldsymbol{C}^{\dagger}\boldsymbol{SC} = \mathbf{1}$, $\boldsymbol{S}$ being the overlap matrix of $\boldsymbol{\sigma}$. Let us assume that the ground state of a system of $2m$ electrons is a closed shell, described by the $\phi_1 \ldots \phi_m$ orbitals, and consider the promotion of one electron from the highest occupied orbital ϕ_m to the first virtual orbital ϕ_{m+1} (ϕ_m and ϕ_{m+1} belong to monodimensional irreducible representations). The open shell thus obtained can be described by a combination of two detors, D_1 and D_2, which correspond to the two configurations [core]$\phi_m\alpha\phi_{m+1}\beta$ and [core]$\phi_m\beta\phi_{m+1}\alpha$. (D_1+D_2) and (D_1-D_2) combinations represent the triplet and singlet states respectively. This is a very poor approximation, as the true orbital ϕ'_{m+1} of the excited state is quite different from the first virtual orbital ϕ_{m+1} of the closed shell. Moreover, because of changes in the charge density, the first m orbitals will also undergo some variations. The wavefunction of this excited state will be built up by $\phi'_1 \ldots \phi'_m, \phi'_{m+1}$ orbitals, which are different from the previous ones. The open shell orbitals can be related to the closed shell ones by the relationship $\boldsymbol{\phi}' = \boldsymbol{\phi} U$($U$ is a rectangular $n \times m+1$ matrix), or to the basis functions by $\boldsymbol{\phi}' = \boldsymbol{\sigma} \boldsymbol{C}'$.

In order to determine the new orbitals $\boldsymbol{\phi}'$, it is necessary to take into account the orthogonality constraint of the excited state wavefunction with that of the ground state. The triplet state wavefunction always satisfies this constraint automatically, while the singlet state one satisfies it only if ϕ_m and ϕ_{m+1} belong to different irreducible representations. Otherwise, the determinant of the overlaps between $\phi_1 \ldots \phi_m$ and $\phi'_1 \ldots \phi'_m$ orbitals or between $\phi_1 \ldots \phi_m$ and $\phi'_1 \ldots \phi'_{m-1}, \phi'_{m+1}$ orbitals must be zero.[1] The first condition has no physical significance, therefore we impose the condition for vanishing the second determinant. We shall fulfil this condition by reducing the variation field of the orbital which describes the excited level. Although it is not a general procedure, it seems highly preferable to us as it can be easily executed and does not cause any significant worsening of the value of the energy and of the form of the orbital.

2. First Excited Singlet State

Let $\phi_1^{(r)} \ldots \phi_n^{(r)}$ be the molecular orbitals of r'th iteration; the first $m-1$ are doubly occupied, ϕ_m and ϕ_{m+1} are singly occupied, $\phi_{m+2} \ldots \phi_n$ are functions orthogonal

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[1] In a rigorous form, the orthogonality constraint must be imposed with the exact wavefunction of the ground state. We limit ourselves to the approximate condition of the orthogonality with the single detor ground state wavefunction. This approximation will be applied to the successive excited states also.

to the preceding ones. $\phi_1^{(0)} \dots \phi_n^{(0)}$ are the ground state MO's (occupied and virtual). Let $\boldsymbol{C}^{(r)}$ be the matrix of the coefficients of the $\boldsymbol{\phi}^{(r)}$ orbitals: $\boldsymbol{\phi}^{(r)} = \boldsymbol{\sigma}\boldsymbol{C}^{(r)}$. Following the formulae of Ref. [27], one can build up the matrices $\boldsymbol{d}$, $\boldsymbol{a}$, $\boldsymbol{b}$ relative to the operators $\mathscr{F}_d, \mathscr{F}_a, \mathscr{F}_b$ employing $\boldsymbol{\phi}^{(r)}$ orbitals. In order to get the new iteration $\boldsymbol{\phi}^{(r+1)}$ MO's, the following steps must be executed:

a) Doubly occupied orbitals – virtual orbitals combinations.
A rectangular matrix $\boldsymbol{C}$ is obtained from $\boldsymbol{C}^{(r)}$ by drawing the columns of the doubly occupied and virtual orbitals and by it the transformation $\boldsymbol{C}^{\dagger}\boldsymbol{d}\boldsymbol{C}$ is performed. If $\boldsymbol{U}$ diagonalizes this last matrix, the rectangular matrix $\boldsymbol{C}_1 = \boldsymbol{C}\boldsymbol{U}$ is calculated and then it is substituted for the previously removed columns of $\boldsymbol{C}^{(r)}$.

b) First singly occupied orbital – virtual orbitals combinations.
A rectangular matrix $\boldsymbol{C}$ is obtained from the new matrix $\boldsymbol{C}^{(r)}$ by drawing the columns of the first singly occupied orbital and of the virtual orbitals, and by it the transformation $\boldsymbol{C}^{\dagger}\boldsymbol{a}\boldsymbol{C}$ is performed. If $\boldsymbol{U}$ diagonalizes this last matrix, the rectangular matrix $\boldsymbol{C}_1 = \boldsymbol{C}\boldsymbol{U}$ is calculated and then it is substituted for the previously taken off columns of $\boldsymbol{C}^{(r)}$.

c) Doubly occupied orbitals – first singly occupied orbital combinations.
A rectangular matrix $\boldsymbol{C}$ is obtained from $\boldsymbol{C}^{(r)}$ by drawing the columns of the doubly occupied orbitals and of the first singly occupied orbital, and by it the transformation $\boldsymbol{C}^{\dagger}(\boldsymbol{d}-\boldsymbol{a})\boldsymbol{C}$ is performed. If $\boldsymbol{U}$ diagonalizes this last matrix, the rectangular matrix $\boldsymbol{C}_1 = \boldsymbol{C}\boldsymbol{U}$ is calculated and then it is substituted for the previously removed columns of $\boldsymbol{C}^{(r)}$.

d) Orthogonalization of the virtual orbitals to the doubly occupied ones of the ground state.
Let $\boldsymbol{C}$ be the matrix obtained by removing from $\boldsymbol{C}^{(r)}$ the columns of the two singly occupied orbitals, and $\boldsymbol{C}'$ the matrix of the first m columns of $\boldsymbol{C}^{(0)}$. The rectangular $(m \times n-2)$ matrix $\boldsymbol{T} = \boldsymbol{C}'^{\dagger}\boldsymbol{S}\boldsymbol{C}$ is constructed. From this, $n-m-1$ square matrices are obtained by putting together the first $m-1$ columns and the k'th column, where $k = m$, $m+1 \dots n-2$. Their determinants are Δ_1, $\Delta_2 \dots \Delta_{n-m-1}$ (we observe that the calculation of these determinants can be very easily performed once the Gauss elimination method is applied). The two columns m and $m+1$ of $\boldsymbol{C}$ are then substituted in the following way:

$$\boldsymbol{C}_{.m} \leftarrow \boldsymbol{C}_{.m} \cos\theta + \boldsymbol{C}_{.m+1} \sin\theta$$

$$\boldsymbol{C}_{.m+1} \leftarrow -\boldsymbol{C}_{.m} \sin\theta + \boldsymbol{C}_{.m+1} \cos\theta,$$

where $\mathrm{tg}\,\theta = -\Delta_1/\Delta_2$. The Δ_1 and Δ_2 determinants become:

$$\Delta_1' = 0$$

$$\Delta_2' = -\Delta_1 \sin\theta + \Delta_2 \cos\theta$$

The same combination can be made between the $m+1$ column just modified and the $m+2$, with $\mathrm{tg}\,\theta = -\Delta_2'/\Delta_3$ and so on until $\Delta_{n-m-2}' = 0$. The resulting $\boldsymbol{C}$ matrix is substituted for the previously removed columns of $\boldsymbol{C}^{(r)}$.

e) Second singly occupied orbital – virtual orbitals combinations.
A rectangular matrix $\boldsymbol{C}$ is obtained from $\boldsymbol{C}^{(r)}$ by drawing the columns of the second singly occupied orbital and all the virtual orbitals, except the last, and by it the transformation $\boldsymbol{C}^{\dagger}\boldsymbol{b}\boldsymbol{C}$ is performed. If $\boldsymbol{U}$ diagonalizes this last matrix, the rectangular matrix $\boldsymbol{C}_1 = \boldsymbol{C}\boldsymbol{U}$ is calculated and then it is substituted for the previously removed columns of $\boldsymbol{C}^{(r)}$. The new matrix $\boldsymbol{C}^{(r+1)}$ thus obtained shall be employed in the next iteration. We remark that combination between the two singly occupied orbitals and those between the second singly occupied orbital and the doubly occupied orbitals cannot be performed without violating the orthogonality condition in our simplified form.

3. Second and Following Excited Singlet States

Let $\phi_1, \phi_2 \ldots \phi_m, \phi_{m+1}, \phi_{m+2} \ldots \phi_n$ be the orbitals resulting from the SCF iterative process to build up the wavefunctions of the first excited singlet state. So one can start from them to build up the wavefunction of the second excited singlet state, considering the singly occupied orbitals as ϕ_m and ϕ_{m+2}. As an electron moves from a ϕ_{m+1} orbital to a ϕ_{m+2} one, the inner $\phi_1 \ldots \phi_m$ orbitals undergo some changes. If they are frozen, then ϕ_{m+2} should lie completely in the space orthogonal to ϕ_{m+1}. It is reasonable to assume that the variations of $\phi_1 \ldots \phi_m$ are small, since the more relevant variations of the charge density take place in an external region where they are not significant. So we regard it a very good approximation to exclude the ϕ_{m+1} orbital from the space spanned by the remaining $n-1$ orbitals. This approximation certainly does not bring any noticeable errors on the energy and the wavefunction, and allows a very remarkable simplification of the SCF process to obtain the new orbitals. The exclusion of the ϕ_{m+1} orbital indeed assures that the new state is orthogonal to the underlying excited one. So the SCF process is the same as that previously described.

The calculation of the third and the following excited states is carried out in a similar way, starting every time from the orbitals obtained for the preceding state and excluding the last singly occupied orbital. The reduction of the space dimension leads to a progressive worsening of the calculated wavefunction. Nevertheless, we observe that this worsening is not very important if the basis set σ is adequate to describe the various orbitals.

4. Excited Triplet States

The first excited triplet state does not offer any difficulty as regards the orthogonality with the ground state wavefunction. So our recently proposed method of calculation for open shells can be followed throughout. Regarding the upper triplet states, one can follow the same procedure, starting from the orbitals of the previous triplet state and excluding the last singly occupied orbital from the SCF process.

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Received July 13, 1977/December 21, 1977