



Recent Developments in the Method of Different Orbitals for Different Spins

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ABSTRACT

The alternant molecular orbital method and the nonpaired spatial orbital method have been compared. Some recent applications of the AMO method have been reported.

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INTRODUCTION

During recent years various extensions of the Hartree-Fock SCF method have been considered; for a general review we refer to the paper of Löwdin.¹ Among the extensions the alternant molecular orbital (AMO) method has gained considerable interest. The general characteristics of the method and its applications to conjugated systems have been discussed by the author² quite recently. The aim of the present note is to consider some recent applications of the method to non-alternant systems, as well as to contrast it with another approach, the Non Paired Spatial Orbital (NPSO) method, which seems to be even more powerful, when applied to small conjugated systems. The AMO method is closely related to the molecular orbital (MO) method, the other approach is more close to the valence bond (VB) treatment. For a comparison and critical evaluation of these two basic methods and their modifications, we refer to the paper of Slater given at the Symposium³.

Alternant Molecular Orbital Method

The method has been suggested by Löwdin⁴; for a general review of the method and its applications we refer to Ref. 2. Here we would like to mention a few points only which will be needed for the comparison with the NPSO method.

Let us take a conjugated system consisting of $2n$ centers and $2n$ electrons. We have to choose $2n$ orbitals which form an orthonormal system. Next we select n orthogonal two-dimensional subspaces spanned by the

pair of orbitals, which will be denoted by ψ_i , and $\bar{\psi}_i$, respectively ($i=1, \dots, n$). In each two-dimensional subspace we form two non-orthogonal linear combinations of ψ_i and $\bar{\psi}_i$ in the following way:

$$\begin{aligned} a_I &= \cos \vartheta_i \psi_i + \sin \vartheta_i \bar{\psi}_i \\ \bar{a}_I &= \cos \vartheta_i \bar{\psi}_i - \sin \vartheta_i \psi_i \end{aligned} \quad (1)$$

The new set obtained consists of two subsets (a_I ; \bar{a}_I), $I=1, \dots, n$. We have orthogonality within each subset, as well as between orbitals a_I and \bar{a}_J for $I \neq J$; the only non-orthogonality will exist between the pairs a_I and \bar{a}_I , $i=1, \dots, n$.

$$\int a_I^* \bar{a}_I dv = \cos 2\vartheta_i = \lambda_i \quad (2)$$

We emphasize this point because it has important consequences in the calculation of the energy and the applicability of the method to larger systems.

The final wavefunction is built up by associating one set of orbitals (a_I) with $\underline{\alpha}$ spin functions, while the other set (\bar{a}_I) with $\underline{\beta}$ spin functions. As the determinantal function is not a proper eigenfunction of S^2 , we have to select the proper spin component. This is conveniently done by the use of the projection operator method, as proposed by Löwdin⁵.

$$\underline{\Psi}^{(s)} = A a_I^{(1)} \dots a_N^{(n)} \bar{a}_I^{(n+1)} \dots \bar{a}_N^{(2n)} \times \alpha(1) \dots \alpha(n) \beta(n+1) \dots \beta(2n) \quad (3)$$

The use of the projection operator in the construction of the wavefunction has important implications both with respect to the effective treatment of the correlation problem and with respect to the calculation of the energy; these aspects have been discussed extensively in Ref. 2.

The matrix element of the Hamiltonian is given by the following expression

$$\langle \underline{\Psi} | \mathcal{H} | \underline{\Psi} \rangle = \sum_P (-1)^P C_{q(P)}^{(S)} \int \underline{\Phi}^* \mathcal{H} P^N \underline{\Phi} d\tau \quad (4)$$

where P^N means permutation of the spatial variables. Because of the orthogonality properties mentioned before, only certain permutations will lead to nonvanishing contributions, so it is easy to classify the possible integrals and their coefficients. Eventually the integrals are expressed in terms of integrals over the basic orbitals and certain functions of the parameters λ_i

So far we have not specified how to choose the basic orbitals and the n two-dimensional subspaces. The best selection would be one which would lead to the lowest energy value obtainable, subject to the limitation that the trial function is given in form (3) and (1). This problem is still unsolved; investigations in this direction are in progress. A few guiding principles which help in choosing the orbitals are the following:

- a) If the parameters λ_i reduce to zero, the functional form given in Eq. (3) goes over to a MO description with doubly filled orbitals. This suggests the choice of the SCF orbitals as a natural starting point, because any other choice would mean a higher energy for this limiting point, but it should be observed that it is not necessarily the best choice. \checkmark

b) The criterion given in a) does not specify the orbitals uniquely. An arbitrary unitary transformation would leave the energy value of the Hartree-Fock-Roothaan function invariant. This transformation could be performed in such a way that the orbitals would be localized, see Edmiston and Ruedenberg's paper⁷. The selection of the orbital pairs should be done such that the alternant orbital pairs would be well separated in space, so as to yield a better correlation between electrons possessing parallel spins.

c) It is desirable that the total wavefunction, which belongs to a given irreducible representation of the symmetry group, should be represented as a spin projection of a single Slater determinant. This is important because it preserves the direct connection with the independent particle model¹. It leads also to a considerable simplification in the calculation of the energy.

In the previous applications to alternant conjugated systems, the selection of the orbital pairs was related to those pairs of orbitals, which in the Hückel approximation have the following form:

$$\begin{aligned} \psi_i^+ &= \sum_{\mu}^* \chi_{\mu} c_{\mu i}^+ + \sum_{\nu}^0 \chi_{\nu} c_{\nu i}^+ \\ \psi_i^- &= \sum_{\mu}^* \chi_{\mu} c_{\mu i}^- - \sum_{\nu}^0 \chi_{\nu} c_{\nu i}^- \end{aligned} \quad (5)$$

Here the two summations \sum_{μ}^* and \sum_{ν}^0 refer to the two subsystems, each of which has the properties that no two atoms in the subsystems are neighbors to each other.

Recent Applications of the AMO Method

There are two recent applications of the AMO method to which we would like to draw attention. The first is concerned with applications

of the method to non-alternant systems, as azulene and fulvene⁸. In these cases we cannot select the pairs in the same way, as has been done in alternant molecules. In the calculation the starting orbitals were formed from the eigenvectors of the overlap matrix, these are somewhat inferior to the SCF orbitals, but they present considerable simplification in the evaluation of electron repulsion integrals over the molecular orbitals. The selection of the pairs have been made on the basis of principles b) and c). In the case of azulene, when using five different mixing parameters, (λ_i) the energy improvement for the ground state was obtained as 3.066 eV, while a configuration interaction treatment, based on the same orbitals, using 24 configurations yielded only 1.928 eV. Full details of the calculations will be published in a separate note.

The second application has been made to naphthalene, using five different parameters (λ_i) and comparing the result with a rather extensive configuration interaction study which included 50 configurational functions⁹. The AMO method using 5 nonlinear parameters turned out to be more effective than the CI treatment with 49 linear parameters. The corresponding energy improvements for the ground state were as follows:

$$E = 5.045 \text{ eV (AMO)}; 3.393 \text{ (CI)}.$$

We cannot claim that these configurations have been the 50 most important configurations, they have been chosen mostly on the basis of their energy values and it is well known that this criterion is insufficient to determine their effectiveness in lowering the energy. Still it is rather impressive that the AMO with a small number of parameters can surpass the limited CI treatment for a medium size system. The orbitals used in this calculations were SC-LCAO-MO orbitals. It is interesting to compare

the results with that relating to the isoelectronic non-alternant system, azulene. We see that because of the peculiar geometrical structure in the case of azulene, the energy improvement was smaller than in naphthalene, but still substantial.

The Non-Paired Spatial Orbital Method

Another important development during recent years has been the application of the Non-Paired Spatial Orbital (NPSO) method to a number of molecules. The method has been suggested by Hirst and Linnett¹⁰ and tested in a number of applications by Linnett and coworkers. For a comprehensive bibliography we refer to the paper of Hirst and Linnett in this issue¹¹.

The main objective of the method is similar to that of the AMO method: to take into account the correlation between electrons with antiparallel spins and to represent the total wavefunction by a functional form which contains a small number of adjustable parameters. The basic orbitals are two-center semilocalized orbitals of the type considered by Mueller and Eyring¹², and by Coulson and Fischer¹³, in the case of the hydrogen molecule. Taking the benzene case, as an example (Empedocles and Linnett¹⁴) we have the following spatial orbitals.

$$\begin{aligned}\Phi_{11} &= (a + kb, b + kc, \dots, f + ka) \\ \Phi_{12} &= (ka + b, kb + c, \dots, kf + a)\end{aligned}\tag{6}$$

The spatial orbitals are combined with appropriate spin functions and the total wave function has the following form¹⁵:

$$\underline{\Psi} = A(\underline{\Phi}_1 + \underline{\Phi}_2) O_{SO} (c_1 \underline{\psi}_1^G + c_2 \underline{\psi}_2^G) \quad (7)$$

where

$$\underline{\psi}_1^G = \underline{\alpha\beta\alpha\beta\alpha\beta}$$

$$\underline{\psi}_2^G = (\underline{\alpha\beta\alpha\beta\alpha\beta} - \alpha\alpha\alpha\beta\beta\beta + \beta\alpha\alpha\beta\beta\beta - \beta\beta\alpha\alpha\alpha\beta) / G$$

The functional form is more general than that used by the AMO method in two respects: a) The spatial part is a sum of two products instead of the single product occurring in Eq. (3); b) The linear combination of two independent spin projections have been used. The nonlinear parameter k will determine the shape of the basic two center orbitals; the linear parameter gives the relative weight of the two spin functions $\underline{\psi}_1^G$ and $\underline{\psi}_2^G$. The best value of k for the ground state was equal to 3.69. The result obtained was very good, it surpassed the corresponding AMO treatment with two parameters. The same result has been obtained in the case of the allyl ions and radical¹⁶, the NPSO usually halves the distance between the AMO result and that of a full configuration interaction treatment. The reason for the better result seems to lie in the more general functional form. From the two aspects considered before, the first one is probably the more important. Preliminary studies in the AMO treatment of the benzene case indicate that the admission of other spin functions leads to an improvement which is still smaller than the one obtained by the use of two different λ_1 parameters. This question has to be studied in other systems too.

The results of the NPSO method seem to open a new possibility in describing and interpreting the structure of molecules¹⁷. The approach is closely related to the valence-bond method, but it differs from it in important respects. One is the use of two center bond orbitals instead of the atomic ones, the second difference lies in the use of a different

spin coupling scheme. The use of the best spin function, as Linnett and coworkers point out, deserves further careful study.

The method suffers a serious drawback from the computational point of view: we have to include all the permutations in the energy expression (like Eq. (4)), as we have no orthogonality properties among the spatial orbitals. This will limit the applicability of the method to small systems. This is the same drawback that prevented the valence bond method from nonempirical calculations of large systems. The remedy suggested by McWeeny¹⁸, the introduction of orthogonalized atomic orbitals instead of the original ones, does not look promising in the case of NPSO, but it may be worth trying. Another possibility would be the use of the pairing principle (Löwdin¹⁹), according to which we can find two transformations which will replace the orbitals associated with α or β spinfunctions in the unprojected determinant in such a way that the new functions will exhibit the same properties, as expressed in Eq. (2). This would lead to simplifications in the calculation of the matrix elements, but it could not be used in such a natural way as in the case of the AMO method.

In contrast to the NPSO method, the AMO is better adapted to the treating of large conjugated systems. In fact, even an infinite linear chain can be satisfactorily treated by the use of the AMO method²⁰. Applications to two dimensional systems are in progress²¹.

Conclusion

In conclusion we can say that the use of different spatial orbitals in connection with different spinfunctions has showed that a suitably chosen functional form with a small number of non-linear variational

parameters can successfully approximate a configuration interaction wavefunction with a high number of linear parameters. This is an important achievement because for larger systems the full CI treatment becomes unmanageable.

At the same time the method gave new problems to solve as the search for the best spinfunctions. From the two methods considered in this note the NPSO gives better results for small systems, but the AMO has wider possibilities for applications.

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