

Commentationes

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On the Connection between the Alternant Molecular Orbital Method and the Separated-Pair Theory

By

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It is shown that the alternant molecular orbital method can be entirely fitted into the separated-pair theory. The total wave function can be taken as a linear combination of antisymmetrized product functions constructed of strongly orthogonal geminals. In the single parameter case, however, these strongly orthogonal geminals cannot be uniquely defined by the criterion of minimum energy alone. The separated-pair formalism may prove more favorable when the one-electron basis is to be extended in order to include, e. g., "vertical" correlation effects.

Es wird gezeigt, daß die AMO-Methode einen Sonderfall der Methode der Elektronenpaare darstellt, denn die zugehörige Wellenfunktion kann in eine Linearkombination antisymmetrischer Geminalprodukte umgeformt werden. Diese im starken Sinn orthogonalen Geminals sind jedoch bei nur einem freien Parameter im AMO-Ansatz durch die Bedingung minimaler Energie nicht vollständig bestimmt. Der Geminalformalismus könnte dann Vorteile bieten, wenn die Einelektronenbasis erweitert werden soll.

On montre que la méthode des orbitales moléculaires alternantes peut être comprise dans la théorie des paires séparées. La fonction d'onde totale s'écrit comme combinaison linéaire de produits antisymétrisés de géminals fortement orthogonales. Cependant, au cas d'un seul paramètre, ces géminals ne sont pas définies uniquement par le critère d'énergie minimum. Le formalisme pourrait se montrer avantageux si la base des fonctions monoélectroniques est étendue pour comprendre, par exemple, la corrélation «verticale».

It is well known that both the separated-pair (SP) theory and the alternant molecular orbital (AMO) method are equivalent to introducing special configurational interactions. It is not generally known, however, that the AMO method can be readily fitted into the SP scheme.

In the SP theory [7, 8, 9, 15, 17] the total wave function is written in the form

$$\Psi = \left[\frac{2^N}{(2N)!} \right]^{\frac{1}{2}} \sum_P (-1)^P \psi_1(1, 2) \psi_2(3, 4) \dots \psi_N(2N-1, 2N), \quad (1)$$

where the geminals ψ_K , $K = 1, 2, \dots, N$, are required to be antisymmetrical, normalized to unity and mutually orthogonal in the strong sense

$$\int \psi_K^*(1, 2) \psi_L(1, 3) d\tau_1 = 0, \quad \text{if } K \neq L. \quad (2)$$

The permutations P interchange electrons between the geminals. As can be shown the N strongly orthogonal geminals $\psi_K(1, 2)$ lie in mutually perpendicular subspaces of the total Hilbert space [2, 13]. A single geminal product function of

type (1) accounts for only N SP correlations. It includes, however, all the corresponding "unlinked" two-electron clusters. The best possible geminals, which can be determined from integrodifferential equations [10], need not represent pure spin states nor should they belong to given symmetry species. Making use of suitable projection operators we can obtain total wave functions of pure spin state and of given symmetry species. If there are n_K (linearly independent) geminals ψ_{Kk} , $k = 1, 2, \dots, n_K$, in the corresponding subspace, the most general total wave function can be taken as the linear combination of $\prod_{K=1}^N n_K$ linearly independent functions of type (1) each containing one geminal from every subspace:

$$\Psi = \sum_{a, b, \dots, n} C_{ab \dots n} \Psi_{ab \dots n},$$

$$\Psi_{ab \dots n} = \left[\frac{2^N}{(2N)!} \right]^{\frac{1}{2}} \sum_P (-1)^p P \psi_{1a}(1, 2) \psi_{2b}(3, 4) \dots \psi_{Nn}(2N-1, 2N). \quad (3)$$

The coefficients $C_{ab \dots n}$ can be determined by minimizing the energy expression. They are not all independent, however, when Ψ is required to be of pure spin state and of given symmetry species.

The calculation of the matrix elements of the Hamilton operator is very easy. As the geminals ψ_{Kk} within every subspace are mutually orthogonal in the usual sense, non-vanishing matrix elements arise only between functions (3) differing in not more than two geminals [9, 15].

A linear combination of geminal product functions can account for some many-electron correlations, too. It allows for all many-electron effects which leave two electrons in every subspace. The characteristic feature of the SP formalism is that the number of electrons in every subspace is strictly conserved.

The AMO method [4, 5, 12, 16] is usually applied to "alternant" systems containing a half-filled "band". One starts with the molecular orbitals χ_κ , $\kappa = 1, 2, \dots, 2N$, of this half-filled "band" which are mutually orthogonal belonging to different irreducible representations or to different rows of the same irreducible representation of the symmetry group of the system.

Combining each MO χ_κ in the lower half of the "band" with its antibonding MO "pair" χ_κ (usually symmetrically positioned in the upper half of the "band") one gets the AMO's

$$\begin{aligned} \varphi_K &= \chi_\kappa \cos \Theta_K + \bar{\chi}_\kappa \sin \Theta_K, \\ \bar{\varphi}_K &= \chi_\kappa \cos \Theta_K - \bar{\chi}_\kappa \sin \Theta_K, \\ K &= 1, 2, \dots, N; \quad 0 \leq \Theta \leq \pi/2. \end{aligned} \quad (4)$$

The antisymmetric total wave function (of a mixed spin state) can be taken in the form

$$\Phi_0 = [(2N)!]^{-\frac{1}{2}} \text{des} [\varphi_1 \alpha \varphi_2 \alpha \dots \varphi_N \alpha \bar{\varphi}_1 \beta \bar{\varphi}_2 \beta \dots \bar{\varphi}_N \beta]. \quad (5)$$

By using the projection operator 1O defined in [12] we obtain the so-called parallel-spin singlet component

$${}^1\Phi = {}^1O \Phi_0.$$

Minimizing the energy expression calculated with the wave function ${}^1\Phi$ we get the best parallel-spin singlet state energy which shows the correct asymptotic behavior for separated atoms [3]. If the system possesses symmetry the variational parameters Θ_K may not be all different in order for ${}^1\Phi$ to belong to given symmetry species.

As a consequence of the orthogonality properties of the AMO's

$$\int \varphi_K^* \varphi_L d\tau = \int \bar{\varphi}_K^* \bar{\varphi}_L d\tau = \delta_{KL},$$

and

$$\int \bar{\varphi}_K^* \varphi_L d\tau = \delta_{KL} \cos 2\Theta_K = \lambda_K \delta_{KL}, \tag{6}$$

we can form N mutually perpendicular subspaces each spanned by the 4 two-electron functions

$$\begin{aligned} \varphi_{K1} &= [2(1 + \lambda_K^2)]^{-\frac{1}{2}} [\bar{\varphi}_K(1)\varphi_K(2) + \bar{\varphi}_K(2)\varphi_K(1)] 2^{-\frac{1}{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)], \\ \varphi_{K2} &= [2(1 - \lambda_K^2)]^{-\frac{1}{2}} [\bar{\varphi}_K(1)\varphi_K(2) - \bar{\varphi}_K(2)\varphi_K(1)] 2^{-\frac{1}{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)], \\ \varphi_{K3} &= [2(1 - \lambda_K^2)]^{-\frac{1}{2}} [\bar{\varphi}_K(1)\varphi_K(2) - \bar{\varphi}_K(2)\varphi_K(1)] \alpha(1)\alpha(2), \\ \varphi_{K4} &= [2(1 - \lambda_K^2)]^{-\frac{1}{2}} [\bar{\varphi}_K(1)\varphi_K(2) - \bar{\varphi}_K(2)\varphi_K(1)] \beta(1)\beta(2). \end{aligned} \tag{7}$$

They are antisymmetrical, normalized to unity and represent pure spin states.

The function Φ_0 can be put in the form

$$\Phi_0 = \left[\frac{2^N}{(2N)!} \right]^{\frac{1}{2}} \sum_P (-1)^P P \bar{\psi}_1(1, 2) \bar{\psi}_2(3, 4) \dots \bar{\psi}_N(2N-1, 2N),$$

where

$$\bar{\psi}_K = [(1 + \lambda_K^2)/2]^{\frac{1}{2}} \varphi_{K1} + [(1 - \lambda_K^2)/2]^{\frac{1}{2}} \varphi_{K2}.$$

The geminals $\bar{\psi}_K$ are mutually orthogonal in the strong sense and have a triplet component in addition to the singlet. As the projection operator 1O acts on the spin functions only it does not mix the two-electron functions of different subspaces. Hence the parallel-spin singlet function ${}^1\Phi$ fits also into the SP framework, namely, it can be represented as the linear combination of functions of type (3) each containing one two-electron function of the four (7) from every subspace

$${}^1\Phi = \sum_{a, b, \dots, n} A_{ab \dots n} \Psi_{ab \dots n}, \tag{8}$$

where

$$\Psi_{ab \dots n} = \left[\frac{2^N}{(2N)!} \right]^{\frac{1}{2}} \sum_P (-1)^P P \psi_{1a}(1, 2) \psi_{2b}(3, 4) \dots \psi_{Nn}(2N-1, 2N), \tag{9}$$

and

$$a, b, \dots, n = 1, 2, 3, 4.$$

The coefficients $A_{ab \dots n}$ are all fixed except for a common factor.

It seems now clear that the AMO method is entirely consistent with the SP theory. The $4N$ dimensional space of the spin orbitals $\chi_{\nu\alpha}, \chi_{\nu\beta}, \nu = 1, 2, \dots, 2N$, is decomposed into N mutually perpendicular subspaces and each of the configurations taken into account has two spin orbitals from every subspace.

There are many more configurations still consistent with the SP theory which are left out from the AMO wave function. These can be easily included by the above geminal product formalism. First we make up all possible singlets by projection operator techniques or by using directly the CLEBSCH-GORDAN coefficients which transform the basis functions (9) into a new basis corresponding to the spin eigenstates [6]. The simplest function is the so-called valence bond singlet which is just the function $\Psi_{1\bar{1} \dots 1\bar{1}}$. It shows incorrect asymptotic behavior for separated atoms, but may be energetically more favourable than ${}^1\Phi$, for finite lattice spacing, in certain localized systems [3].

Since the 4^N functions $\Psi_{ab \dots n}$ form an orthonormalized set

$$\int \Psi_{ab \dots n}^* \Psi_{a'b' \dots n'} d\tau = \delta_{aa'} \delta_{bb'} \dots \delta_{nn'}$$

the calculation of matrix elements of (spin independent) one- and two-particle operators is relatively easy. In case of one-particle operators the matrix element for two different functions (9) always vanishes. For two-particle operators non-vanishing matrix elements may arise between functions (9) differing in not more than two two-electron functions [9, 15].

To get the best results for the given basis functions (9) one should mix all the possible singlets

$$\sum_{\alpha} C_{\alpha} {}^1\Phi_{\alpha}$$

The coefficients C_{α} and the parameters Θ_K have to be determined by minimizing the energy expression.

We can show now that, when $\Theta_1 = \Theta_2 = \dots = \Theta_N = \Theta$, the strongly orthogonal geminals ψ_{Kk} cannot be uniquely defined by the criterion of minimum energy alone. Namely, the function Φ_0 as a determinant is invariant (except for a phase factor) under any unitary transformation of the elements. Thus, we can apply a unitary transformation to the "lower half" MO's $\chi_{\kappa} \rightarrow \chi'_{\kappa}$, $\kappa = 1, 2, \dots, N$. This change of the orbitals leaves the Hartree-Fock energy and wave function invariant. Applying the same unitary transformation to the "upper half" MO's the new AMO pairs have the form

$$\begin{aligned} \varphi'_K &= \chi'_{\kappa} \cos \Theta + \bar{\chi}'_{\kappa} \sin \Theta, \\ \bar{\varphi}'_K &= \chi'_{\kappa} \sin \Theta - \bar{\chi}'_{\kappa} \cos \Theta, \end{aligned}$$

and possess the same orthogonality properties as the old ones. Consequently, the new geminals ψ'_{Kk} based on the transformed AMO's are also mutually strongly orthogonal and can equally well be used for constructing the same total wave function as the old ones. This result, which is not confined to the AMO case, suggests that inclusion of simple configuration interaction may not always suffice to define uniquely the strongly orthogonal geminals of the system.

As we have seen the SP theory is just a change of the formalism, it does not add anything new to the AMO method. This situation may greatly alter, however, if we want to extend the method in order to include other correlation effects, too. This involves that we have to complete our one-electron basis functions with MO's of higher "bands". As has been pointed out [11, 13] we should include MO's constructed of $3d$ atomic orbitals in order to take into account the "vertical" correlation effects. Whereas the number of the basis functions (4) increases within every subspace, the total wave function still retains the form of eq. (8).

LÖWDIN has pointed out [14] that in the method of different orbitals for different spins one may choose the orbitals, without loss of generality, so that they have the same orthogonality properties as the AMO's. It means that this method (somewhat more general than the AMO method) can also be fitted in the SP theory.

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