

Use of Orthogonal Functions in Non-Paired Spatial Orbital (NPSO) Wave Functions

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The NPSO theory originally proposed by LINNETT [1] has proved remarkably successful for producing good single parameter wave functions for small molecules (see Ref. [2] for full references). The Alternant Molecular Orbital (AMO) method, which is also a "different orbitals for different spins" wave function, is less successful than NPSO for small molecules but becomes more manageable for larger molecules [3]. A weakness of the NPSO approach is that no quantitative empirical or semi-empirical methods have so far been proposed. One difficulty which is probably relevant here is the lack of orthogonality between the functions used to construct NPSO wave functions. CHONG and LINNETT [4] suggested the use of orthogonal atomic orbitals (OAO) although PAUNZ has suggested that their use "does not look promising in the case of NPSO" [3].

The use of OAO's in NPSO and other approximate functions has therefore been tested for two simple systems — the allyl cation studied by HIRST and LINNETT [5] and the bridge region of the diborohydride anion studied by DUKE and LINNETT [6]. These two systems are of a very different character. One is a π -system the other a σ -system and the largest overlap integrals range from 0.26 for allyl to 0.75 for $B_2H_7^-$. They should give a good guide to the value of this approach for other systems. The OAO's are obtained as described in the appendix. For $B_2H_7^-$ a new method Eq. (4) is required. A transformation matrix is then used either to transform the valence bond basis set to an OAO basis set or to transform an OAO approximate function to the original valence bond basis set. Both methods are equivalent.

Table. *Energy of functions using atomic orbitals (AO) and orthogonalised atomic orbitals (OAO)*

	Allyl cation ^a		Diborohydride ion ^b	
	AO	OAO	AO	OAO
VB(A)	-27.842	-26.781	-1.475	-1.294
VB(B)	-29.302	-28.423	-1.448	-1.317
MO	-29.432	-29.432	-1.481	-1.481
NPSO(B)	-30.200	-29.670	-1.464	-1.441
NPSO(A)	-30.031	-29.509	-1.486	-1.439
CI	-30.396	-30.306	-1.496	-1.496

^a $E - 2W_{2p}$ in eV; ^b E in a.u.

Results are shown in the table. The functions are as defined by HIRST and LINNETT [5] and in each case the energy has been minimised with respect to a single parameter. The molecular orbital (MO) function is, of course, invariate under the transformation to OAO's. In other cases the function changes and the OAO functions are all worse than the corresponding AO functions. CHONG and LINNETT [7] found that the AMO function for allyl improved when transformed to OAO's. For allyl the ordering of functions remains the same. The small overlap integrals for this system lead to small changes when functions are transformed to OAO's. NPSO(B) is still the best function considered. For $B_2H_7^-$ the large overlap integrals lead to large changes. Both NPSO functions now have higher energies than the MO function which is the best function considered using OAO's.

The use of OAO's in NPSO calculations does not seem very promising and this work has not been extended to other systems.

Appendix [8]

A set of OAO's are related to the set of AO's by

$$\chi' = \chi T \quad (1)$$

where

$$T = S^{-1/2} \quad (2)$$

and S is the overlap matrix over AO's. Following LÖWDIN [9] T has been obtained by a series expansion

$$T = I - \frac{1}{2}Z + \frac{3}{8}Z^2 \dots \quad (3)$$

where

$$Z = S - I.$$

(I is the unit matrix). It is necessary for convergence that S is positive definite and that the largest eigenvalue of S (λ_{\max}) is less than 2 and sufficient that the maximum row sum of S , a , is less than 2. These conditions are not universally fulfilled although Eq. (3) is adequate in the majority of cases. Convergence can however be obtained if Eq. (3) is generalised to

$$T = \sqrt{\frac{2}{r}} \{I - \frac{1}{2}Z' + \frac{3}{8}Z'^2 \dots\} \quad (4)$$

where

$$Z' = \frac{2}{r} \cdot S - I. \quad (5)$$

r must be chosen to be greater than λ_{\max} and can therefore be set equal to a to ensure convergence. Optimum convergence is obtained if

$$r = \lambda_{\max} + \lambda_{\min} \quad (6)$$

where λ_{\min} is the smallest eigenvalue of S . For matrices where Eq. (3) is adequate $\lambda_{\max} + \lambda_{\min}$ appears to be close to 2 in a number of cases studied. Eq. (3), which is identical to Eq. (4) for $r = 2$, is thus close to optimum for these cases. In other cases a appears to be a good estimate of $\lambda_{\max} + \lambda_{\min}$ and rapid convergence can be obtained if r is set equal to a in these cases.

T can be obtained, although probably less efficiently, from the solution of an eigenvalue problem. If

$$S C = C \lambda \quad (7)$$

then

$$\mathbf{T} = \mathbf{C} \boldsymbol{\lambda}^{1/2} \mathbf{C}^\dagger \quad (8)$$

\mathbf{C} is the matrix of eigenvectors and \mathbf{C}^\dagger its transpose. $\boldsymbol{\lambda}$ is the diagonal matrix of eigenvalues. Eq. (8) has been used to check results obtained by Eq. (4). It is thus possible to obtain OAO's in cases where the usual method does not converge.

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