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Use of Single Determinant Wave Functions Constructed from Localized Orbitals in the Mapping Analysis of Concerted Reactions*

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Wave functions expressed as a single determinant of completely localized orbitals make possible considerable simplification in the mapping analysis of concerted reactions. The formal basis for and several examples of such simplification are presented.

While increasingly accurate wave functions for polyatomic systems are becoming available [1], it seems clear that chemical speculations are still profoundly influenced by the simple valence bond representation of molecules as assemblies of bonded atoms. Hybridization, used widely to explain diverse chemical phenomena, is rigorously definable only for these localized functions [2]. Delocalization, while highly significant, can be usefully considered a deviation from a basically localized system [3] for all but aromatic molecules. Still the conceptual utility of the SDLO representation of molecules does not imply that these functions provide a quantitatively realistic account of all chemical properties. Thus some test of the simple wave function in each new chemical application is called for. It is the purpose of this report to explore the utility of the SDLO function in the recently developed mapping analysis of concerted reactions.

The one attribute which the SDLO wave function shares with the true wave function for all cases but those in which more than one VB structure is necessary for a qualitatively correct description (e.g., benzene) is its nodal structure. This assertion is supported by the existance of perturbation calculations which use such SDLO functions as a starting point [3]. If the nodal structure of the true wave function differed from that of the reference function, then such a perturbation expansion would fail. We may surmise that the very simple SDLO functions are suitable to calculations which depend for the most part on the nodal structure. Such a calculation, described in detail elsewhere [4], is the mapping analysis of concerted chemical reactions. Here a transform T is sought which produces the product wave function from the reactant wave function: The constraint on T is that it be a topological identity. That is, the nodal structure of the reactant wave function must not be altered in the course of the mapping toward the product function. If the mapping is successful, the transition from the assumed state of the reactants to

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the products is "thermally allowed". This analysis has been successfully applied to a number of cases for which the symmetry arguments which support the related Hoffmann-Woodward analyses [5] cannot be employed.

The mapping transform is allowed to alter hybridization and orientation of basis functions under the constraint that it remain a topological identity. The only demand on the wave functions is that they have proper nodal structure. These mild requirements suggest that the SDLO functions can serve as a convenient starting point for the study of concerted reactions.

The SDLO form of the wave functions of the products and reactants makes possible a considerable computational simplification in the mapping calculation. The mapping transformation can be written as $\boldsymbol{U}=\boldsymbol{I}+\boldsymbol{A}_{\mathrm{KK}}$ where $\boldsymbol{A}_{\mathrm{KK}}$ is a matrix associated with the K-th atom, of dimension μ_{K} where μ_{K} is the number of atomic basis orbitals on the atom K. That is, $\boldsymbol{U}$ is of block diagonal form, each block transforming orbitals on a single atom among themselves. The general derivation [4] for the operator which maximises the overlap of the mapped function with the product function leads to the expression

$$\boldsymbol{A}_{\mathrm{KK}}=(\boldsymbol{P}^{\mathrm{A}}\boldsymbol{P}^{\mathrm{B}}-\boldsymbol{P}^{\mathrm{B}}\boldsymbol{P}^{\mathrm{A}})/\mathrm{Tr}(\boldsymbol{P}^{\mathrm{A}}\boldsymbol{P}^{\mathrm{B}}+\boldsymbol{P}^{\mathrm{B}}\boldsymbol{P}^{\mathrm{A}})\,. \tag{1}$$

The SDLO form of the functions leads to a block form of the density matrices. The total density matrix of molecule A, $\boldsymbol{P}^{\mathrm{A}}$, is a "matrix of submatrices" $\boldsymbol{P}^{\mathrm{A}}_{\mathrm{KL}}$ of dimension $\mu_{\mathrm{K}}\times\mu_{\mathrm{L}}$. $\boldsymbol{P}^{\mathrm{A}}_{\mathrm{KL}}$ is the null matrix $\mathbf{0}$ unless atom K is bonded to atom L in the molecule A. We can rewrite $\boldsymbol{A}_{\mathrm{KK}}$ as

$$\boldsymbol{A}_{\mathrm{KK}}=\sum_{\substack{\mathrm{L\ bound}\\ \mathrm{to\ K\ in\ both}\\ \mathrm{A\ and\ B}}}(\boldsymbol{P}^{\mathrm{A}}_{\mathrm{KL}}\boldsymbol{P}^{\mathrm{B}}_{\mathrm{LK}}-\boldsymbol{P}^{\mathrm{B}}_{\mathrm{KL}}\boldsymbol{P}^{\mathrm{A}}_{\mathrm{LK}})/\mathrm{Tr}\left\{\sum_{\mathrm{KL}}\boldsymbol{P}^{\mathrm{A}}_{\mathrm{KL}}\boldsymbol{P}^{\mathrm{B}}_{\mathrm{LK}}+\boldsymbol{P}^{\mathrm{B}}_{\mathrm{KL}}\boldsymbol{P}^{\mathrm{A}}_{\mathrm{LK}}\right\}. \tag{2}$$

While the notation of Eq. (2) seems more complicated than that of Eq. (1), manipulation of the small submatrices $\boldsymbol{P}^{\mathrm{A}}_{\mathrm{KL}}$ and $\boldsymbol{P}^{\mathrm{B}}_{\mathrm{KL}}$ is much less time consuming than that the multiplication of the much larger matrices $\boldsymbol{P}^{\mathrm{A}}$ and $\boldsymbol{P}^{\mathrm{B}}$.

During the overlap maximization of the mapping analysis, the expression (3) plays a central role:

$$\sigma=\mathrm{Tr}\left\{\sum_{\mathrm{KL}}(\boldsymbol{I}_{\mathrm{KK}}+\boldsymbol{A}_{\mathrm{KK}})^{tr}\boldsymbol{P}^{\mathrm{A}}_{\mathrm{KL}}(\boldsymbol{I}_{\mathrm{LL}}+\boldsymbol{A}_{\mathrm{LL}})\boldsymbol{P}^{\mathrm{B}}_{\mathrm{LK}}\right\}. \tag{3}$$

If the bond K–L is simply reoriented during the reaction, it seems apparent that the maximum KL contribution to σ will occur when the $\boldsymbol{A}$ matrices are such that

$$(\boldsymbol{I}_{\mathrm{KK}}+\boldsymbol{A}_{\mathrm{KK}})^{tr}\boldsymbol{P}^{\mathrm{A}}_{\mathrm{KL}}(\boldsymbol{I}_{\mathrm{LL}}+\boldsymbol{A}_{\mathrm{LL}})=\boldsymbol{P}^{\mathrm{B}}_{\mathrm{KL}}\,. \tag{4}$$

In that case the contribution to the trace σ from reoriented bonds is simply $\mathrm{Tr}(\sum(\boldsymbol{P}^{\mathrm{B}}_{\mathrm{KL}})^2)$, or the number of reoriented bonds N. The existance of these integer contributions to σ, and the associated unit roots in the equivalent orbital computations discussed in [4] has been a recurring numerical feature of mapping computations.

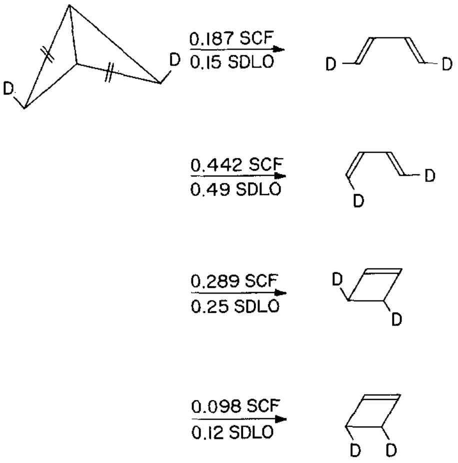

Fig. 1. Permissibilities (see text) for various thermal rearrangements of bicyclobutane, as determined by mapping analyses of (CNDO) SCF and valence bond (SDLO) wave functions

The computational advantage of relation (4) is that it allows direct attention to the relatively small number of bonds which are actually broken or suffer substantial changes in hybridization during the reaction in question. This advantage would be particularly marked for large molecules, where the reaction affects only a small portion of the total charge distribution.

To illustrate the above remarks we have made mapping analyses of the thermal interconversion of prismane and Dewar benzene and the disrotatory and conrotatory thermal closures of butadiene to cyclobutene, using (a) CNDO-SCF wave functions and (b) SDLO wave functions constructed from orthogonalized atomic orbitals with the Pople-Segal approximations to integrals [6]. For these examples we find that the symmetry-dictated reaction routes are reproduced in all computations. The closure of butadiene proceeds in a conrotatory fashion with a permissibility of 0.61 according to SCF computations; the corresponding SDLO value is 0.68. The permissibility toward the rearrangement of prismane to Dewar benzene and the disrotatory closure of butadiene is zero according to both computations. These results are in agreement with the symmetry-based analyses of Hoffmann and Woodward.

Confirmation of symmetry-dictated results by direct computation does not verify the present analysis, of course. It is essential to consider a problem free of symmetry which could force a correct answer. As a more rigorous test, a comparison of SCF and SDLO mapping analyses of the rearrangements of bicyclobutane was made; the results are summarized in Fig. 1. Note that according to arguments presented elsewhere [4] we associate a high value for the mapping parameter with an easy reaction. The agreement between the SCF and SDLO-permissibilities is quantitatively satisfactory. The savings of time effected by the SDLO procedure relative to the SCF mapping was roughly 50% in these cases; the savings were due to the ease of constructing SDLO functions as opposed to a CNDO-SCF computation. The consideration of larger molecules would provide more dramatic examples of the speed of the SDLO mapping.

Recommendation

Due to the simplicity of the SDLO wave functions and its conformity with the assumptions of the mapping analysis of concerted reactions, it is suggested that a fruitful means of studying complicated reactions is to employ the SDLO function in the mapping analysis. Where the qualitative conclusions of the mapping require further explication, a perturbative refinement of the SDLO wave function would supply the necessary detail. In this way attention can be given the critical points along a reaction coordinate with relative economy.

References

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