

The Orbital Phase Continuity Principle and Selection Rules for Concerted Reactions

Sir:

In recent years the GI method¹ for electronic wavefunctions has been used to improve upon Hartree-Fock and yet retain the orbital interpretation. In the GI method we allow every orbital to be different (no double occupation restriction) and yet retain the correct spin symmetry.² The result is one electron per orbital and two orbitals per bond, with the orbitals generally localized near one or two nuclei (for nonaromatic systems). These orbitals are solved for self-consistency; however, we find that for many molecules the orbitals tend to be qualitatively similar to the familiar valence-bond functions. For example, the π orbitals of *trans*-1,3 butadiene are shown² in Figure 1. Orbitals ϕ_{1a} and ϕ_{1b} form one bonding pair and ϕ_{2a} and ϕ_{2b} form a symmetrically related bonding pair.

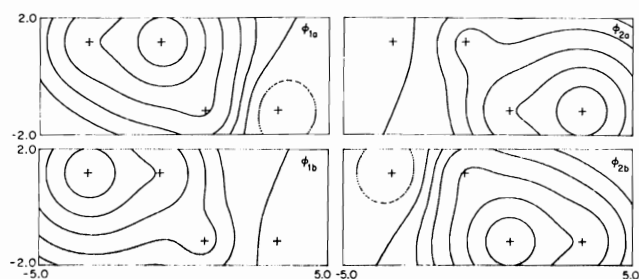


Figure 1. The GI orbitals for *trans*-1,3-butadiene. (The plot is for 1.06 bohrs above the molecular plane. The dashed line represents negative amplitude and the first solid contour is the nodal line. The other contours correspond to amplitudes of 0.01, 0.021, 0.0441, 0.0926, and 0.1945; thus a purely exponential function would have equal spacings between the contours.) The crosses represent projections of the nuclei.

From consideration of *ab initio* GI calculations on reactions of small molecules, we have found that paired bonding orbitals remain paired and nonbonding orbitals change phase as the orbitals and bonds interchange centers during the reaction.³ For reactions involving the π electrons of molecules, this principle implies that as the bond between A and B is transferred to B-C, the π orbital concentrated on C must change phase as it is transferred to A. Using this *orbital phase continuity principle* (OPCP), we obtain selection rules for chemical reactions in general agreement with both the Woodward-Hoffmann rules^{4,5} and

(1) W. A. Goddard III, *Phys. Rev.*, **157**, 81 (1967); *J. Chem. Phys.*, **48**, 5337 (1968); W. E. Palke and W. A. Goddard III, *ibid.*, **50**, 4524 (1969); R. C. Ladner and W. A. Goddard III, *ibid.*, **51**, 1073 (1969); R. J. Blint, W. A. Goddard III, R. C. Ladner, and W. E. Palke, *Chem. Phys. Lett.*, **5**, 302 (1970); R. C. Ladner and W. A. Goddard III, manuscript in preparation.

(2) G. Levin, W. J. Hunt, W. A. Goddard III, and T. H. Dunning, manuscript in preparation. These orbitals were obtained using the SOGI method (ref 1).

(3) This phase change would not occur if electrons were Bosons or if they had an intrinsic spin larger than one-half; hence the phase relationships can be considered a consequence of the basic properties of electronic systems. The orbital flips can also be discussed approximately in terms of changes in the spin coupling angles. Further details will be presented in a subsequent paper.

(4) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

(5) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

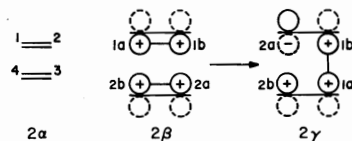


Figure 2. 2 + 2 cycloaddition.

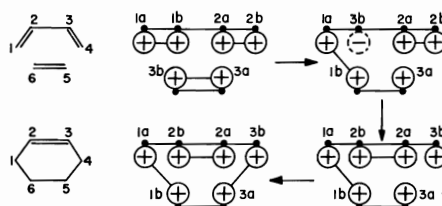


Figure 3. 4 + 2 cycloaddition.

experiment. The details of the calculations leading to the basis of OPCP will be presented elsewhere. The principles are simple to use and can be applied to systems with symmetry too low for the Woodward-Hoffmann approach, and hence we will illustrate the use of OPCP with some simple examples.

Consider first the 2 + 2 addition reaction of Figure 2. (Here we schematically represent the GI orbitals by a simplified contour plot; a bonding pair is indicated by a line connecting two GI orbitals.) In Figure 2b we show the plane of the two ethylenes and the schematic contours of the four occupied π orbitals. To obtain the product, Figure 2c, we transfer the 1a-1b bond from centers 1-2 to centers 2-3, but we see that according to OPCP, orbital ϕ_{2a} must simultaneously move from 3 to 1 and change phase. But now in the product the phase of ϕ_{2a} is not consistent with retaining the 2a-2b bond (*i.e.*, ϕ_{2a} and ϕ_{2b} have opposite phases) and hence the thermal reaction is unfavored (*i.e.*, it should require a large activation energy; a twist of the top ethylene would be required to match the phases of 2a and 2b).⁶

Now consider the 4 + 2 addition of Figure 3. Here we have illustrated the recouplings of the bonding orbitals by moving one bond at a time. As we move the 1a-1b and 2a-2b bonds, orbital 3a moves first to center 2 and then to center 4, changing phase twice; hence, in the product, 3a and 3b are adjacent and have the same phase. Thus the phase changes required to preserve the 1a-1b and 2a-2b bonds are in this case consistent with retaining the 3a-3b bond and the reaction is favored. Of course, in the real reaction the changes in all bonds occur simultaneously. We have examined these changes one at a time in order to determine if they are all consistent, and find that they are. Note that these considerations do *not* depend upon the exact geometry of the transition state (TS) and do *not* require the preservation of, say, a C_2 axis during the reaction.⁷

(6) In the transition state of the 2 + 2 cycloaddition, the ϕ_{2a} and ϕ_{2b} orbitals become essentially orthogonal; thus we have essentially broken one bond, obtaining the diradical (in this case the phases between the orbitals of the products need not be related to the phases of the reactants). An alternative concerted path could be obtained by displacing center 4 above the plane and twisting by 180° during the reaction, which would allow orbitals ϕ_{2a} and ϕ_{2b} to retain their phases during the reaction. It would appear that the diradical path predominates.

(7) In competition with the 4 + 2 concerted cycloaddition is the 2 + 2 cycloaddition.⁶ The latter reaction involves a diradical intermediate and requires about 7 kcal/mol greater activation energy. However,

We see that the selection rule for such addition reactions depends on whether an even or odd number of phase changes are made, and thus such *addition reactions are favored where there are an odd number of π bonds in the relevant segments*. This is the same rule obtained by Woodward and Hoffmann⁴ from a completely different type of analysis using correlation diagrams for Hartree-Fock orbitals. An application of this same orbital phase continuity principle (OPCP) to electrocyclic and hydrogen-migration reactions again leads to the rules found by Woodward and Hoffmann for thermal reactions.^{4,5}

In the Woodward-Hoffmann approach one determines the symmetries of the bonding and antibonding molecular orbitals (essentially minimum basis set Hartree-Fock orbitals) and constructs a correlation diagram. In this approach molecular and orbital symmetry are crucial. In the OPCP approach we use just the bonding GI orbitals (for many cases these are very much like valence-bond orbitals). Here molecular and orbital symmetry are irrelevant. Thus the OPCP approach

for C_2F_4 plus butadiene the energy of the diradical intermediate is much lower and 2 + 2 cycloaddition dominates: P. D. Bartlett, *Science*, **159**, 833 (1968).

may be useful even for reactions along low-symmetry reaction paths and involving molecules of low symmetry and may provide a convenient means of predicting and discussing such reactions.

Woodward and Hoffmann⁵ have generalized their rules to cases for which correlation diagrams would be difficult or impossible to construct. For thermal reactions these rules are in general agreement with the predictions from OPCP. Trindle⁸ has proposed a way of using the nodal structure of MO's to analyze low-symmetry reactions. Since OPCP is based upon GI-type wave functions, it is more akin to valence-bond wave functions than to MO's, and there is no direct connection between these MO approaches and OPCP. More significant differences result for excited states, where the GI wave function can lead to descriptions quite different from the MO or Hartree-Fock wave functions.

(8) C. Trindle, *J. Amer. Chem. Soc.*, **92**, 3251, 3255 (1970).

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