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The Conservation of Orbital Symmetry

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Prof. Robert Burns Woodward
Department of Chemistry, Harvard University
12 Oxford Street
Cambridge, Mass. 02138 (USA)

Prof. Roald Hoffmann
Department of Chemistry, Cornell University
Ithaca, N. Y. 14850 (USA)

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Errata

Page 80, formula (173): the asterisk should be placed at the CH_2 group of the five-membered ring, as in (174).

Page 83, line 1: replace calicenes by sesquifulvalenes.

Page 86, footnote [100], last reference: read 88, 2880 (1966).

Page 103, line 9: read (273) instead of (278).

Page 120, footnote [142], first reference: read 89, 5503 (1967).

Page 125, figure 36: the two formulae must be interchanged.

Page 130, footnote [177]: read 1966, 6393.

Page 142, footnote [185]: add *E. E. van Tamelen*, *R. S. Dewey*, and *R. J. Timmons*, *ibid.* 83, 3725 (1961).

Page 143, footnote [187]: add *K. Schaffner*, personal communication.

Page 176, line 11: read *Laidler* [249a] and *Shuler* [249b].

Page 176, footnote [249]: insert a) in front of the first reference and add b) *K. E. Shuler*, *J. chem. Physics* 21, 624 (1953).

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1. Introduction

Of the various ways in which the phenomena of chemical bonding have been treated from the theoretical point of view, the molecular orbital method may fairly be deemed to have been the most fruitful in the hands of the organic chemist, and most adaptable to his needs. None the less, the method, with a few conspicuous exceptions, has been used mainly in the study of the static properties of molecules — in ground and excited states — and only rarely have its potentialities been explored in relation to reacting systems.

In 1965, in a series of preliminary communications^[1-3], we laid down some fundamental bases for the theoretical treatment of all concerted reactions. The history of the genesis of these ideas has been described elsewhere^[4]. The basic principle enunciated was that reactions occur readily when there is congruence between orbital symmetry characteristics of reactants and products, and only with difficulty when that congruence does not obtain — or to put it more succinctly, *orbital symmetry is conserved in concerted reactions*. This principle has met with widespread interest; the applications made of it, the tests which it has survived, and the corollary predictions which have been verified are already impressive. In this paper we develop our views at some length, survey some of the developments — in our hands and those of others — of the three years just past, and make some new projections.

[1] R. B. Woodward and Roald Hoffmann, J. Amer. chem. Soc. 87, 395 (1965).

[2] Roald Hoffmann and R. B. Woodward, J. Amer. chem. Soc. 87, 2046 (1965).

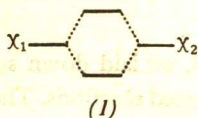
[3] R. B. Woodward and Roald Hoffmann, J. Amer. chem. Soc. 87, 2511 (1965).

[4] R. B. Woodward: Aromaticity. Special Publication No. 21. The Chemical Society, London 1967, p. 217.

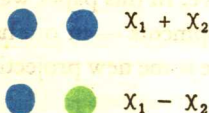
2. Orbitals and Bonding

nonbonding

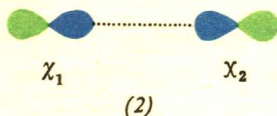
It is worth while to review the elementary aspects of the molecular orbital theory of bonding^[5]. Molecular orbitals are constructed as combinations of atomic orbitals, and are then populated by electron pairs. When two equivalent atomic orbitals, χ_1 and χ_2 , combine, they always yield a bonding combination and a corresponding antibonding orbital (1).



The bonding combination is characterized by positive overlap, and by concentration of electron density in the region between the nuclei. By contrast, the antibonding combination exhibits negative overlap, and a nodal surface in the region between the nuclei. When χ_1 and χ_2 are s orbitals, the bonding combination is $\chi_1 + \chi_2$, and the antibonding one $\chi_1 - \chi_2$.



When χ_1 and χ_2 are p orbitals interacting in a σ manner, and oriented as shown in (2) the bonding combination is again $\chi_1 + \chi_2$ and the antibonding combination $\chi_1 - \chi_2$.

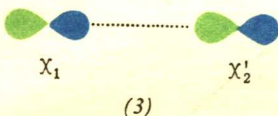


Throughout this paper, the phases of wave-functions are color-coded: positive = blue, negative = green. When phase relationships are not relevant, the orbitals are presented in solid gray.

[5] In addition to the classical text by *C. A. Coulson* (Valence, 2nd ed., Oxford University Press, London 1961), we recommend: *C. A. Coulson and E. T. Stewart* in *S. Patai: The Chemistry of Alkenes*, Wiley-Interscience, New York 1964, *E. Heilbronner and H. Bock: Das HMO-Modell und seine Anwendung*, Verlag Chemie, Weinheim 1968, and *R. S. Mulliken*, *Science* 157, 13 (1967); *Angew. Chem.* 79, 541 (1967).



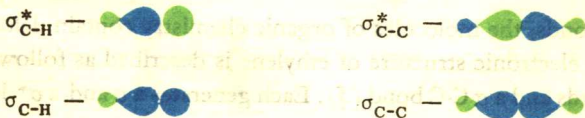
It is important to realize, however, that were the basis orbitals initially arbitrarily oriented in some other fashion, such as (3), then, since $\chi'_2 = -\chi_2$, the bonding



combination would be $\chi_1 - \chi'_2$, and the antibonding one $\chi_1 + \chi'_2$. It should also be kept in mind that multiplying an entire wave function by -1 does not affect its energy. Thus, overlap of minus with minus lobes is precisely equivalent to plus with plus lobes, and $-\chi_1 - \chi_2$ is the *same* bonding orbital as $\chi_1 + \chi_2$.

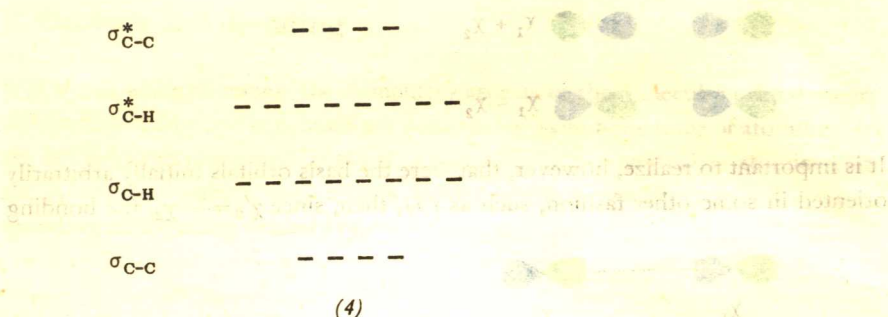


The description of σ bonds in hydrocarbons is simple. Each formal chemical bond engenders a σ and a σ^* orbital. The C-H and C-C cases are:



The molecular orbitals are represented in our drawings as the overlap of two hybrids of unspecified hybridization. It should be emphasized that this is only intended as an artistic mnemonic device: the only essential features of a σ orbital are that it is approximately cylindrically symmetrical around the bond axis, that it concentrates electron density in the region between the nuclei, and that there is no nodal plane between the atoms.

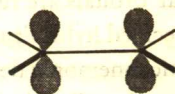
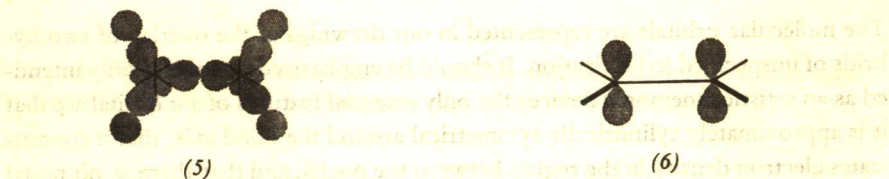
Our simple picture of bonding in, say, cyclobutane, shows four C-C σ levels, and eight C-H σ levels, each with a matching σ^* level (4). The carbon $1s$ orbitals are



not considered. Each of the σ levels is occupied by two electrons. Spectroscopic studies indicate that the gap between occupied and unoccupied levels must be of the order of 10 electron volts.

The orbitals we have constructed are semi-localized. They are delocalized over only two atoms. Such orbitals are satisfactory for an analysis of some properties of the molecules — those which depend on all of the occupied molecular orbitals: bond lengths, energies, dipole moments. They are not the proper molecular orbitals of the molecule. The latter are completely delocalized, subject to the full symmetry of the molecule. For a discussion of physical properties depending on one or two specific molecular orbitals, such as spectra or ionization, it is absolutely necessary to construct these equivalent delocalized orbitals. The mechanics of delocalization will be described in Section 3.

In addition to σ bonds, the molecules of organic chemistry contain delocalized π orbitals. Thus, the electronic structure of ethylene is described as follows: There are four σ C-H bonds and a σ C-C bond (5). Each generates a σ and a σ^* level, and



five pairs of electrons are placed in the σ levels. There remain two electrons and two atomic p orbitals perpendicular to the plane of the molecule (6). These com-

bine to give π and π^* orbitals, differentiated by the absence or presence of a node between the atoms (Figure 1).

There are two independent symmetry operations which may be used to classify these orbitals; the mirror plane m , perpendicular to the molecular plane and bisecting the molecule, and the two-fold rotation axis C_2 , passing through the center of the carbon-carbon bond. It should be noted carefully that the symmetry proper-

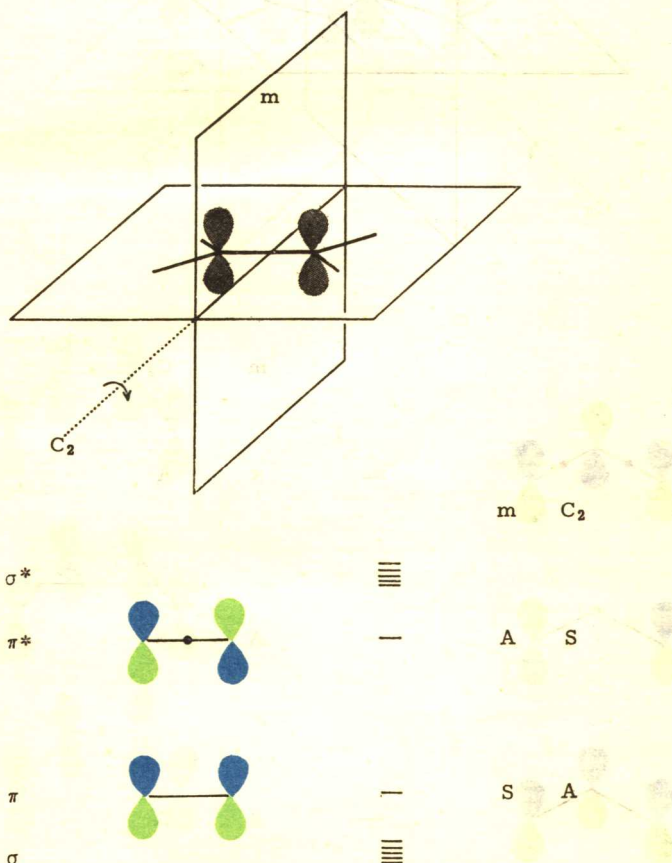


Figure 1. Molecular orbitals of ethylene and symmetry properties of the π and π^* orbitals. A = antisymmetric, S = symmetric. The horizontal bars indicate the relative orbital energies.

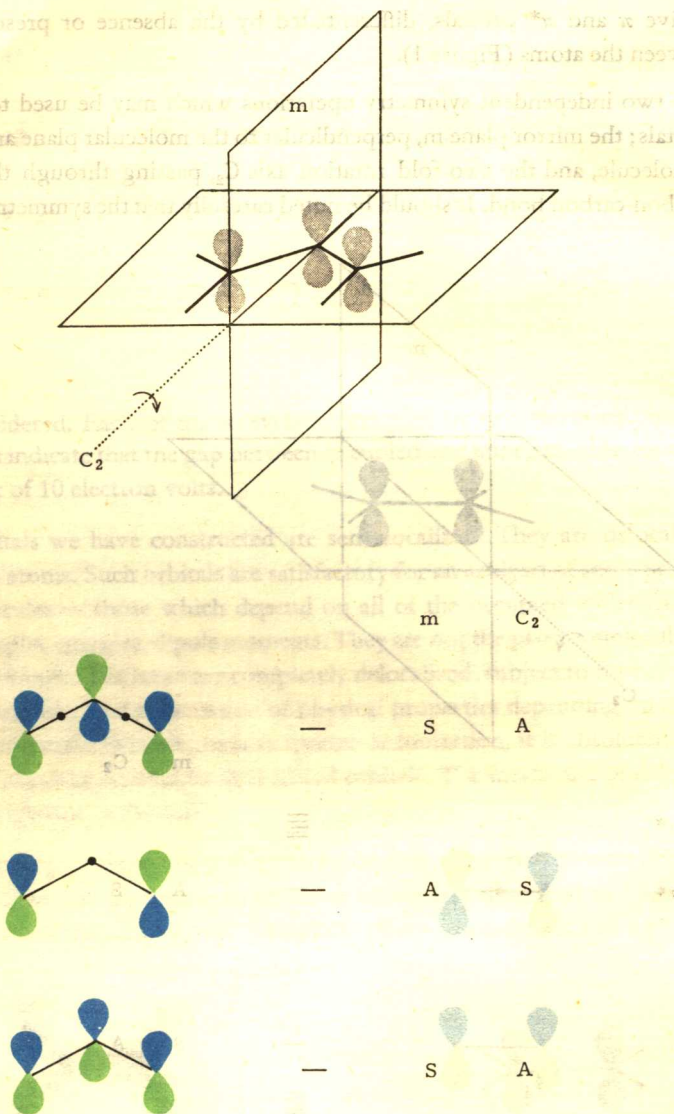
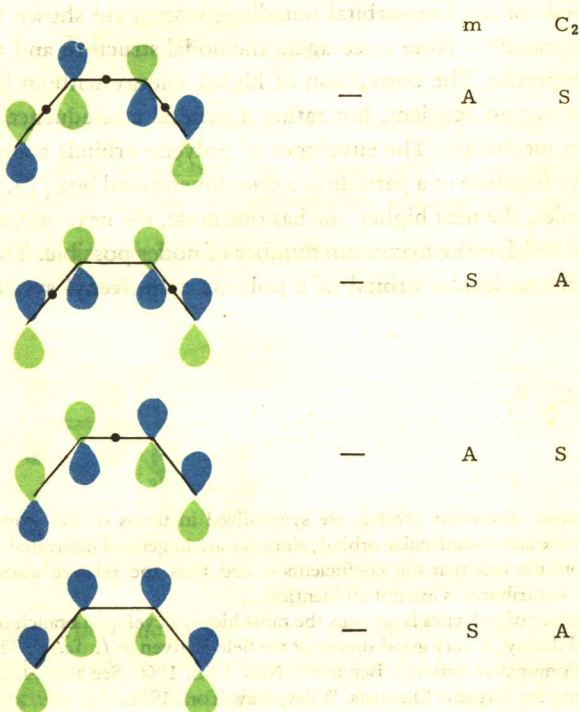
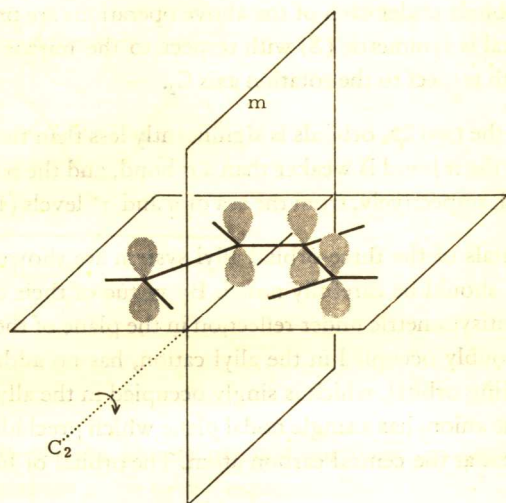


Figure 2. π molecular orbitals of the allyl system. A = antisymmetric, S = symmetric.

Figure 3. π molecular orbitals of *s-cis*-butadiene. A = antisymmetric, S = symmetric.



ties of the ethylene orbitals under each of the above operations are precisely opposite. Thus, the π orbital is symmetric (S) with respect to the mirror plane m , and antisymmetric (A) with respect to the rotation axis C_2 .

The overlap between the two $2p_z$ orbitals is significantly less than that involved in σ interactions, and so the π bond is weaker than a σ bond, and the π and π^* levels are raised and lowered, respectively, from the sea of σ and σ^* levels (Figure 1).

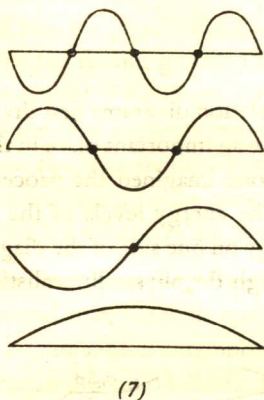
The π molecular orbitals of the three-orbital allyl system are shown in Figure 2. Their nodal structure should be carefully noted. By virtue of their character as π orbitals, they all are antisymmetric under reflection in the plane of the allyl system. The lowest orbital, doubly occupied in the allyl cation, has no additional nodes. The middle, nonbonding orbital, which is singly occupied in the allyl radical, and doubly occupied in the anion, has a single nodal plane which precludes any contribution of the $2p$ orbital at the central carbon atom. The orbital of highest energy has two nodes.

The molecular orbitals of the four-orbital butadiene system are shown in Figure 3 for an *s-cis* arrangement^(6,7). Note once again the nodal structure and the alternating symmetry properties. The correlation of higher energy with an increasing number of nodes is not an accident, but rather a general consequence of either classical or quantum mechanics. The envelopes of polyene orbitals coincide with the curve of the wave function of a particle in a one-dimensional box (7). The lowest orbital has no nodes, the next higher one has one node, the next two, and so on until the highest orbital has the maximum number of nodes possible. The general expression for the k^{th} molecular orbital of a polyene or polyenyl system with n carbon atoms is

$$\psi_k = \sum_{i=1}^n C_{ki} \phi_i,$$

[6] Throughout this paper molecular orbitals are symbolized in terms of the atomic orbitals whose interaction gives the actual molecular orbital; since we are in general interested only in nodal properties, we ignore the fact that the coefficients — and thus the relative sizes — of the resultant atomic orbital contributions are not all identical.

[7] The electronic structure of polyenes is perhaps the most highly developed branch of semi-empirical molecular orbital theory. A very good survey of the field is given in *L. Salem: The Molecular Orbital Theory of Conjugated Systems*. Benjamin, New York 1966. See also *A. Streitwieser: Molecular Orbital Theory for Organic Chemists*. Wiley, New York 1961.



(7)

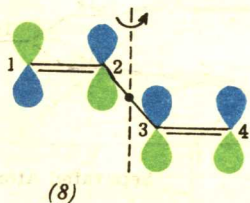
where the Φ_i are the atomic orbitals numbered consecutively from one end. The coefficients are given by the expression^[7]

$$c_{ki} = \sqrt{\frac{2}{n+1}} \sin \frac{\pi ki}{n+1}$$

The orbitals alternate in symmetry with increasing energy.

If n is even, there are $n/2$ bonding π orbitals and $n/2$ antibonding. If n is odd, there are $(n-1)/2$ bonding, $(n-1)/2$ antibonding, and one nonbonding orbital.

A final point of much importance is that no molecular orbital may be at the same time symmetric and antisymmetric with respect to any existing molecular symme-



(8)

try element. Thus, the orbital (8) is symmetric under rotation by 180° if atoms 2 and 3 are viewed, but antisymmetric if 1 and 4 are considered; it is not an acceptable molecular orbital of butadiene.

3. Correlation Diagrams

The united atom-separated atoms diatomic correlation diagrams first drawn in the early nineteen-thirties by *Hund* and *Mulliken* have an important place in theoretical chemistry^[8]. In constructing such a diagram, one imagined the process of two atoms approaching each other from infinity. The energy levels of the separated atoms were placed in approximate order of energy on one side of the diagram. One then imagined the approach of the atoms through the physically realistic molecu-

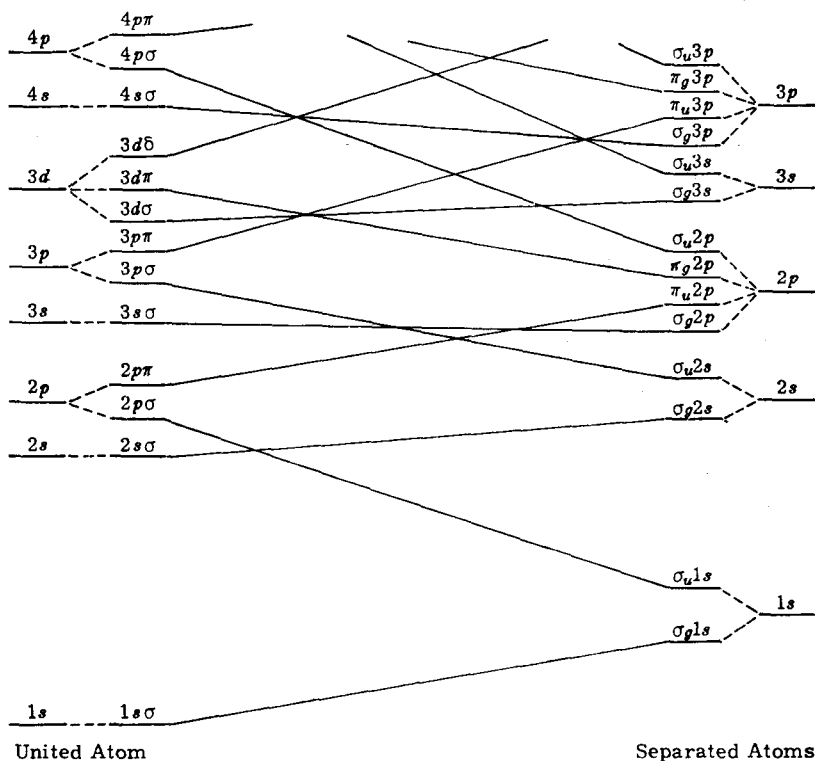


Figure 4. A typical atomic correlation diagram.

[8] *F. Hund*, *Z. Phys.* 40, 742 (1927); 42, 93 (1927); 51, 759 (1928); *R. S. Mulliken*, *Phys. Rev.* 32, 186 (1928); *Rev. Mod. Phys.* 4, 1 (1932). See also *G. Herzberg*: *The Electronic Structure of Diatomic Molecules*. 2nd edition, Van Nostrand, Princeton 1950.

lar region into the physically impossible process of nuclear coalescence. The energy levels of the resulting united atom were once again known. They were placed on the other side of the diagram. One then proceeded to classify the initial separated and the final united atom orbitals with respect to the symmetry maintained throughout the hypothetical reaction. Levels of like symmetry were connected, paying due attention to the quantum mechanical noncrossing rule — that is, only levels of unlike symmetry are allowed to cross (Figure 4).

In this way, from the relatively well-known level structures of the separated atoms and the united atom valuable information was obtained about the level structure of the intermediate region corresponding to the molecule. It was this kind of diagram which provided a rationalization for the existence of the oxygen molecule as a ground-state triplet.

In an exactly analogous manner a correlation diagram may be drawn for a concerted reaction such as cycloaddition. On one side one writes down the approximately known energy levels of the reactants, on the other side those of the product. Assuming a certain geometry of approach one can classify levels on both sides with respect to the symmetry maintained throughout the approach, and then connect levels of like symmetry. Such a molecular correlation diagram yields valuable information about the intermediate region, which represents in this case the transition state for the reaction.

We would like to illustrate in some detail the construction of a molecular correlation diagram. The first example we choose is the maximum-symmetry approach of two ethylene molecules, leading to cyclobutane (Figure 5). As usual in theoretical discussions, maximum insight into the problem at hand is gained by simplifying

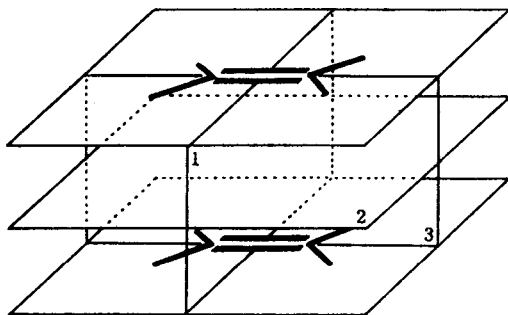


Figure 5. Parallel approach of two ethylene molecules.

the case as much as possible, while maintaining the essential physical features. In this instance we treat in the correlation diagram *only four* orbitals—the four π orbitals of the two ethylenes. In the course of the reaction these four π orbitals are transformed into four σ orbitals of cyclobutane. We may safely omit the C-H and the C-C σ bonds of the ethylene skeleton from the correlation diagram because, while they undergo hybridization changes in the course of the reaction, their number, their approximate positions in energy, and in particular their symmetry properties are unchanged.

The first step in the construction of a correlation diagram involves isolating the essential bonds and placing them at their approximate energy levels in reactants and

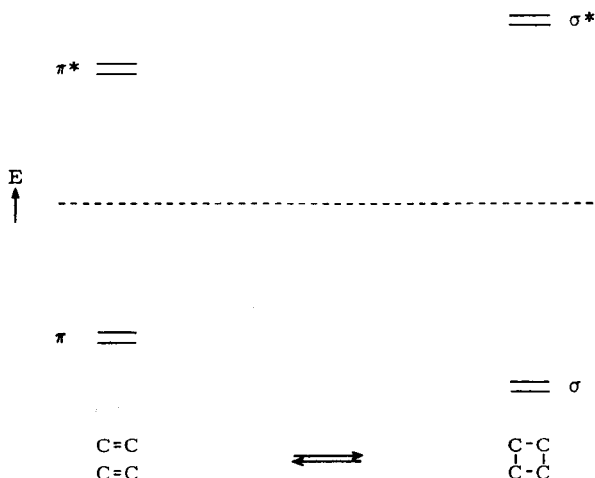


Figure 6. Energy levels of the orbitals essential for the formation of cyclobutane from two ethylene molecules in the geometry shown in Figure 5.

products; the result is shown for the case at hand in Figure 6, in which the dashed horizontal line is the nonbonding level—approximately the energy of an electron in a free carbon $2p$ orbital. We have separated σ and σ^* by an energy greater than that between π and π^* ; although there is little reason to question this assignment, it is important to emphasize that it is in no way essential to the subsequent argu-