In 1965 R. B. Woodward and Roald Hoffmann of Harvard University proposed and demonstrated that concerted reactions proceed most readily when there is congruence between the orbital symmetries of the reactants and products. In other words, when the bonding character of all occupied molecular orbitals is preserved at all stages of a concerted molecular reorganization, that reaction will most likely take place. The greater the degree of bonding found in the transition state for the reaction, the lower will be its activation energy and the greater will be the reaction rate.

A general introduction to molecular orbitals was presented earlier. The simple compound ethene is made up of six atoms held together by six covalent bonds, as described in the following illustration. A molecular orbital diagram of ethene is created by combining the twelve atomic orbitals associated with four hydrogen atoms and two sp² hybridized carbons to give twelve molecular orbitals. Six of these molecular orbitals (five sigma & one pi-orbital) are bonding, and are occupied by the twelve available valence shell electrons. The remaining six molecular orbitals are antibonding, and are empty.

Proper molecular orbitals are influenced by all the nuclei in a molecule, and require consideration of the full structure and symmetry of a molecule for their complete description. For most purposes, this level of treatment is not needed, and more localized orbitals serve well. In the case of ethene and other isolated double bonds, descriptions of the localized π orbitals will be displayed by clicking on the above diagram. Several important characteristics of molecular orbitals need to be pointed out, and this diagram will serve to illustrate them.

1. The spatial distribution of electron density for most occupied molecular orbitals is discontinuous, with regions of high density separated by regions of zero density, e.g. a nodal plane. The π-orbital on the left has one nodal plane (colored light blue), and the π* -orbital on the right has a second nodal plane (colored yellow). As a rule, higher energy molecular orbitals have a larger number of nodal surfaces or nodes.

2. The wave functions that describe molecular orbitals undergo a change in sign at nodal surfaces. This phase change is sometimes designated by plus and minus signs associated with discrete regions of the orbital, but this notation may sometimes be confused for an electric charge. In the above diagram, regions having one phase sign are colored blue, while those having an opposite sign are colored red.

3. These localized orbitals may be classified by two independent symmetry operations ; a mirror plane perpendicular to the functional plane and bisecting the the molecule (colored yellow above), and a two-fold axis of rotation (C₂) created by the intersection of this mirror plane with the common nodal plane (colored light blue). The π-orbital on the left is symmetric (S) with respect to the mirror plane, but antisymmetric (A) when rotated 180º, a C₂ operation. The opposite is true for the π* -orbital on the right, which has a mirror plane symmetry of A and a C₂ symmetry of S. Such symmetry characteristics play an important role in creating the orbital diagrams used by Woodward and Hoffmann to rationalize pericyclic reactions.

The original approach of Woodward and Hoffmann involved construction of an "orbital correlation diagram" for each type of pericyclic reaction. The symmetries of the appropriate reactant and product orbitals were matched to determine whether the transformation could proceed without a symmetry imposed conversion of bonding reactant orbitals to
antibonding product orbitals. If the correlation diagram indicated that the reaction could occur without encountering such a **symmetry-imposed barrier**, it was termed **symmetry allowed**. If a symmetry barrier was present, the reaction was designated **symmetry-forbidden**. Two related methods of analyzing pericyclic reactions are the **transition state aromaticity** approach, and the **frontier molecular orbital** approach. Each of these methods has merit, and a more detailed description of each may be examined by clicking the appropriate button below.

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**Contributors**