A classical example of the application of these ideas concerns the thermal equilibrium between 1,3(Z),5-hexatriene and cyclohexadiene:

The overall course of the interconversion is summarized in the first line of the figure, using the "curved arrow notation" frequently employed by organic chemists to signify the movement of an electron pair. It should be stressed that this reaction is an isomerization, involving changes of hybridization in the carbon skeleton and the reorganization of electrons and C—C bonds. Three C—C π bonds are lost, while a new C—C σ bond and two new C—C π bonds are formed. No atoms are added or subtracted, nor do hydrogen atoms move from the carbon atoms to which they are bonded. The second line offers a more three-dimensional depiction of the process, showing how the terminal sp² carbon atoms of the hexatriene become the sp³ carbon atoms of the cyclohexadiene.

From the above it will be clear that while the methine (CH) groups at the four internal positions remain fundamentally static throughout the transformation, the terminal methylene (CH₂) groups must rotate 90° out of the plane. In principle, such rotation might take place in a conrotatory fashion (both methylene groups rotating in the same sense — clockwise or counterclockwise — relative to one another), or in a
disrotatory fashion (the methylene groups rotating in opposite senses, relative to one another); or the relative sense of rotation might be random:

conrotatory versus disrotatory motion

One cannot differentiate between these two pathways on the basis of the (same) product obtained in this (unsubstituted) case. However, what is of extraordinary interest is the sharply partitioned stereochemical outcome when there is substitution — for example, as in the figure below, methyl substitution. 2(Z),4(Z),6(E)-octatriene equilibrates thermally only with trans-5,6-dimethyl-1,3-cyclohexadiene. In contrast, both 2(E),4(Z),6(E)-octatriene and 2(Z),4(Z),6(Z)-octatriene (just the former is shown) equilibrate thermally only with cis-5,6-dimethyl-1,3-cyclohexadiene. There is no crossing over: so long as the reactions are carried out thermally, that is, initiated by heat (but not, for example, by light), the Z,Z,E triene does not yield the cis-substituted cyclohexadiene, and vice versa; nor do the E,Z,E and Z,Z,Z trienes give the trans-substituted ring compound, or vice versa. In sum, we must infer — from these cases where the methyl substituents provide a
frame of reference — that the disrotatory motion somehow is preferred, while the conrotatory motion somehow is not allowed:

If we now consider the orbitals involved, a remarkably simple explanation presents itself: that the observed result is a consequence of the nodal properties (and hence, ultimately, the symmetry properties) of $\chi_3$ — the frontier orbital, the HOMO, of hexatriene and substituted hexatrienes. As one imagines $\chi_3$ (with its two electrons) being transformed into the required $\sigma$ bonding orbital (again, with its two electrons), it is necessary that a bonding interaction develop. This can happen only as a result of disrotatory motion, for conrotatory motion will lead to an antibonding interaction, as the following figure makes clear:
A completely reversed stereochemical result is observed under photochemical conditions: \(2(Z),4(Z),6(E)\)-octatriene is found to equilibrate photochemically with cis-5,6-dimethyl-1,3-cyclohexadiene, while both \(2(E),4(Z),6(E)\)-octatriene and \(2(Z),4(Z),6(Z)\)-octatriene equilibrate photochemically with trans-5,6-dimethyl-1,3-cyclohexadiene. Now the motion is conrotatory!
Assuming that the (forward) photochemical reaction is initiated by excitation of the substituted hexatriene to its first excited state, the HOMO becomes $\chi_4^*$, which correctly predicts the observed photochemical result:

Several modes of interpretation have been developed to explain the panoply of results described above. Differing in their qualitative thrust, these various theories have been shown to be, in fact, mathematically equivalent at the level of a rigorous quantum mechanical analysis. Here we have concentrated on the frontier orbital approach. Another treatment is based on the principle that orbital symmetry must be conserved throughout such a concerted reaction, as the entire orbital array of the starting material is transformed into the entire orbital array of the product, each
starting orbital being correlated with a specific product orbital having the same symmetry.

Yet another useful point of view develops through application of the concept of aromaticity to the problem. As the following figure attempts to illustrate in pictorial fashion, the thermal hexatriene—cyclohexadiene interconversion has a transition state that is aromatic in the sense of obeying Hückel’s Rule, if and only if it occurs in a disrotatory fashion. The figure makes the case that for the disrotatory thermal reaction the transition state orbitals will be exactly the Hückel benzene aromatic orbitals of Segment 8.03. (Note that in the Hückel aromatic orbital corresponding to $\chi_3$ of 1,3,5-hexatriene the orbital fades away at the nodes.) In contrast, the orbitals of the conrotatory thermal hexatriene—cyclohexadiene transition state would have odd numbers of nodes in combination with $4n+2$ ($n=1$) electrons, and would be anti-aromatic.
TRANSITION STATE orbitals for disrotatory thermal hexatriene — cyclohexadiene interconversion are Hückel aromatic.