Quantum Chemistry

Lecture 28

Fukui function
Frontier Molecular Orbital
Woodward-Hoffman Rules

NC State University

Fukui function

The electrostatic potential that results from a quantum chemical calculation of a molecule contains a great deal of information. The interpretation of the electrostatic potential is facilitated by a function that can add or remove a small amount of charge from the total electron density in order to determine which regions are the most electron rich (nucleophilic) or poor (electrophilic). One way to approach this kind analysis of the electron density is to use the Fukui function. The Fukui function is defined as the differential change in electron density caused by

$$f(\mathrm{r}) = \left(\frac{\partial \rho(\mathrm{r})}{\partial \mathrm{N}}\right)_{\nu(\mathrm{r})}$$

Nucleophilicity/Electrophilicity

In practice, the Fukui function is calculated by approaching the density either from above,

$$f^{+}(\mathrm{r}) = \left(\frac{\partial \rho(\mathrm{r})}{\partial N}\right)^{+}_{\nu(\mathrm{r})} = \lim_{\varepsilon \to 0^{+}} \frac{\rho_{N+\varepsilon}(\mathrm{r}) - \rho_{N}(\mathrm{r})}{\varepsilon}$$

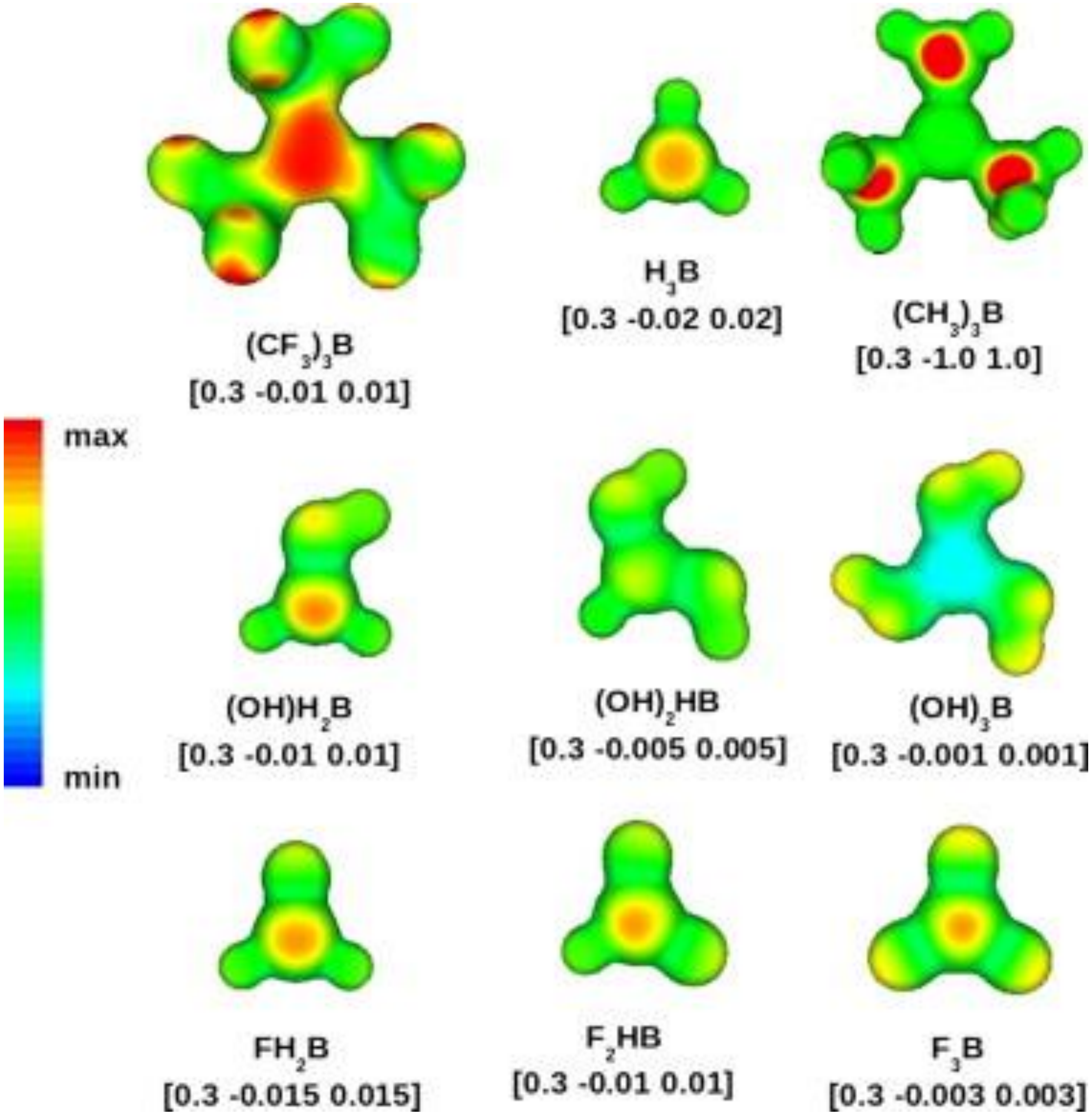
or below.

$$f^{-}(\mathrm{r}) = \left(\frac{\partial \rho(\mathrm{r})}{\partial N}\right)^{-}_{\nu(\mathrm{r})} = \lim_{\varepsilon \to 0^{-}} \frac{\rho_{N}(\mathrm{r}) - \rho_{N-\varepsilon}(\mathrm{r})}{\varepsilon}$$

An increase in electron density on the molecule localizes proportional to the magnitude of $f^{+}(r)$. Consequently, nucleophilic attack will occur at sites where $f^{+}(r)$ is large. Conversely, removal of charge will tend to occur to the greatest extent where $f^{-}(r)$ is the largest. Electrophilic attack occurs at locations where $f^{-}(r)$ is the largest.

Lewis Acidity/Basicity

The Fukui function is a an important indicator of the locations where electron transfer can occur. The function is illustrated as a color-coded map that shows the locations where f+(r) is The largest. In the example shown below the Fukui function For various boron derivatives have been plotted. The can be interpreted in terms of the Lewis acidity. The red color indicates a strong Lewis acid, while the blue color indicates a Lewis base. A molecular such as BH_3 is a weak Lewis acid as indicated by the yellow color of the B atom. However, $B(CF_3)_3$ is a very strong Lewis acid as indicated by the large value of f+(r). Of the molecules shown only $B(OH)_3$ has Lewis basicity. This is due to the donation of electron density from the OH moieties.


$(CF_3)_3B$
[0.3 -0.01 0.01]
H_3B
[0.3 -0.02 0.02]
$(CH_3)_3B$
[0.3 -1.0 1.0]
max
min
$(OH)H_2B$
[0.3 -0.01 0.01]
$(OH)_2HB$
[0.3 -0.005 0.005]
$(OH)_3B$
[0.3 -0.001 0.001]
FH_2B
[0.3 -0.015 0.015]
F_2HB
[0.3 -0.01 0.01]
F_3B
[0.3 -0.003 0.003]

Frontier Molecular Orbital Theory

The concept of an electron density function that denotes reactive regions is related to an theory developed by Fukui on reactivity in aromatic hydrocarbons. The theory defines the reactivity in terms of the frontier orbitals, the HOMO and the LUMO. The theory is based on the following principles. As two molecules interact:

- The occupied orbitals of different molecules repel each other.
- Positive charges of one molecule attract the negative charges of the other.
- The HOMO and LUMO interact causing attraction if the symmetry is conserved, but there is no attraction if symmetry is not conserved.

Woodward-Hoffman Rules

Frontier orbitals help to explain the predictions of the Woodward–Hoffmann rules for thermal pericyclic reactions, which are summarized in the following statement:

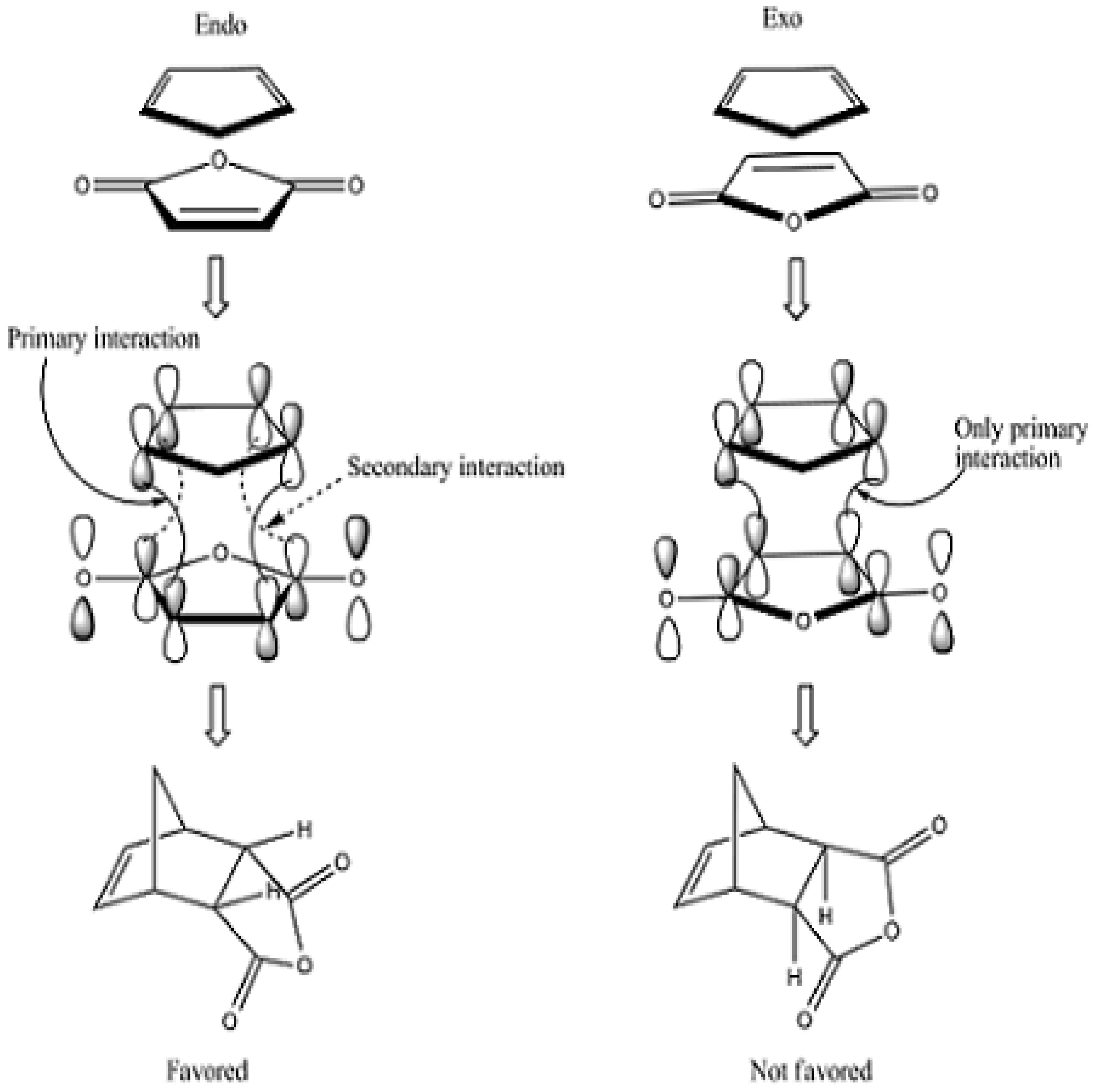
"A ground-state pericyclic change is symmetry-allowed when the total number of $(4q+2)_s$ *and* $(4r)_a$ *components is odd"*

The symbols $(4q+2)_s$ and $(4r)_a$ refer to the number of aromatic (suprafacial) and antiaromatic (antarafacial) electron systems, respectively. A cycloaddition is a reaction that simultaneously forms at least two new bonds. If the electron motion in the reaction involves the same side of the π-system, it is called suprafacial. On the other hand, if the motion involves a transition to the opposite side of the π-system it is called antarafacial.

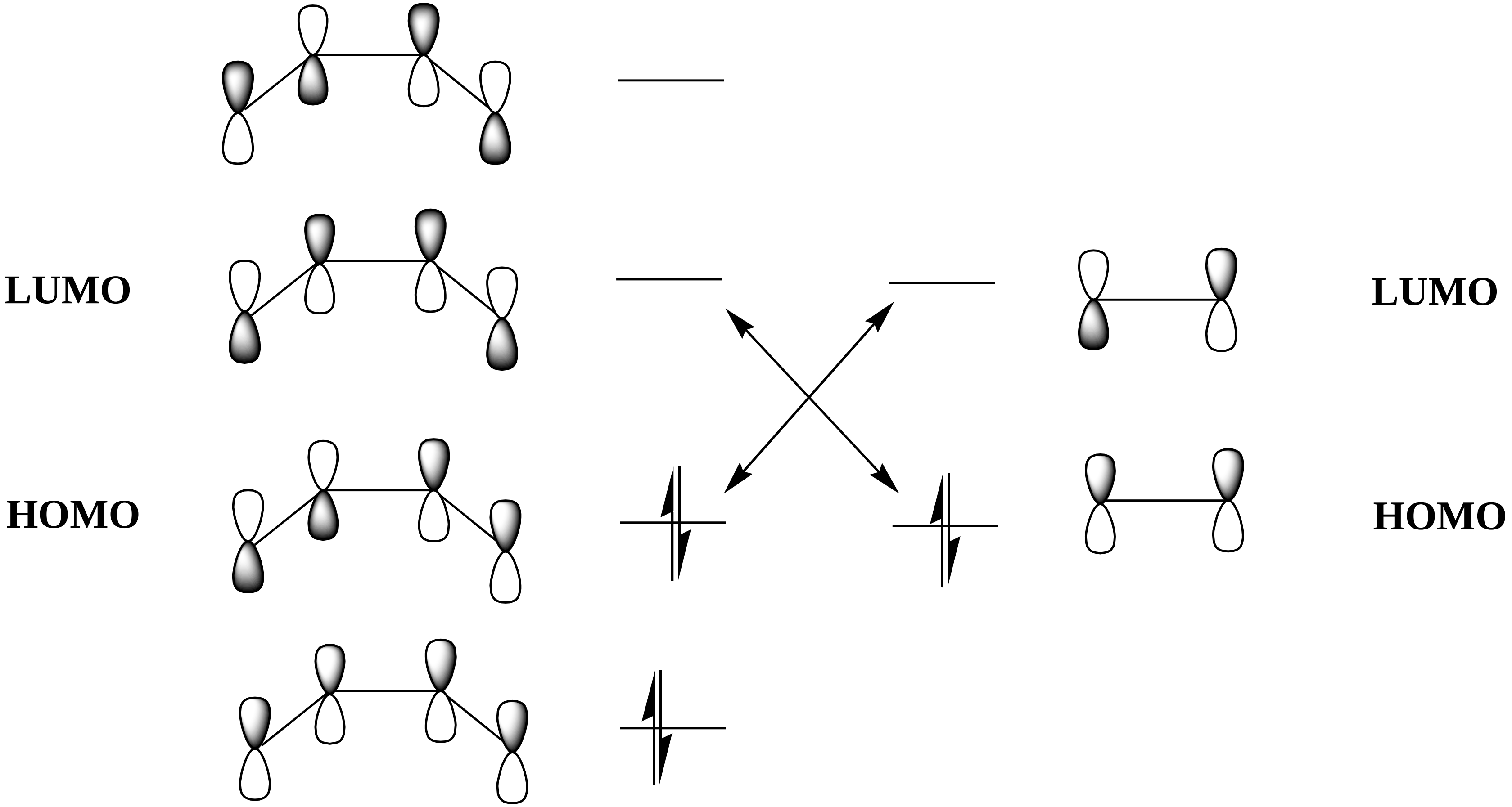
Woodward-Hoffman Rules

The process of cycloaddition converts two or more open-chain molecules into rings. The transition states for these reactions involves circulation of the electrons in continuous rings, making them pericyclic reactions. The electron count includes all of the π electrons in the system. For example, the Diels-Alder reaction between maleic anhydride (MA) and cyclopentadiene (CP) involves the addition of the 2-electron π system of MA to the 4-electron π system of CP. Such a cycloaddition has total of 6 π electrons and is allowed by the Woodward–Hoffmann rules because the electrons move suprafacially. Thus, there is one $(4q + 2)_s$ component and no $(4r)_a$ component. According to the rule this means that the reaction is thermally allowed.

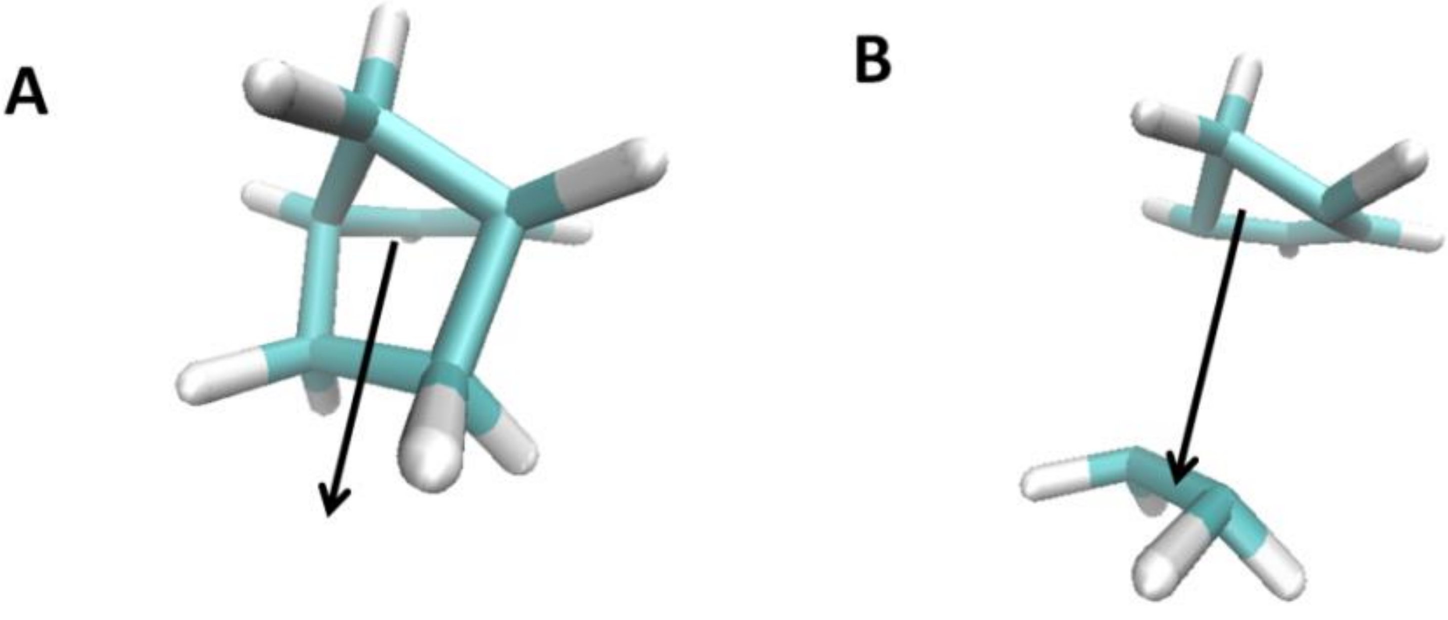
Frontier molecular orbital (FMO) theory also finds that this reaction is allowed and furthermore predicts its stereoselectivity. For example, the reaction between maleic anhydride and cyclopentadiene, shown in Figure 14.2, gives rise to the *endo*-product . Maleic anhydride is an has electron-withdrawing groups that make the p bond electron deficient. Therefore, in the Diels–Alder reaction the p bond of maleic anhydride is termed the dienophile (diene-friendly). Thus, only the reaction between the HOMO of cyclopentadiene and the LUMO of maleic anhydride is allowed. Furthermore, although the *exo*-product is the more thermodynamically stable isomer, there are secondary (non-bonding) orbital interactions in the *endo*- transition state, lowering its energy and making the reaction towards the *endo*- product faster, and therefore more kinetically favorable. Since the *exo*-product has primary (bonding) orbital interactions it can still form, but since the *endo*-product forms faster it is the major product.


Endo
Exo
Primary interaction
Secondary interaction
Only primary interaction
O
H
Favored
Not favored

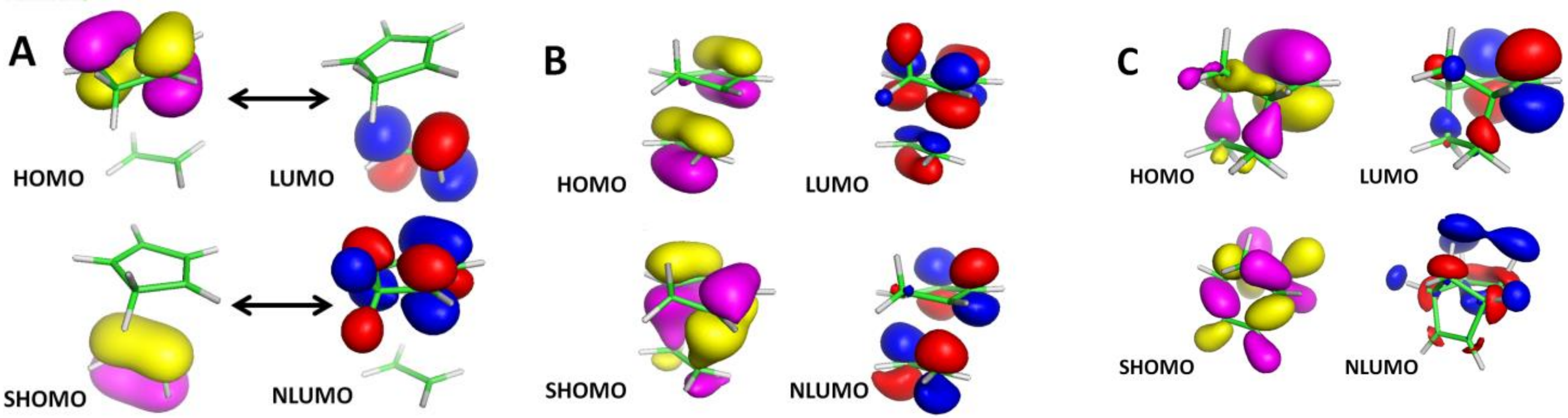
Since the Diels-Alder reaction is a [4 + 2] cycloaddition, the reaction can be simplified by considering the reaction between butadiene and ethene. The HOMO of butadiene and the LUMO of ethene are both antisymmetric (rotationally symmetric), meaning the reaction is allowed.



The Diels-Alder reaction is a classic example that has been studied intensely. Therefore, it provides an excellent example for consideration of application of methods. We have applied DMol3 using the PBE basis set to calculate the geometry optimized structure of norbornene, which is the product of the Diels-Alder reaction between cyclopentadiene and ethene. We then removed the ethene molecule using the average bond vector shown below.



Calculated Frontier Orbitals

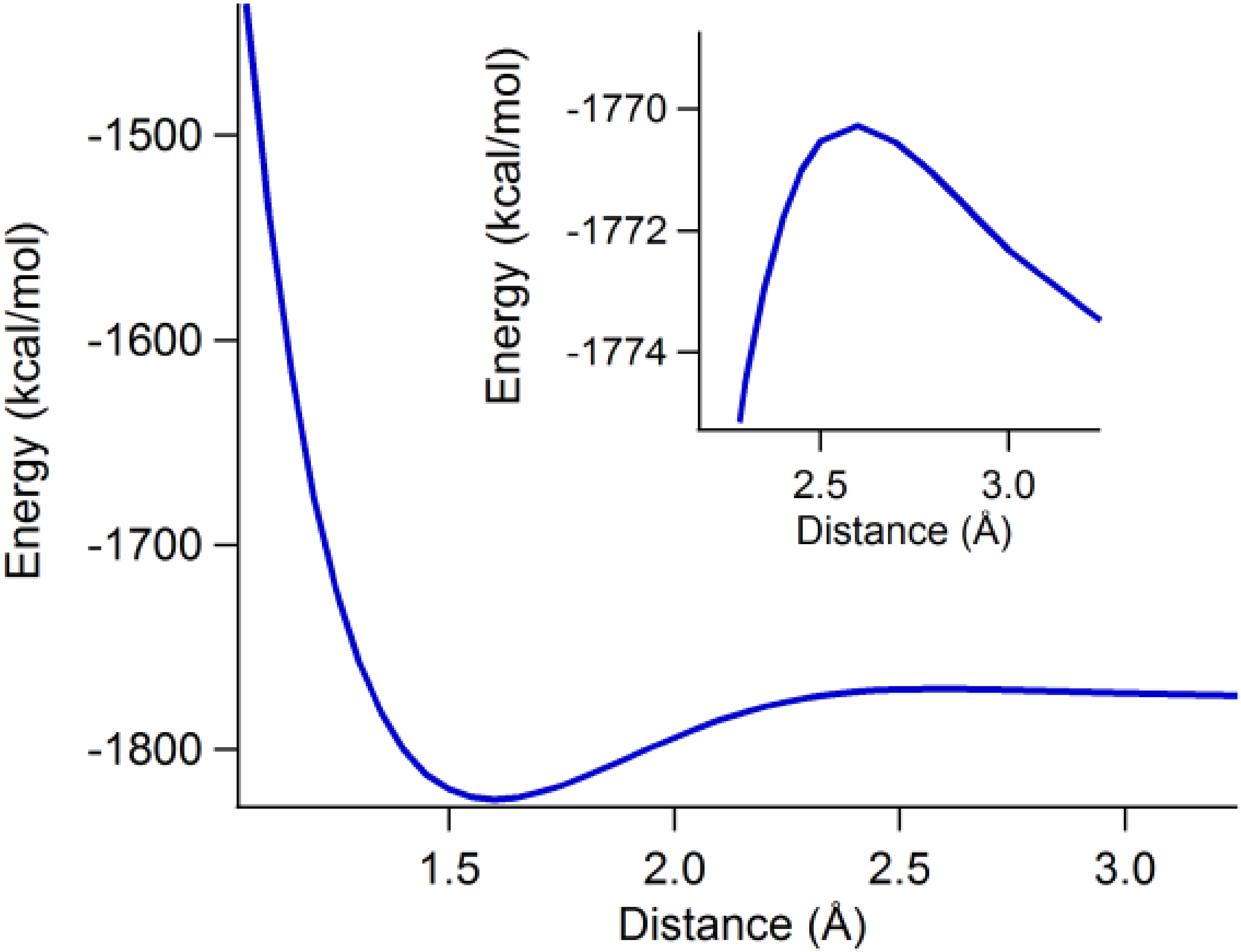


Structures and molecular orbitals along the MEP for the Diels-Alder reaction. The three panels in the figure are A.) the reactant, B.) the transition state and C.) the product.

Computational approaches

Note that the geometries were geometry optimized at each separation distance with four carbon atoms held fixed in order to ensure that the molecule would not drift either towards the reactants or the products. Once a maximum along the separation vector has been identified one can conduct a frequency calculation to determine the mode(s) with negative eigenvalues, which are the modes that describe motion along the transition state.

It is straightforward to create a number of structures for which the pulling distances is varied. These can then be used to calculate a potential energy surface for the binding of ethene. One possible method for searching for the transition state is to find the local maximum in the potential energy surface.



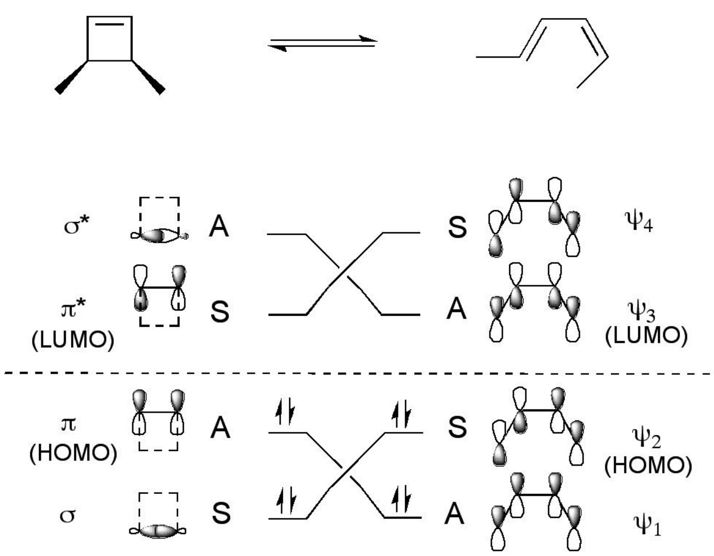
Potential energy surface for the separation of ethene from norbornene.

The purpose of such calculations is to understand the nature of the reaction path, barrier height and therefore possible strategies for catalysis, effects of chemical substitution and so on. For example, one question that has been posed for the Diels-Alder reaction is whether the bonds form simultaneously or sequentially. An electrocyclic reaction is a pericyclic reaction involving the net loss of a π bond and the creation of a σ bond that forms a ring by rotations the pivot around two bonded atoms. Electrocyclic reactions can proceed through either a conrotatory or disrotatory mechanism. In the conrotatory ring opening of cyclobutene, there are two electrons moving suprafacially (on the π bond) and two moving antarafacially (on the σ bond). This means there is one $4q + 2$ suprafacial system and no 4r antarafacial system. Thus the conrotatory process is thermally allowed by the Woodward–Hoffmann rules.

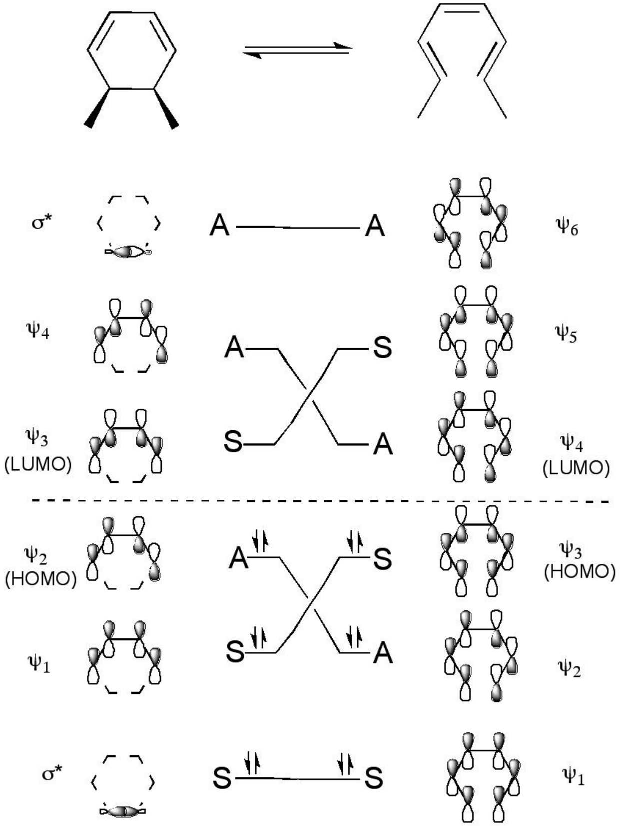
The Woodward-Hoffman rules can be illustrated using a correlation diagram .

Conrotatory

Disrotatory



Correlation diagram for the allowed conrotatory ring opening of 3,4-dimethylcyclobutene



Correlation diagram for the allowed disrotatory ring opening of 5,6-dimethylcyclohexa-1,3-diene

S = symmetric to symmetry element
A = antisymmetric to symmetry element

Woodward-Hoffman Rules
By Frontier Orbital Approach

To see the relationship between the Woodward-Hoffman rules and FMO theory we can consider the cyclic molecule to be made up of two parts. The LUMO of the σ bond on the reactant and the HOMO of the π bond on the product must have appropriate overlap with product orbitals. When compared to the picture drawn for the Diels-Alder reaction we can see that the conrotatory sense of rotation of the atoms in the σ bond that corresponds to the HOMO in the product. Consequently, this reaction will be thermally allowed.

Disrotatory transition

When the same reasoning is applied to the ring opening of cyclohexadiene to make hexatriene the sense of the favored rotation is opposite. The LUMO of the reactant is shown and the HOMO of the product is shown to illustrate the correspondence of the orbitals involved in the rotation.

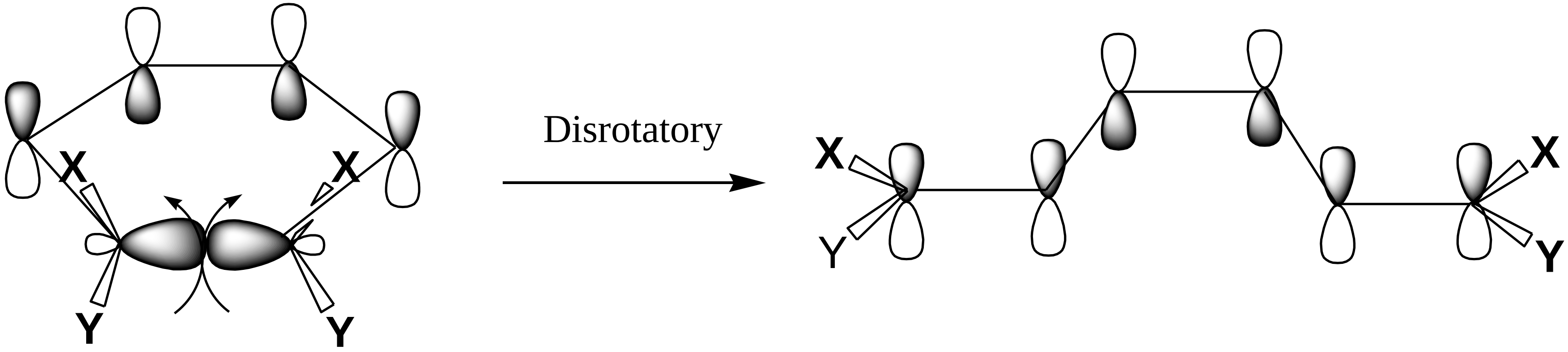


Illustration of the requirement for disrotatory ring opening in the ring opening reaction of a disubstituted cyclohexadiene to form a disubstituted hexatriene.