

# Quantum Chemistry

## Lecture 23

### Orbital Interactions

**NC State University**

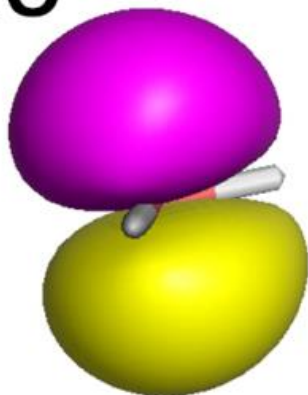
# A look at MO calculations of H<sub>2</sub>O

The ability to calculate the electronic structure at a given nuclear geometry paves that way for comparisons of the energies of different structures. The simplest example of this type calculation is the potential energy for the hydrogen molecule ion, H<sub>2</sub><sup>+</sup>. We have shown how to approach the H<sub>2</sub>O MOs using the LCAO approach and the C<sub>2v</sub> point group.

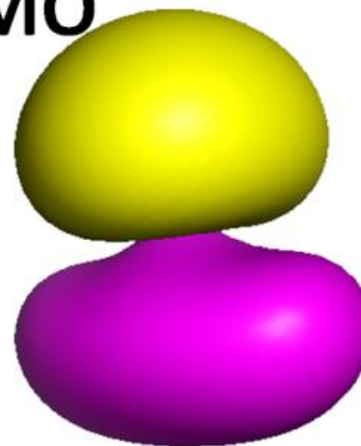
The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are numbers 5 and 6, respectively. Orbital 4 is the second HOMO or SHOMO and orbital 7 is the next LUMO or NLUMO.

# Frontier orbitals of H<sub>2</sub>O

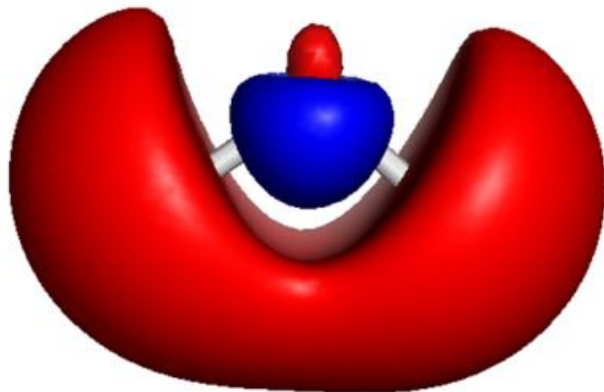
**HOMO**



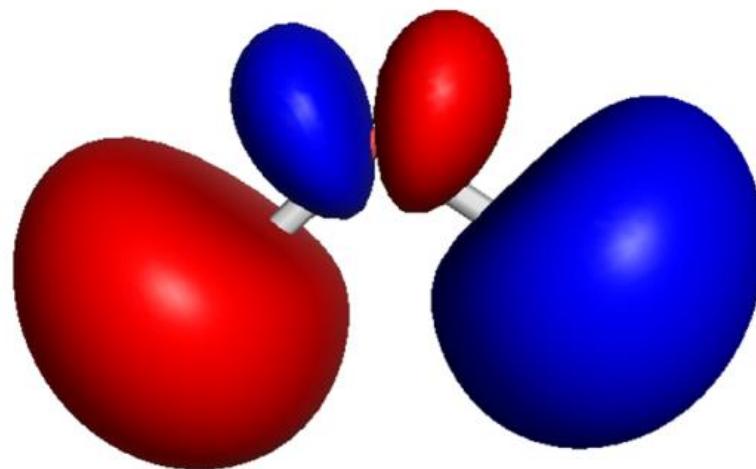
**SHOMO**



**LUMO**



**NLUMO**



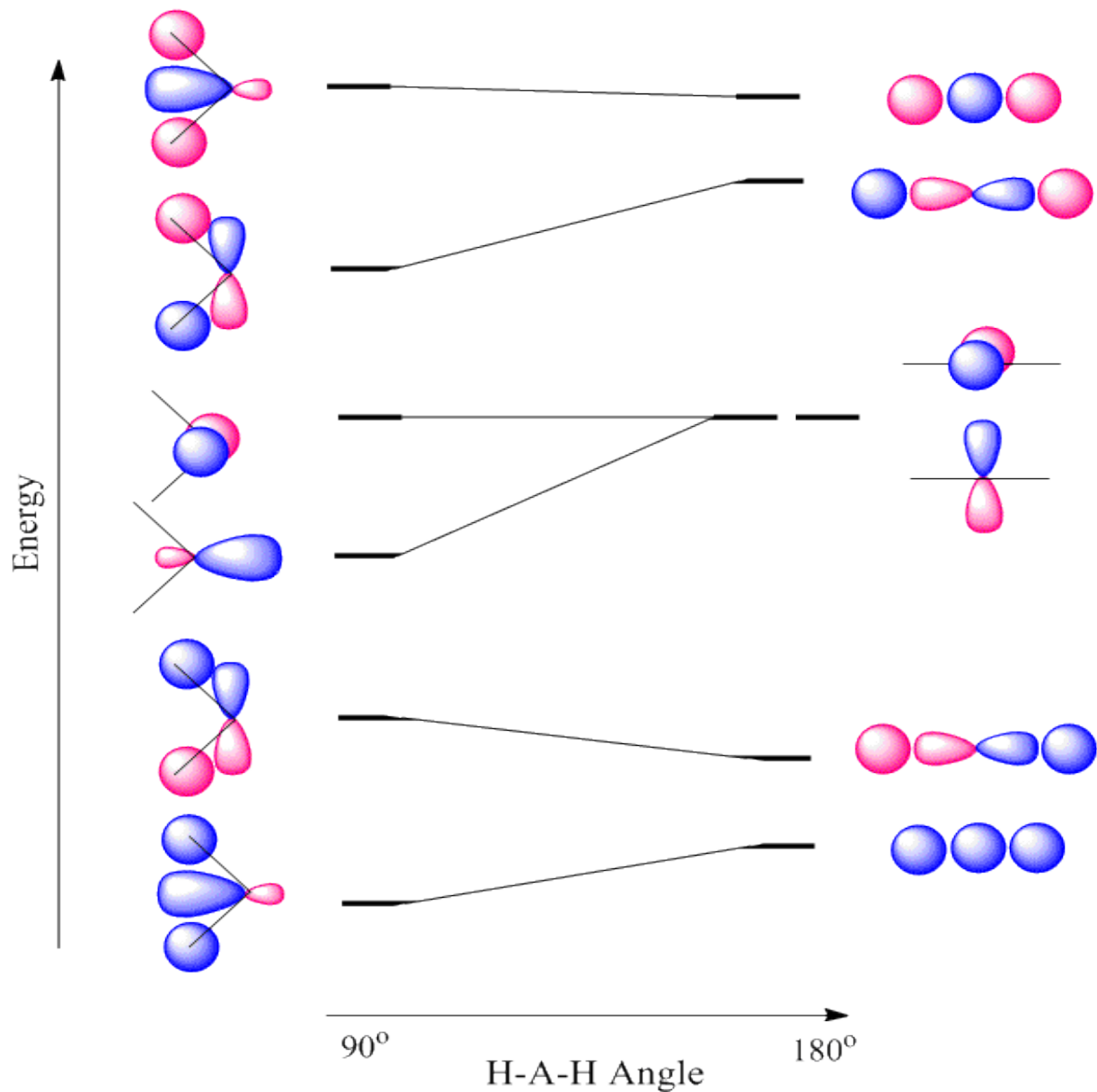
The energies and irreducible representations of the MOs of H<sub>2</sub>O in its equilibrium geometry are given in the Table. For small molecules such as H<sub>2</sub>O we have already shown that group theory can be used to create the MOs and to rank order them. However, the energies of the MOs require a quantum chemical calculation.

MO	Irrep	Hartrees	eV	Occup
1	a <sub>1</sub>	-18.7485	-512.172	2
2	a <sub>1</sub>	-0.91755	-24.968	2
3	b <sub>1</sub>	-0.47179	-12.838	2
4	a <sub>1</sub>	-0.33324	-9.068	2
5	b <sub>2</sub>	-0.25314	-6.888	2
6	a <sub>1</sub>	0.023886	0.65	0
7	b <sub>1</sub>	0.093912	2.555	0
8	b <sub>2</sub>	0.563271	15.327	0

# Walsh diagram observes reactivity

Once we have obtained ground and excited state energies, we can use such information to ask questions about molecular reactivity. However, once we begin to consider the complexity of molecules it is clear that we must identify the most important coordinate(s) for the purpose of comparison of energies and reactivities. At an early stage in the interpretation of MO theory Walsh proposed a presentation of the energy of small molecules as a function of their bend angle. The Walsh diagram for HAH type molecules will be presented using H<sub>2</sub>O as the example. We will consider the energies of the valence level MOs as a function of the H-O-H bend angle ranging from 90° to 180°. The energies change as a function angle as indicated in the diagram on the next slide.

# Walsh diagram for AH<sub>2</sub> molecules



# Analysis of the Walsh diagram

It is evident that the character of certain MOs changes. The  $p_y$  does not change much since it is orthogonal to the changing angle and it is non-bonding for all geometries. However, the  $p_x$  orbital changes substantially since it is a bonding orbital in the bent configuration, but non-bonding in the linear configuration.

# Molecules in the $AH_3$ classification

Molecules that have the  $AH_3$  classification belong to the  $C_{3v}$  point group. We have shown that the sets of three s orbitals related by symmetry on the peripheral atoms transform as  $a_1 + e$ . Thus, the 1s and 2s orbitals both will have LCAOs that have the form,

$$\psi_{a_1} = \frac{1}{\sqrt{3}} (\phi_1 + \phi_2 + \phi_3)$$

$$\psi_{e1} = \frac{1}{\sqrt{6}} (2\phi_1 - \phi_2 - \phi_3)$$

$$\psi_{e2} = \frac{1}{\sqrt{2}} (\phi_1 - \phi_3)$$



# Application of $C_{3v}$ symmetry

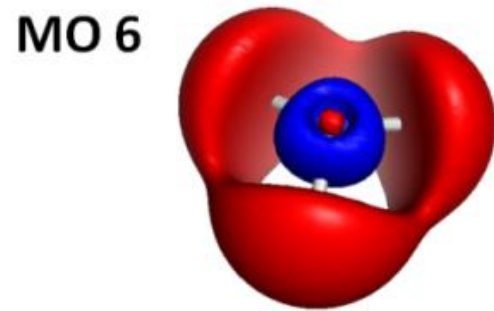
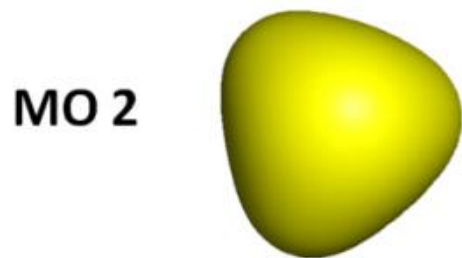
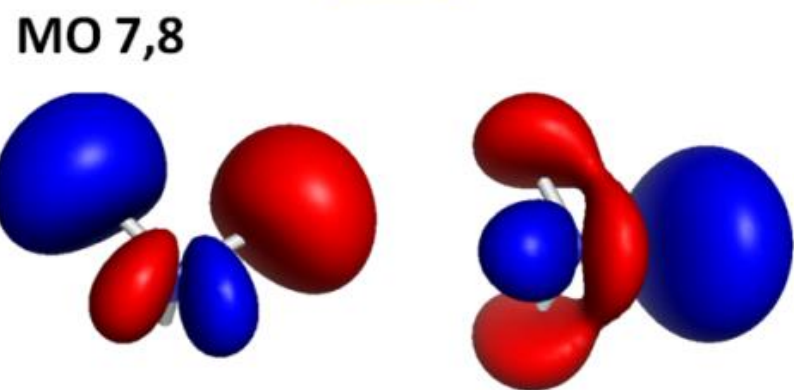
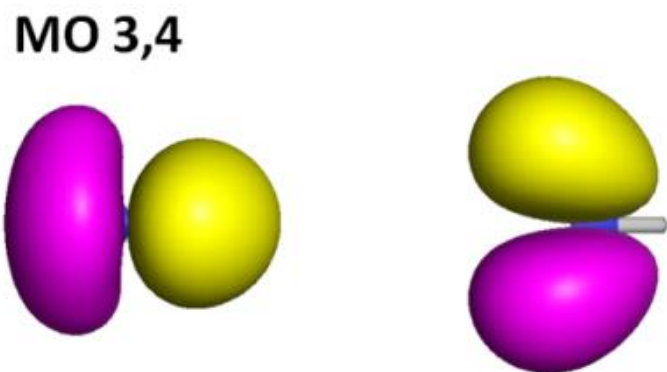
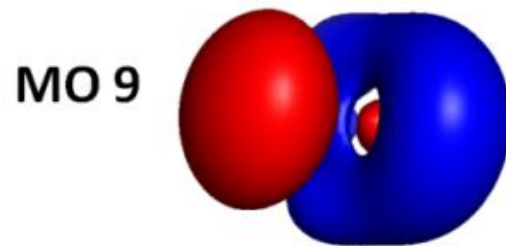
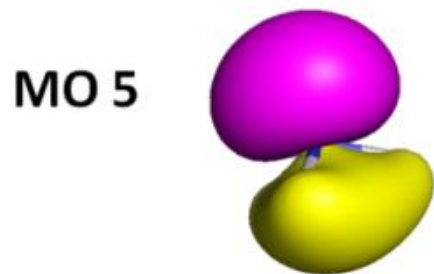
The irreps of the orbitals on the central N atom are:

$1s, 2s, 2p_z$   $a_1$

$2p_{x,y}$   $e$

Using DMol3 we calculate the MOs of  $NH_3$ . Ignoring the core  $1s$  orbital on the N atom, we have the following MOs. The bonding MOs are shown on the left and the anti-bonding MOs are on the right. We can see that these MOs are formed from combinations of the SALCs.

# MOs for NH<sub>3</sub>



# MO coefficients for NH<sub>3</sub>

Although we cannot determine the coefficients by inspection, we can see the linear combinations of the SALCs in the orbitals output by the DFT program DMol3.

$$\text{MO2} = c_{21}\phi_{\text{N},2s} + c_{22}(\phi_{\text{H1},1s} + \phi_{\text{H2},1s} + \phi_{\text{H3},1s})$$

$$\text{MO3} = c_{31}\phi_{\text{N},2p_x} + c_{32}(2\phi_{\text{H1},1s} - \phi_{\text{H2},1s} - \phi_{\text{H3},1s})$$

$$\text{MO4} = c_{41}\phi_{\text{N},2p_y} + c_{42}(\phi_{\text{H2},1s} - \phi_{\text{H3},1s})$$

$$\text{MO5} = c_{51}\phi_{\text{N},2p_z} + c_{52}(\phi_{\text{H1},1s} + \phi_{\text{H2},1s} + \phi_{\text{H3},1s})$$

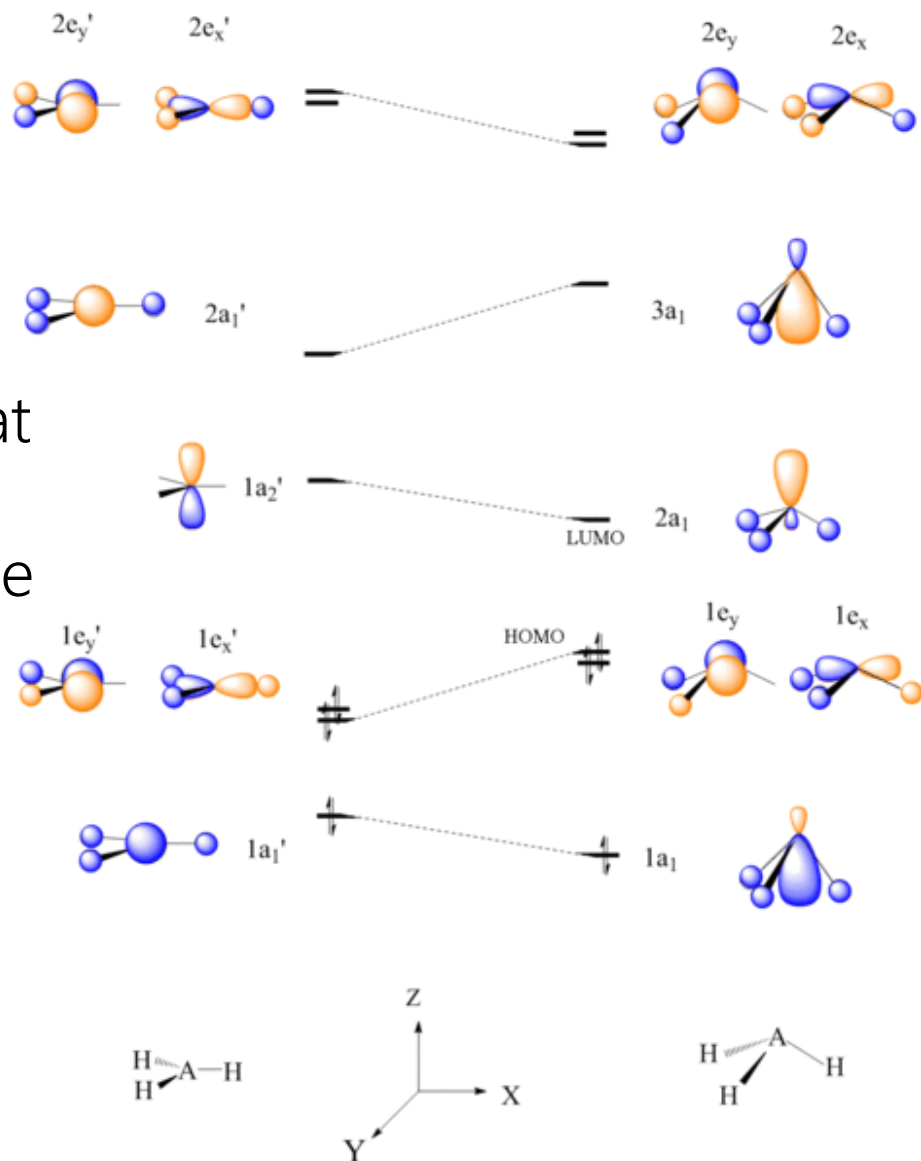
$$\text{MO6} = c_{61}\phi_{\text{N},2p_z} - c_{62}(\phi_{\text{H1},1s} + \phi_{\text{H2},1s} + \phi_{\text{H3},1s})$$

$$\text{MO7} = c_{71}\phi_{\text{N},2p_x} - c_{72}(2\phi_{\text{H1},1s} - \phi_{\text{H2},1s} - \phi_{\text{H3},1s})$$

$$\text{MO8} = c_{81}\phi_{\text{N},2p_y} - c_{82}(\phi_{\text{H2},1s} - \phi_{\text{H3},1s})$$

Walsh diagrams can be combined with MO theory to predict reactivity.

Six electron  $AH_3$  molecules should have a planar conformation. It can be seen that the HOMO,  $1e'$ , of planar  $AH_3$  is destabilized upon bending of the A-H bonds to form a pyramid shape, due to disruption of bonding. The LUMO, which is concentrated on one atomic center, is a good electron acceptor and explains the Lewis acid character of  $BH_3$  and  $CH_3^+$ .



# Polyenes in the free electron model

Polyenes are found in nature as dyes that have important functional roles in photosynthesis, vision, proton pumping to name a few. These are the quintessential "particle-in-a-box" molecules that can be treated approximately using the free electron model. We can see a pattern emerging in terms of the electronic structure from the comparison of ethene, butadiene, and hexatriene. The p-symmetry MOs start with zero nodes and have an increasing number of nodes up to  $N + 1$ , where  $N$  is the number of carbon atoms in the polyene. We can easily predict that the HOMO and LUMO will have  $N/2 - 1$  and  $N/2$  nodes, respectively. For all-trans even polyenes, the point group will be  $C_{2h}$  and the MOs will alternately possess  $b_2$  and  $a_2$  symmetry.

# Polyene wave function

The wavefunction coefficients are derived from the amplitude of the sine function obtained from the solution of the particle in a box. The particle in a box solutions are:

$$\psi_j = \sqrt{\frac{2}{L}} \sin\left(\frac{j\pi x}{L}\right)$$

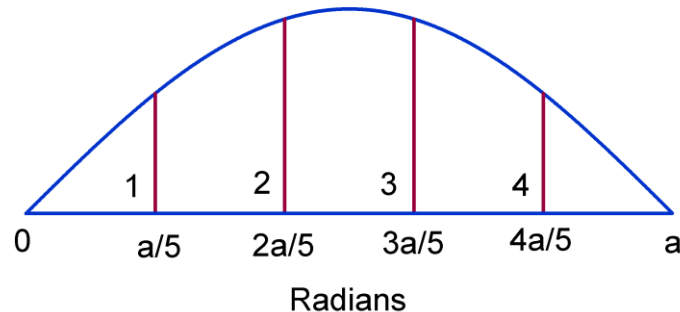
where  $a$  is the length of the box and  $j$  is the quantum number for a given state. If we imagine that an electron is placed in a box that contains  $N$  atoms we can approximate the positions as  $nL/(N+1)$  along the length of the box. Note that it is impossible for an atom to be at the edge or end of the box so we have increased the number  $N$  by 1.

With this approximation the free electron model (FEM) states that the wavefunction coefficients for a polyene will be given by:

$$\psi_j = \sum_{n=1}^N c_{nj} \phi_n$$

$$c_{nj} = \sqrt{\frac{2}{N+1}} \sin\left(\frac{jn\pi}{N+1}\right)$$

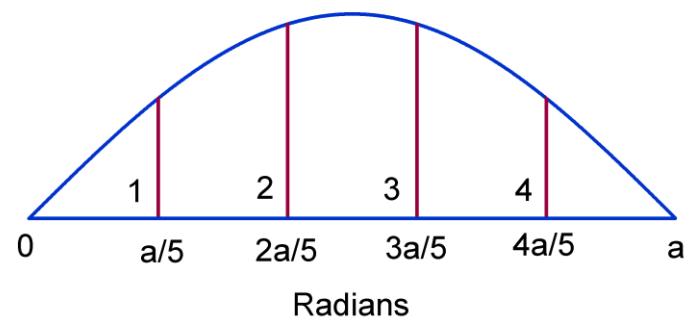
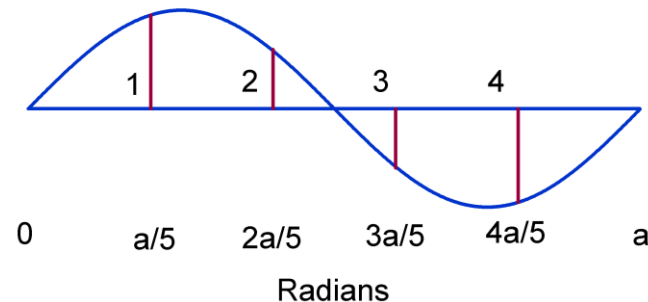
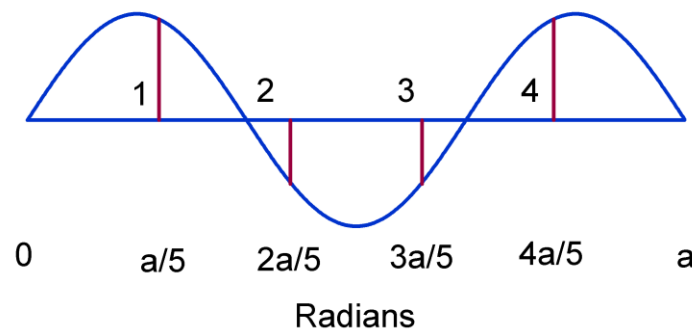
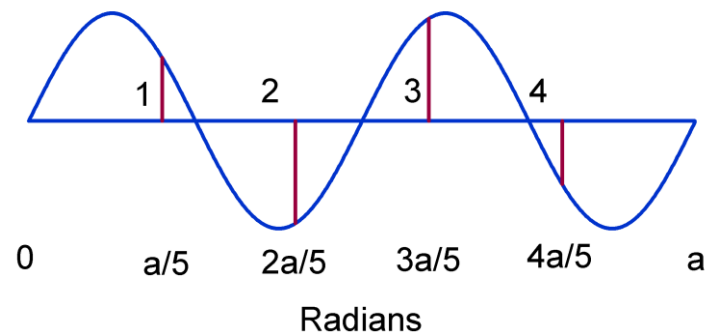
This is illustrated for butadiene below.



# MOs in the free Electron model

The free electron model for the butadiene  $\pi$  orbitals is shown. Not only is the trend in the number of nodes correct, but the overall Shapes are also correct, which means that the orbital coefficients obtained by this model agree with those obtained from Hückel theory.

These general features of butadiene are observed for any level of theory used to describe the molecule.





# Electronic Transition Energies

Using particle in a box energies, the FEM can be used to model the spectral transitions of polyenes. For a transition from level  $j$  to level  $j + 1$  we find that:

$$\Delta E = E_{j+1} - E_j = \frac{(j+1)^2 h^2}{8mL^2} - \frac{j^2 h^2}{8mL^2} = \frac{(2j+1)h^2}{8mL^2}$$

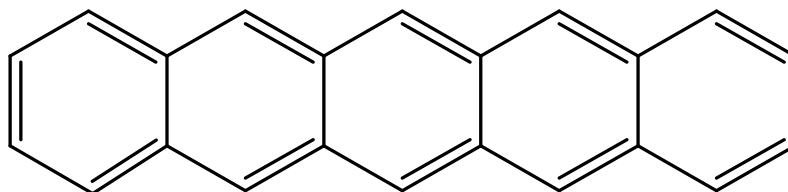
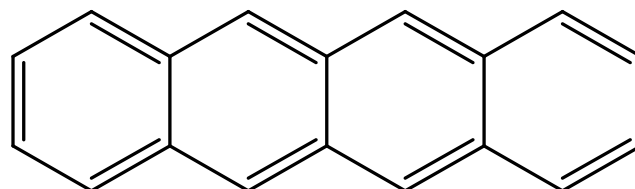
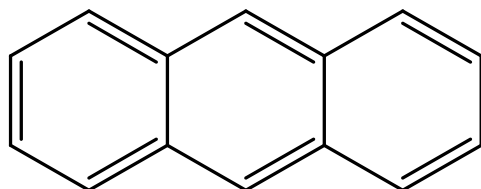
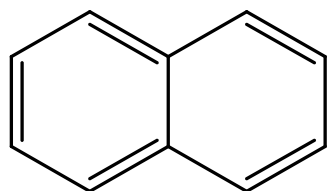
This model has predictive power for polyenes of any length. We can estimate the energy levels, electronic transitions and even the wave functions for the entire  $\pi$  system. It is illustrative to compare this simple model with the results for hexatriene obtained using Hückel theory.

# Aromatic molecules

The class of aromatic molecules is enormous, comprising all molecules that contain ring systems that obey the  $4n + 2$  rule. The optical properties of these molecules are dominated by the  $\pi-\pi^*$  absorption bands. Chemically they are hydrophobic and typically have similar reactivity with electrophiles to benzene. There are two general additional features that we wish to consider in this brief survey of molecular structure. The first is the role of the size of the conjugated system.

# Linear chains of fused aromatic rings

The second is the role of heteroatoms in the ring. The fused ring systems consisting of a linear chain of 2, 3 4 and 5 rings shown in the Figure have the names naphthalene, anthracene, tetracene and pentacene, respectively.



Series of fused ring aromatic molecules.

# Two-dimensional particle-in-a-box models

In addition to the particle on a circle model, there is a two-dimensional particle in a box model that is applicable. This is particularly useful for the long molecules in the series naphthalene, anthracene, tetracene, pentacene, etc. Assuming the box has length  $K$  along  $y$  and width  $L$  along  $x$ , the energy is given by:

$$E_{n,m} = \frac{n^2 h^2}{8mL^2} + \frac{m^2 h^2}{8mK^2}$$

# Allyl vs Cyclopropenyl Radical

We can apply group theory to two possible conformations of the 3-carbon  $\pi$ -system. Since we are only considering the energy of the  $\pi$ -bonding MOs our basis will consist only of a single p orbital contributed by each carbon atom in the molecule. The "linear" (or extended) polyene with 3 carbons is known as allyl radical. If the three carbons form a 3-membered ring then we have cyclopropenyl radical. Allyl radical is not linear, of course, and it has bond angle of approximately  $120^\circ$ . Thus, it belongs to the  $C_{2v}$  point group. Cyclopropenyl radical has bond angles of  $60^\circ$  and forms an equilateral triangle. Thus, it belongs to the  $D_{3h}$  point group.

# Hückel Theory Application to Allyl vs Cyclopropenyl Radical

Based on the Hückel theory analysis we find the energy level diagrams shown below. For allyl radical the energies of the bonding and anti-bonding orbitals are  $E = \alpha + \sqrt{2}\beta$  and  $E = \alpha - \sqrt{2}\beta$  and for the non-bonding orbital it is  $E = \alpha$ . For cyclopropenyl radical the energies  $E = 2\beta$  for the bonding and  $E = -\beta$  for the anti-bonding. Since each molecule has three electrons, the total energies are  $E = \sqrt{2}2\beta$  and  $E = 2\beta$  for allyl and cyclopropenyl radical, respectively. While both are stable molecules, we predict a stabilization of  $\Delta E = 0.172\beta$  for the cyclic molecule.

# Allyl radical analysis

Allyl radical belongs to the  $C_{2v}$  point group. The p-orbitals that comprise the  $\pi$  system can be divided into two groups, terminal and central.

$C_{2v}$	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	Total
$\Gamma_p$	2	-1	-2	1	
$A_1$	1	1	1	1	0
$A_2$	1	1	-1	-1	4
$B_1$	1	-1	1	-1	0
$B_2$	1	-1	-1	1	4

$$\Gamma_p = a_2 + b_2$$

$$\psi_{b_2} = \frac{1}{\sqrt{2}}(\phi_1 + \phi_3) \quad \psi_{a_2} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3) \quad \psi_{2,b_2} = \phi_2$$

$$\langle \psi_{b_2} | H | \psi_{b_2} \rangle = \frac{1}{2} (\langle \phi_1 | H | \phi_1 \rangle + \langle \phi_3 | H | \phi_3 \rangle) = \alpha$$

$$\text{Since } \langle \phi_1 | H | \phi_3 \rangle = 0$$

$$\langle \psi_{2,b_2} | H | \psi_{2,b_2} \rangle = \langle \phi_2 | H | \phi_2 \rangle = \alpha$$

$$\langle \psi_{b_2} | H | \psi_{2,b_2} \rangle = \langle \phi_1 | H | \phi_2 \rangle + \langle \phi_2 | H | \phi_3 \rangle = 2\beta$$

$$\langle \psi_{2,b_2} | H | \psi_{b_2} \rangle = \langle \psi_{b_2} | H | \psi_{2,b_2} \rangle$$

$$\begin{vmatrix} \alpha - E & 2\beta \\ 2\beta & \alpha - E \end{vmatrix} = 0$$

This determinant is sufficiently simple that we do not need to use the Hückel substitution to simplify it. We find that:

$$E_{b_2} = \alpha \pm \sqrt{2}\beta$$

$$E_{a_2} = \alpha$$



# Cyclopropenyl radical analysis

Cyclopropenyl radical belongs to the  $D_{3h}$  point group. The p-orbitals that comprise the  $\pi$  system are identical.

$D_{3h}$	E	$2C_3$	$3C'_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	Total
$\Gamma_p$	3	0	-1	-3	0	1	0
$A'_1$	1	1	1	1	1	1	0
$A'_2$	1	1	-1	1	1	-1	0
$E'$	2	-1	0	2	-1	0	0
$A''_1$	1	1	1	-1	-1	-1	0
$A''_2$	1	1	-1	-1	-1	1	12
$E''$	2	-1	0	-2	1	0	12

$$\Gamma_p = a''_2 + e''$$

# Cyclopropenyl SALCs

$$\psi_{e''} = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)$$

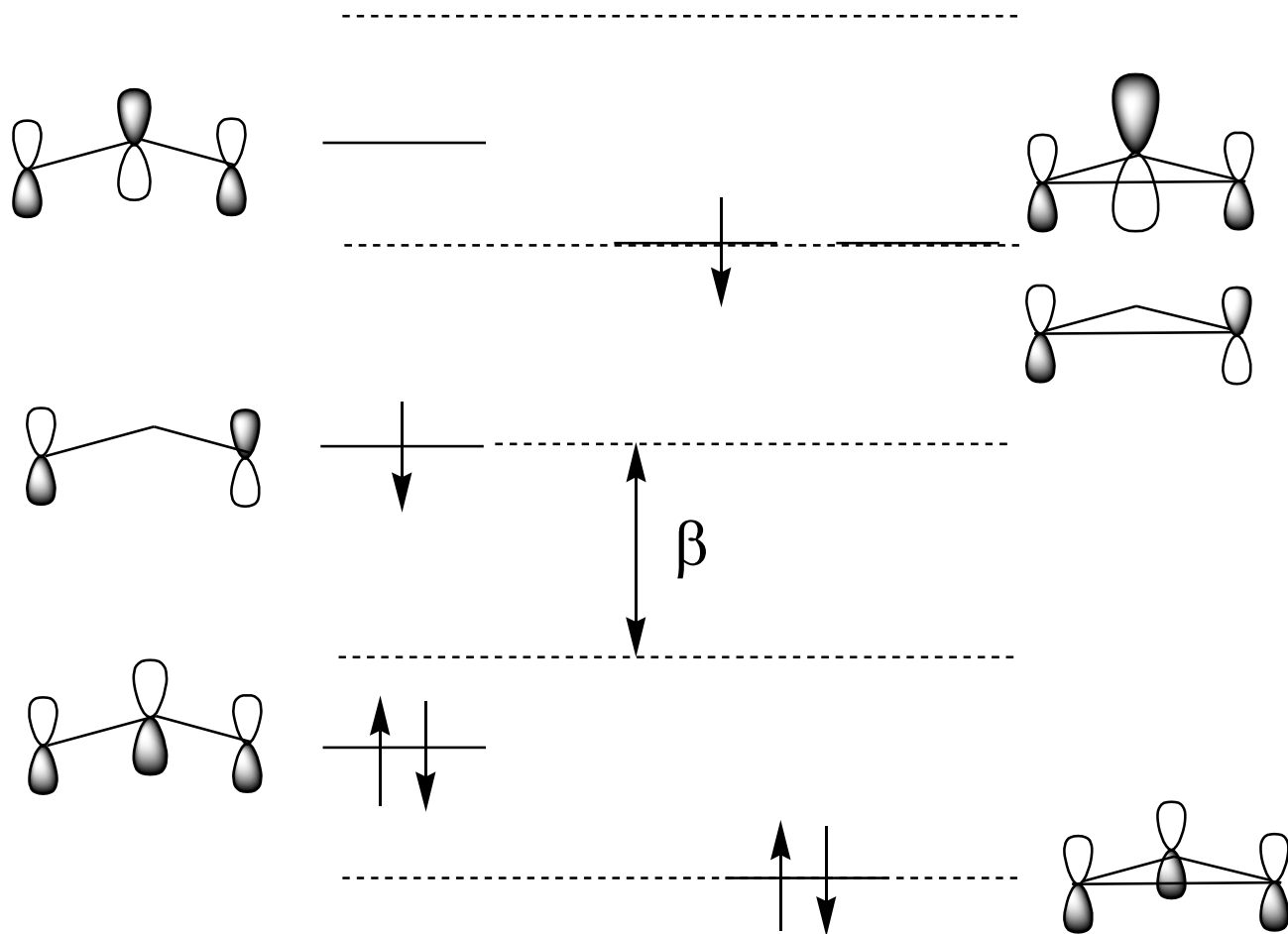
$$\psi_{e''} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3)$$

$$\psi_{a''_2} = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)$$

$$\langle \psi_{a''_2} | H | \psi_{a''_2} \rangle = \frac{1}{3} (\langle \phi_1 | H | \phi_1 \rangle + \langle \phi_2 | H | \phi_2 \rangle + \langle \phi_3 | H | \phi_3 \rangle)$$

$$+ \frac{1}{3} (2\langle \phi_1 | H | \phi_2 \rangle + 2\langle \phi_2 | H | \phi_3 \rangle + 2\langle \phi_1 | H | \phi_3 \rangle) = \alpha + 2\beta$$

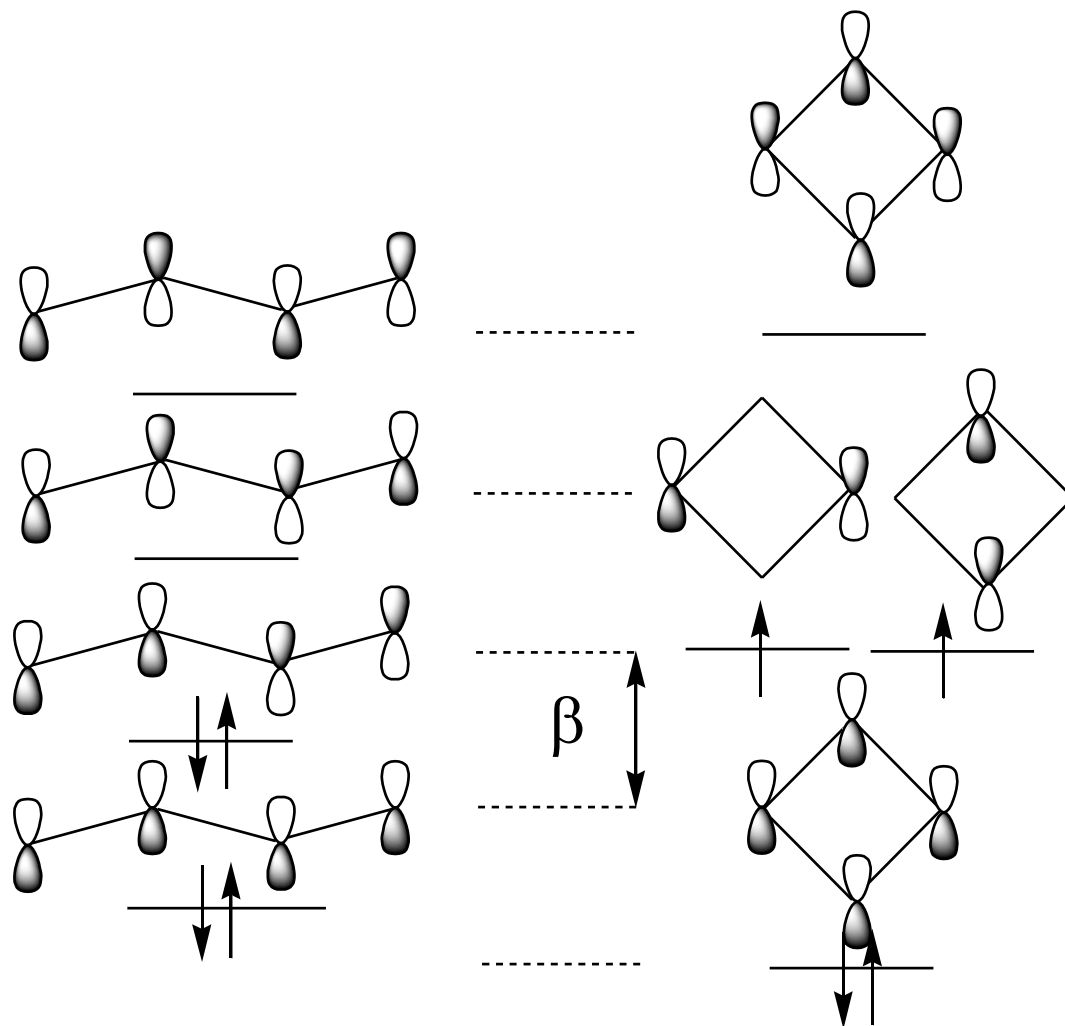
$$\langle \psi_{e''} | H | \psi_{e''} \rangle = \frac{1}{2} (\langle \phi_1 | H | \phi_1 \rangle + \langle \phi_3 | H | \phi_3 \rangle - 2\langle \phi_1 | H | \phi_3 \rangle) = \alpha - \beta$$



Energy level diagram for the comparison between allyl radical and cyclopropenyl radical. The energy level diagram is given in units of the Hückel resonance parameter  $\beta$ .

# Butadiene vs Cyclobutadiene

We can take a similar approach to compare the energies of the extended and cyclic system consisting of 4 carbons. Once again, we consider only the p-orbitals for this analysis. The energy diagram for these systems in the Hückel approximation is given in Figure. The energy of the  $\pi$ -system in butadiene is  $4.48\beta$ , compared to  $4\beta$  for cyclobutadiene. Thus, the cyclized butadiene is less stable than the corresponding linear molecule. This is an example of anti-aromatic behavior. Cyclic molecules with  $4n$  electrons are not stable relative to their linear counterparts.



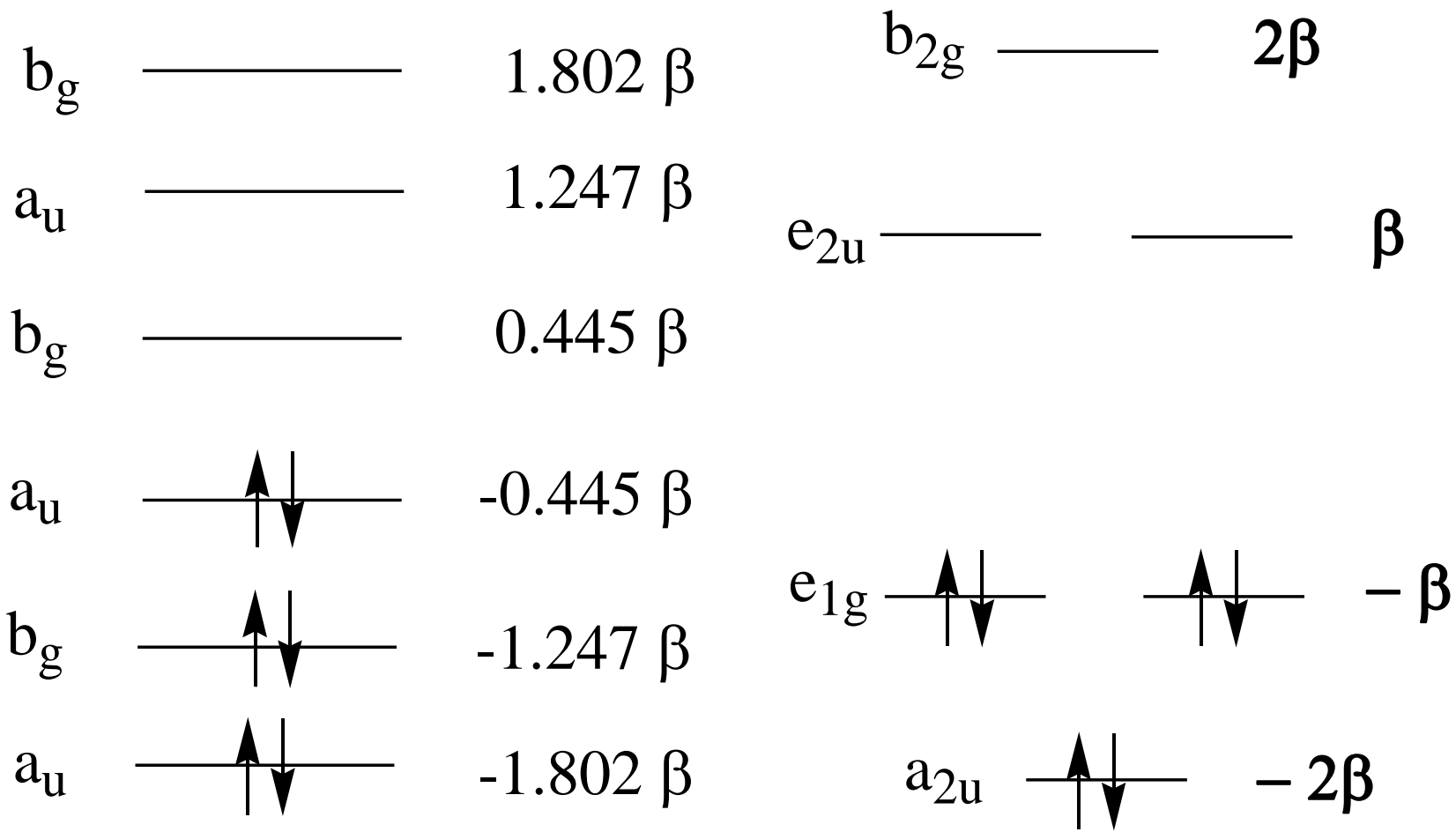
Energy level diagram for the comparison between butadiene and cyclobutadiene. The energy level diagram is given in units of the Hückel resonance parameter  $\beta$ .

# Hexatriene vs Benzene

We continue with the series, although we have omitted the interesting case of pentadienyl radical and its cyclic conformer, cyclopentadienyl radical. The six carbon extended molecule hexatriene can be treated using Hückel theory as either a  $C_{2v}$  or  $C_{2h}$  molecule (depending on whether it is in the cis or trans conformation). The result is the same at the level of Hückel and we have arbitrarily chosen trans-hexatriene ( $C_{2h}$ ) for the comparison. There are three different symmetry related sets and thus the secular determinant is a 3 x 3 matrix. Numerical methods must be used to solve it. Benzene is, of course, a well-studied highly symmetrical molecule that belongs to the  $D_{6h}$  point group. The energies and occupations of the MOs for each molecule are shown in the Figure.

# Hexatriene vs Benzene

The energy of the  $\pi$ -system in hexatriene is  $6.98\beta$ , compared to  $8\beta$  for benzene. Thus, the cyclized 6-membered ring is more stable than the corresponding linear molecule. This is an example of aromatic behavior. The consideration of related aromatic molecules leads to the  $4n + 2$  rule. Molecules that have  $4n + 2$   $\pi$  electrons are stable as cyclic molecules relative to their linear counterparts.

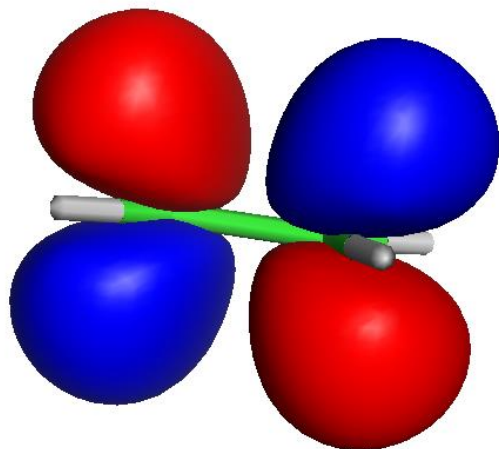


Comparison of the energy levels for hexatriene and benzene calculated using the Hückel approximation.

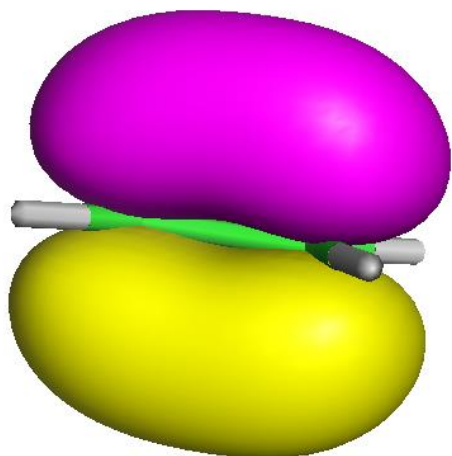


# Ethene DFT Energies and MOs

$b_{2g}$



$b_{3u}$



MO	irrep	Ha	eV	Occup
1	ag	-9.881290	-268.884	2.000
2	b1u	-9.880624	-268.866	2.000
3	ag	-0.685800	-18.662	2.000
4	b1u	-0.520221	-14.156	2.000
5	b2u	-0.418055	-11.376	2.000
6	ag	-0.371634	-10.113	2.000
7	b3g	-0.311322	-8.471	2.000
8	b3u	-0.242838	-6.608	2.000
9	b2g	-0.030348	-0.826	0.000
10	ag	0.093546	2.546	0.000
11	b2u	0.096304	2.621	0.000
12	b1u	0.122793	3.341	0.000

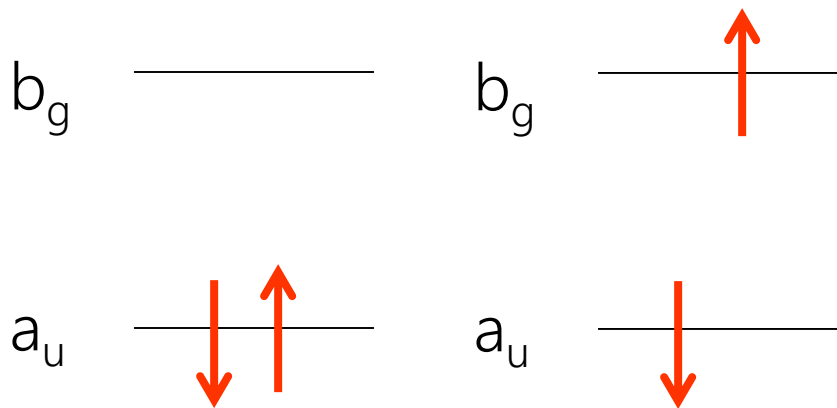
HOMO -> LUMO

$$\Delta E = 5.78 \text{ eV}$$

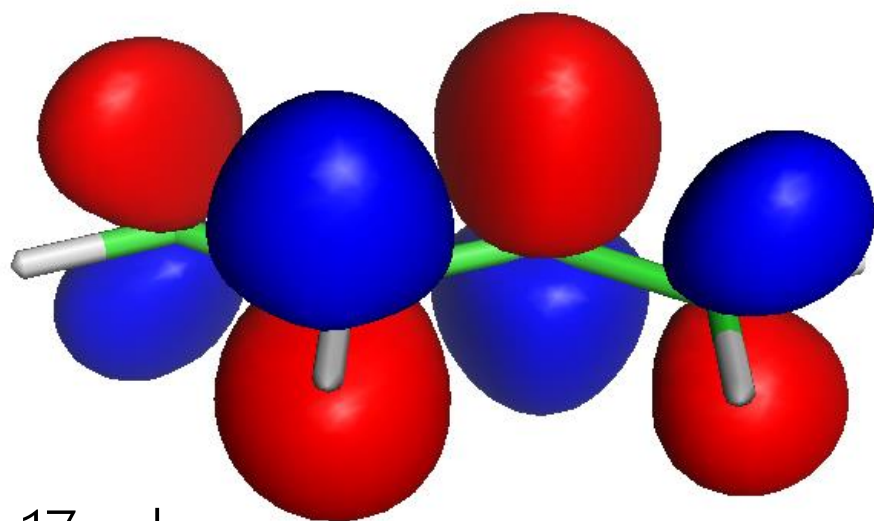
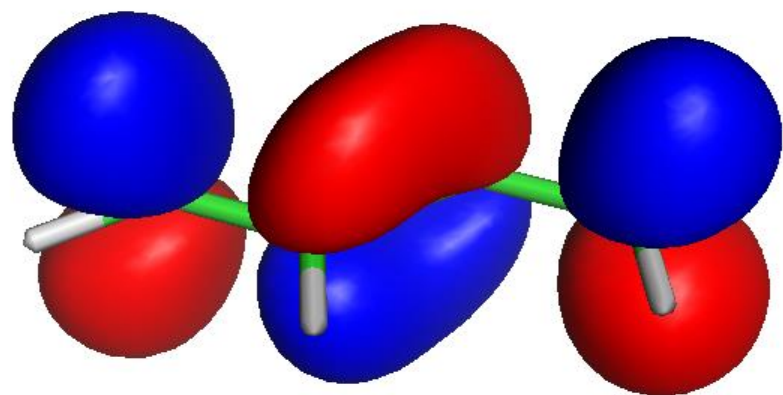
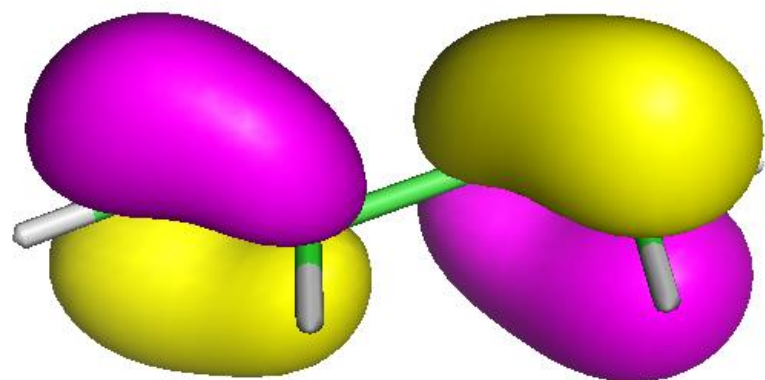
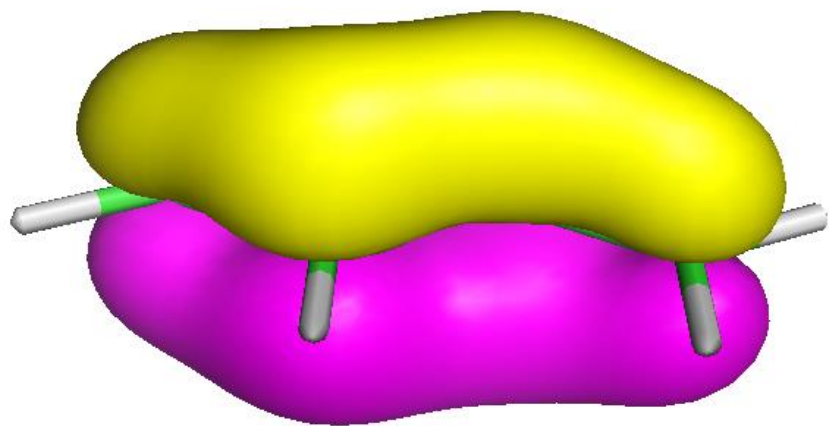
# Trans butadiene Molecular orbitals

$C_{2h}$	E	$C_2$	i	$\sigma_h$	linear	Quadrat
$A_g$	1	1	1	1	$R_z$	$x^2, y^2, z^2, xy$
$B_g$	1	-1	1	-1	$R_x, R_y$	$xz, yz$
$A_u$	1	1	-1	-1	z	
$B_u$	1	-1	-1	1	x, y	

$$\Delta E = 3.94 \text{ eV}$$

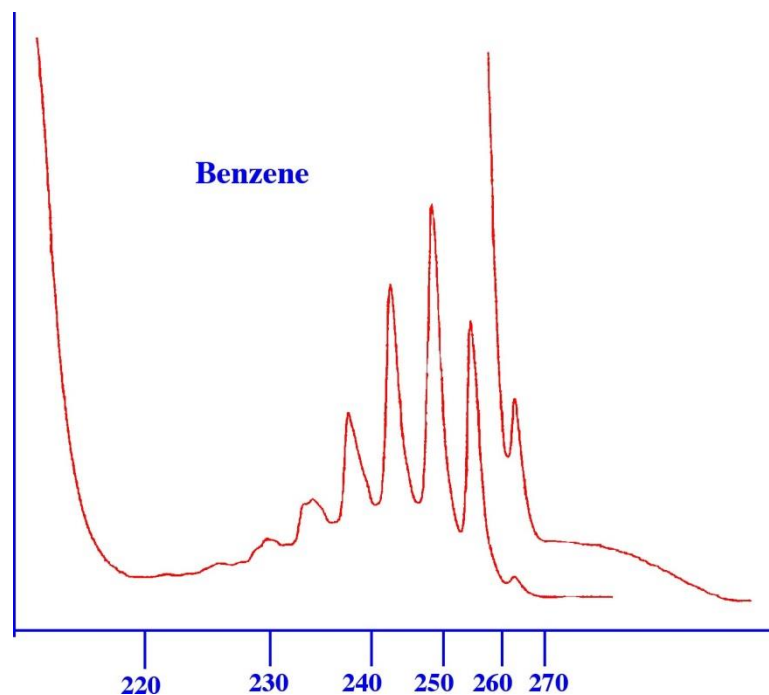


MO	Irrep	eV	Occupation
1	$a_g$	-269.085	2.000
2	$b_u$	-269.078	2.000
3	$a_g$	-268.876	2.000
4	$b_u$	-268.875	2.000
5	$a_g$	-19.916	2.000
6	$b_u$	-18.033	2.000
7	$a_g$	-14.871	2.000
8	$b_u$	-13.504	2.000
9	$b_u$	-11.354	2.000
10	$a_g$	-11.276	2.000
11	$a_g$	-9.463	2.000
12	$b_u$	-9.299	2.000
13	$a_g$	-8.308	2.000
14	$a_u$	-7.962	2.000
15	$b_g$	-5.719	2.000
16	$a_u$	-1.783	0.000
17	$b_g$	0.850	0.000
18	$b_u$	1.932	0.000



# The important role of benzene in structure and spectroscopy studies

Benzene is reactive via electrophilic substitutions. There is a large number of substituted benzenes that are important molecules in everyday experience and even more that are synthetic intermediates. The stability of the aromatic ring is a key aspect of the reactivity. The spectrum of benzene is a model for all molecular spectroscopy of aromatic molecules. It consists of a weak vibronic band shown on the right at 240-270 nm. There is also a very strong absorption at 168 nm.



# Benzene transitions

In benzene both the HOMO and LUMO are doubly degenerate. This is a common pattern observed in all aromatic molecules. The allowed transitions will have

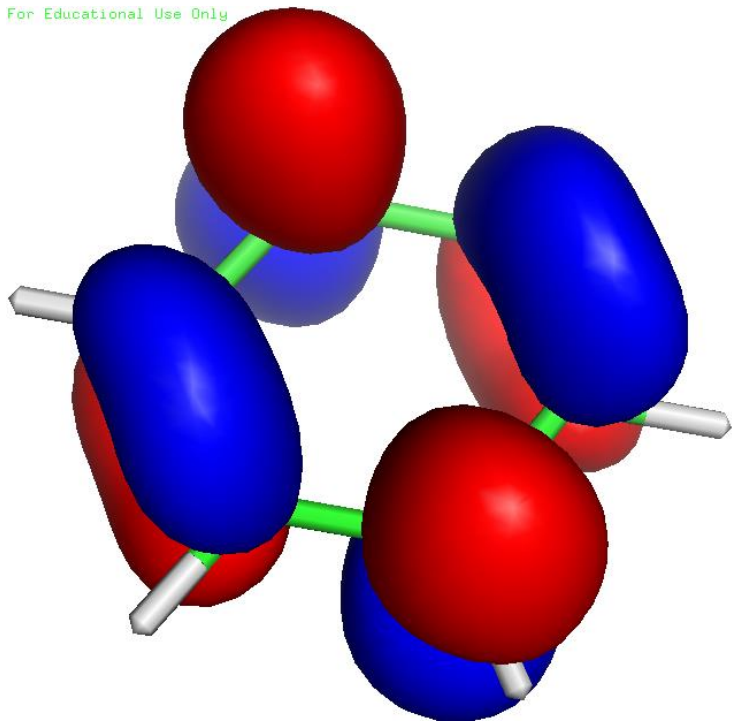
$$\Gamma_{\text{homo}} \Gamma_{x,y \text{ or } z} \Gamma_{\text{lumo}} = A_{1g}$$

Since it can be tedious to perform separate calculations for x, y and z, we can also use the shortcut:

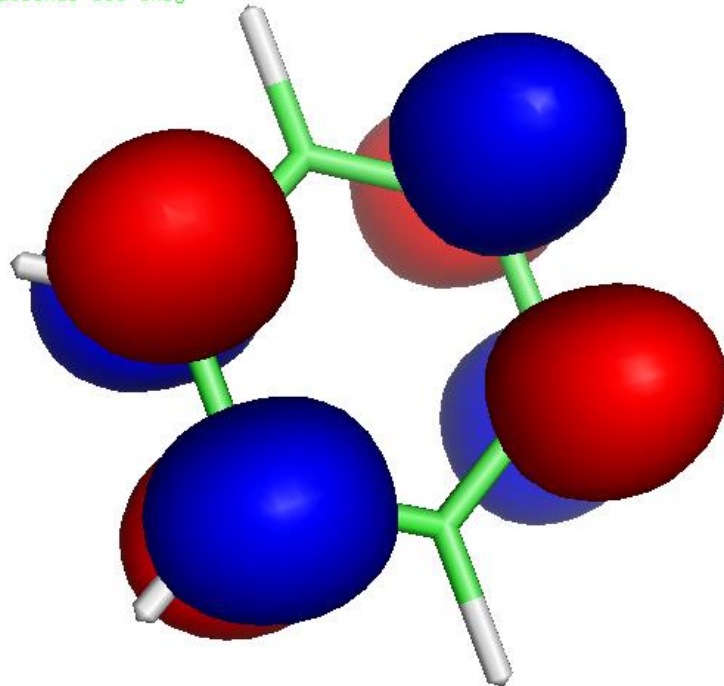
$$\Gamma_{\text{homo}} \Gamma_{\text{lumo}} = \Gamma_{x,y \text{ or } z}$$

MO	Irrep	eV	Occupation
7	a <sub>1g</sub>	-21.136	2.000
8	e <sub>1u</sub>	-18.361	2.000
10	e <sub>2g</sub>	-14.759	2.000
12	a <sub>1g</sub>	-12.839	2.000
13	b <sub>1u</sub>	-11.145	2.000
14	b <sub>2u</sub>	-10.844	2.000
15	e <sub>1u</sub>	-10.189	2.000
17	a <sub>2u</sub>	-8.946	2.000
18	e <sub>2g</sub>	-8.204	2.000
20	e <sub>1g</sub>	-6.231	2.000
22	e <sub>2u</sub>	-1.065	0.000
24	a <sub>1g</sub>	1.500	0.000
25	e <sub>1u</sub>	2.857	0.000
27	b <sub>2g</sub>	2.927	0.000
28	e <sub>2g</sub>	4.039	0.000

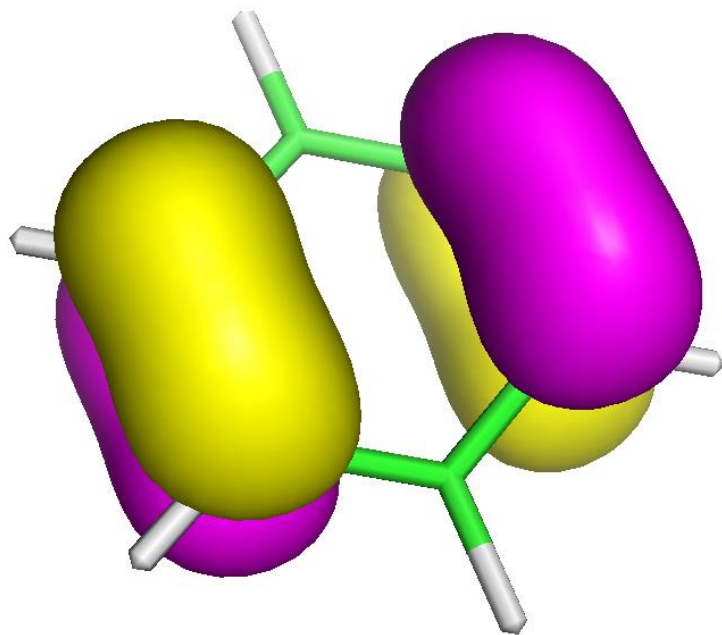
For Educational Use Only



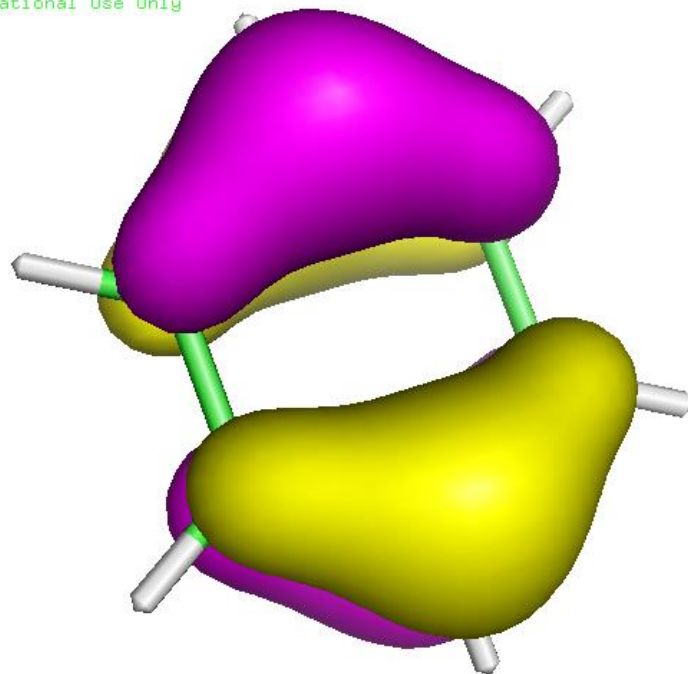
For Educational Use Only



For Educational Use Only

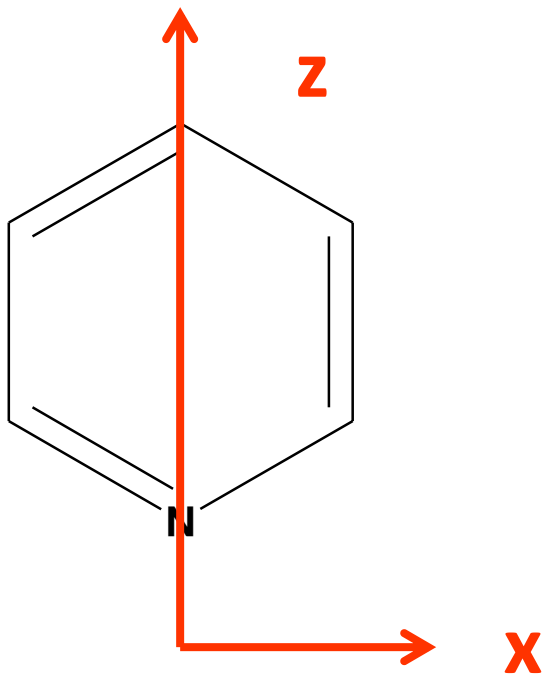


For Educational Use Only



# Pyridine

Pyridine has many of the spectroscopic characteristics of Benzene. However, pyridine has the lone pair of the N atom, Which leads to the possibility of  $n-\pi^*$  transitions in addition To the  $\pi-\pi^*$  transitions of benzene. Pyridine belongs to the  $C_{2v}$  point group.



$C_{2v}$	E	$C_2$	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
$A_1$	1	1	1	1
$A_2$	1	1	-1	-1
$B_1$	1	-1	1	-1
$B_2$	1	-1	-1	1

# Pyridine transitions

The n- $\pi^*$  is:

21 a<sub>1</sub> -> 22 b<sub>2</sub>

Weak absorption 280 nm

The  $\pi$ - $\pi^*$  transitions are similar to benzene:

19 b<sub>2</sub> -> 22 b<sub>2</sub> or 23 a<sub>2</sub>

20 a<sub>2</sub> -> 22 b<sub>2</sub> or 23 a<sub>2</sub>

Moderate absorption

274 nm, 230 nm

Strong absorption

169 nm

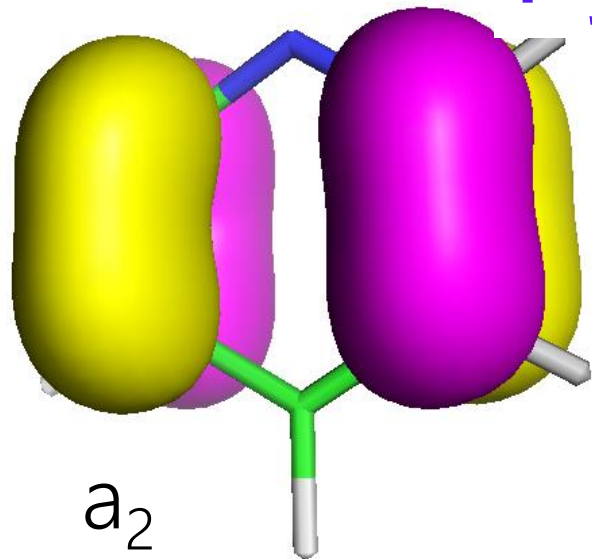
MO	Irrep	eV	Occupation
11	a <sub>1</sub>	-15.520	2.000
12	a <sub>1</sub>	-13.042	2.000
13	b <sub>1</sub>	-11.820	2.000
14	a <sub>1</sub>	-11.487	2.000
15	b <sub>1</sub>	-10.459	2.000
16	b <sub>2</sub>	-9.824	2.000
17	a <sub>1</sub>	-9.816	2.000
18	b <sub>1</sub>	-8.800	2.000
19	b <sub>2</sub>	-7.222	2.000
20	a <sub>2</sub>	-6.623	2.000
21	a <sub>1</sub>	-5.896	2.000
22	b <sub>2</sub>	-1.778	0.000
23	a <sub>2</sub>	-1.412	0.000
24	a <sub>1</sub>	1.519	0.000
25	b <sub>2</sub>	2.421	0.000



# Pyridine

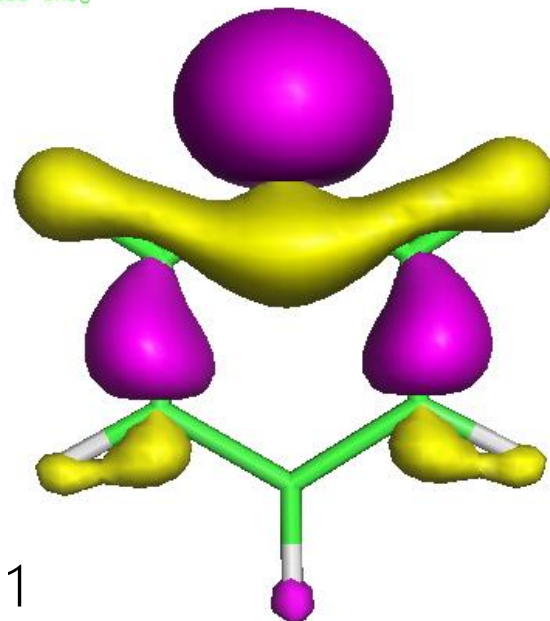
20

$a_2$



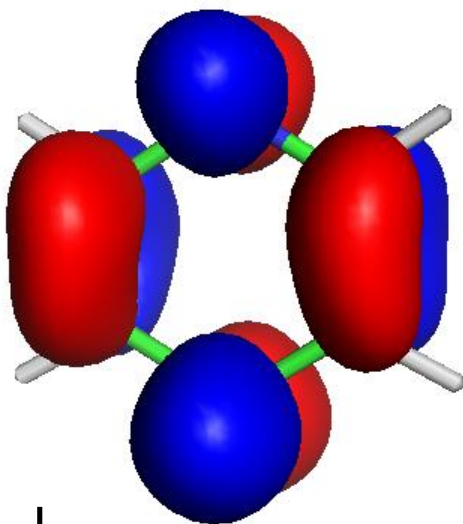
21

$a_1$



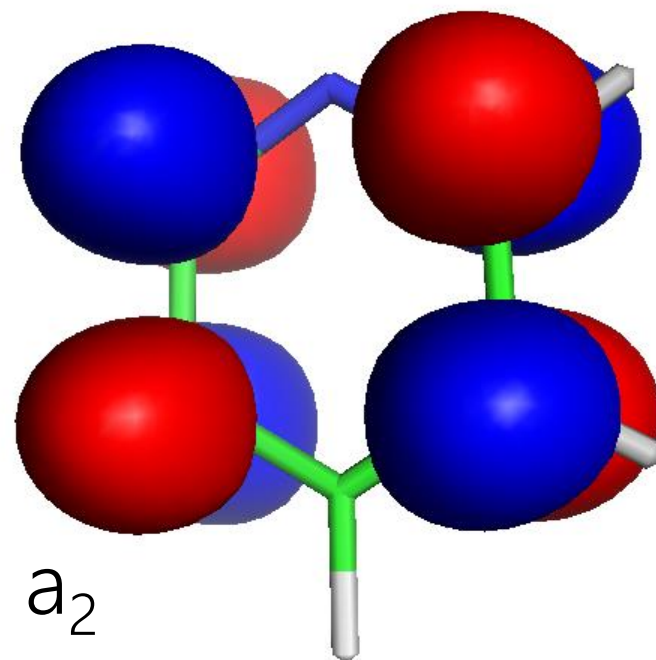
22

$b_2$



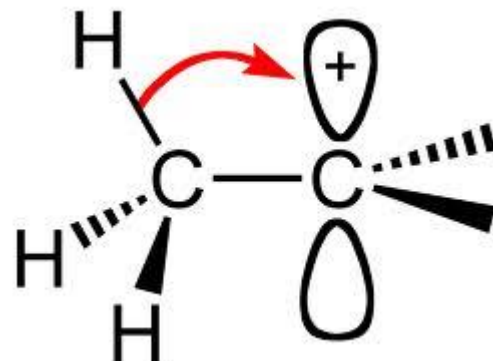
23

$a_2$



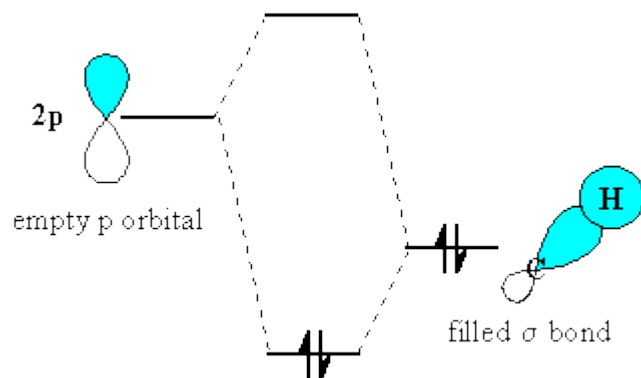
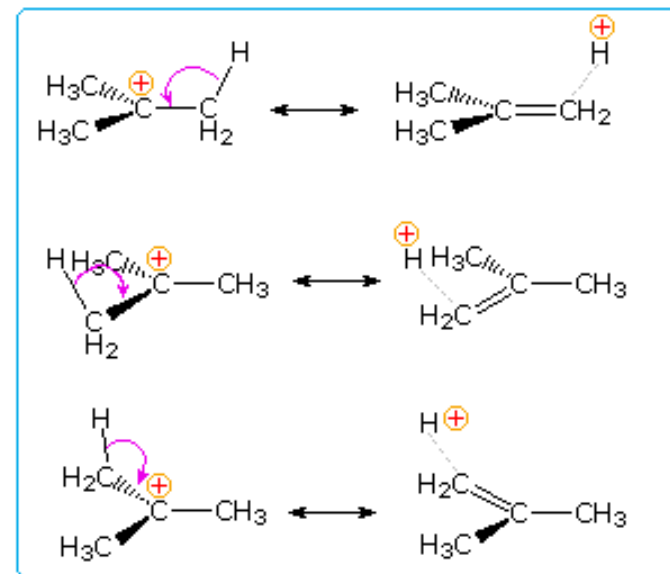
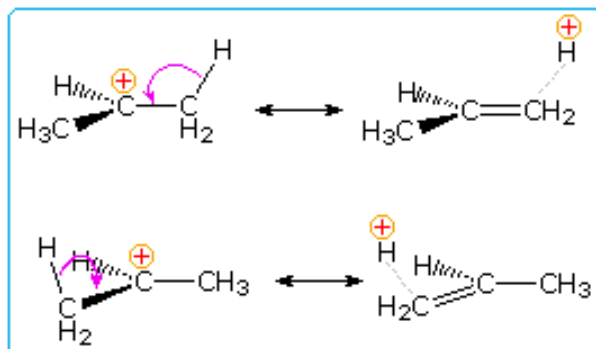
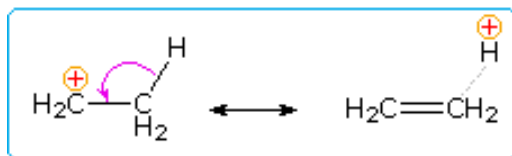
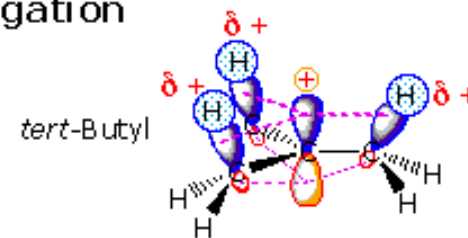
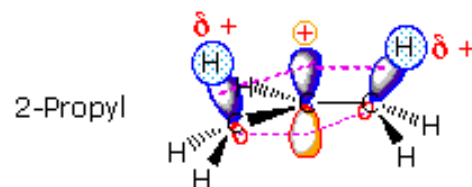
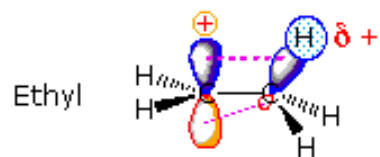
# Hyperconjugation

Hyperconjugation is the interaction of the electrons in C-H or C-C sigma bond with an adjacent empty (or partially filled) non-bonding p-orbital, anti-bonding p-orbital or even filled bonding p-orbital to give an extended molecular orbital that increases the stability of the system. Only electrons in bonds that are adjacent to the positively charged carbon can stabilize a carbocation by hyperconjugation.



# Hyperconjugation

## Stabilization of Carbocations by Hyperconjugation



**Mechanism for stabilization**

# Effect of Hyperconjugation on Thermochemistry

In 1937, Kistiakowsky and co-workers studied the effect of hyperconjugation on thermochemistry of addition reactions to unsaturated and cyclic compounds.

They noticed that heats of hydrogenation for gas-phase reactions of various molecules containing one a single double bond were affected by the bonding of an adjacent C-C bond. For example, the monosubstituted alkene compounds propylene, 1-butene, 1-heptene, isopropyl-ethylene all had similar heat of hydrogenation, which were lower than the that for ethene. They concluded that any C-C bonded group is equally effective in stabilizing the adjacent alkene. The overall range of the  $\Delta H$  for hydrogenation for these compounds was only 0.8 kcal/mol.