

Quantum Chemistry

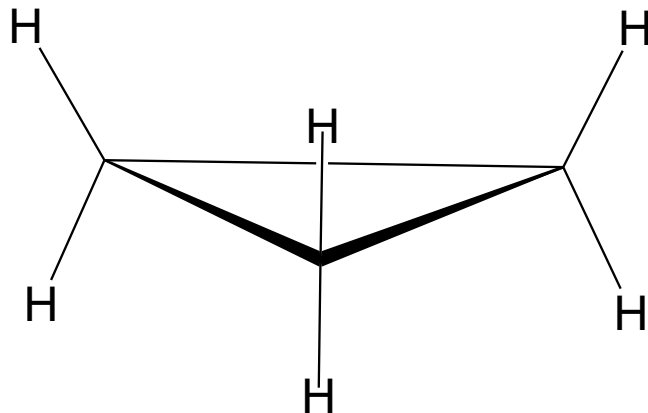
Lecture 30

Orbital Interactions
Chemical reactivity

NC State University

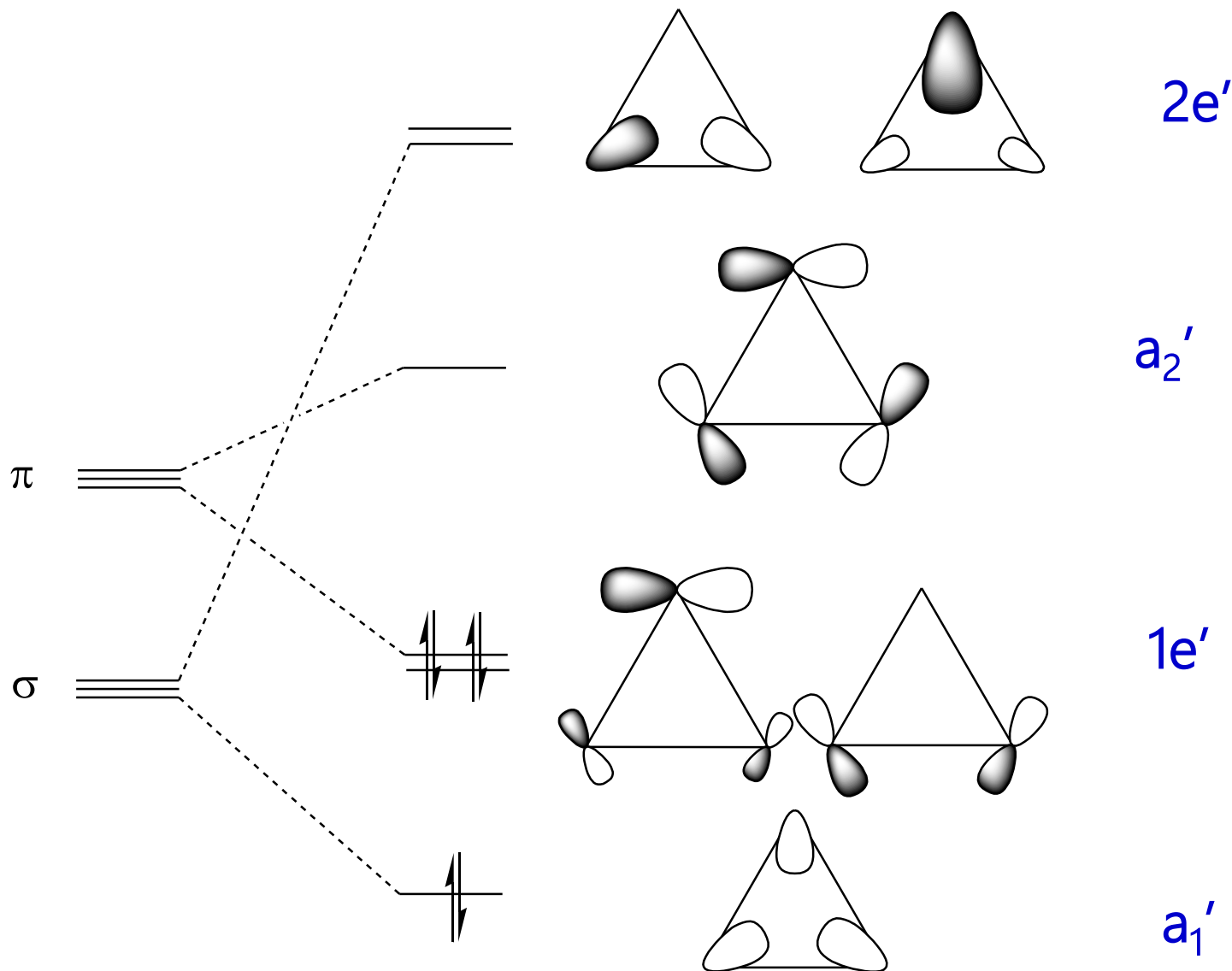
Relationship between orbital interactions and reactivity

The importance of understanding symmetry and basic orbital interactions is evident when we examine chemical reactions. Examination of structure and “shortest distance” paths for reactions can be misleading. Only when we examine the orbital interactions do the reasons for particular reaction path and transition state geometries become clear. For this reason we return to orbital interactions from the vantage point of understanding reaction pathways.



Cyclopropane

D_{3h}



Mixing of orbitals

This analysis starts with two different sets of in-plane orbitals derived from the 2p set. The σ set is directed towards the center of symmetry and the π set is perpendicular to the center of symmetry.

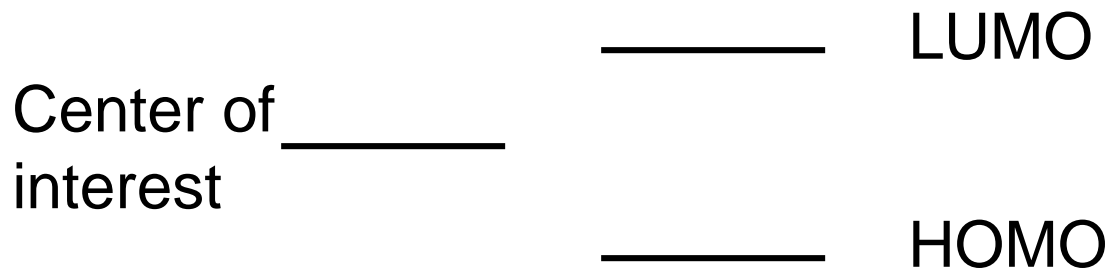
The e' orbitals can mix since they have the same symmetry. There are both bonding (+) and anti-bonding (-) linear combinations of these orbitals.

In this molecule the bulk of the electron density lies off of the C-C bond axis. The so-called banana bonds are the equivalent of ring strain, which is quite large in this system.

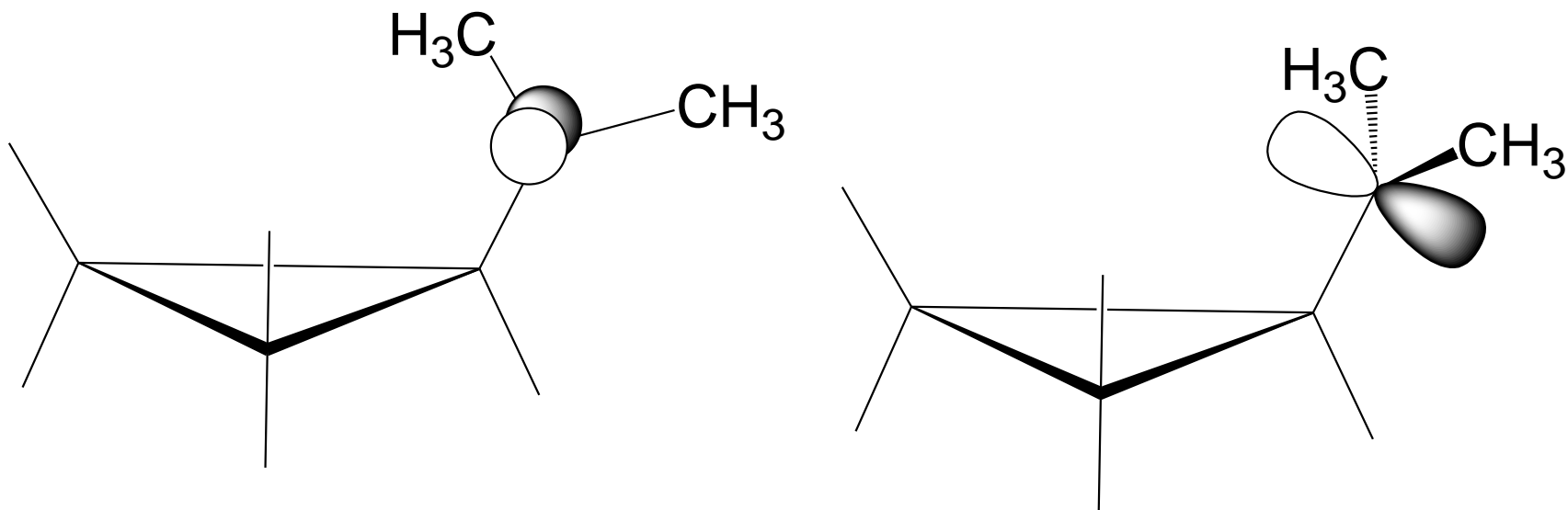
Orbital perturbations

We can think of the interaction of the orbitals in a molecular and an appendage as a perturbation. We could think of a coupling V between a group and the orbitals, but there is also an energy ΔE . The perturbation in the wave function is approximately equation to $V/\Delta E$. Using this kind of thinking we can reason out how electron density in orbitals can stabilize vacant orbitals (i.e. cations) or how two spins are coupled.

Often the spin or vacant orbital is somewhere between the HOMO and LUMO. If this is the case then the coupling can be to the HOMO for cationic centers and to the LUMO for lone pairs.



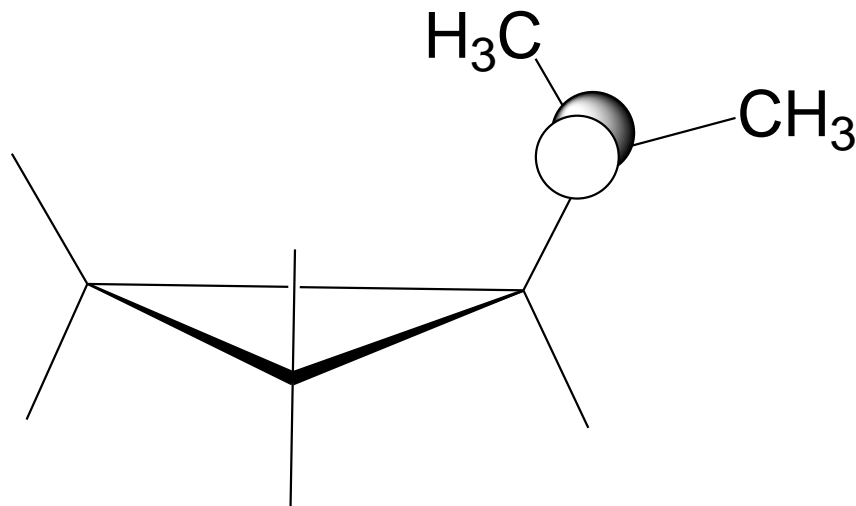
Stabilization of carbocation



The cyclopropane ring stabilizes one carbocation geometry. The p-orbital shown is the empty orbital in the cation. The orientation that maximizes overlap with occupied orbitals will be the most stable since there can be electron transfer from the filled orbital to the empty p orbital. The orbital on the left has overlap with e' and is therefore more stable.

Cyclopropane stabilization of carbocation by hyperconjugation

The logic behind the e' coupling to the carbocation is the fact that the HOMO is much closer in energy to the vacant p orbital. The a_1' orbital is significantly lower in energy and therefore has much weaker coupling. The d' dominates.



The coupling of remote orbitals

One of the ways we can analyze a molecule is in terms of fragments. This is particularly useful for understanding spin coupling and electron transfer (charge transfer) systems. In order to analyze a molecule in terms of the coupling of electrons on remote centers for the purposes of charge transfer we can think of the orbital of a donor and acceptor as well as bridge. For spin-spin coupling we call the remote orbitals center 1 and center 2.



Conceptual decomposition of a molecule. A and D could be s, p or d orbitals on atoms that are connected by bonds.

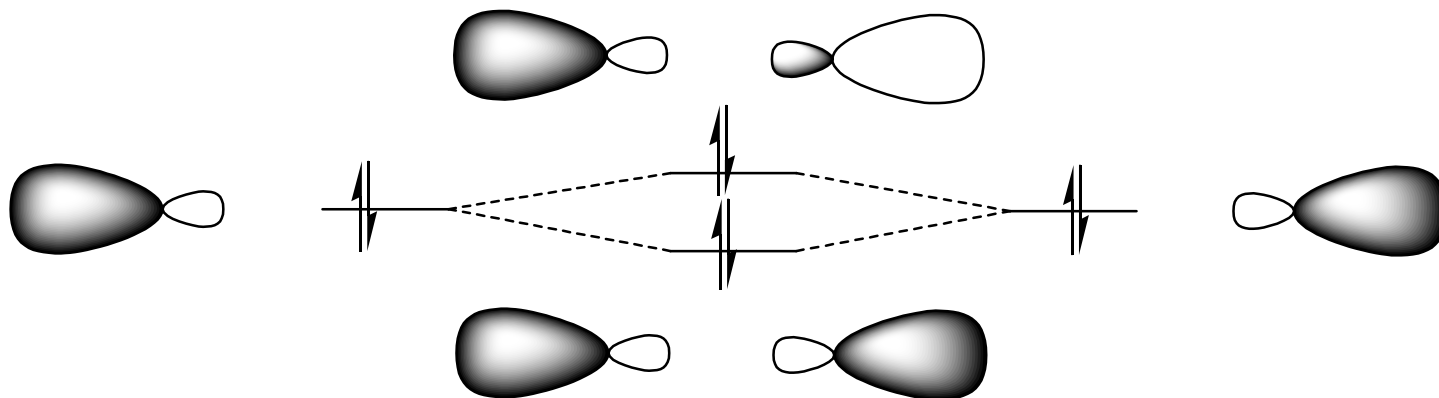
Through-bond vs. Through-space

Since all bonding involves interactions of orbitals we can compare the role of molecule bridge (a collection of bonds and their associated electron density) with the interaction of the remote orbitals when only empty space is present between them. We call the molecular bridge a through-bond interaction and, obviously, the empty space is a through space interaction. Clearly, as with all interactions that depend on overlap, the larger the distance, the smaller the interaction.

The important point here is that the molecular bridge can strongly affect the energy ordering and strength of interaction of two remote sites.

Through-space interaction

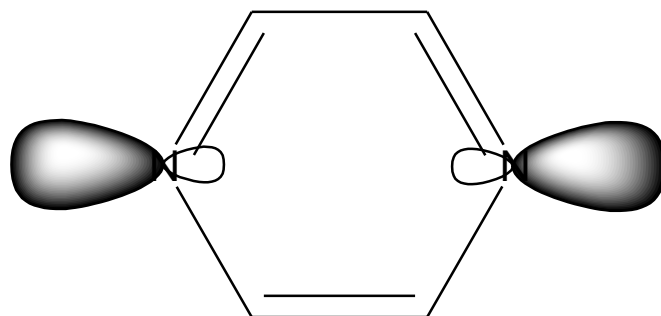
We examine the interaction of two p-orbitals a relatively large distance (e.g. $\sim 4 \text{ \AA}$). There will be two linear combinations as with all such interactions, however, the interaction energy will be expected to be very small because the overlap is small. This example is shown in the figure below.



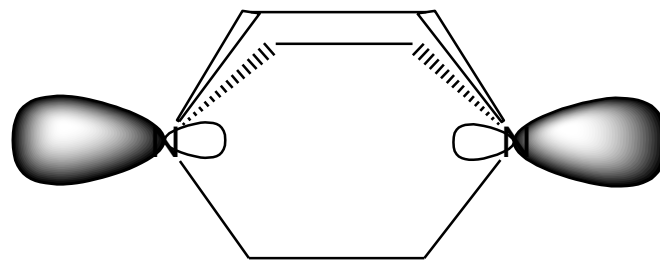
Since both orbitals are filled we find that both the linear combinations are also filled. The interesting comparison can be made with a bridged through bond interaction.

Through-bond interaction

We can compare two p-orbitals in a molecule such as pyrazine or diazabicyclooctane (DABCO). In each of these cases there is a series of bonds that connect two lone pairs.



Pyrazine



DABCO

The role bridging orbitals

In the example shown we can imagine the σ -bonding network will be important for the through bond interaction of the two remote p-orbitals. Comparison using DFT calculations shows that the effect of through-bond coupling is much larger than through space coupling (orders of magnitude larger!).

Moreover, in some cases the symmetry of bonding “pathways” can even change the order of the energy interactions.

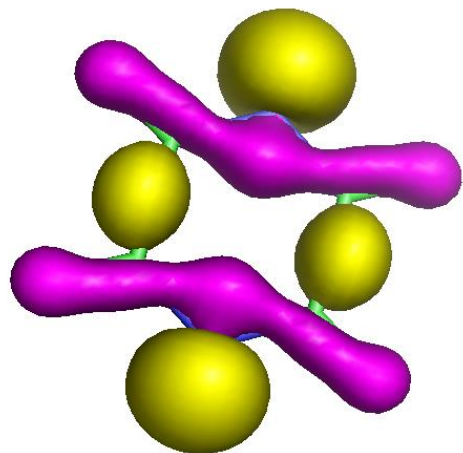
DABCO is an example of this and that is given as a homework problem.

The key point of the problem is ask how the energy level splitting and ordering in DABCO compares to our expectation based on the through space configuration. We actually do not have a quantitative value for the through-space interaction, but we can guess it will be a very small splitting indeed at such a large distance (on the atomic scale).

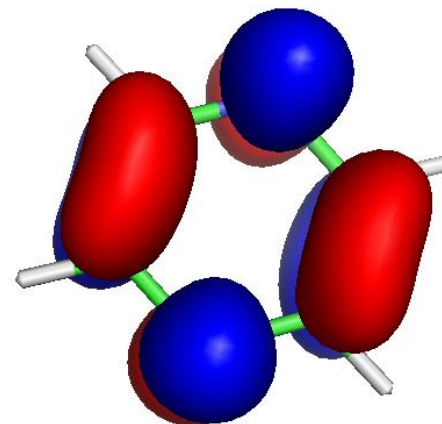
Types of bridging orbitals

In addition to σ -bonding, there are also π -bonding through-bond “pathways”. We can use the word pathways since we can imagine that electrons can virtually occupy the LUMO and NLUMO of the bridge in their coupling with a remote site. The lower the energy of the LUMO/NLUMO, the greater the coupling. Since the splitting of π - π^* is typically smaller than σ - σ^* , the π -system can often be important for through-bond coupling. The analysis must carefully consider the orbital interactions of the donor/acceptor with the bridge. For example, in pyrazine, the remote p orbitals of the lone pairs cannot couple through the π -system by symmetry. In pyrazine the π -system is a spectator to the through-bond coupling.

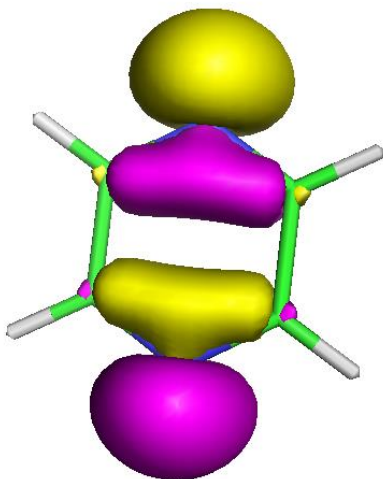
Molecular orbitals of pyrazine



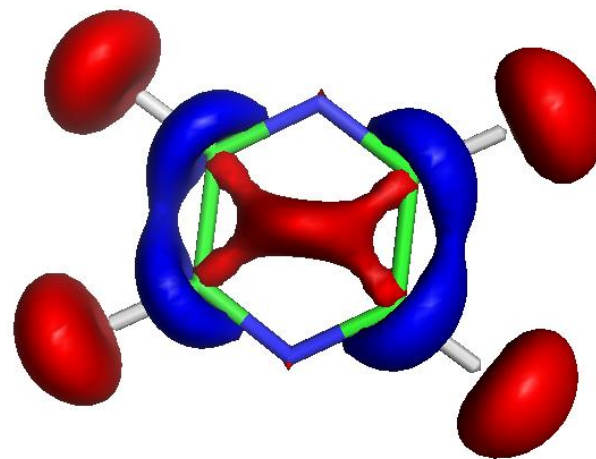
HOMO



LUMO



HOMO - 1



LUMO + 1

Types of bridging orbitals

Note that ordering of the remote p-orbital linear combinations is the reverse of what we would have expected based on the through-space consideration. This is because the remainder of the σ -framework has at least one node in its wave function at this energy. The mixing of the remote p-orbitals with the σ -framework then requires the remote p-orbitals to couple through the nodal structure of the available σ -bonding network. We can think of that network as giving rise to even and odd combinations depending on whether there is an even or odd number of nodes in the intervening s-bonding system. It so happens that the lowest energy bridge orbital that is close to the p-orbital energies has a 3 nodes (see the HOMO – 1). The HOMO has 4 nodes, an even number and hence a positive linear combination for the two remote p-orbitals.

The concept of superexchange

The exchange integral is operative mainly for orbitals that have overlap. Distant orbitals considered above do not have significant overlap except through the bridge. Thus, we can consider the very small direct exchange of D and A (through space) to be:

$$\langle A|H|D\rangle$$

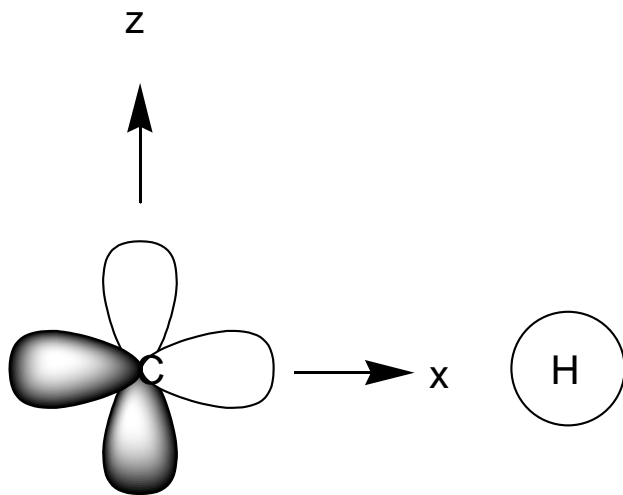
The effect of the bridge B can be understood using perturbation theory. The exchange via the bridge is known as superexchange. It is given by:

$$\sum_B \frac{\langle A|H|B\rangle\langle B|H|D\rangle}{E_B - E_D} + \frac{\langle A|H|B\rangle\langle B|H|D\rangle}{E_B - E_A}$$

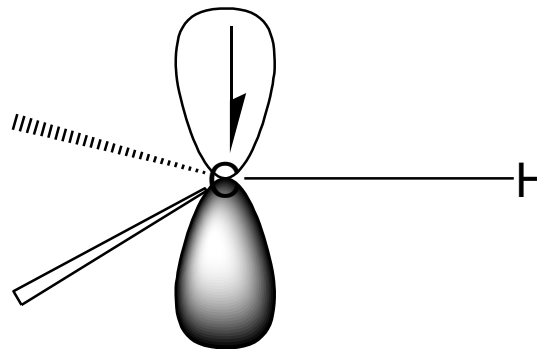
Superexchange is important in the theory of anti-ferromagnetic coupling or other spin coupling mechanisms in EPR and even NMR as well as in long distance electron transfer.

Spin polarization

In considering how unpaired spins can “communicate” through a molecular bridge, we can first examine a simple system to understand how spin polarization can be transmitted in a molecule. We examine C-H system. This system consists of three bonds and three electrons. We consider the p_x and p_z orbital on carbon and a $1s$ orbital on H.



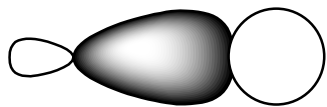
Orbitals involved



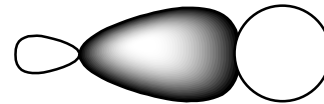
Unpaired spin

Spin polarization

If we consider the possible orbital interactions we can distinguish between a case that has no spin polarization and a case that has spin polarization. These are shown below.



— ϕ_3



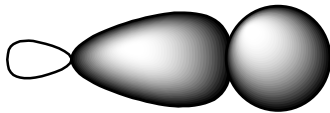
— ϕ_3



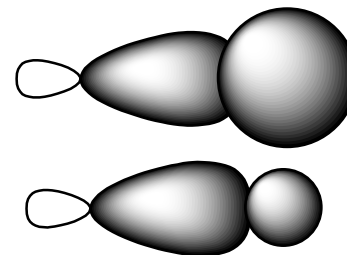
— ϕ_2



— ϕ_2



— ϕ_1



— ϕ_1

No spin polarization

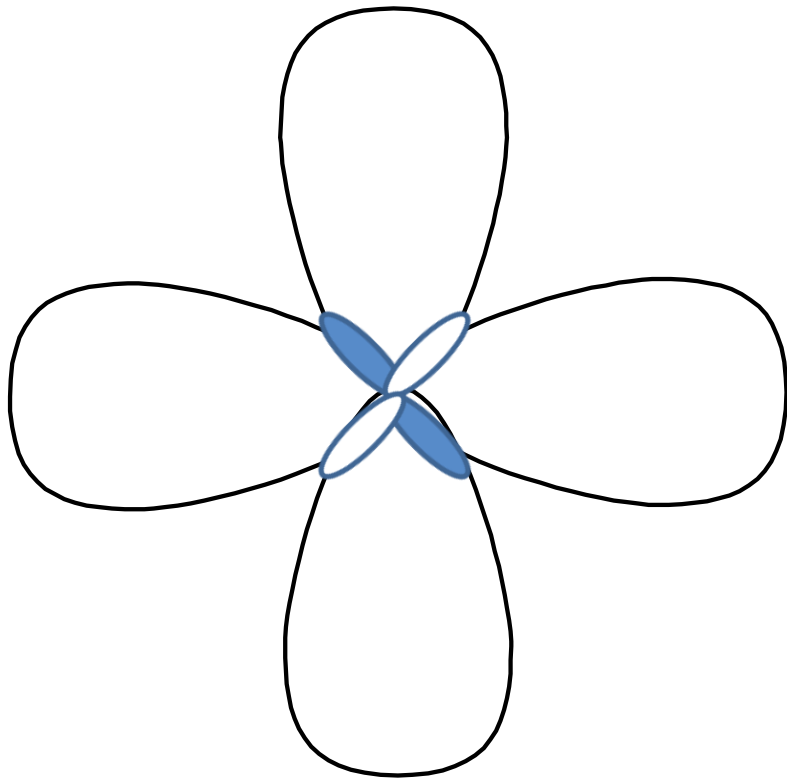
spin polarization

Origin of spin polarization: Experimental significance

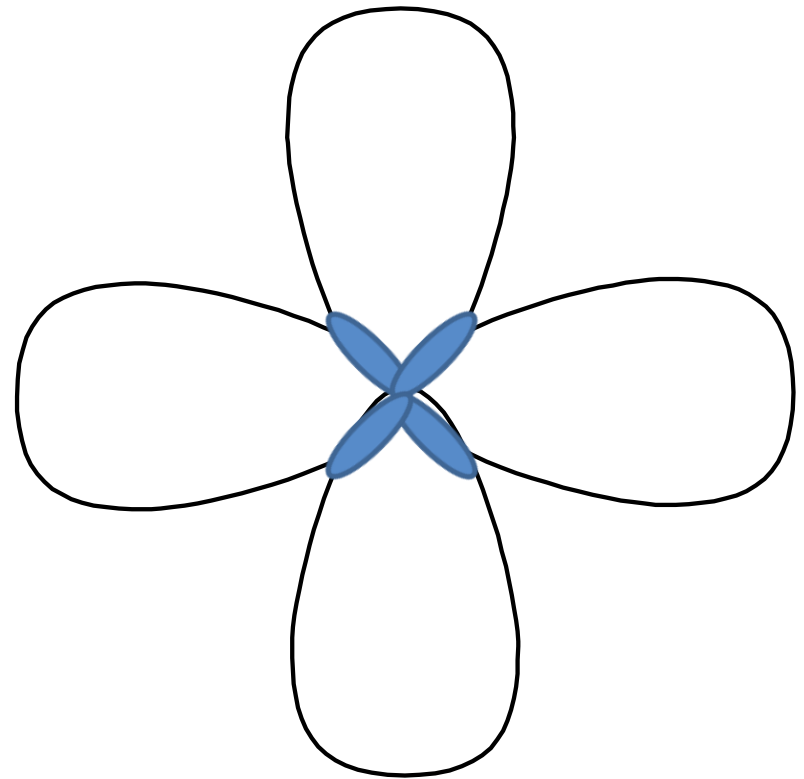
Of course, the overlap of the p_z and p_x orbitals is zero. The origin of spin polarization is not overlap, but rather it is from electron exchange. The differential interaction of the spin up spin down electrons in the $p\sigma$ orbital (ϕ_1) arises because of exchange with the spin down electron in ϕ_2 . This interaction lowers the energy of the spin down electron in ϕ_1 . The prediction is that there will be some spin density in an “orthogonal” orbital. It is observed by electron spin resonance (ESR) that there is some density of unpaired spins on H atoms that are nominally orthogonal to a π -system (represented the p orbital in the C-H model system).

Key point for bonding pathways

This example underscores a key point that we can illustrate with two orthogonal p orbitals. Spin density can be communicated to an orthogonal orbital via exchange.



Overlap is zero



Exchange is not zero

Spin states in diradicals

The relative energy of the triplet and singlet state in a diradical is usually a complicated result of configuration interaction. To get the correct ordering and energy splitting between the singlet and triplet one must use high level CI. Typically, the CCSD(T) level would be considered adequate for small systems.

We define the singlet-triplet splitting as spin-exchange parameter J .

$$\Delta E = {}^1E - {}^3E \equiv J$$

Note that J is negative if the singlet state is the ground state and positive if the triplet state is the ground state. We can consider J to be a combination of ferromagnetic and anti-ferromagnetic contributions.

$$J = J_F + J_{AF}$$

J-coupling

The ferromagnetic term favors the triplet state and the anti-ferromagnetic term favors the singlet state. The ferromagnetic J coupling term is a result of the exchange interaction.

$$J_F = -2K_{12}$$

The anti-ferromagnetic coupling is proportional to the square of the overlap.

$$J_{AF} = (S_{12})^2$$

The criterion for determining which of these terms dominates in a molecule is to examine whether highest occupied orbital(s) that interact with an orbital containing an unpaired spin have significant density on the atom that contains the spin. This criterion is called disjoint (no similarity in the density) and non-disjoint (similarity in the density). Disjoint = singlet ground state and non-disjoint = triplet ground state.

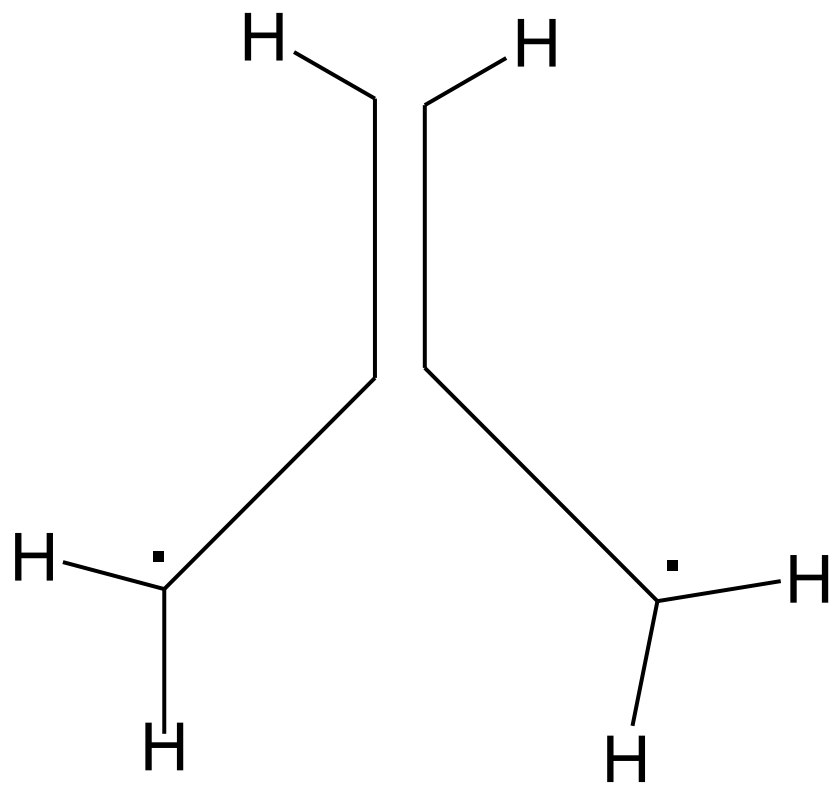
Disjoint and non-disjoint criteria

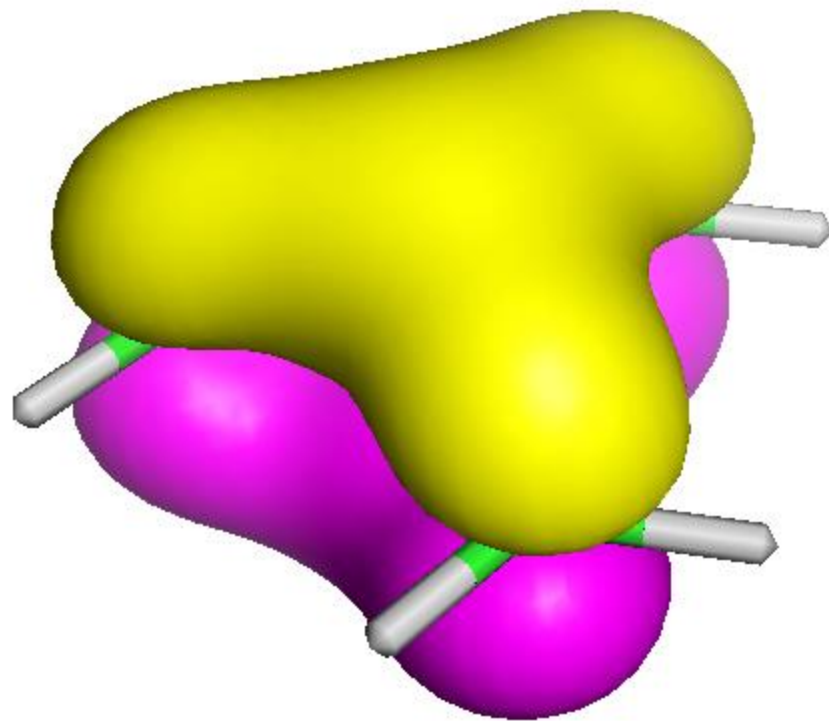
We can examine the trimethylmethylene (TMM) biradical. This is an example of a non-disjoint molecule. This means that the two orbitals that contain the unpaired electrons occupy similar space although their overlap is small. Recall that the density is proportional to the square of the wave function so the phases do not matter when considering the density. The only consideration is whether the orbitals occupy the same general region of space. The following molecule orbitals show this. Pay attention to the HOMO and HOMO-1 since these are the MOs that contain the unpaired electrons.

We can contrast the case of TMM with tetramethylene ethane. In that case the HOMO and HOMO-1 have essentially no common density. The considerations predict that this molecule will have a singlet ground state.

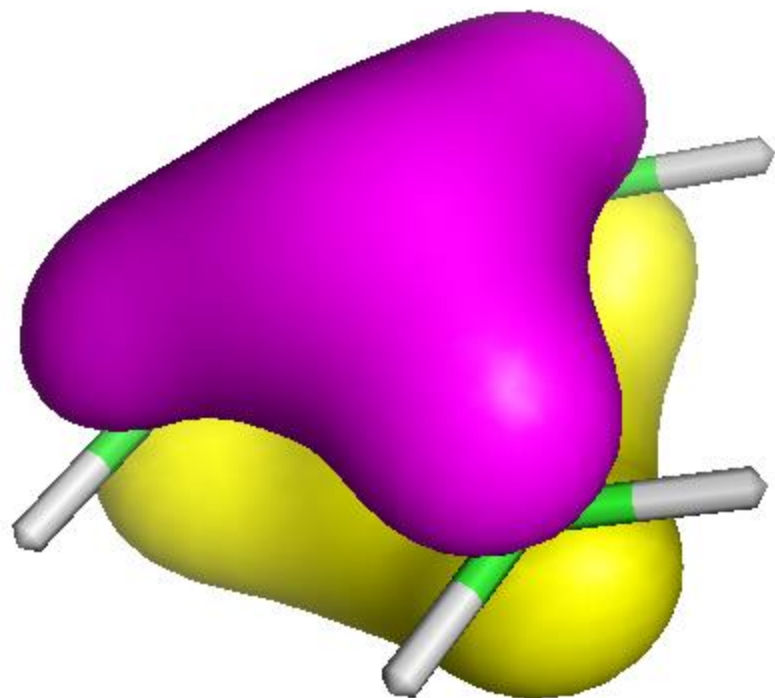
Triethylene methane

An example of a triplet ground state

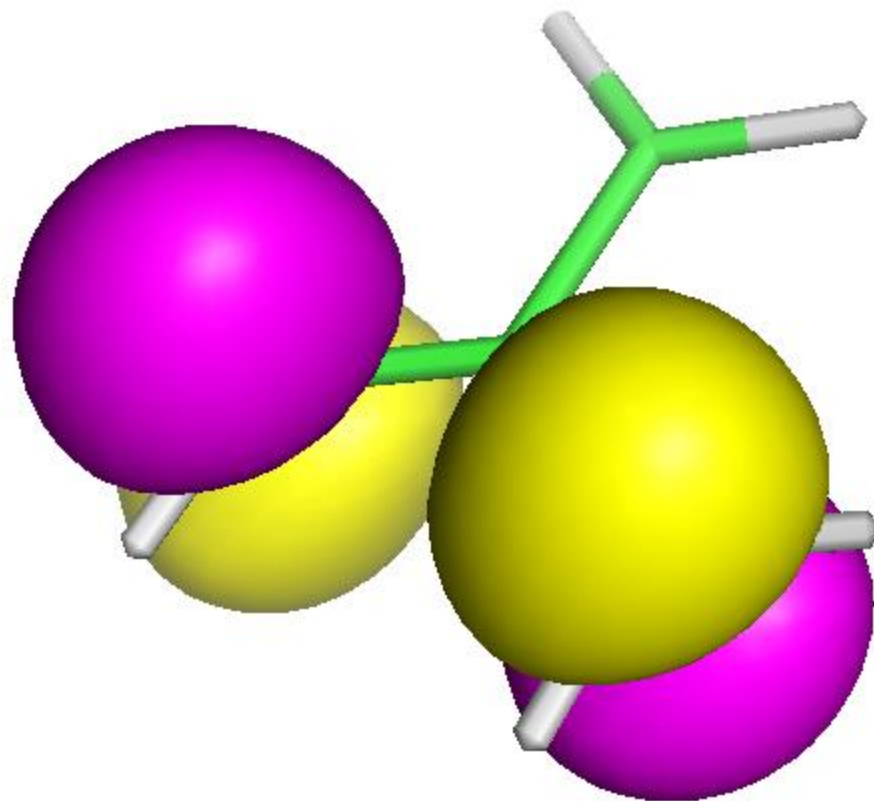




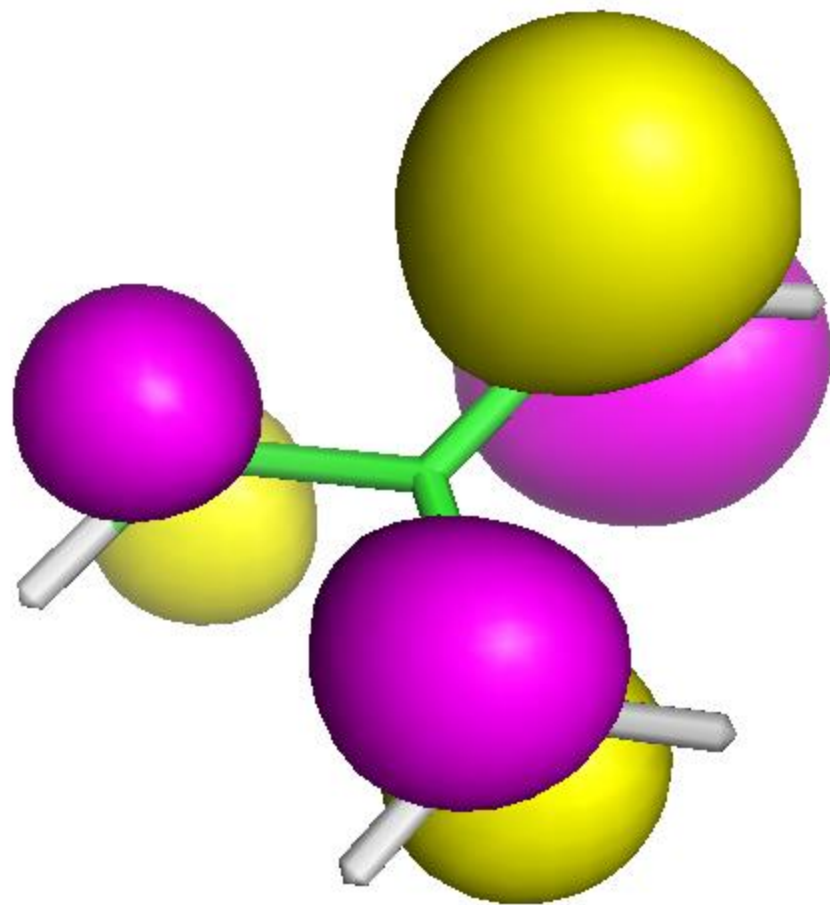
MO 27



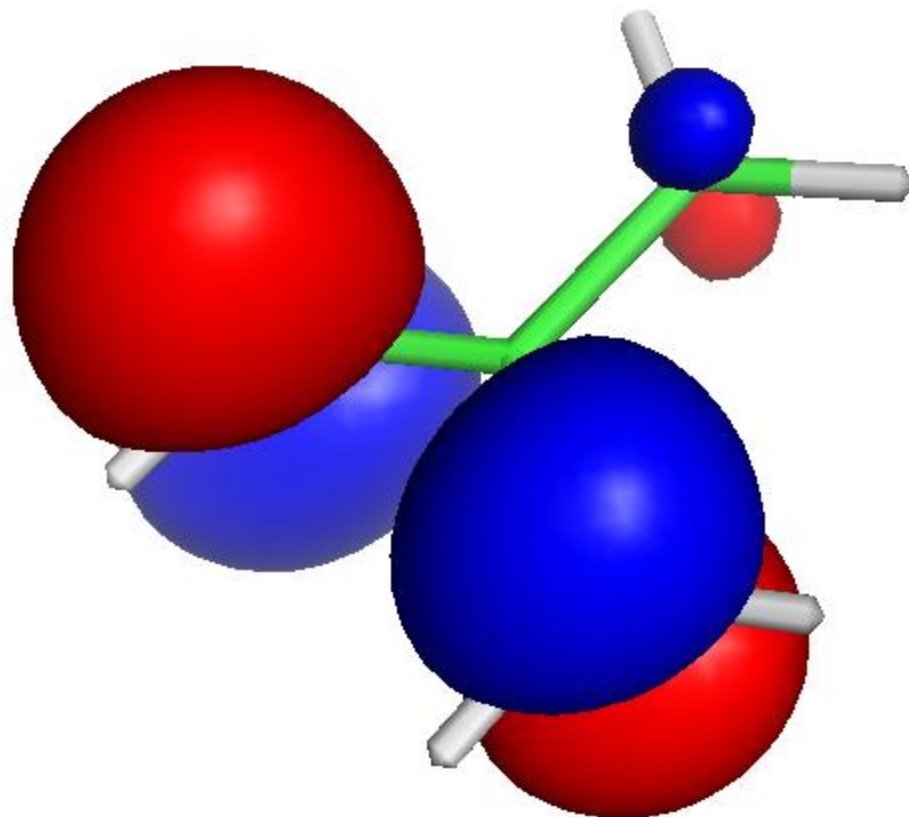
MO 28



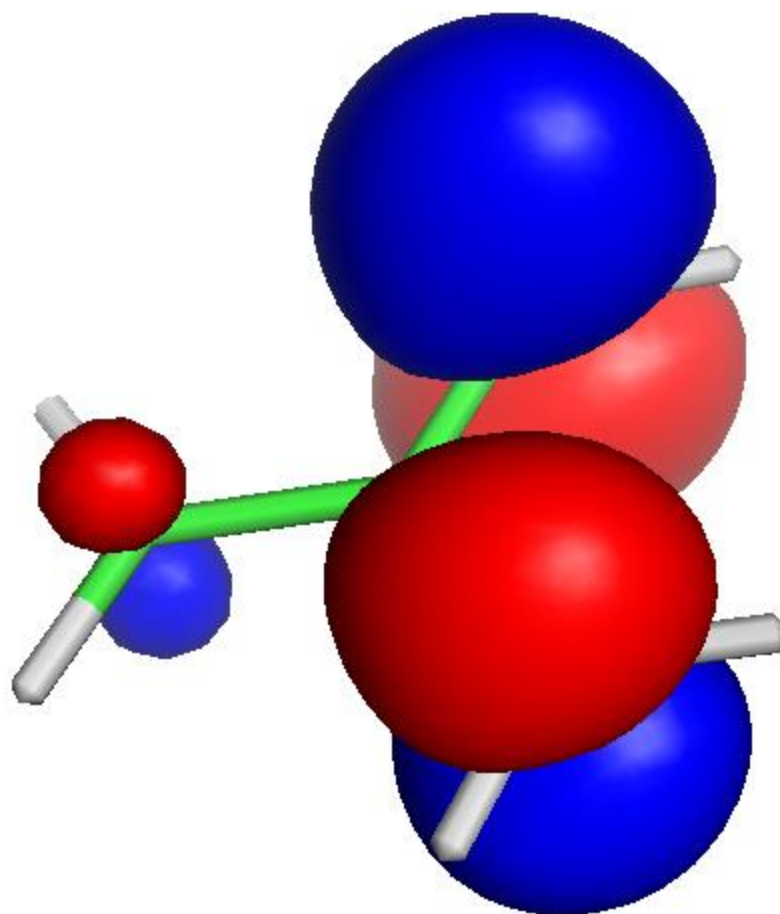
MO 29 HOMO - 1



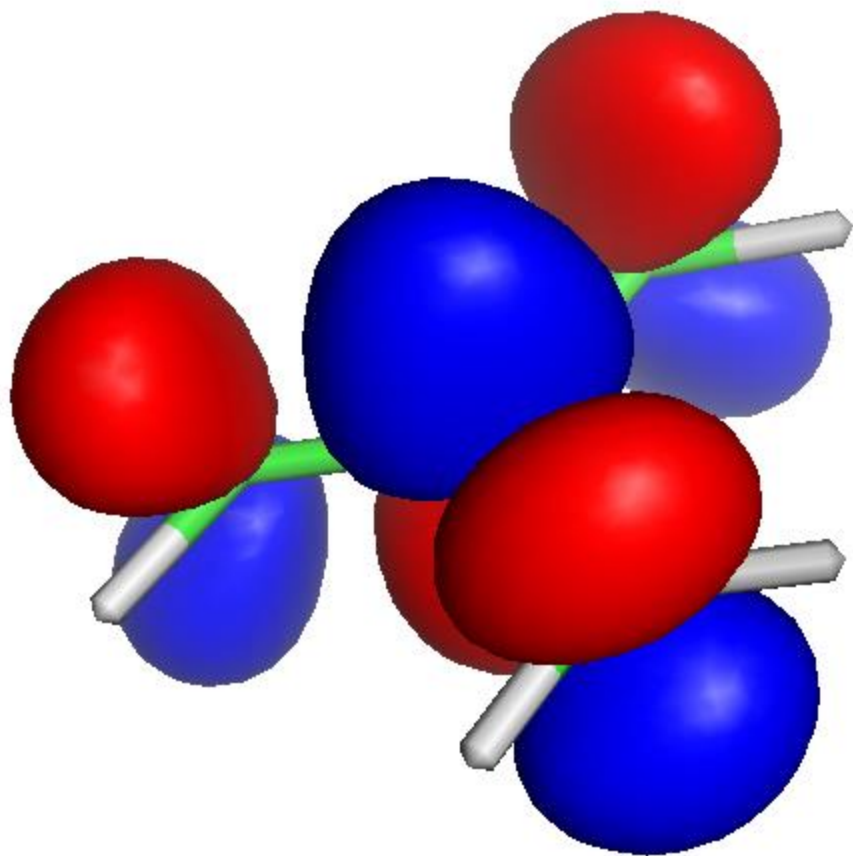
HOMO



LUMO



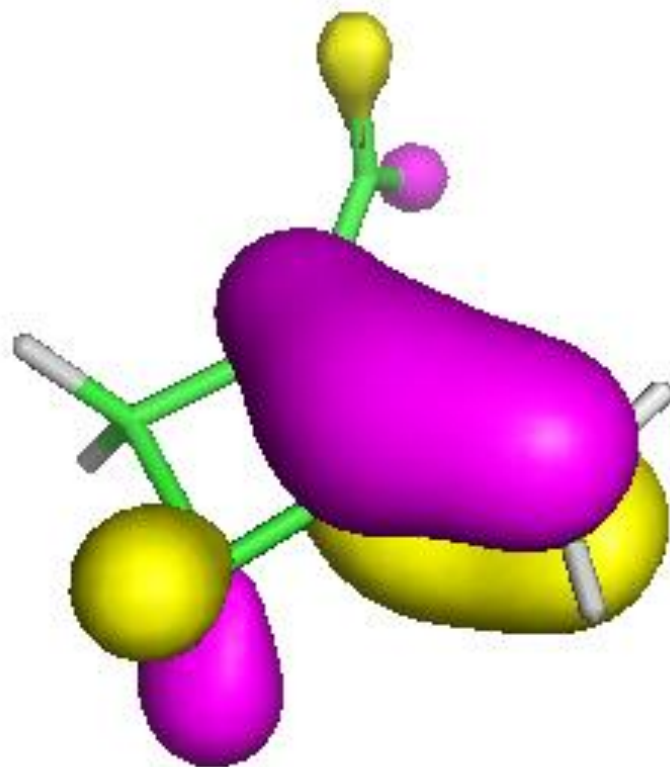
MO 32 LUMO + 1



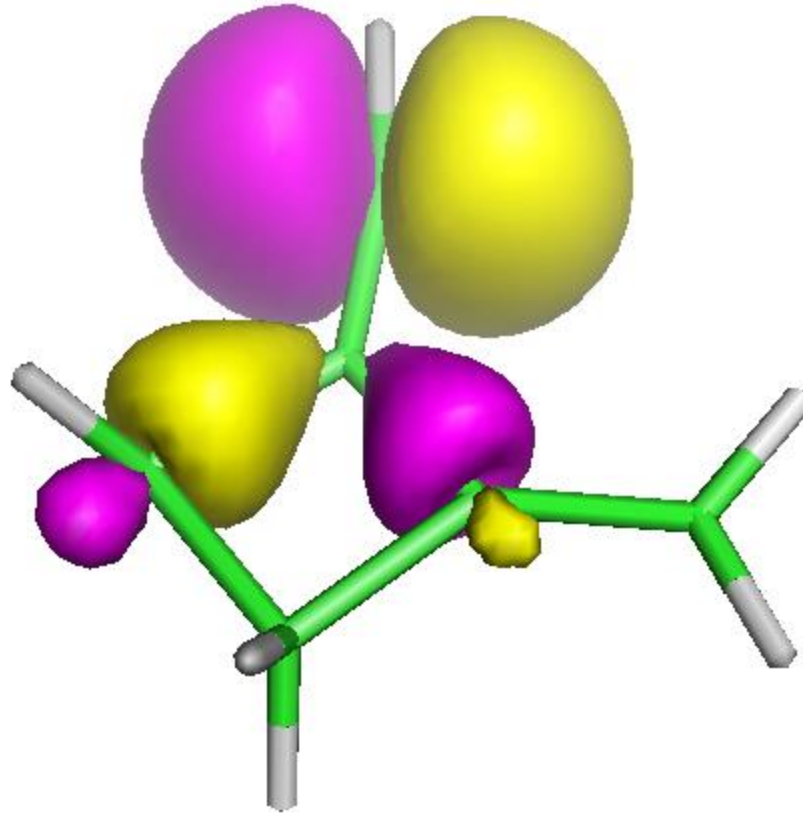
MO 33

Tetramethylene ethane

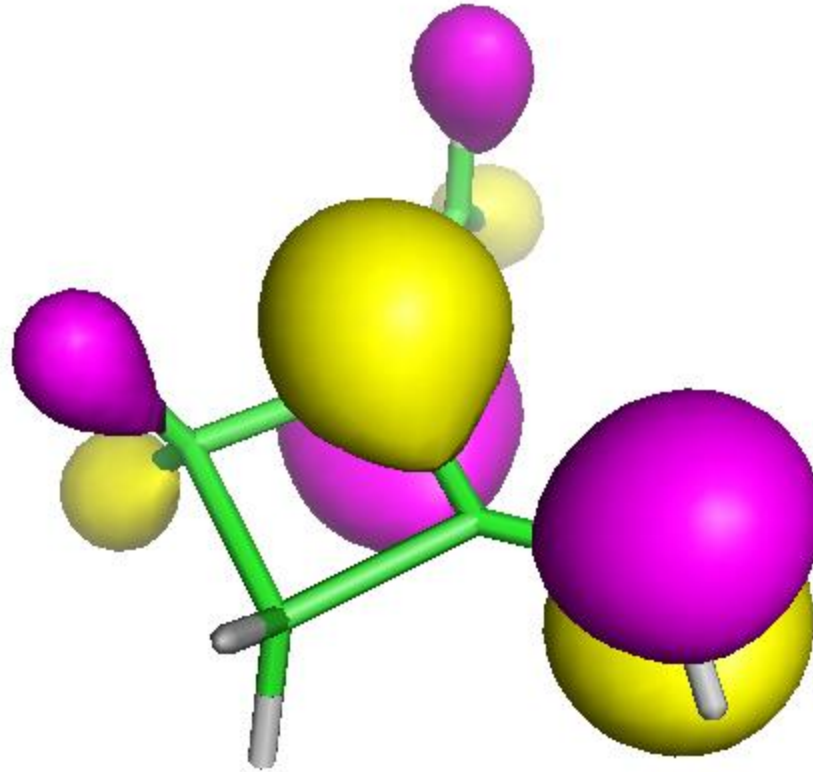
An example of a singlet ground state



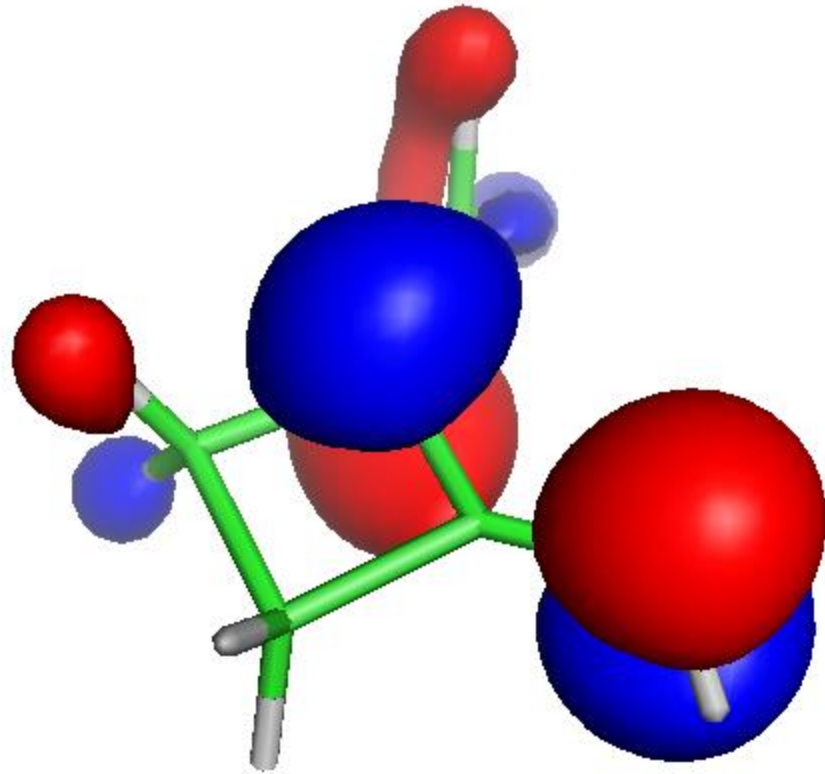
HOMO-2



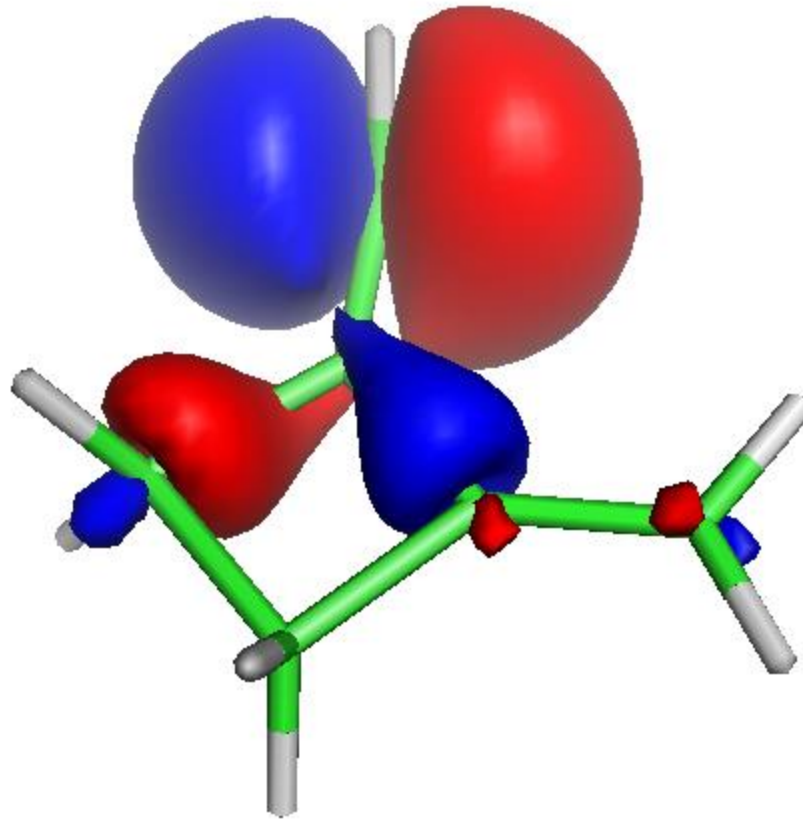
HOMO-1



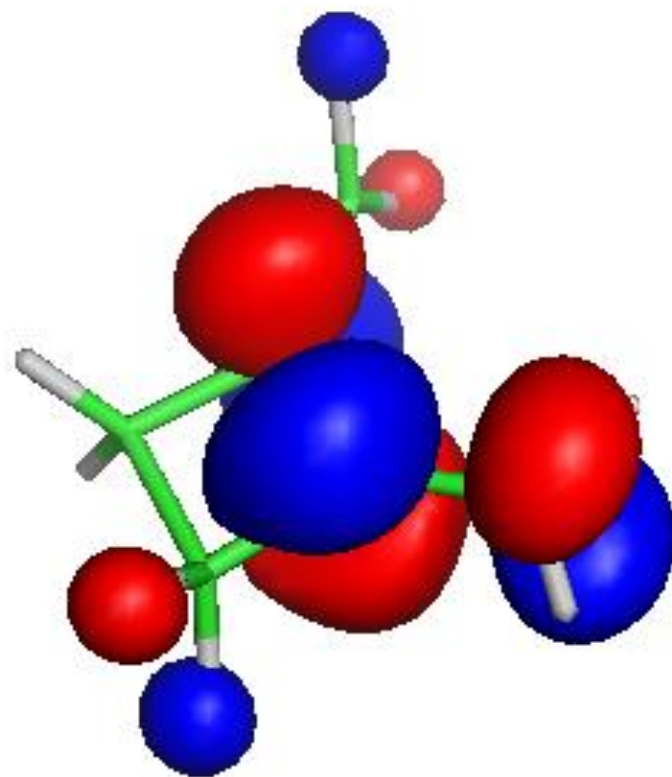
HOMO



LUMO



LUMO+1



LUMO+2