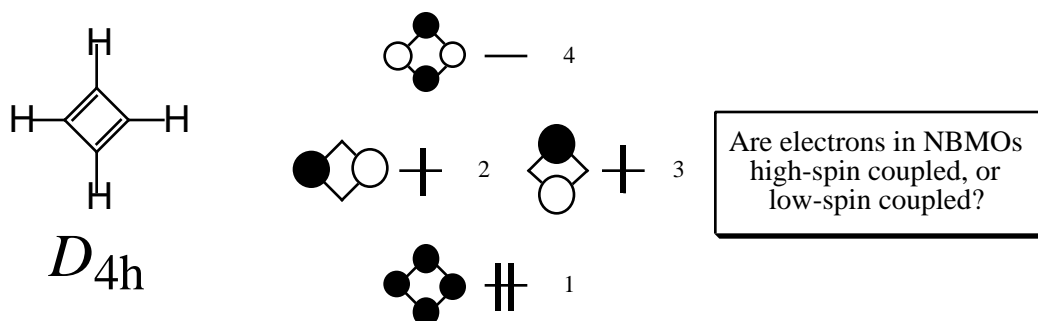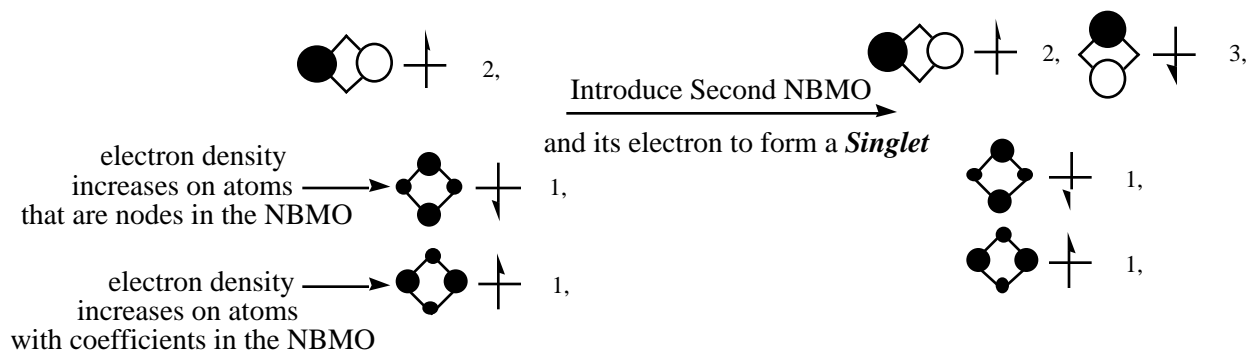# SPIN POLARIZATION

I. Dynamic or Double Spin Polarization[1-6]

The understanding of electron-electron repulsion in open-shell species with $S > 1/2$ can often be enhanced using the concept of double (or dynamic) spin polarization (DSP). This model requires different orbitals for different spins. DSP results in two scenarios. Additive DSP occurs when multiple unpaired electrons polarize filled orbitals in the same way. Competitive DSP arises when an unpaired electron polarizes filled shells in the opposite fashion from the previous electron. Additive DSP will lower the electron-electron repulsion, while that electron configuration having competitive DSP will have a higher energy.

Take square planar cyclobutadiene as an example

D_{4h}

4

2

3

1

Are electrons in NBMOs high-spin coupled, or low-spin coupled?

If one places an α electron into the first NBMO (ψ_2), then ψ_1 will be spin polarized as shown. This polarization reduces coulombic repulsions between $\psi_1(\alpha)$ and NBMO(α) and enhances exchange repulsions between $\psi_1(\beta)$ and NBMO(α). Both of these effects reduce the total energy. Now introduce the second NBMO and its electron making a singlet state, i.e. use a β spin electron. Introduction of a second, β electron polarizes ψ_1 in exactly the same way as the first, α electron. The DSP is said to be additive.

2,

Introduce Second NBMO

2, 3,

and its electron to form a *Singlet*

electron density increases on atoms that are nodes in the NBMO

1, 1,

electron density increases on atoms with coefficients in the NBMO

1, 1,

The spin polarized orbitals $\psi_1(\alpha)$ and $\psi_1(\beta)$ are formed by mixing ψ_4 in-phase with ψ_1 to give $\psi_1(\alpha)$ and out-of-phase to give $\psi_1(\beta)$. For alternant hydrocarbons, any virtual orbital may be used to create the spin polarized orbitals.

To continue, now consider adding the second NBMO and its electron to make a triplet, *i.e.*, add the second electron with   spin. The polarization caused by the second   electron **negates** the polarization caused by the first electron.
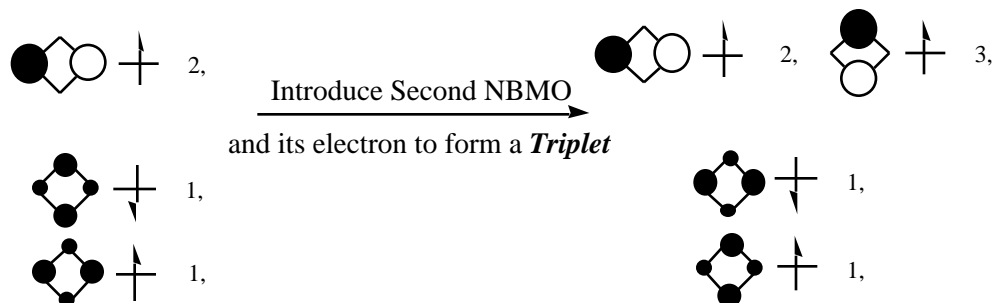

Compared to the singlet configuration, the triplet experiences greater electron-electron repulsion, and therefore has a greater total energy. In this case we would expect the singlet to lie well below the triplet.

As a second example, consider trimethylenemethane.

D_{3h}

Are electrons in NBMOs high-spin coupled, or low-spin coupled?
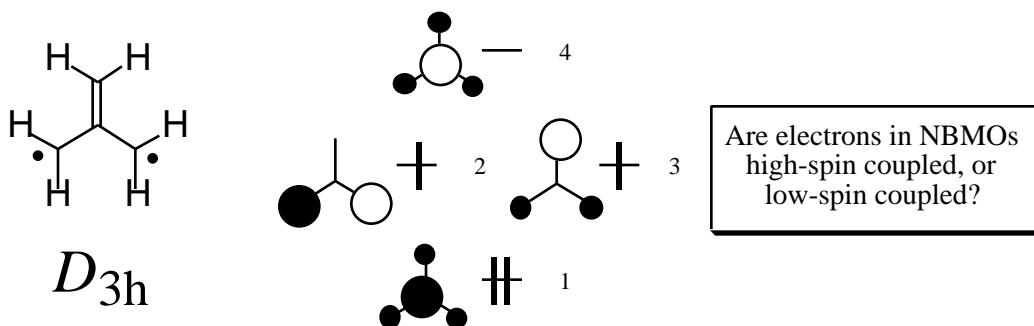
SPIN POLARIZED TRIPLET   SPIN POLARIZED SINGLET
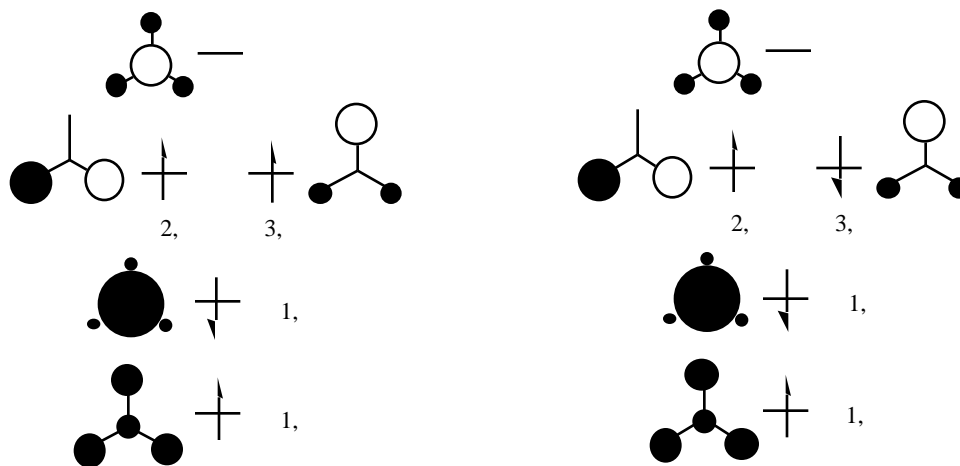
Here, the DSP is additive for the triplet, and a triplet ground state is predicted and observed. Note that in the case of TMM,   spin density greater than that predicted by Hückel calculations would be predicted for each of the CH_2 carbons, while   spin density is predicted for the central carbon atom.

EXERCISE: Draw MOs for spin-polarized allyl radical. What are the expected spin densities for each carbon atom?
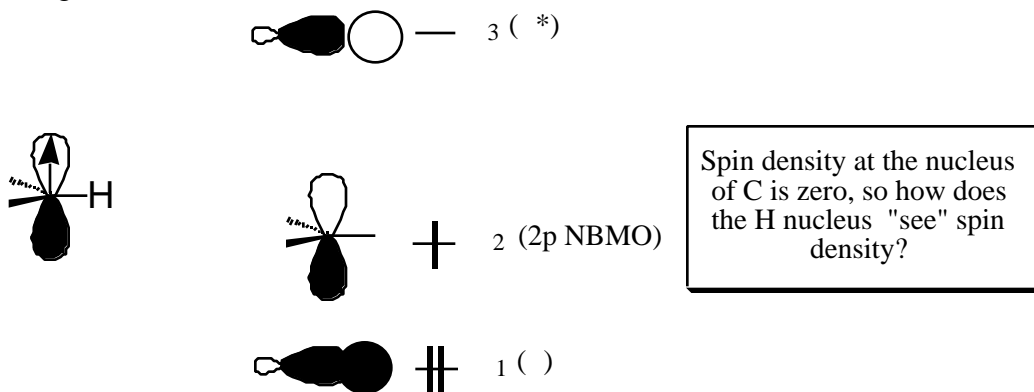
MO diagrams like those above lead to the schematic diagrams that show   spin polarization:

CH₂•

CH₂•

=

=
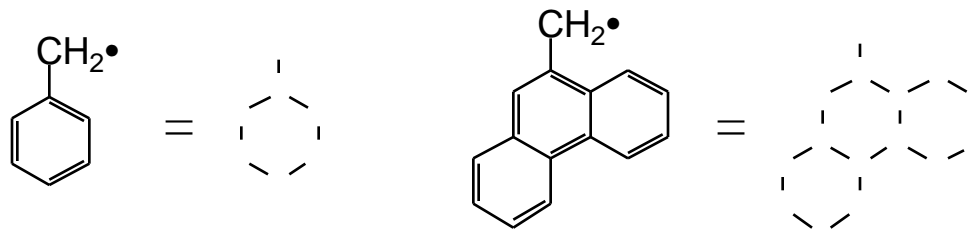
Generally, cross-conjugated biradicals will exhibit additive DSP and will be triplet ground-state biradicals.

II. Spin Polarization of the Sigma Framework: Hyperfine Coupling

Analogous MO diagrams analogous to those above can be drawn for   -systems. The most common is a
 -CH bond that shows how spin density "leaks" onto the hydrogen atom and leads to hyperfine coupling in EPR spectra of organic radicals.

―   ₃ (*)

—H

+   ₂ (2p NBMO)

┼┼   ₁ ( )

> Spin density at the nucleus of C is zero, so how does the H nucleus "see" spin density?

The answer to the question in the box above is again to lower the total energy by polarizing the   ₁
electrons:

―   ₃ (*)

+   ₂ (2p NBMO)

+   1,

+   1,
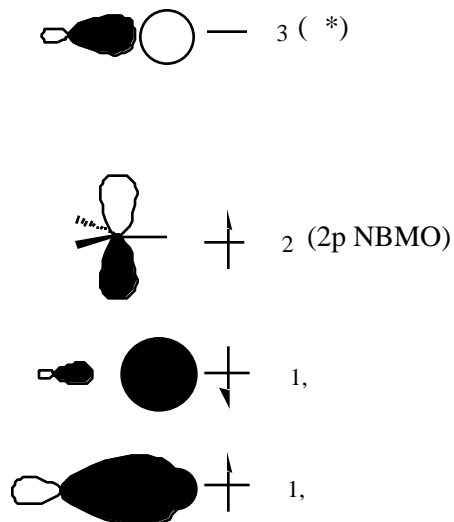
You must keep in mind that the hybrid orbital that makes up the CH bond overlaps the 2p orbital. In this way, - spin polarization increases   spin density at carbon and creates   spin density at hydrogen. This spin density is "seen" by the hydrogen nucleus, and results in hyperfine structure in the EPR spectrum. Thus, the proportionality constant, Q, in the McConnell equation (hyperfine coupling constant at H is directly proportional to the spin density at the carbon to which it is attached)[7] is a measure of the spin polarization.

$$\mathbf{a}(H) = Q \rho_C$$

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