

# Quantifying and characterizing the (poly)radical nature of molecules

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# Singlet diradicals

- In the case of systems such as singlet diradicals the spin density is not sufficient to describe unpaired electrons, as  $\rho^s(\vec{r}) = 0$  for any pure singlet.
- Density of effectively unpaired electrons

$$u(\vec{r}) = 2\rho(\vec{r}) - \int \rho(\vec{r}; \vec{r}')\rho(\vec{r}'; \vec{r})d\vec{r}'$$

$$\int u(\vec{r})d\vec{r} = N_D = \sum_i 2n_i - n_i^2$$

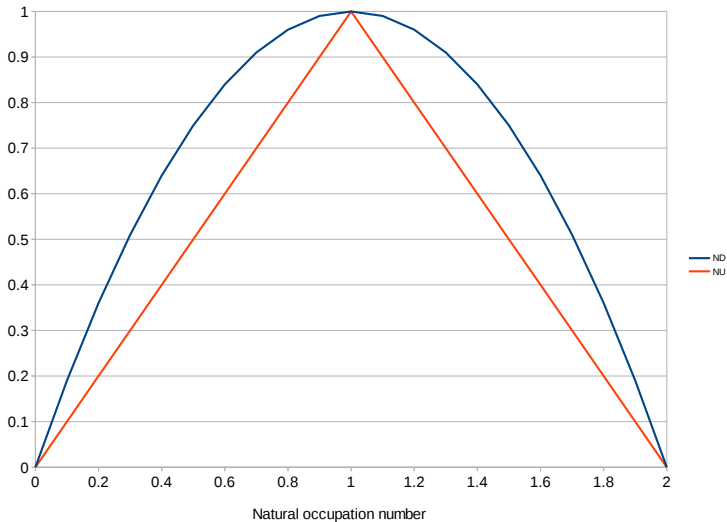
$$0 \leq N_D \leq 2N$$

Table: Number of effectively unpaired electrons ( $N_D$ ) and local spin values for the O atoms,  $\langle \hat{S}^2 \rangle_O$ , at the dissociation limit of several O<sub>2</sub> molecular electronic states.

Molecular elec. state	$N_D$	$\langle \hat{S}^2 \rangle_{O_1} / \langle \hat{S}^2 \rangle_{O_2}$	Atomic elec. state <sup>a</sup>
$^3\Sigma_g^-$	5	2 / 2	$^3P/^3P$
$^1\Delta_g$	4	2 / 2	$^3P/^3P$
$^1\Sigma_g^+$	5	2 / 2	$^3P/^3P$
$^1\Sigma_u^-$	5	2 / 2	$^3P/^3P$
$^3\Pi_u$	4	2 / 2	$^3P/^3P$
$^1\Pi_g$	5	2 / 2	$^3P/^3P$
$^1\Pi_u$	5	2 / 2	$^3P/^3P$
$^1\Delta_u$	5.33	0 / 0	$^1D/^1D$
$^1\Pi_u$	4.99	0 / 0	$^1D/^1D$

<sup>a</sup> Atomic electronic states at the dissociation limit

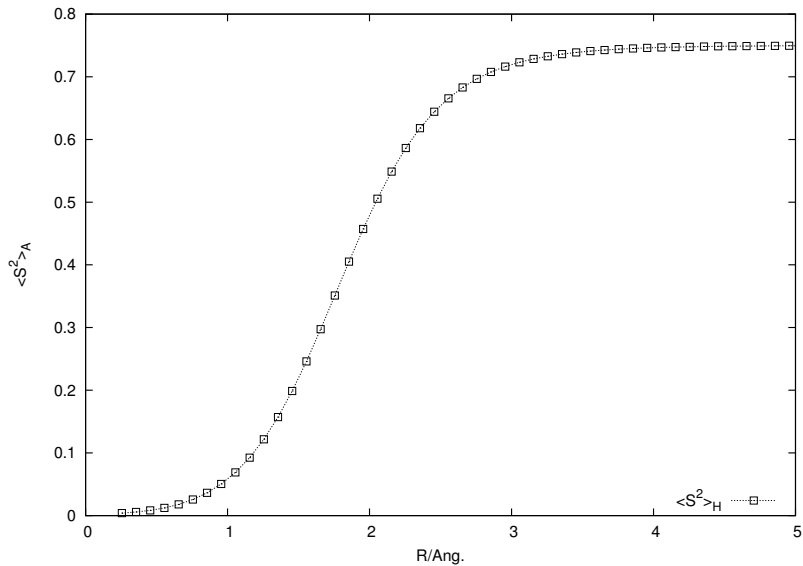
$$N_U = \sum_i \min(n_i, 2 - n_i)$$



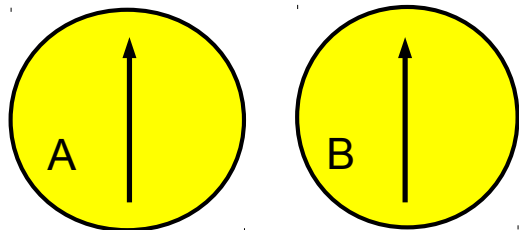
## Introduction: Local Spin

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A, B \neq A} \langle \hat{S}^2 \rangle_{AB}$$

- The spin density can be used to characterize the spin properties of molecular systems.
- In the case of systems such as singlet diradicals the spin density is not sufficient to describe unpaired electrons, as  $\rho^s(\vec{r}) = 0$  for any pure singlet.
- Density of effectively unpaired electrons



## The ideal picture: Triplet diradical

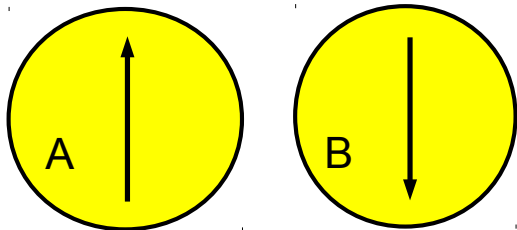


$$\langle \hat{S}^2 \rangle = 2$$

$$\langle \hat{S}^2 \rangle_A = \langle \hat{S}^2 \rangle_B = \frac{3}{4}$$

$$\langle \hat{S}^2 \rangle_{AB} = \langle \hat{S}^2 \rangle_{BA} = \frac{1}{4}$$

# Singlet diradical



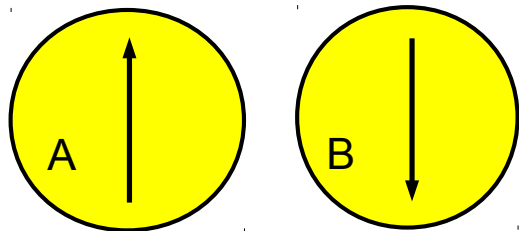
$$\langle \hat{S}^2 \rangle = 0$$

$$\langle \hat{S}^2 \rangle_A = \langle \hat{S}^2 \rangle_B = \frac{3}{4}$$

$$\langle \hat{S}^2 \rangle_{BA} = \langle \hat{S}^2 \rangle_{AB} = -\frac{3}{4}$$



## Broken symmetry singlet diradical



$$\langle \hat{S}^2 \rangle = 1$$

$$\langle \hat{S}^2 \rangle_A = \langle \hat{S}^2 \rangle_B = \frac{3}{4}$$

$$\langle \hat{S}^2 \rangle_{BA} = \langle \hat{S}^2 \rangle_{AB} = -\frac{1}{4}$$

# Introduction: Local Spin

## Clark and Davidson

- Local spin operators  $\hat{S}_A$  by projection of the overall spin vector operator.

$$\hat{S} = \sum_A \hat{S}_A \quad \langle \hat{S}_A \hat{S}_A \rangle \quad \langle \hat{S}_A \hat{S}_B \rangle$$

- Leads to significant local spin contributions for genuine closed-shell diamagnetic molecular systems.

## Introduction: Local Spin

- An alternative procedure proposed by Mayer consists in the partition of  $\langle \hat{S}^2 \rangle$  in atomic and diatomic terms.

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A,B \neq A} \langle \hat{S}^2 \rangle_{AB}$$

- Several formulations for single-determinant and correlated wave functions have been proposed (non fully satisfactory)

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I. Mayer, *Chem. Phys. Lett.*, **440**, 357 (2007)

I. Mayer, *Chem. Phys. Lett.*, **478**, 323 (2009).

I. Mayer, E. Matito, *Phys. Chem. Chem. Phys.*, **12**, 11308 (2010)

## Introduction: Physical requirements

- Zero local spins for closed-shell restricted wave functions
- For a properly dissociating wave function in the dissociation limit the atoms should have the same local  $\langle \hat{S}^2 \rangle$  value as the respective free atoms
- For non-singlet states, the formula should be independent of the  $S_z$  value in the absence of a magnetic field

This general expression cannot be used

$$\langle \hat{S}^2 \rangle = \frac{3}{4} \int \rho(\vec{r}_1) d\vec{r}_1 - \frac{1}{4} \iint \rho_2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 - \frac{1}{2} \iint \rho_2(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) d\vec{r}_1 d\vec{r}_2$$

## Introduction: Formulation

$$\langle \hat{S}^2 \rangle = \frac{3}{8} \int u(\vec{r}_1) d\vec{r}_1 - \frac{1}{4} \int \int \Lambda(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 - \frac{1}{2} \int \int \Lambda(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) d\vec{r}_1 d\vec{r}_2$$

Using the effectively unpaired density of Takatsuka

$$u(\vec{r}) = 2\rho(\vec{r}) - \int \rho(\vec{r}; \vec{r}') \rho(\vec{r}'; \vec{r}) d\vec{r}'$$

and the cumulant expansion

$$\rho_2(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2) = \rho(\vec{r}_1; \vec{r}'_1) \rho(\vec{r}_2; \vec{r}'_2) - \frac{1}{2} \rho(\vec{r}_1; \vec{r}'_2) \rho(\vec{r}_2; \vec{r}'_1) + \Lambda(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2)$$

where

$$\Lambda(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2) = -\frac{1}{2} \rho^s(\vec{r}_1; \vec{r}'_2) \rho^s(\vec{r}_2; \vec{r}'_1) + \Gamma(\vec{r}_1, \vec{r}_2; \vec{r}'_1, \vec{r}'_2)$$

is the so-called spin-free cumulant.

## Introduction: Formulation

$$\langle \hat{S}^2 \rangle = \frac{3}{8} \int u(\vec{r}_1) d\vec{r}_1 - \frac{1}{4} \int \int \Lambda(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 - \frac{1}{2} \int \int \Lambda(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) d\vec{r}_1 d\vec{r}_2$$

Using  $u(\vec{r}_1) = -2 \int \Lambda(\vec{r}_1, \vec{r}_2) d\vec{r}_2$  in the second term

### Alcoba's expression

$$\langle \hat{S}^2 \rangle = \frac{1}{2} \int u(\vec{r}_1) d\vec{r}_1 - \frac{1}{2} \int \int \Lambda(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) d\vec{r}_1 d\vec{r}_2$$

- The one- and two-center decomposition fulfills all requirements

## Alternative formulation

One can use  $u(\vec{r}_1) = -2 \int \Lambda(\vec{r}_1, \vec{r}_2) d\vec{r}_2$  freely in the first and second term

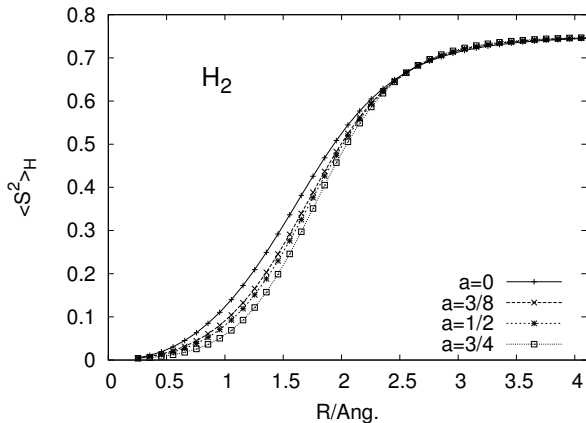
Appropriate form, but depends on  $a$

$$\langle \hat{S}^2 \rangle = a \int u(\vec{r}_1) d\vec{r}_1 - (1-2a) \int \int \Lambda(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 - \frac{1}{2} \int \int \Lambda(\vec{r}_1, \vec{r}_2; \vec{r}_2, \vec{r}_1) d\vec{r}_1 d\vec{r}_2$$

- Zero local spins for closed-shell restricted wave functions
- Independent of the  $S_z$  value for nonsinglets

## Alternative formulation

- Proper asymptotic behavior for any value of  $a$



- We need to impose an extra condition in order to derive a unique formulation



## Towards a unique formulation

### One-electron system

$$\langle \hat{S}^2 \rangle = \frac{3}{4} \int \rho^s(\vec{r}_1) d\vec{r}_1$$
$$\langle \hat{S}^2 \rangle \equiv \sum_A \frac{3}{4} \int_{\Omega_A} \rho^s(\vec{r}_1) d\vec{r}_1 = \sum_A \langle \hat{S}^2 \rangle_A$$

- No diatomic terms (no spurious self-coupling of the single electron)
- Only if one selects the parameter  $a=3/4$

## New formulation (3D-space analysis)

### One-center terms

$$\langle \hat{S}^2 \rangle_A = \frac{3}{4} \left( 2 \text{tr}(\mathbf{D}\mathbf{S}^A) - \text{tr}(\mathbf{D}\mathbf{S}^A\mathbf{D}) \right) + \frac{1}{2} \sum_{ijkl} \Lambda_{ijkl} S_{ki}^A S_{lj}^A - \frac{1}{2} \sum_{ijkl} \Lambda_{ijkl} S_{li}^A S_{kj}^A$$

### Two-center terms

$$\langle \hat{S}^2 \rangle_{AB} = \frac{1}{2} \sum_{ijkl} \Lambda_{ijkl} S_{ki}^A S_{lj}^B - \frac{1}{2} \sum_{ijkl} \Lambda_{ijkl} S_{li}^A S_{kj}^B$$

Atomic overlap matrix (in the MO/NO basis)

$$S_{ij}^A = \int_{\Omega_A} \phi_i^*(\vec{r}) \phi_j(\vec{r}) d\vec{r}$$

# New formulation (Hilbert-space analysis)

## One-center term

$$\begin{aligned}\langle \hat{S}^2 \rangle_A &= \frac{3}{4} \sum_{\mu \in A} \left( 2 [DS]_{\mu\mu} - [DSDS]_{\mu\mu} \right) \\ &\quad - \frac{1}{4} \sum_{\mu, \nu \in A} [P^S S]_{\mu\nu} [P^S S]_{\nu\mu} + \frac{1}{4} \sum_{\mu, \nu \in A} [P^S S]_{\mu\mu} [P^S S]_{\nu\nu} \\ &\quad + \frac{1}{2} \sum_{\mu, \sigma \in A} \sum_{\nu, \lambda} (\Gamma_{\mu\sigma\nu\lambda} - \Gamma_{\mu\sigma\lambda\nu}) S_{\lambda\sigma} S_{\nu\mu},\end{aligned}$$

## Two-center term

$$\begin{aligned}\langle \hat{S}^2 \rangle_{AB} &= -\frac{1}{4} \sum_{\mu \in A, \nu \in B} [P^S S]_{\mu\nu} [P^S S]_{\nu\mu} + \frac{1}{4} \sum_{\mu \in A, \nu \in B} [P^S S]_{\mu\mu} [P^S S]_{\nu\nu} \\ &\quad + \frac{1}{2} \sum_{\mu \in A, \sigma \in B} \sum_{\nu, \lambda} (\Gamma_{\mu\sigma\nu\lambda} - \Gamma_{\mu\sigma\lambda\nu}) S_{\lambda\sigma} S_{\nu\mu}.\end{aligned}$$

## AIM comparison

Table: Comparison of the One- And Two-Center Local- Spin Values for the NO Molecule at the UHF/cc-pVTZ Level Using Different Atoms in Molecules Definitions

		Becke	Becke-rho	Hirsh	Hirsh-it	Qtaim
NO	N	0.540	0.497	0.531	0.527	0.547
	O	0.232	0.272	0.241	0.244	0.229
	NO	-0.003	-0.002	-0.002	-0.002	-0.005

## Basis set dependency

Table: Atomic  $\langle \hat{S}^2 \rangle_C$  components for acetylene molecule computed at the CISD level of theory with different basis sets.

Basis set	$\langle \hat{S}^2 \rangle_C$	$\langle \hat{S}^2 \rangle_C^\lambda$	$\langle \hat{S}^2 \rangle_C^{3D}$
STO-3G	0.012	0.179	0.159
6-31G	-0.074	0.119	0.114
6-31G**	-0.136	0.082	0.084
6-31G**(6d)	-0.139	0.080	0.083
6-311G	0.030	0.119	0.113
6-311G**	-0.118	0.085	0.085
6-311G**(6d 10f)	-0.143	0.091	0.084
cc-pVDZ	-0.162	0.078	0.085
cc-pVTZ	-0.271	0.087	0.079
cc-pVTZ(6d 10f)	-0.146	0.104	0.078
aug-cc-pVDZ	0.729	0.078	0.087
aug-cc-pVTZ	-2.926	0.092	0.078

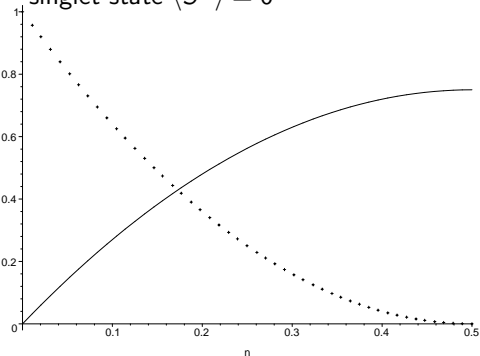
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Molecular elec. state	$N_D$	$\langle \hat{S}^2 \rangle_{O_1} / \langle \hat{S}^2 \rangle_{O_2}$	Atomic elec. state <sup>a</sup>
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<sup>a</sup> Atomic electronic states at the dissociation limit

# Local spin and chemical bonding

Ideal system: Minimal basis two electron homonuclear diatomic system in the singlet state  $\langle \hat{S}^2 \rangle = 0$



$$BO = 1 - 2n(1 - n)(1 + 4\delta^2)$$

$$u_A = 4n(1 - n)$$

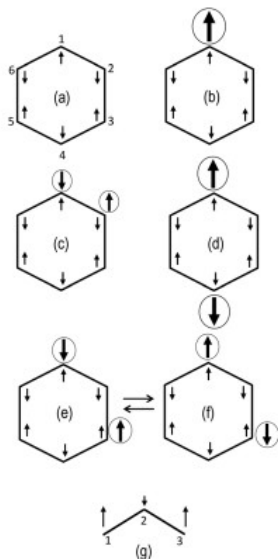
$$\langle \hat{S}^2 \rangle_A = -\langle \hat{S}^2 \rangle_{AB} = \frac{3}{2}n(1 - n)(1 + 4\delta^2)$$

- $\langle \hat{S}^2 \rangle_A = \frac{3}{4}(1 - BO)$
- Always  $\langle \hat{S}^2 \rangle_A = -\langle \hat{S}^2 \rangle_{AB}$

Evolution of the BO (dotted) and  $\langle \hat{S}^2 \rangle_A$  (solid) (assuming  $\delta = 1/2$ ) with respect to the natural spin orbital occupation,  $n$

# Results: Quantification of diradical character

	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	$C_6$
<b>Benzene</b>						
$C_1$	0.114	-0.101	0.079	-0.069		
<b>Phenyl radical</b>						
$C_1$	0.968	-0.145	0.100	-0.103		
$C_2$		0.129	-0.102	0.079	-0.071	0.078
$C_3$			0.127	-0.102	0.080	
$C_4$				0.118		
<b><i>o</i>-Benzyne</b>						
$C_1$	0.324	-0.304	0.086	-0.075	0.080	-0.110
$C_3$			0.130	-0.107	0.079	
$C_4$				0.115	-0.092	
<b><i>m</i>-Benzyne</b>						
$C_1$	0.540	-0.101	-0.344	-0.056	0.069	-0.104
$C_2$		0.133		0.066	-0.065	
$C_4$				0.116	-0.097	0.074
$C_5$					0.121	
<b><i>p</i>-Benzyne</b>						
$C_1$	0.962	-0.171	0.125	-0.862		
$C_2$		0.145	-0.106		-0.072	0.078
<b>Allyl radical</b>						
$C_1$	0.440	-0.145	0.151			
$C_2$		0.145				





## Results: A general measure of polyradical character

We have introduced a general measure of  $k$ -radical character making use of the  $\langle \hat{S}^2 \rangle_A$  values obtained for an actual molecular system as

$$\Delta^{(k)} = \sqrt{\frac{\sum_A (\langle \hat{S}^2 \rangle_A - \langle \hat{S}^2 \rangle_A^{id})^2}{n}}$$

- $\langle \hat{S}^2 \rangle_A^{id}$  indicate reference atomic ideal values
- $n$  is the total number of atoms/fragments considered in the local spin analysis
- The smaller the  $\Delta^{(k)}$  value the closer the system is to a reference picture of  $k$  perfectly localized spin centers.

# Diradicals

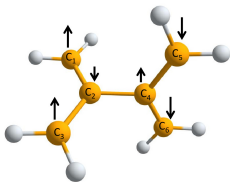


Figure: Numbering scheme of trimethyleneethane (TME)

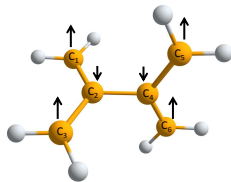
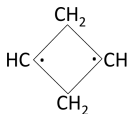
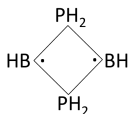


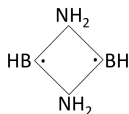
Figure: Numbering scheme of trimethyleneethane (TME triplet)



(a)



(b)



(c)

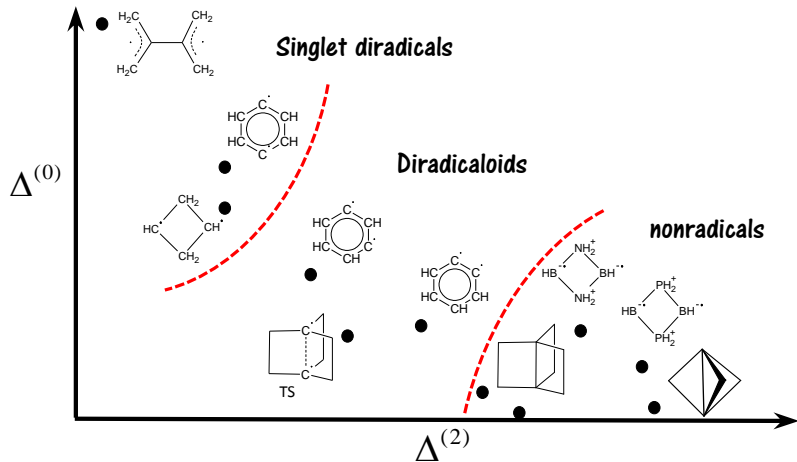
Figure: Four-member ring (planar) diradicaloids considered in this work. (a)  $(\text{CH})_2(\text{CH}_2)_2$ , (b)  $(\text{BH})_2(\text{PH}_2)_2$  and (c)  $(\text{BH})_2(\text{NH}_2)_2$

# Diradicals

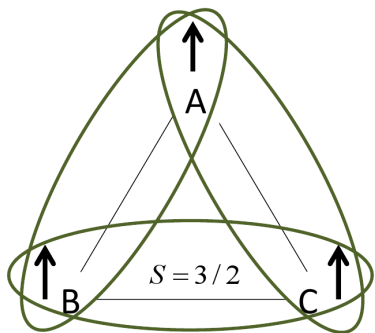
Table:  $k$ -radical character index,  $\Delta^{(k)}$ , for a set of diradicaloids. Values in parenthesis computed at the UB3LYP level of theory.

Molecule	Singlet		Triplet
	$\Delta^{(0)}$	$\Delta^{(2)}$	$\Delta^{(2)}$
o-benzyne	0.18	0.28	0.14
m-benzyne	0.28	0.19	0.13
p-benzyne	0.49	0.12	0.12
TME	0.77	0.02	0.05
(CH) <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub>	0.41 (0.42)	0.12 (0.12)	0.12 (0.12)
(BH) <sub>2</sub> (PH <sub>2</sub> ) <sub>2</sub>	0.10 (0.00)	0.46 (0.53)	0.39 (0.34)
(BH) <sub>2</sub> (NH <sub>2</sub> ) <sub>2</sub>	0.17 (0.18)	0.41 (0.40)	0.38 (0.36)

# Results: Quantification of diradical character



# Triradicals



$$\begin{array}{c} \text{A} \\ \text{B} \\ \text{C} \end{array} \begin{pmatrix} \text{A} & \text{B} & \text{C} \\ \frac{3}{4} & +\frac{1}{4} & +\frac{1}{4} \\ +\frac{1}{4} & \frac{3}{4} & +\frac{1}{4} \\ +\frac{1}{4} & +\frac{1}{4} & \frac{3}{4} \end{pmatrix}$$

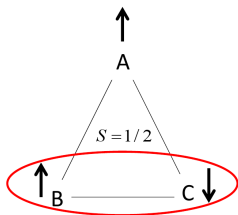
$$\langle \hat{S}^2 \rangle = 15/4$$

$$\begin{array}{c} \text{A} \\ \text{B} \\ \text{C} \end{array} \begin{pmatrix} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{pmatrix}$$

$$\langle \hat{S}_z \rangle = 3/2$$

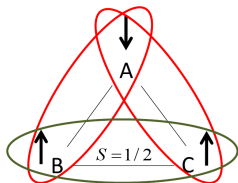
Pictorial representation of the local spin analysis for perfectly localized spins in quartet state

# Triradicals



$$\begin{array}{c}
 \text{A} \\
 \text{B} \\
 \text{C}
 \end{array}
 \begin{pmatrix}
 \frac{3}{4} & 0 & 0 \\
 0 & \frac{3}{4} & -\frac{3}{4} \\
 0 & -\frac{3}{4} & \frac{3}{4}
 \end{pmatrix}
 \begin{array}{c}
 \text{A} \\
 \text{B} \\
 \text{C}
 \end{array}
 \begin{pmatrix}
 \frac{1}{2} \\
 0 \\
 0
 \end{pmatrix}$$

$$\langle \hat{S}^2 \rangle = 3/4 \qquad \langle \hat{S}_z \rangle = 1/2$$

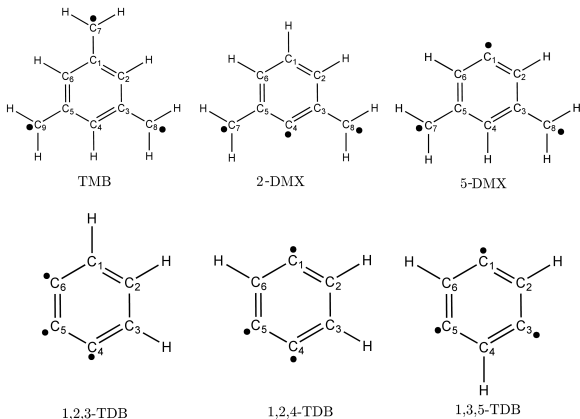


$$\begin{array}{c}
 \text{A} \\
 \text{B} \\
 \text{C}
 \end{array}
 \begin{pmatrix}
 \frac{3}{4} & -\frac{1}{2} & -\frac{1}{2} \\
 -\frac{1}{2} & \frac{3}{4} & +\frac{1}{4} \\
 -\frac{1}{2} & +\frac{1}{4} & \frac{3}{4}
 \end{pmatrix}
 \begin{array}{c}
 \text{A} \\
 \text{B} \\
 \text{C}
 \end{array}
 \begin{pmatrix}
 -\frac{1}{6} \\
 \frac{1}{3} \\
 \frac{1}{3}
 \end{pmatrix}$$

$$\langle \hat{S}^2 \rangle = 3/4 \qquad \langle \hat{S}_z \rangle = 1/2$$

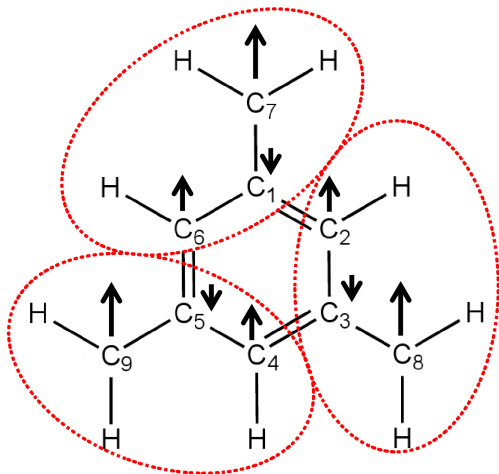
Pictorial representation of the local spin analysis for perfectly localized spins in doublet states

# Triradicals



Numbering scheme of trimethylenebenzene (TDB), dehydro-*m*-xylylene isomers (2-DMX and 5-DMX), and tridehydrobenzene isomers (1,2,3-TDB, 1,2,4-TDB, and 1,3,5-TDB)

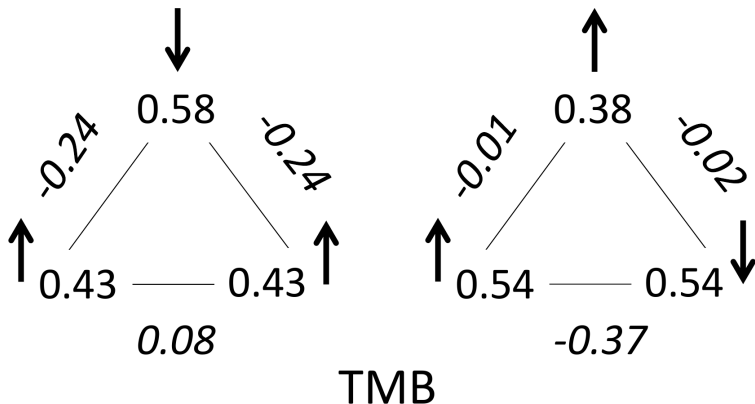
# Triradicals



Numbering scheme of TMB and local spin distribution of the quartet state.  
Three pseudo-allyl moieties are encircled in red

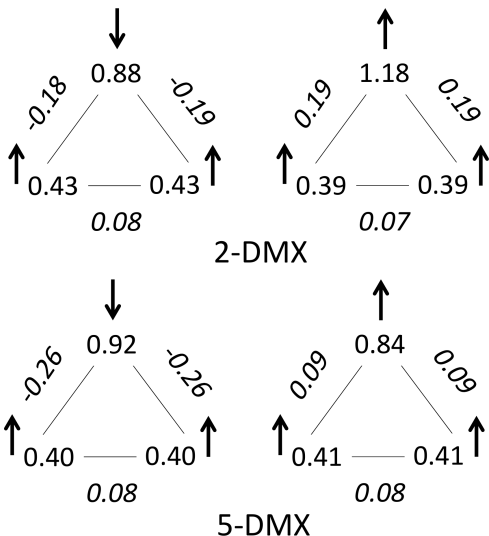


## Triradicals



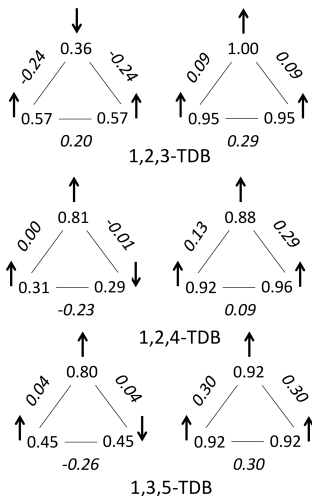
Pictorial local spin representation of the lowest-lying  $^2A_2$  (left) and  $^2B_1$  (right) doublet states of the TMB  $\pi, \pi, \pi$ -triradical

## Triradicals



Pictorial representation of the local spin distribution of the 2-DMX and 5-DMX  $\sigma, \pi, \pi$ -triradicals in their lowest lying doublet ( ${}^2B_2$ , left) and quartet ( ${}^4B_2$ , right) states

# Triradicals



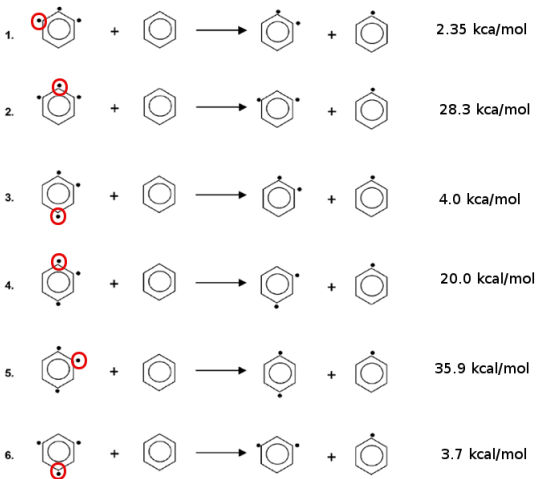
Representation of the local spin distribution of the 1,2,3-TDB, 1,2,4-TDB and 1,3,5-TDB  $\sigma, \sigma, \sigma$ -triradicals in their lowest lying doublet (left) and quartet (right) states

## Triradicals

$k$ -radical character index,  $\Delta^{(k)}$ , for a set of molecules. The value in parenthesis for TMB corresponds to the lowest-lying  ${}^2B_1$  state.

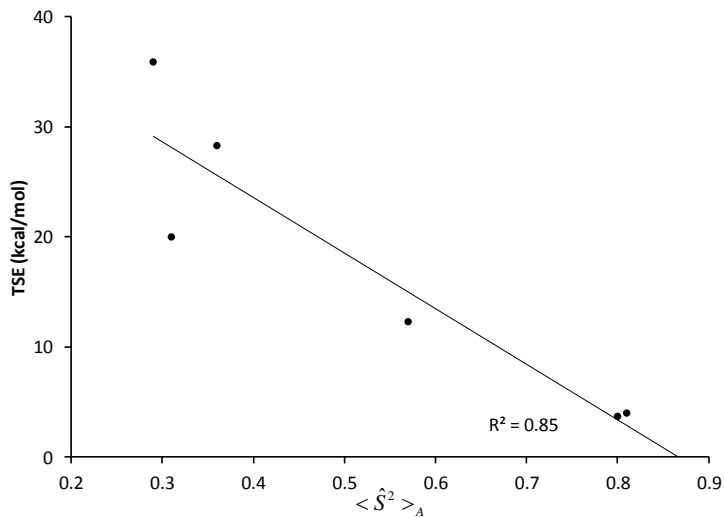
Molecule	$k$	$\Delta^{(k)}$	
		Doublet	Quartet
TMB	3	0.232 (0.231)	0.248
2-DMX	3	0.227	0.287
5-DMX	3	0.263	0.253
1,2,3-TDB	3	0.207	0.181
1,2,4-TDB	3	0.279	0.165
1,3,5-TDB	3	0.200	0.168

# Triradicals



From Krylov A. J. Phys. Chem. A 2005, 109, 10638-10645

# Triradicals



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