Characterizing Unpaired Electrons in Molecular Systems

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Doublet Radical

- e.g. phenyl radical, NO, CN, CH3, CO^+,...
- Visualization of singly occupied molecular orbital (SOMO)
- The spin density can be used to characterize the spin properties doublet radicals.

$$\rho^s(\vec{r}) = \rho^\alpha(\vec{r}) - \rho^\beta(\vec{r})$$

$$\rho^s(\vec{r}) = \sum_\Omega \int_\Omega \rho^s(\vec{r})d\vec{r} = \sum_\Omega \rho^s_\Omega(\vec{r})$$

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

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

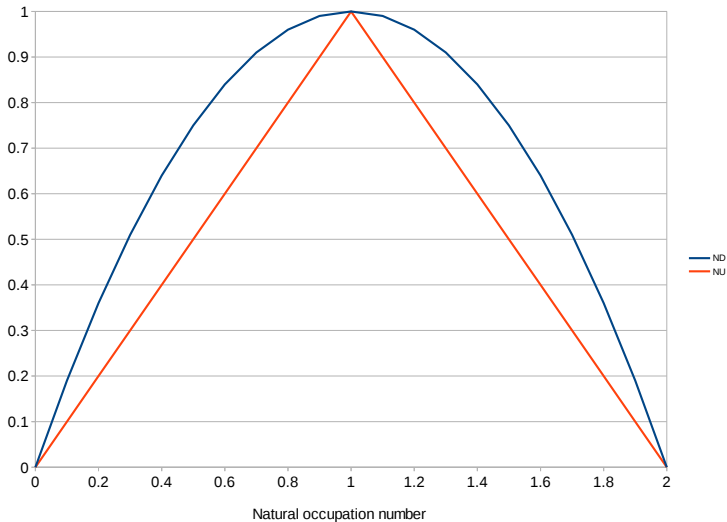$$\int u(\vec{r})d\vec{r} = N_D = \sum_i 2n_i - n_i^2$$

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

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_2 molecular electronic states.

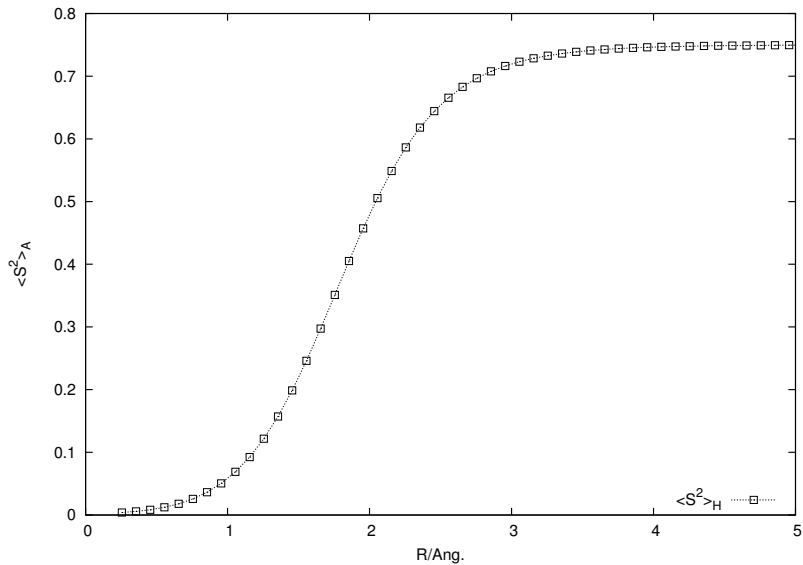| Molecular elec. state	N_D	$\langle \hat{S}^2 \rangle_{O_1}$ / $\langle \hat{S}^2 \rangle_{O_2}$	Atomic elec. state[a]
$^3\Sigma_g^-$	5	2 / 2	$^3P/^3P$
$^1\Delta_g$	4	2 / 2	$^3P/^3P$
$^1\Sigma_g^+$	5	2 / 2	$^3P/^3P$
$^1\Sigma_u^-$	5	2 / 2	$^3P/^3P$
$^3\Pi_u$	4	2 / 2	$^3P/^3P$
$^1\Pi_g$	5	2 / 2	$^3P/^3P$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

[a] Atomic electronic states at the dissociation limit
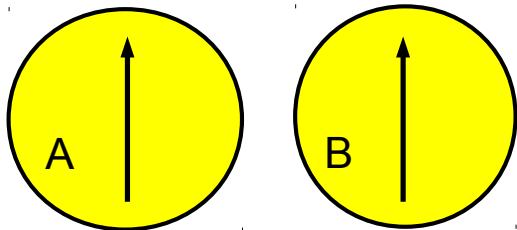
4

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

Natural occupation number

$$\langle \hat{S}^2 \rangle = \sum_A \langle \hat{S}^2 \rangle_A + \sum_{A, B \neq A} \langle \hat{S}^2 \rangle_{AB}$$
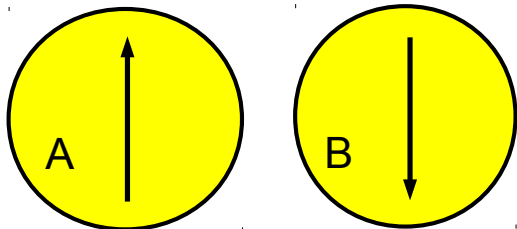
The ideal picture: Triplet diradical

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

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

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

Singlet diradical

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

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

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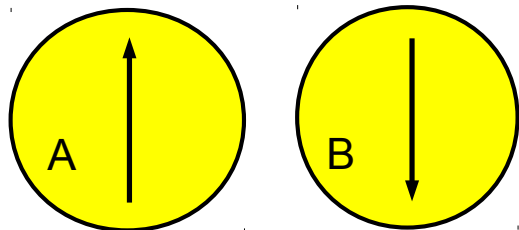
Broken symmetry singlet diradical

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

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

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

Introduction: Local Spin

Clark and Davidson

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

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

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

A. E. Clark, E. R. Davidson, *J. Chem. Phys.* **115**, 7382 (2001).

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)

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

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D. R. Alcoba, A. Torre, L. Lain, R. C. Bochicchio *J. Chem. Theory Comput.*, **7**, 3560 (2011)

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
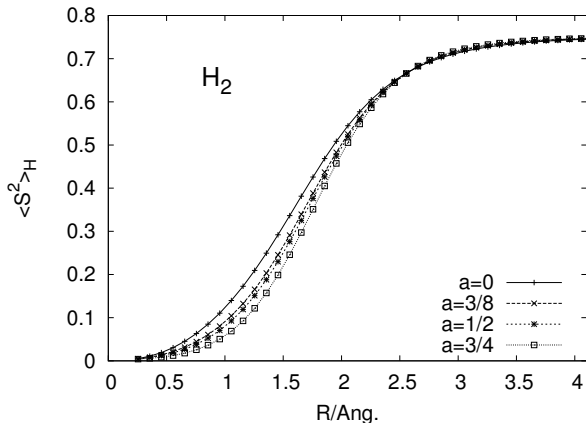
Appropriate form, but depends on a

$$\langle \hat{S}^2 \rangle = a \int u(\vec{r_1}) d\vec{r_1} - (1-2a) \int \int \Lambda(\vec{r_1}, \vec{r_2}) d\vec{r_1} d\vec{r_2} - \frac{1}{2} \int \int \Lambda(\vec{r_1}, \vec{r_2}; \vec{r_2}, \vec{r_1}) d\vec{r_1} d\vec{r_2}$$

- 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

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

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

$$\langle \hat{S}^2 \rangle_A = \frac{3}{4} \sum_{\mu \in A} \left(2 \left[DS \right]_{\mu\mu} - \left[DSDS \right]_{\mu\mu} \right)$$

$$-\frac{1}{4} \sum_{\mu,\nu \in A} \left[P^s S \right]_{\mu\nu} \left[P^s S \right]_{\nu\mu} + \frac{1}{4} \sum_{\mu,\nu \in A} \left[P^s S \right]_{\mu\mu} \left[P^s S \right]_{\nu\nu}$$

$$+\frac{1}{2} \sum_{\mu,\sigma \in A} \sum_{\nu,\lambda} \left(\Gamma_{\mu\sigma\nu\lambda} - \Gamma_{\mu\sigma\lambda\nu} \right) S_{\lambda\sigma} S_{\nu\mu},$$

Two-center term

$$\langle \hat{S}^2 \rangle_{AB} = -\frac{1}{4} \sum_{\mu \in A, \nu \in B} \left[P^s S \right]_{\mu\nu} \left[P^s S \right]_{\nu\mu} + \frac{1}{4} \sum_{\mu \in A, \nu \in B} \left[P^s S \right]_{\mu\mu} \left[P^s S \right]_{\nu\nu}$$

$$+\frac{1}{2} \sum_{\mu \in A, \sigma \in B} \sum_{\nu,\lambda} \left(\Gamma_{\mu\sigma\nu\lambda} - \Gamma_{\mu\sigma\lambda\nu} \right) S_{\lambda\sigma} S_{\nu\mu}.$$

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

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_2 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[a]
$^3\Sigma_g^-$	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	$^1D/^1D$

[a] 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 $\langle \hat{S}^2 \rangle_A = -\langle \hat{S}^2 \rangle_{AB}$
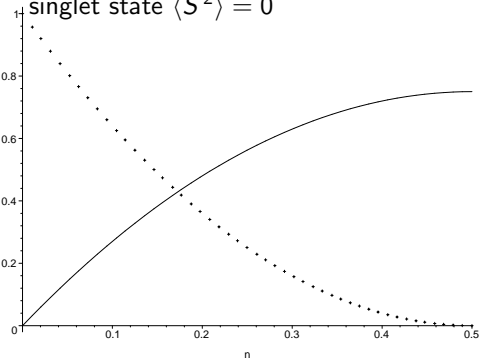
Evolution of the BO (dotted) and $\langle \hat{S}^2 \rangle_A$ (solid) (assuming

$\delta = 1/2$) with respect to the natural spin orbital occupation, n

Ramos-Cordoba, E.; Salvador, P.; Reiher, M. *Chem. Eur. J.* **2013**, *19*, 15267–15275

Results: Quantification of diradical character

	C_1	C_2	C_3	C_4	C_5	C_6
Benzene						
C_1	0.114	−0.101	0.079	−0.069		
Phenyl radical						
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		
o-Benzyne						
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	
m-Benzyne						
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	
p-Benzyne						
C_1	0.962	−0.171	0.125	−0.862		
C_2		0.145	−0.106		−0.072	0.078
Allyl radical						
C_1	0.440	−0.145	0.151			
C_2		0.145				

25
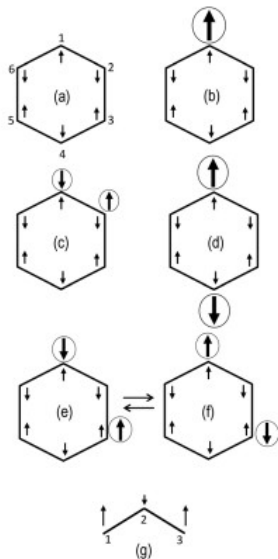
Results: A general measure of polyradical character

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.

Ramos-Cordoba, E.; Salvador, P *J. Chem. Theory Comput.* **10**, 634 (2014)
Ramos-Cordoba, E.; Salvador, P *Phys. Chem. Chem. Phys.* DOI: 10.1039/C4CP00939H, (2014)
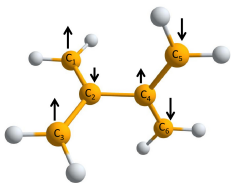
Diradicals

Figure: Numbering scheme of trimethyleneethane (TME)
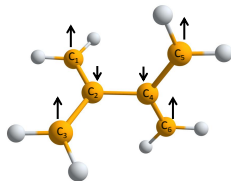
Figure: Numbering scheme of trimethyleneethane (TME triplet)
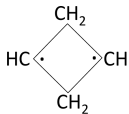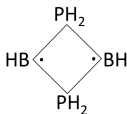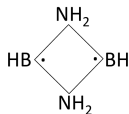
Figure: Four-member ring (planar) diradicaloids considered in this work. (a) $(CH)_2(CH_2)_2$, (b) $(BH)_2(PH_2)_2$ and (c) $(BH)_2(NH_2)_2$
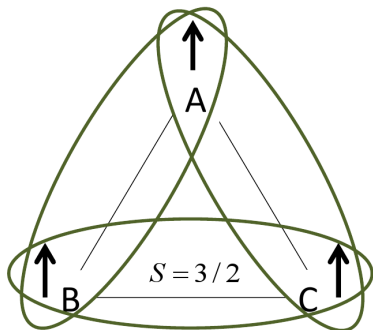
Diradicals

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
$(CH)_2(CH_2)_2$	0.41 (0.42)	0.12 (0.12)	0.12 (0.12)
$(BH)_2(PH_2)_2$	0.10 (0.00)	0.46 (0.53)	0.39 (0.34)
$(BH)_2(NH_2)_2$	0.17 (0.18)	0.41 (0.40)	0.38 (0.36)

Results: Quantification of diradical character
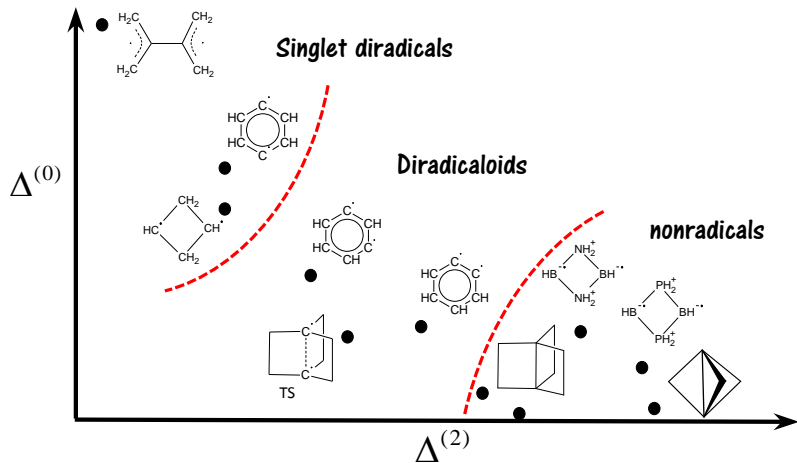
Triradicals

$$
\begin{array}{cccc}
 & \text{A} & \text{B} & \text{C} \\
\text{A} & \dfrac{3}{4} & +\dfrac{1}{4} & +\dfrac{1}{4} \\
\text{B} & +\dfrac{1}{4} & \dfrac{3}{4} & +\dfrac{1}{4} \\
\text{C} & +\dfrac{1}{4} & +\dfrac{1}{4} & \dfrac{3}{4}
\end{array}
\qquad
\begin{array}{cc}
\text{A} & \dfrac{1}{2} \\
\text{B} & \dfrac{1}{2} \\
\text{C} & \dfrac{1}{2}
\end{array}
$$

$$\left\langle \hat{S}^2 \right\rangle = 15/4 \qquad \left\langle \hat{S}_z \right\rangle = 3/2$$

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

Triradicals

$$\begin{array}{c c c}
 & A & B & C \\
A & \dfrac{3}{4} & 0 & 0 \\
B & 0 & \dfrac{3}{4} & -\dfrac{3}{4} \\
C & 0 & -\dfrac{3}{4} & \dfrac{3}{4}
\end{array}
\qquad
\begin{array}{c c}
A & \dfrac{1}{2} \\
B & 0 \\
C & 0
\end{array}$$
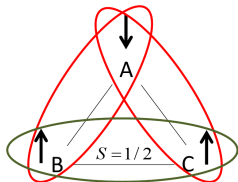
$$\left\langle \hat{S}^2 \right\rangle = 3/4 \qquad \left\langle \hat{S}_z \right\rangle = 1/2$$

$$\begin{array}{c c c}
 & A & B & C \\
A & \dfrac{3}{4} & -\dfrac{1}{2} & -\dfrac{1}{2} \\
B & -\dfrac{1}{2} & \dfrac{3}{4} & +\dfrac{1}{4} \\
C & -\dfrac{1}{2} & +\dfrac{1}{4} & \dfrac{3}{4}
\end{array}
\qquad
\begin{array}{c c}
A & -\dfrac{1}{6} \\
B & \dfrac{1}{3} \\
C & \dfrac{1}{3}
\end{array}$$

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

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

Triradicals

TMB   2-DMX   5-DMX

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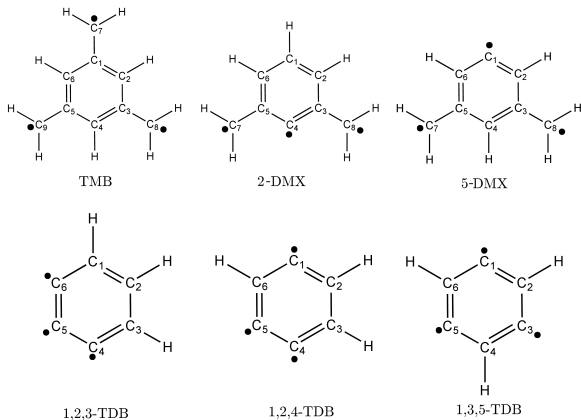
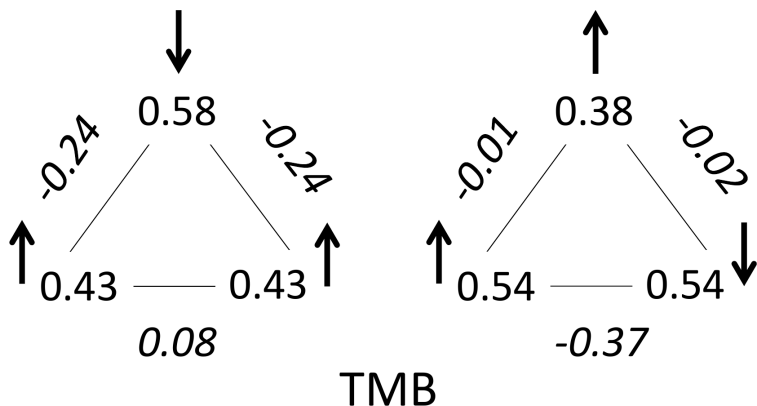Numbering scheme of trimethylenebenzene (TDB), dehydro-m-xylylene isomers (2-DMX and 5-DMX), and tridehydrobenzene isomers (1,2,3-TDB, 1,2,4-TDB, and 1,3,5-TDB)
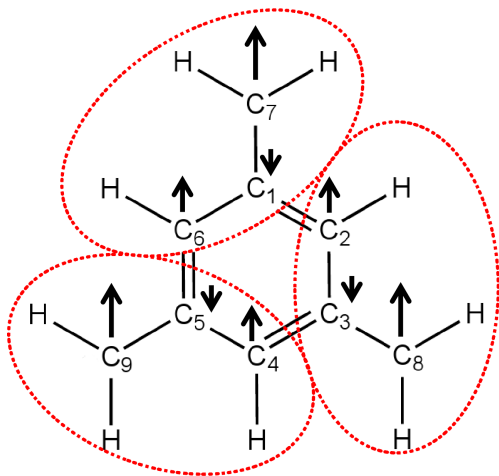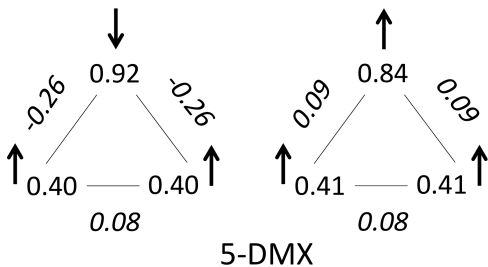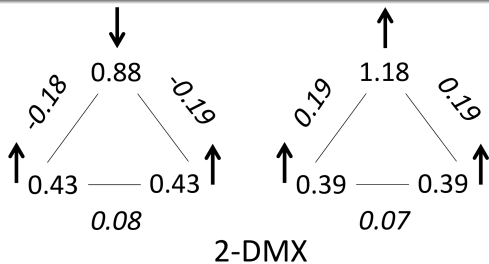
Triradicals

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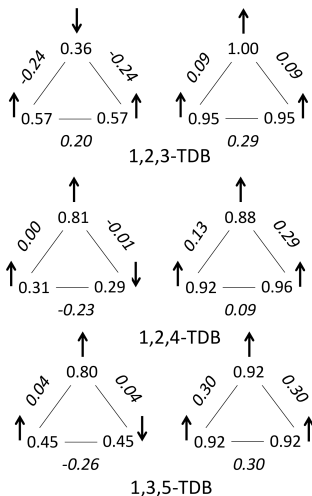Three pseudo-allyl moieties are encircled in red

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

2-DMX

5-DMX

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
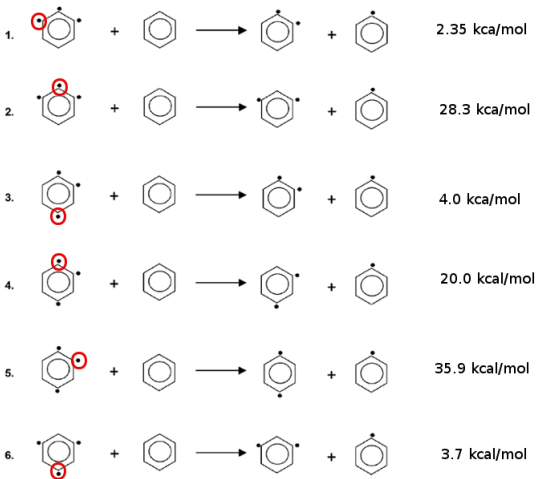
Triradicals

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 parethesis for TMB corresponds to the lowest-lying $^2B_1$ state.
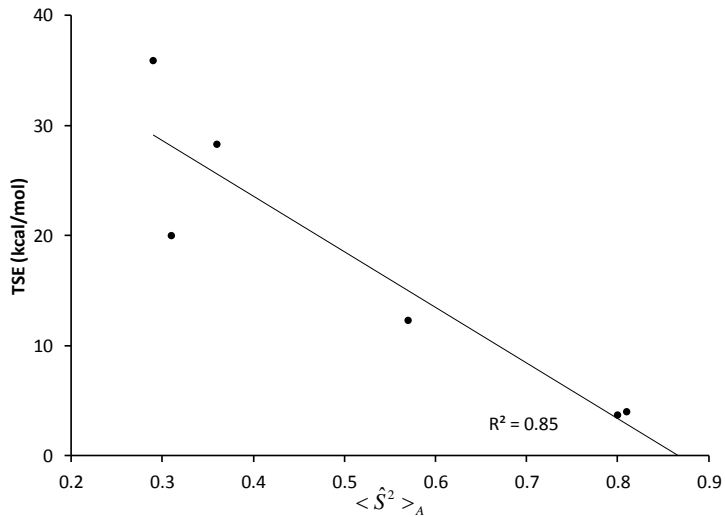
Molecule	k	$\Delta^{(k)}$	
		Doublet	Quartet
TMB	3	0.232 (0.231)	0.248
2-DMX	3	0.227	0.287
5-DMX	3	0.263	0.253
1,2,3-TDB	3	0.207	0.181
1,2,4-TDB	3	0.279	0.165
1,3,5-TDB	3	0.200	0.168

Triradicals

1. 2.35 kca/mol

2. 28.3 kca/mol

3. 4.0 kca/mol

4. 20.0 kcal/mol

5. 35.9 kcal/mol

6. 3.7 kcal/mol

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Triradicals

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