SC(N,M): Spin-Coupled Theory for 'N Electrons in M Orbitals' Active Spaces

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Spin-coupled (SC) wavefunction

Hartree-Fock:

$$\Psi_{HF} = \hat{A}\left[\, \psi_1^2\, \psi_2^2 \ldots \psi_n^2\, \underbrace{(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\ldots(\alpha\beta - \beta\alpha)}_{n \text{ singlet pairs}} \right]$$

SC wavefunction for N electrons SC(N) ≡ SC(N,N):

$$\Psi_{SM} = \hat{A}\left(\psi_1\, \psi_2 \ldots \psi_N\, \Theta_{SM}^N \right)$$

$$\psi_\mu = \sum_{p=1}^{m} c_{\mu p} \chi_p$$

Single product of
N singly-occupied orbitals,
no orthogonality constraints

$$\Theta_{SM}^N = \sum_{k=1}^{f_S^N} C_{Sk}\, \Theta_{SM;k}^N$$

$$\hat{S}^2 \Theta_{SM;k}^N = S(S+1)\Theta_{SM;k}^N$$

$$\hat{S}_z \Theta_{SM;k}^N = M\Theta_{SM;k}^N$$

$$f_S^N = \begin{pmatrix} N \\ \dfrac{N}{2} - S \end{pmatrix} - \begin{pmatrix} N \\ \dfrac{N}{2} - S - 1 \end{pmatrix}$$

SC: J. Gerratt and W. N. Lipscomb, *Proc. Natl. Acad. Sci. (USA)* **59 (**1968) 332

Full-GVB: R. C. Ladner and W. A. Goddard III, *J. Chem. Phys.* **51** (1969) 1073

SC wavefunction with core-valence separation

core component

$$\Psi_{SM} = \hat{A}\left(\overbrace{\varphi_1^2 \varphi_2^2 \ldots \varphi_n^2 \underbrace{\alpha\beta\alpha\beta \ldots \alpha\beta}_{n \; \alpha\beta \; \text{pairs}}} \underbrace{\psi_1 \psi_2 \ldots \psi_N \Theta_{SM}^N}_{\text{valence component}} \right)$$

$$= \hat{A}\left[(\text{core})\psi_1 \psi_2 \ldots \psi_N \Theta_{SM}^N \right]$$

$$E = \frac{\langle \Psi_{SM} | \hat{H} | \Psi_{SM} \rangle}{\langle \Psi_{SM} | \Psi_{SM} \rangle}$$

$$= D^{-1}\left(\sum_{\mu,\nu=1}^{N} D(\mu|\nu)\langle\mu|\,\textcolor{red}{\hat{f}}\,|\nu\rangle + \frac{1}{2}\sum_{\mu,\nu,\sigma,\tau=1}^{N} D(\mu\nu|\sigma\tau)\langle\mu\nu|\sigma\tau\rangle \right)$$

As a rule, quantitatively SC(N) ≡ SC(N,N) comes very close to a CASSCF(N,N) construction.

P. B. Karadakov, J. Gerratt,
D. L. Cooper and M. Raimondi,
J. Chem. Phys. **97** (1992) 7637

Classical VB interpretation of the SC(N) ≡ SC(N,N) wavefunction

$$\Psi_{SM} = \hat{A}\left(\psi_1\,\psi_2\ldots\psi_N \underbrace{\sum_{k=1}^{f_S^N} C_{Sk}\Theta_{SM;k}^{N}}_{\Theta_{SM}^{N}} \right)$$

VB-style structures
(non-orthogonal CSFs)
in *'resonance'*

$$= \sum_{k=1}^{f_S^N} C_{Sk}\hat{A}\left(\psi_1\,\psi_2\ldots\psi_N\Theta_{SM;k}^{N} \right) = \sum_{k=1}^{f_S^N} C_{Sk}\ \boxed{\Psi_{SM;k}}$$

$$\Theta_{SM}^{N} = \sum_{k=1}^{f_S^N} C_{Sk}\ \boxed{\Theta_{SM;k}^{N}}$$

For a VB picture, use **Rumer spin functions**

Kotani
Serber   } the three most frequently used spin bases
Rumer

SC(6) description of benzene

D.L. Cooper, J. Gerratt and
M. Raimondi
Nature **323** (1986) 699

$R_1(K_1)$ ⟷ $R_2(D_1)$ ⟷ $R_3(D_2)$ ⟷ $R_4(K_2)$ ⟷ $R_5(D_3)$
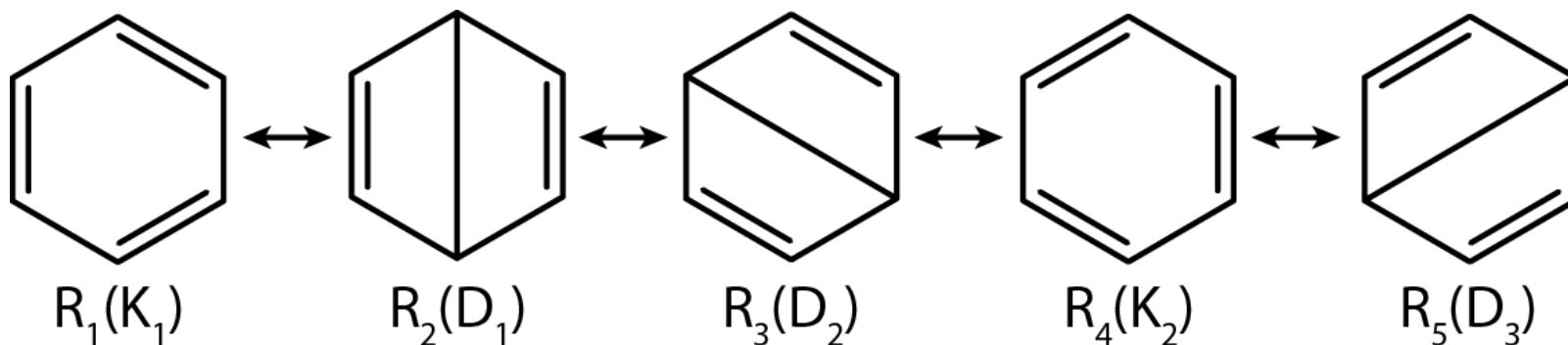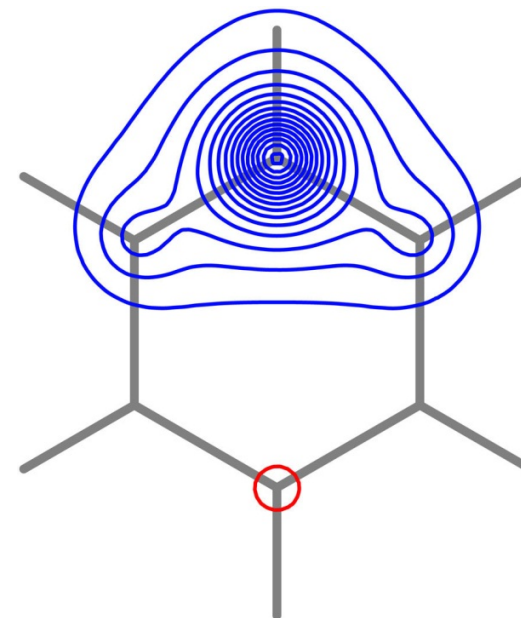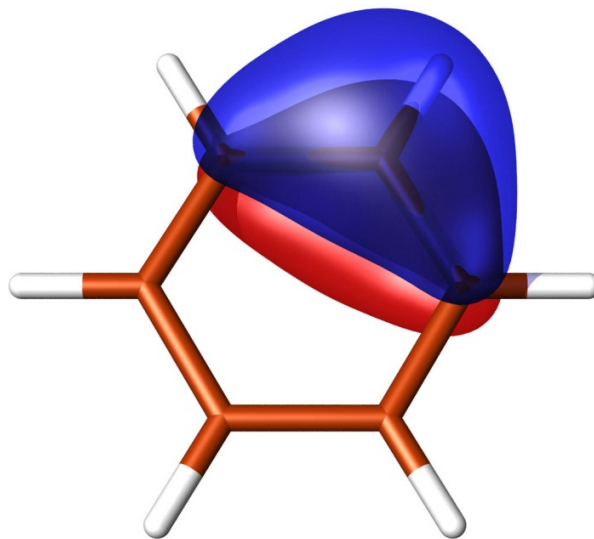
$$\Psi(S_0) \approx \Psi_{K_1} + \Psi_{K_2}$$

$$\Psi(S_1) \approx \Psi_{K_1} - \Psi_{K_2}$$

E.C. da Silva, J. Gerratt,
D.L. Cooper and M. Raimondi
J. Chem.Phys. **101** (1994) 3866

Addition of one electron to SC(N,N) → SC(N + 1,N)

$$\Psi_{SM}(N,N) = \hat{A}\left[(core)\psi_1\,\psi_2\ldots\psi_N\,\Theta_{SM}^N \right]$$

plus one extra electron, taking into account
all possible electron distributions

$$\Psi_{SM_S}(N+1,N) = \hat{A}\left\{ (core)\sum_{v=1}^{N}\left[\textcolor{red}{\psi_v\alpha\psi_v\beta}\left(\prod_{\mu\neq v}^{N}\psi_\mu\right)\Theta_{v;SM_S}^{N-1} \right] \right\}$$

$$\Theta_{v;SM_S}^{N-1} = \sum_{k=1}^{f_S^{N-1}} C_{v;Sk}\Theta_{SM_S;k}^{N-1}$$

P. B. Karadakov, D. L. Cooper,
B. J. Duke and J. Li, *J. Phys.
Chem. A* **116** (2012) 7238

'6 electrons in 5 orbitals' example: $C_5H_5^-$
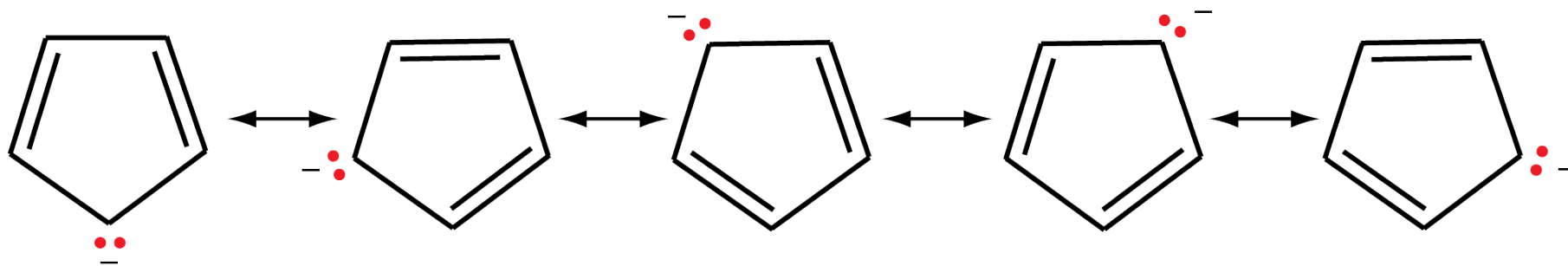
The SC(6,5) wavefunction:

$$\Psi_{00}(6,5) = \hat{A}(\text{core})\Big[\big(\psi_1\alpha\psi_1\beta\psi_2\psi_3\psi_4\psi_5 + \psi_2\alpha\psi_2\beta\psi_3\psi_4\psi_5\psi_1$$

$$+ \psi_3\alpha\psi_3\beta\psi_4\psi_5\psi_1\psi_2 + \psi_4\alpha\psi_4\beta\psi_5\psi_1\psi_2\psi_3$$

$$+ \psi_5\alpha\psi_5\beta\psi_1\psi_2\psi_3\psi_4\big)\big(C_{01}^4\Theta_{00;1}^4 + C_{02}^4\Theta_{00;2}^4\big)\Big]$$
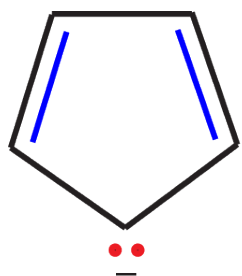
$\Theta_{00;1}^4$
weight 0.165
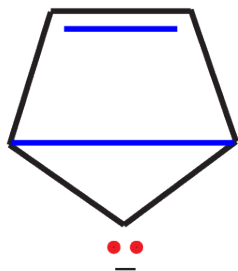
$\Theta_{00;2}^4$
weight 0.035
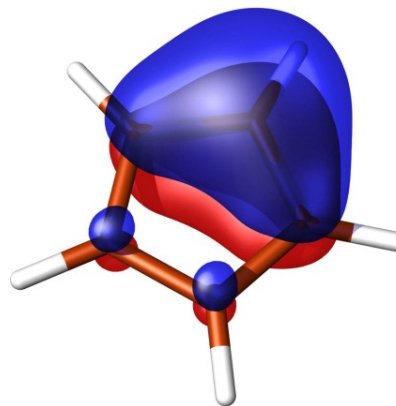
Removal of one electron from SC(N,N) → SC(N − 1,N)

$$\Psi_{SM}(N,N) = \hat{A}\left[(core)\psi_1\,\psi_2\ldots\psi_N\,\Theta_{SM}^N\right]$$

minus one electron, taking into account
all possible electron distributions

$$\Psi_{SM_S}(N-1,N) = \hat{A}\left\{(core)\sum_{v=1}^{N}\left[\left(\prod_{\mu\neq v}^{N}\psi_\mu\right)\Theta_{v;SM_S}^{N-1}\right]\right\}$$

$$\Theta_{v;SM_S}^{N-1} = \sum_{k=1}^{f_S^{N-1}}C_{v;Sk}\,\Theta_{SM_S;k}^{N-1}$$

'6 electrons in 7 orbitals' example, $C_7H_7^+$

7×
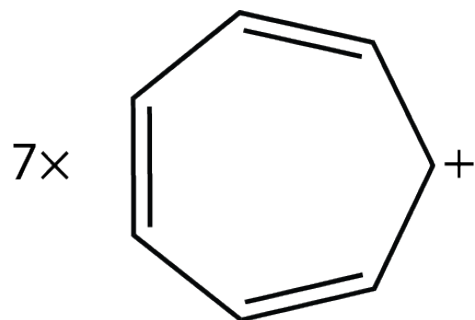
The SC(6,7) wavefunction:

$$\Psi_{00}(6,7) = \hat{A}(\text{core})\Big[\big(\psi_2\psi_3\psi_4\psi_5\psi_6\psi_7 + \psi_3\psi_4\psi_5\psi_6\psi_7\psi_1 + \psi_4\psi_5\psi_6\psi_7\psi_1\psi_2$$

$$+\psi_5\psi_6\psi_7\psi_1\psi_2\psi_3 + \psi_6\psi_7\psi_1\psi_2\psi_3\psi_4 + \psi_7\psi_1\psi_2\psi_3\psi_4\psi_5$$

$$+\psi_1\psi_2\psi_3\psi_4\psi_5\psi_6\big)\sum_{k=1}^{5}C_{0k}\Theta_{00;k}^6\Big]$$
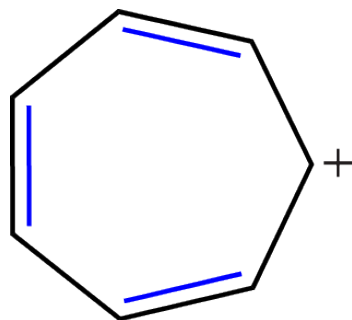
$\Theta_{00;1}^6$

weight 0.072
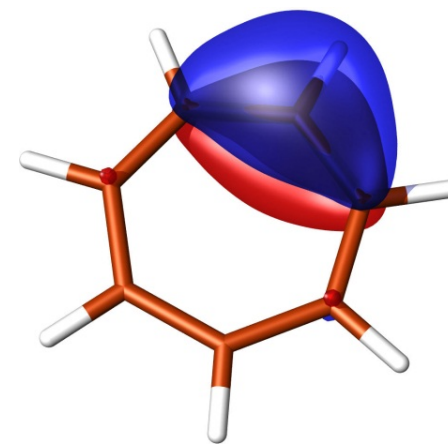
SC orbitals: SC(6,5) for $C_5H_5^-$, SC(6,6) for C_6H_6, SC(6,7) for $C_7H_7^+$

$C_5H_5^-$

C_6H_6

$C_7H_7^+$

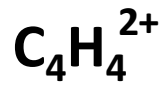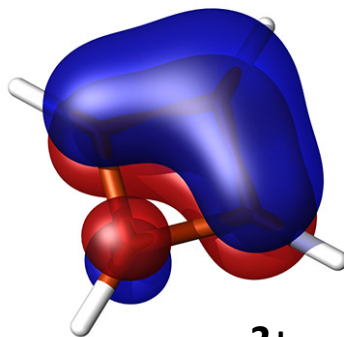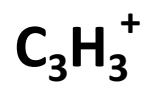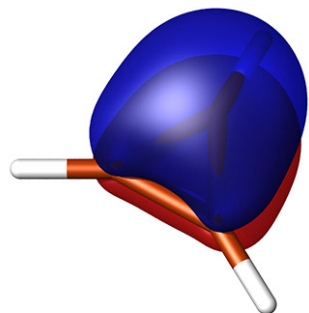**Modern Valence-Bond Description of Aromatic Annulene Ions**
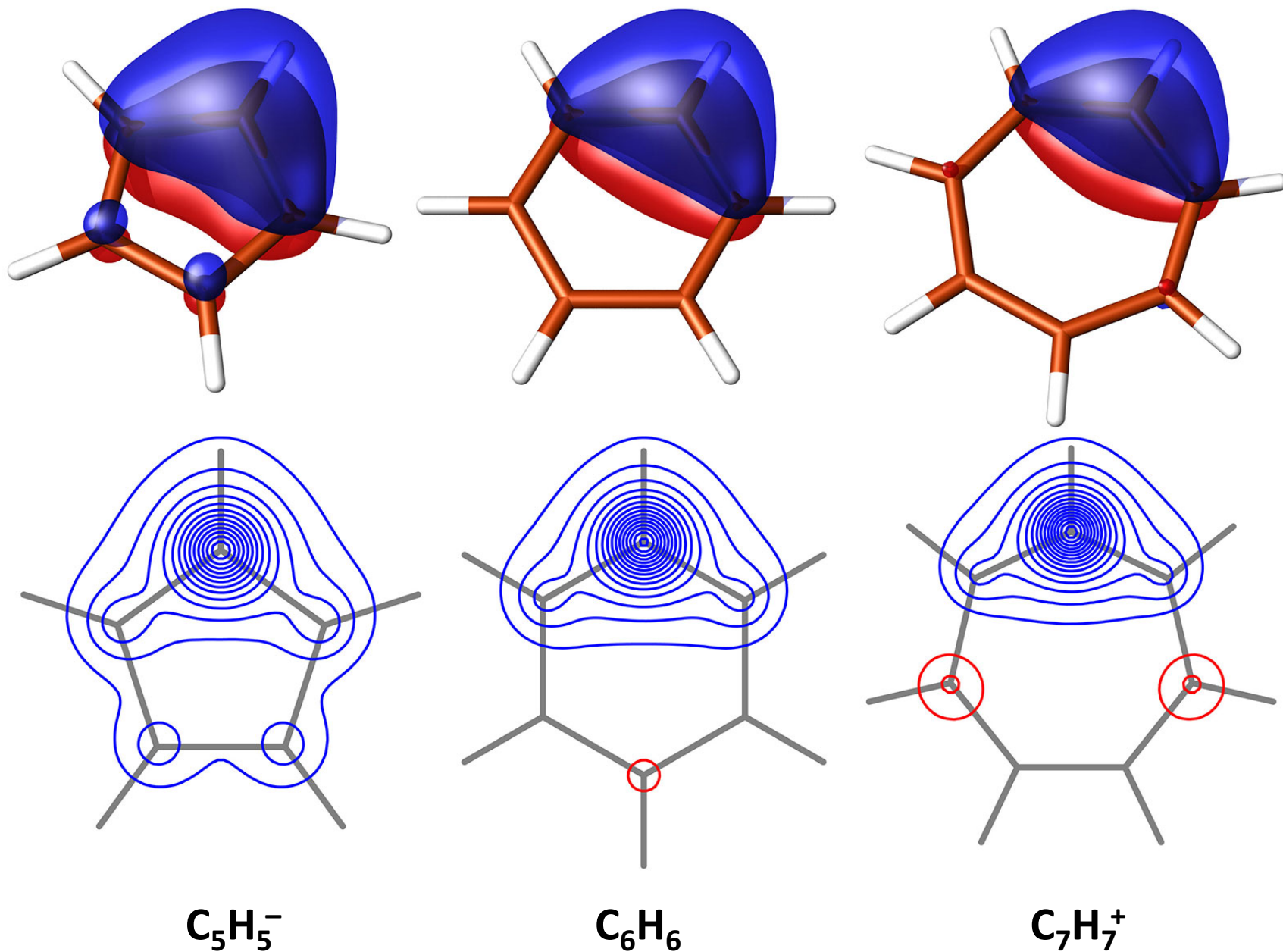
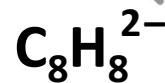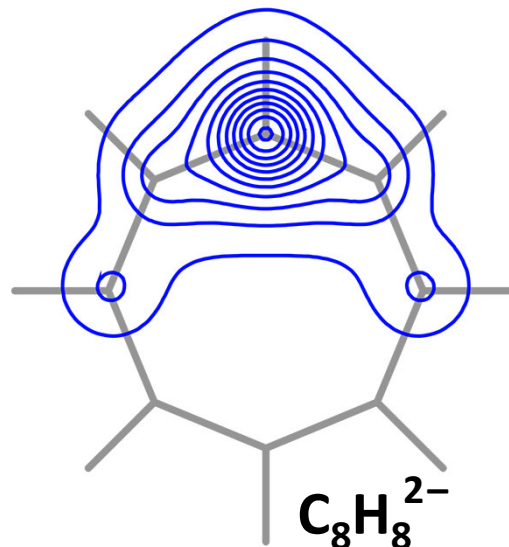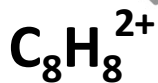CAS(2,3)/6-311G(d,p) D_{3h} LM — $C_3H_3^+$
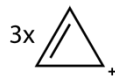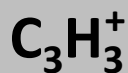
CAS(2,4)/6-311G(d,p) D_{4h} SP(1)
CAS(6,4)/6-311G(d,p) D_{4h} SP(4) — $C_4H_4^{2+,2-}$

CAS(6,5)/6-311G(d,p) D_{5h} LM — $C_5H_5^-$

CAS(6,7)/6-311G(d,p) D_{7h} LM — $C_7H_7^+$

CAS(6,8)/6-311G(d,p) D_{8h} LM
CAS(10,8)/6-311G(d,p) D_{8h} LM — $C_8H_8^{2+,2-}$
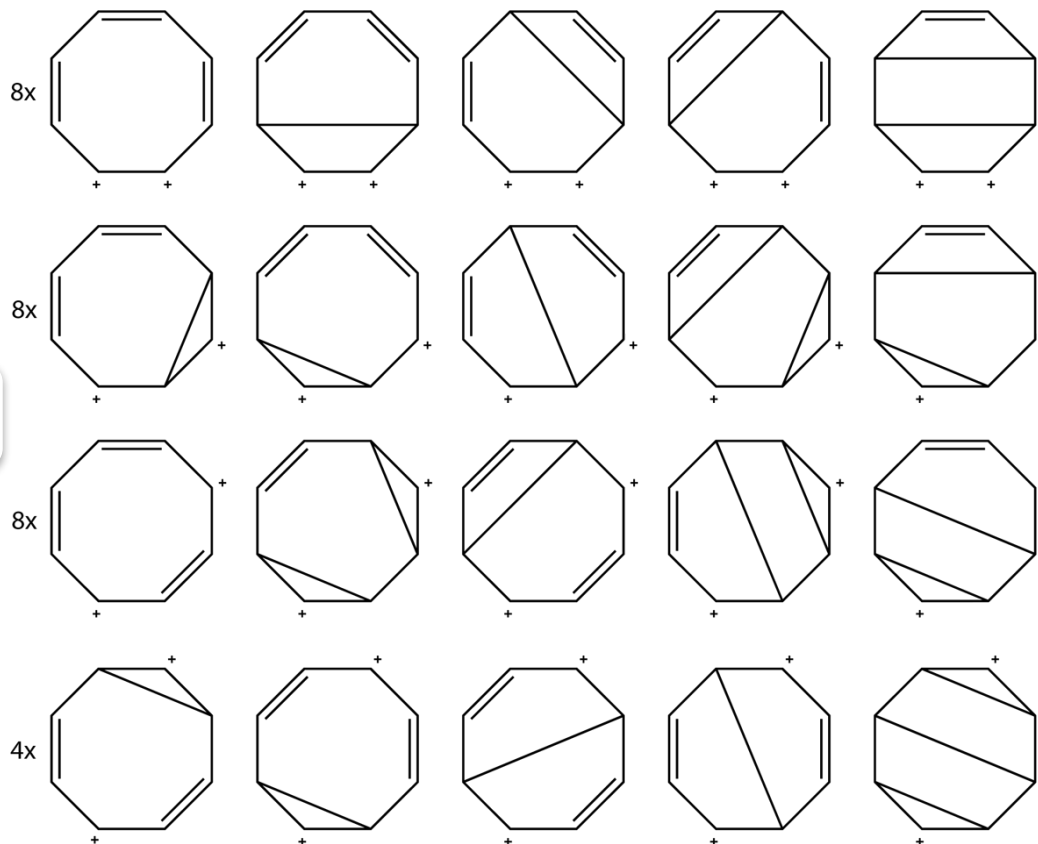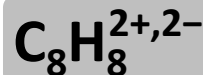
P. B. Karadakov and D. L. Cooper,
Theor. Chem. Acc. **133** (2014) 1421

$C_3H_3^+$ $C_4H_4^{2+}$ $C_4H_4^{2-}$

$C_5H_5^-$ C_6H_6 $C_7H_7^+$

$C_8H_8^{2+}$ $C_8H_8^{2-}$

$C_3H_3^+$ $C_4H_4^{2+}$ $C_4H_4^{2-}$ $C_5H_5^-$ C_6H_6 $C_7H_7^+$ $C_8H_8^{2+}$ $C_8H_8^{2-}$
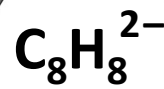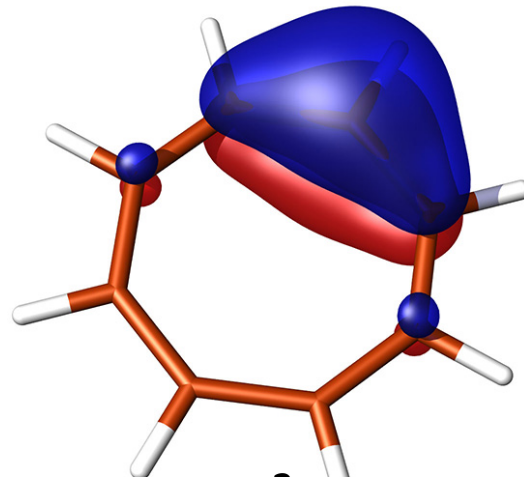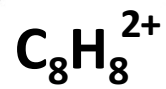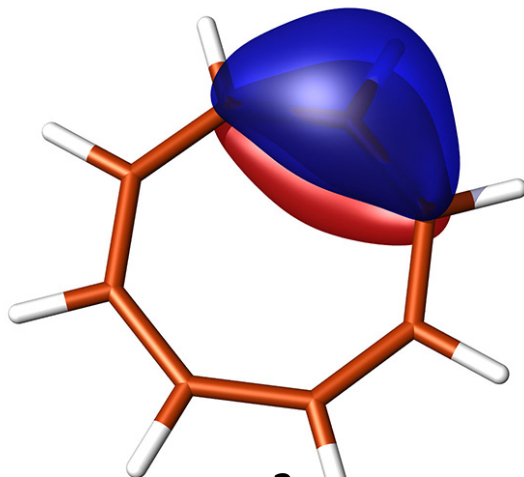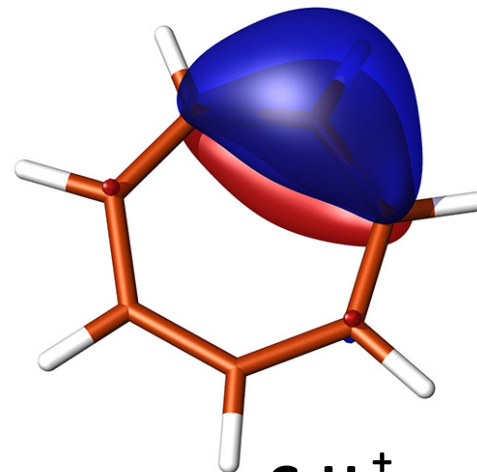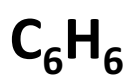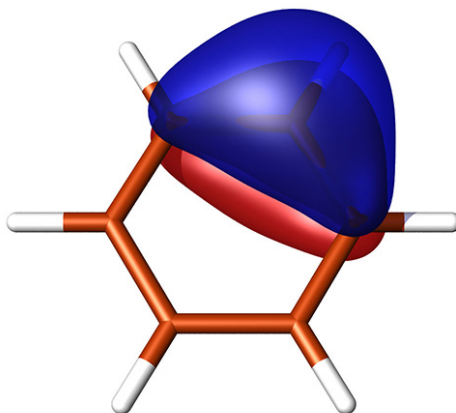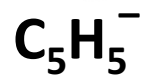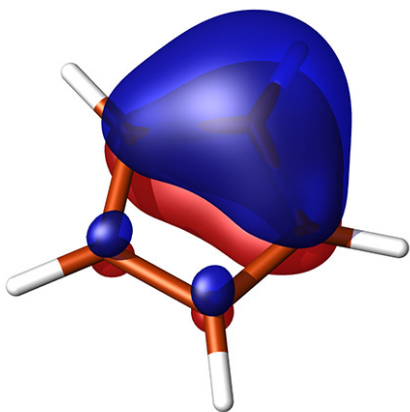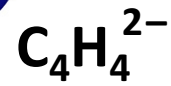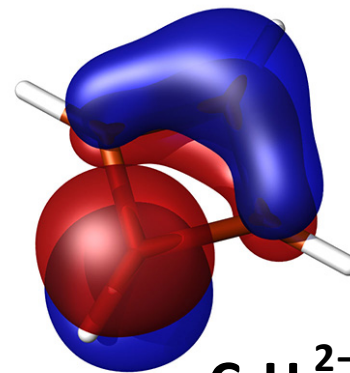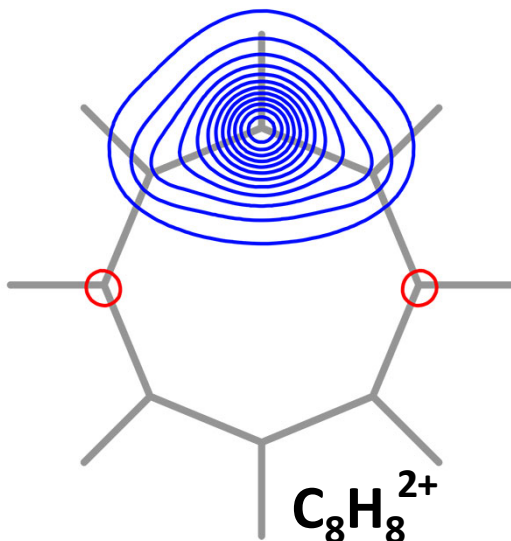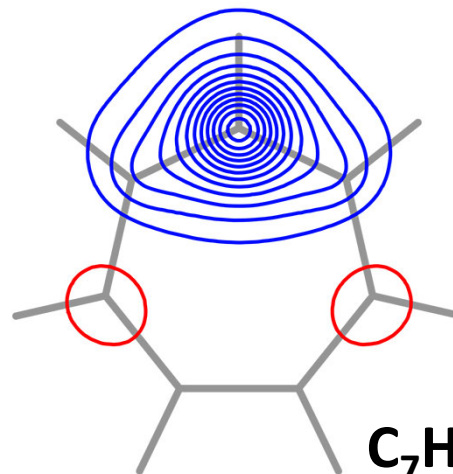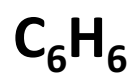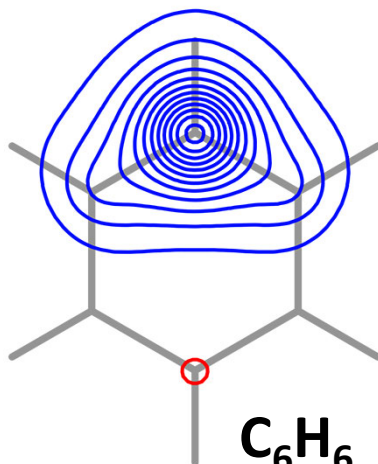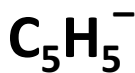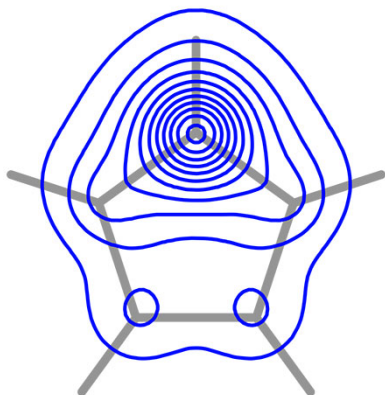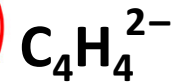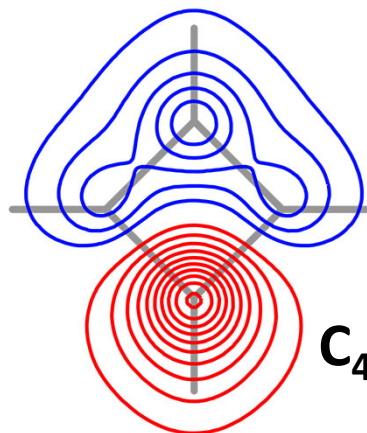
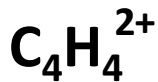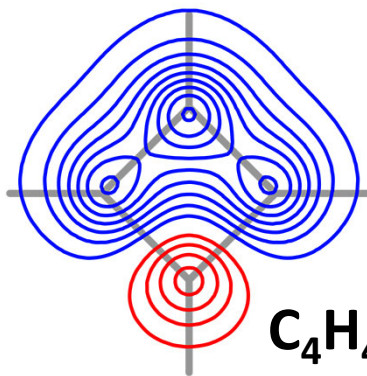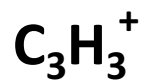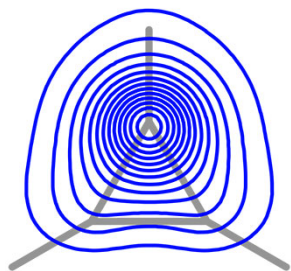| System	Ψ	CSFs	%CASSCF correlation E
Cyclopropenium ion ($C_3H_3^+$)	SC(2,3)	3	100.0%
	CASSCF(2,3)	6	100.0%
Cyclobutadiene dication ($C_4H_4^{2+}$)	SC(2,4)	6	100.0%
	CASSCF(2,4)	10	100.0%
Cyclobutadiene dianion ($C_4H_4^{2-}$)	SC(6,4)	6	100.0%
	CASSCF(6,4)	10	100.0%
Cyclopentadienide anion ($C_5H_5^-$)	SC(6,5)	10	97.6%
	CASSCF(6,5)	50	100.0%
Benzene (C_6H_6)	SC(6)	5	89.6%
	CASSCF(6,6)	175	100.0%
Cycloheptatrienyl cation ($C_7H_7^+$)	SC(6,7)	35	95.4%
	CASSCF(6,7)	490	100.0%
Cyclooctatetraene dication ($C_8H_8^{2+}$)	SC(6,8)	140	96.9%
	CASSCF(6,8)	1176	100.0%
Cyclooctatetraene dianion ($C_8H_8^{2-}$)	SC(10,8)	140	97.5%
	CASSCF(10,8)	1176	100.0%

Modern Valence-Bond Description of Homoaromaticity
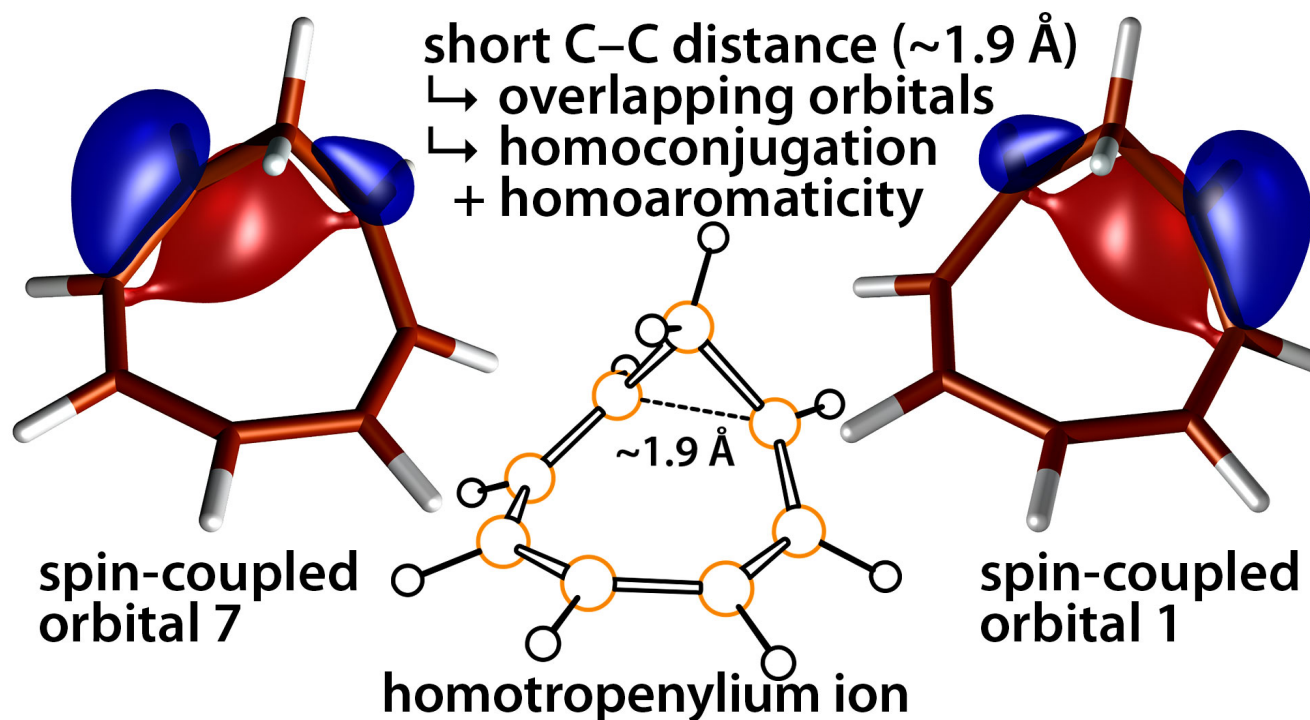
short C–C distance (~1.9 Å)
↳ overlapping orbitals
↳ homoconjugation
 + homoaromaticity

~1.9 Å

spin-coupled orbital 7

spin-coupled orbital 1

homotropenylium ion

$$\Psi_{00}(6,7) = \hat{A}\left[(core)\left(\psi_2\psi_3\psi_4\psi_5\psi_6\psi_7\Theta^6_{1;00} + \psi_3\psi_4\psi_5\psi_6\psi_7\psi_1\Theta^6_{2;00} \right.\right.$$

$$+ \psi_4\psi_5\psi_6\psi_7\psi_1\psi_2\Theta^6_{3;00} + \psi_5\psi_6\psi_7\psi_1\psi_2\psi_3\Theta^6_{4;00} + \psi_6\psi_7\psi_1\psi_2\psi_3\psi_4\Theta^6_{5;00}$$

$$\left.\left. + \psi_7\psi_1\psi_2\psi_3\psi_4\psi_5\Theta^6_{6;00} + \psi_1\psi_2\psi_3\psi_4\psi_5\psi_6\Theta^6_{7;00} \right)\right]$$

SC(6,7) 35 CSFs vs. CASSCF(6,7) 490 CSFs
94.9% of CASSCF correlation energy