SPIN-COUPLED VB AND CASVB METHODS AND THEIR APPLICATIONS

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CLASSICAL VB

- Played an important role in directing early qualitative models of bonding. Many VB concepts are still key components of the language of chemistry.

- Early computational implementations disappointing: (1) slow ($N!$); (2) ionic structures.

- Schism between variants of MO theory, for producing numbers, and simple VB ideas, for visualizing electronic structure. Debate became acrimonious and even entangled with politics. [*Physically and ideologically inadmissible notions formulated by decadent bourgeois scientists*]

- For practical calculations, VB theory has mostly been eclipsed by molecular orbital (MO) theory and, especially, density function theory (DFT).

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COULSON-FISCHER WAVEFUNCTION FOR H_2

Define:

$$\phi_A = 1s_A + \lambda\, 1s_B$$

$$\phi_B = 1s_B + \lambda\, 1s_A$$

Coulson-Fischer wavefunction is of 'covalent-only' VB form:

$$\Psi_{CF} = [\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)]\, \Theta$$

Special cases:

$\lambda = 0$ is Heitler-London function of classical VB

$\lambda = 1$ is $(1\sigma_g)^2$ of MO theory

Instead, λ is variationally optimized.

Ψ_{CF}, with just one spatial configuration, is the *same* wavefunction as 'Heitler-London + ionic' and it is the same as '2 in 2' CASSCF.

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SPIN-COUPLED (SC) THEORY

Most general N-electron wavefunction based on a single orbital product:

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

Orbitals expanded in a suitable basis and spin functions in full spin space:

$$\psi_\mu = \sum_{p=1}^{m} c_{\mu p} \chi_p \qquad\qquad \Theta^N_{SM} = \sum_{k=1}^{f^N_S} C_{Sk} \Theta^N_{SM\,;k}$$

Index k distinguishes between the f^N_S unique spin eigenfunctions sharing the same pair of S

and M values. Can construct spin functions in various ways: Kotani, Rumer, Serber …

Optimal SC orbitals and spin-coupling pattern determined variationally, through simultaneous optimization of the energy expectation value:

$$E = \frac{\langle \Psi_{SM} | \hat{H} | \Psi_{SM} \rangle}{\langle \Psi_{SM} | \Psi_{SM} \rangle} = D^{-1} \Big[\sum_{\mu,\nu=1}^{N} D(\mu|\nu)\langle \mu| \hat{h} |\nu\rangle + \frac{1}{2} \sum_{\mu,\nu,\sigma,\tau=1}^{N} D(\mu\nu|\sigma\tau)\langle \mu\nu|\sigma\tau\rangle \Big]$$

with respect to all $c_{\mu p}$ and C_{Sk}.

Multiple strategies for constructing density matrices: e.g. **U** matrices, cofactors …

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Introduction of *n* doubly-occupied core/inactive orbitals:

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

Energy expectation value:

$$E = E_{\text{c}} + D^{-1}\left[\sum_{\mu,\nu=1}^{N} D(\mu\,|\,\nu)\langle\mu\,|\,\hat{f}_{\text{c}}\,|\,\nu\rangle + \frac{1}{2}\sum_{\mu,\nu,\sigma,\tau=1}^{N} D(\mu\nu\,|\,\sigma\tau)\langle\mu\nu\,|\,\sigma\tau\rangle \right]$$

$$E_{\text{c}} = \sum_{i=1}^{n}\langle i\,|\,\hat{h} + \hat{f}_{\text{c}}\,|\,i\rangle \qquad\qquad \hat{f}_{\text{c}} = \hat{h} + \sum_{i=1}^{n}\left(2\hat{J}_i - \hat{K}_i\right)$$

Fixed or optimized core/inactive orbitals:

$$\varphi_i = \sum_{p=1}^{m} c_{ip}\chi_p$$

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Benzene S_0
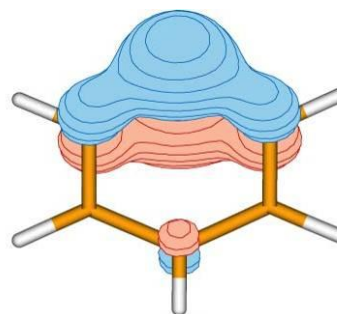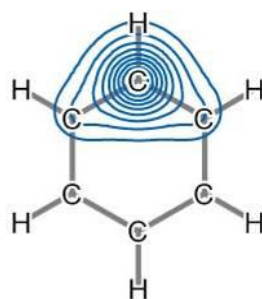
Overlaps: $\qquad$ $\Delta_{12} = 0.52$ $\qquad$ $\Delta_{13} = 0.03$ $\qquad$ $\Delta_{14} = -0.16$

Spin coupling: $\qquad$ $P_1 = P_4 \approx 41\%$ $\qquad$ $P_2 = P_3 = P_5 \approx 6\%$

Resonance energy: ~85 kJ mol^{-1}

S_1

Orbitals resemble those for S_0 (but increased overlaps with other sites).

Overlaps: $\qquad$ $\Delta_{12} = 0.60$ $\qquad$ $\Delta_{13} = 0.29$ $\qquad$ $\Delta_{14} = 0.28$

Spin coupling: $\qquad$ Out-of-phase combination of two Kekulé-like structures.

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SPIN-COUPLED VB (SCVB) THEORY

Virtual orbitals

At convergence, SC orbitals ψ_μ satisfy separate orbital equations based on $(N-1)$–electron operators $\hat{F}_\mu^{eff}$ from which the particular occupied orbital has been excluded:

$$\hat{F}_\mu^{eff}\, \psi_\mu^{(i)} = \varepsilon_\mu^{(i)}\, \psi_\mu^{(i)}$$

Obtain 'stacks' of fairly compact orthonormal virtual orbitals $\psi_\mu^{(i)}$ that correspond closely to the physical situation in actual excited states. [Different stacks overlap]

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SCVB wavefunctions

- Excited configurations mostly constructed by single, double (*etc*) excitations from one or more reference functions, replacing occupied orbitals with their 'own' virtuals.

- Final SCVB wavefunctions obtained from nonorthogonal CI calculations involving reference configuration(s) and excited configurations.

- Very compact.

- Achieve a fairly uniform level of accuracy for many states of one or more spatial symmetries and spin multiplicities over the entire range of nuclear coordinates.

Applications include charge transfer processes in astrophysical environments:

$$A^{q+} + B \rightarrow A^{(q-1)+} + B^+$$
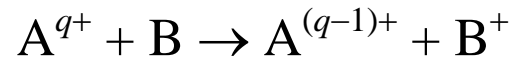
Concerned in adiabatic molecular picture with avoided crossings of **many** AB^{q+} potentials.

Electron transfer corresponds to nonradiative transitions driven by matrix elements $A_{ij} = \langle \Psi_i | \partial/\partial R | \Psi_j \rangle$.

Convenient to transform to p-diabatic representation (**A** is null) for solving scattering problem. Electron capture driven by off-diagonal elements of the potential matrix $\mathbf{U}(R)$.

- Straightforward with SCVB to identify dominant 'atomic' contributions. Good asymptotic energies.

- Compactness of SCVB wavefunctions particularly beneficial for (a) numerical computation of nonadiabatic couplings and (b) for carrying out transformation to diabatic representation.

Example: $O^{7+} + He \rightarrow O^{6+} (n=4) + He^+$
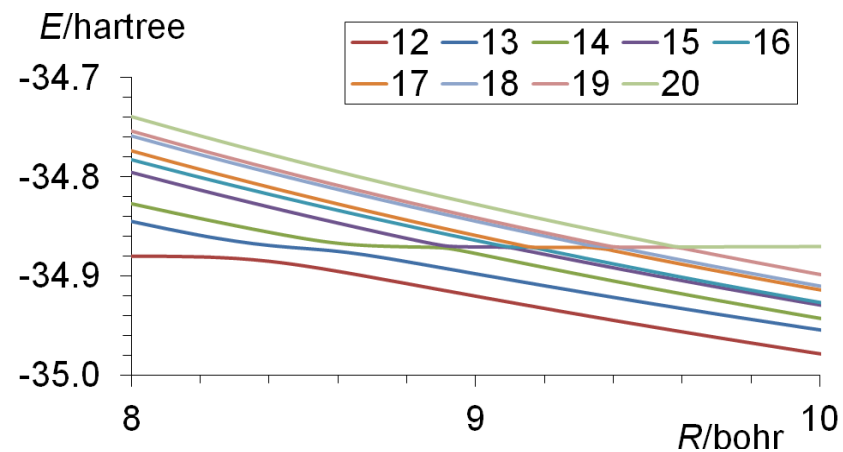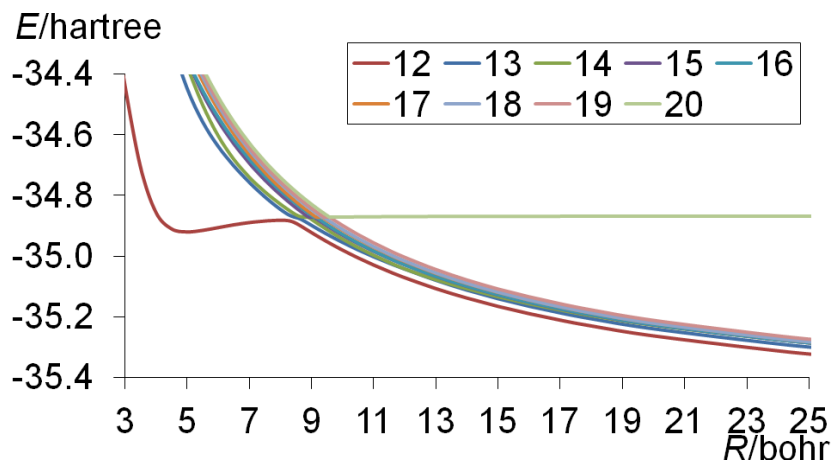
CASVB

Basic idea?

$$\Psi_{\text{CAS}} = \sum_{I}^{N_{\text{CI}}} c_I \Phi_I \qquad \text{(normalized)}$$

Exploit the invariance of full CI wave functions to nonsingular transformations of the defining orbitals:

$$\{\phi'\} = \{\phi\}\boldsymbol{O} \qquad\qquad \{\Phi'\} = \{\Phi\}\boldsymbol{T}(\boldsymbol{O})$$

$$m \text{ orbitals } \phi \qquad\qquad N_{\text{CI}} \text{ structures } \Phi$$

$$\boldsymbol{O} = \boldsymbol{O}_1\boldsymbol{O}_2 \qquad \Leftrightarrow \qquad \boldsymbol{T}(\boldsymbol{O}) = \boldsymbol{T}(\boldsymbol{O}_1)\boldsymbol{T}(\boldsymbol{O}_2)$$

Write $(O_{11}(\lambda_1)O_{12}(\lambda_2)O_{13}(\lambda_3)\ldots O_{mm}(\lambda_{m^2}))^{-1} O = 1$

with $O_{ij}(\lambda): \phi_j \rightarrow \phi_j + \lambda\phi_i$

for which the corresponding transformation of the structure space is very simple – achieved by application of the operator

$$\hat{I} + \lambda\hat{E}_{ij}^{(1)} + \lambda^2\hat{E}_{ij}^{(2)}$$

[$\hat{E}_{ij}^{(1)}$ & $\hat{E}_{ij}^{(2)}$ generate spin-averaged single & double excitations]

$\rightarrow\rightarrow\rightarrow$ Highly efficient strategy for realizing exactly the effects of the structure transformation $T(O)$, without explicit construction.

PLUS: Convenient expressions for the first and second derivatives of $T(O)$ with respect to the λ parameters.

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Optimization criterion?

Want Ψ_{VB} to dominate Ψ_{CAS} in:

$$\Psi_{CAS} = S_{VB}\Psi_{VB} + (1 - S_{VB}^2)^{1/2}\Psi_{VB}^{\perp}$$

So: *maximize* $S_{VB} = \dfrac{\langle\Psi_{CAS}|\Psi_{VB}\rangle}{\langle\Psi_{VB}|\Psi_{VB}\rangle^{1/2}}$

or: *minimize* $E_{VB} = \dfrac{\langle\Psi_{VB}|\hat{H}|\Psi_{VB}\rangle}{\langle\Psi_{VB}|\Psi_{VB}\rangle}$

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- Obtain *exact* representations of 'N in m' CASSCF wavefunctions in which a small number of modern-VB structures dominate.

- Analogous overlap- and energy-optimized wavefunctions typically very similar.

- Embed energy criterion within CASSCF procedure $\rightarrow$ allows fully-variational optimization of general types of modern-VB wavefunction, including (MC)SC, via a linked two-step iterative strategy. [Excited states.]

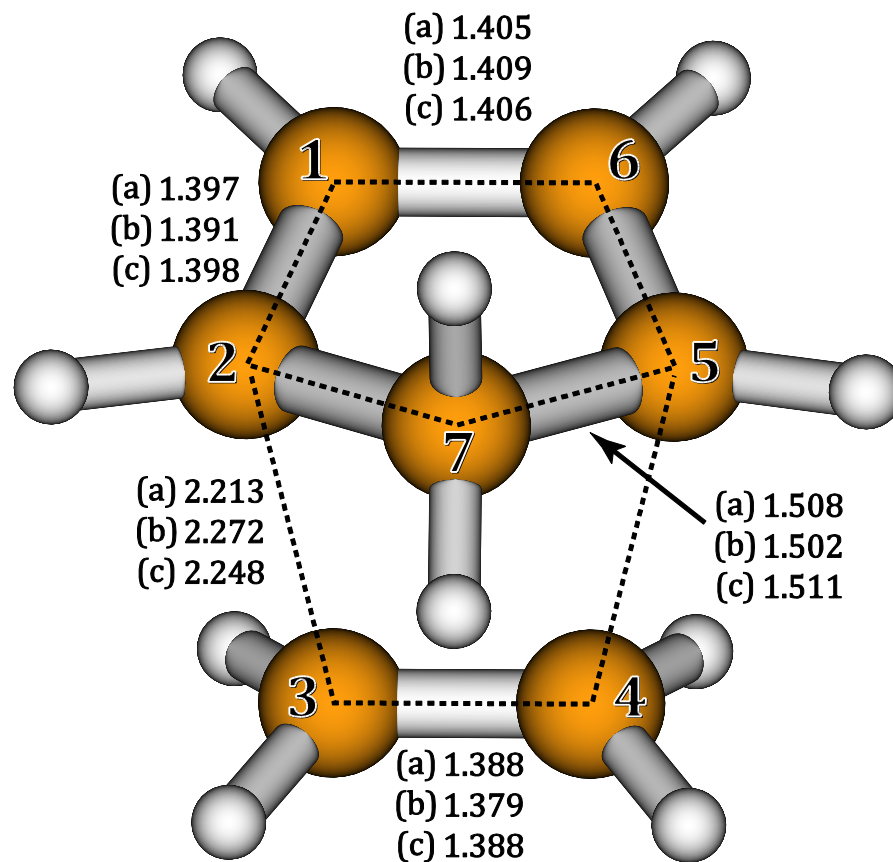- MOLPRO & MOLCAS.

REACTION PATHWAYS

Current procedure for constructing SC model of electronic mechanism of an organic chemical reaction involves two steps:

1. TS and sequence of geometries along the reaction path (or intrinsic reaction coordinate) towards reactants and products are calculated using an existing efficient implementation of an appropriate high-level MO or DFT approach.

2. Series of SC calculations at representative geometries along the IRC. Analysis involves examining the variations in the shapes of the SC orbitals and the overlaps between them, the changes to the pattern of spin coupling, and so on …

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- Useful to compare performance of SC(N) with 'N in N' CASSCF construction. For benzene, amount of 'non-dynamic' '6 in 6' π space CASSCF correlation energy recovered by SC(6) is *ca.* 90%. Along a reaction path, SC typically accounts for consistently more than 90% of the CASSCF correlation energy. Single orbital product provides a reasonably close approximation to its CASSCF counterpart, without the inclusion of ionic structures.

- SC approach requires next to no 'hand-tailoring'. Being the most general wavefunction based on a single orbital product, it arguably represents the highest level of theory at which one can obtain directly orbital models of the bond-breaking and bond-formation processes accompanying organic chemical reactions.

DIELS-ALDER REACTIONS

Retro Diels-Alder Reaction of Norbornene (to Cyclopentadiene and Ethene)

(a) 1.405
(b) 1.409
(c) 1.406

(a) 1.397
(b) 1.391
(c) 1.398

(a) 2.213
(b) 2.272
(c) 2.248

(a) 1.508
(b) 1.502
(c) 1.511

(a) 1.388
(b) 1.379
(c) 1.388

TS: (a) CCSD; (b) MP2; (c) B3LYP

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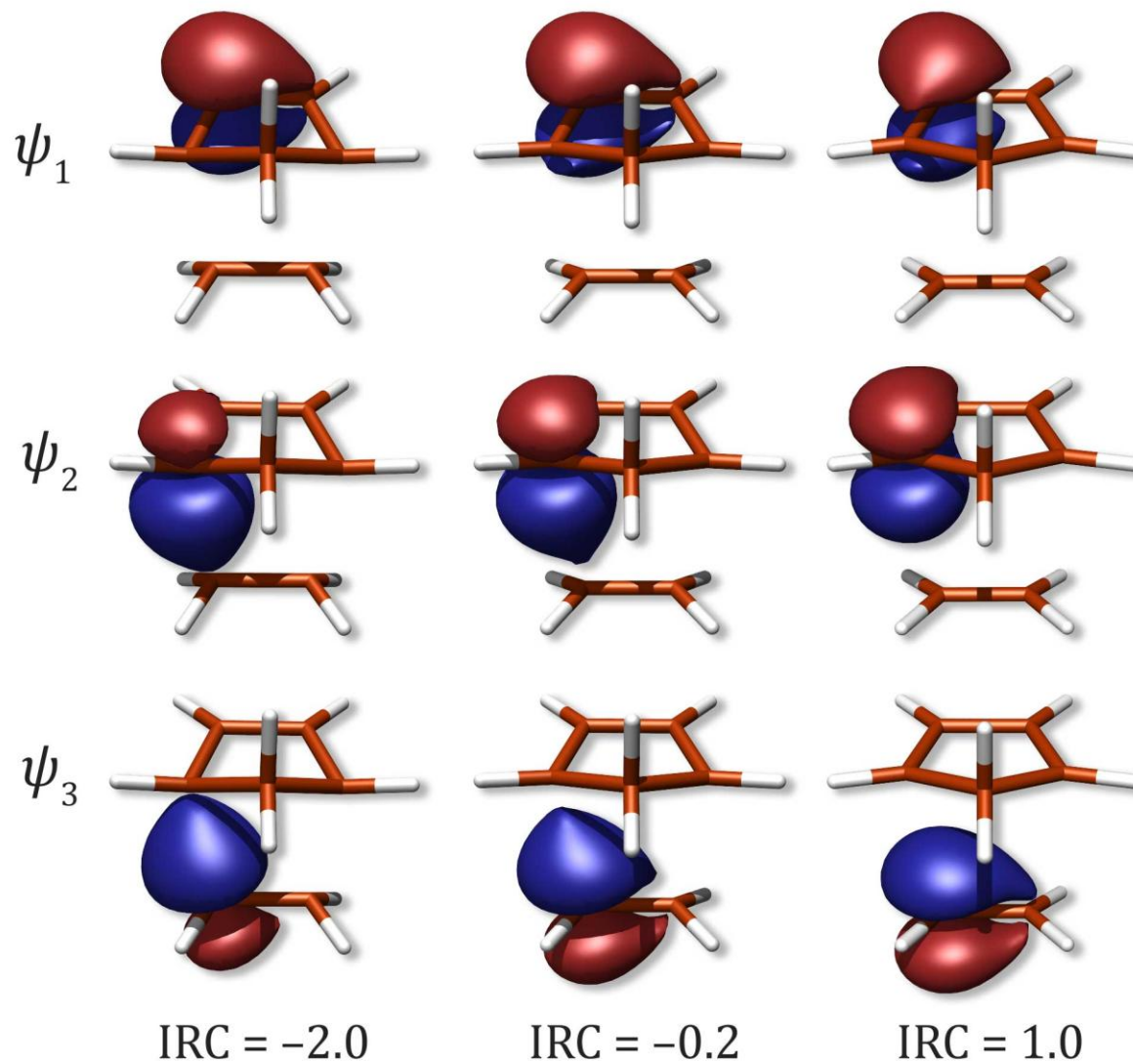Calculate IRC at B3LYP/6-31G(d) level [step size 0.1 amu$^{\frac{1}{2}}$bohr].

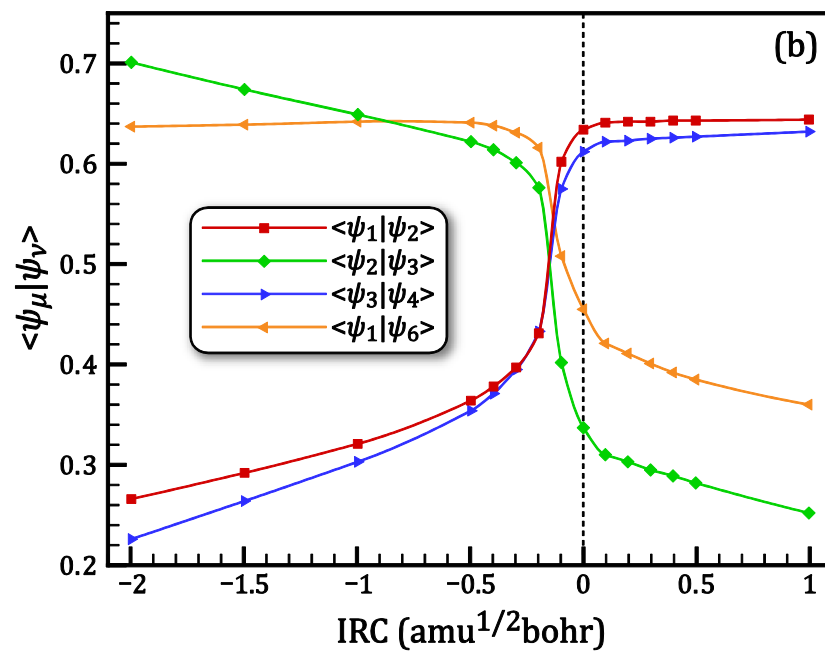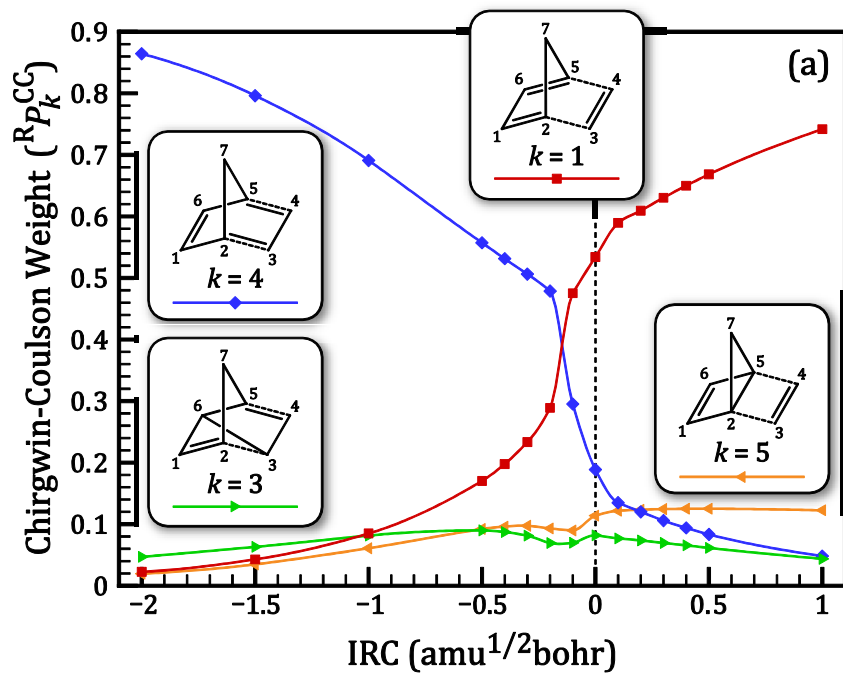Then, monitor the electronic rearrangements along this pathway using SC:

$$\Psi = \hat{A}\left[\left(\prod_{i=1}^{n} \phi_i\alpha\,\phi_i\beta\right)\left(\prod_{\mu=1}^{N} \psi_\mu\right)\Theta_{SM}^{N}\right]$$

Examine evolution of shapes of ψ_μ, active-orbital overlaps, composition of Θ_{SM}^{N}, vertical resonance energy, Wiberg-Mayer indices

$$W_{AB} = \sum_{p \in A}\sum_{q \in B} (\mathbf{DS})_{pq}\,(\mathbf{DS})_{qp}$$

… and so on

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ψ_1

ψ_2

ψ_3

IRC = −2.0　　　IRC = −0.2　　　IRC = 1.0

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(a)

(b)

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- Most dramatic changes to electronic structure in gas phase retro Diels-Alder reaction of norbornene (bicyclo[2.2.1]hept-2-ene) occur in a relatively narrow interval.

- Passes through a geometry, a little before the TS, at which the SC description resembles that of the archetypal aromatic system: benzene.

- Results consistent with a synchronous 'aromatic' mechanism.
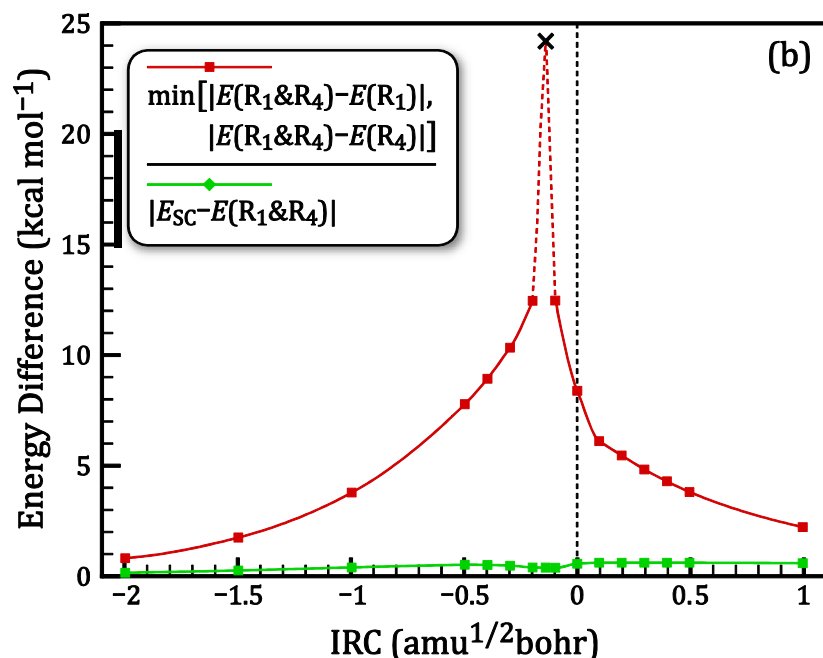
SC THEORY FOR '*N* ELECTRONS IN *M* ORBITALS' ACTIVE SPACES

SC(N,M) retains the essential features of the original SC model:

- As few orbitals as possible, $|N-M|$, are doubly-occupied (for $N>M$) or missing (for $N<M$). All other orbitals are singly occupied;

- Each orbital product is combined with a flexible spin function that allows any mode of coupling of the spins.

Example – one more electron than there are orbitals:

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

N orbital products, each associated with a spin space of dimension f_S^{N-1}.

e.g. $(6,5) - 10 \; vs \; 50$

Example: cyclopentadienyl anion, benzene and tropylium cation:

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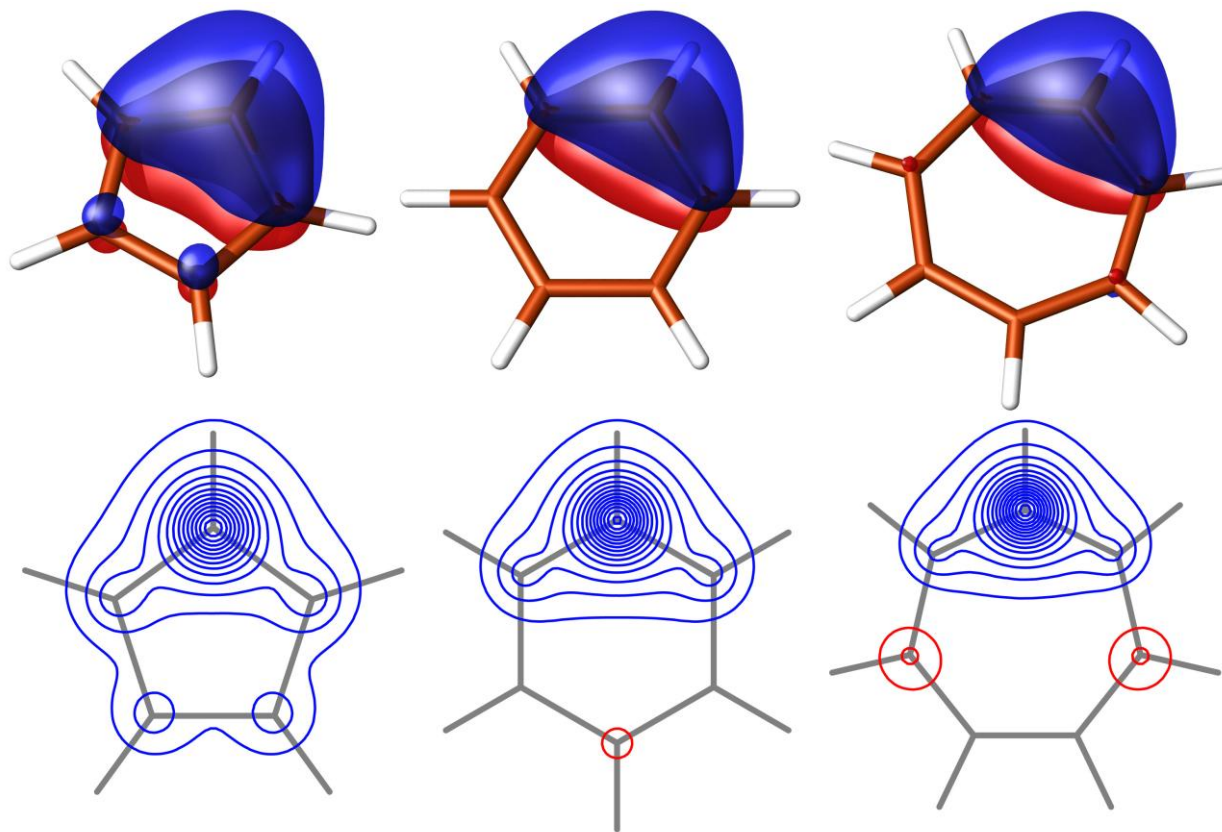
DOMAIN-AVERAGED FERMI HOLE (DAFH) ANALYSIS

- Original idea was to provide information about the behaviour of one electron of a pair when the second one is confined to (or 'averaged over') a fixed domain.

- Departure from quasi-independence of the motion of two electrons arises because of Fermi correlation and (beyond the Hartree-Fock approximation) because of Coulomb correlation.

$$g_A(\mathbf{r}_1,\mathbf{r}_1') = \rho^{(1)}(\mathbf{r}_1,\mathbf{r}_1') \left(\int_{\substack{\mathbf{r}_2=\mathbf{r}_2' \\ \Omega_A}} \rho^{(1)}(\mathbf{r}_2,\mathbf{r}_2') \, d\mathbf{r}_2 \right) - 2 \left(\int_{\substack{\mathbf{r}_2=\mathbf{r}_2' \\ \Omega_A}} \rho^{(2)}(\mathbf{r}_1,\mathbf{r}_1';\mathbf{r}_2,\mathbf{r}_2') \, d\mathbf{r}_2 \right)$$

$$\equiv \sum_{ij} \phi_i^*(\mathbf{r}_1) \, G_A(i,j) \, \phi_j(\mathbf{r}_1')$$

- Diagonalize $\mathbf{G}_A = \{G_A(i,j)\}$

- Isopycnic localization procedure
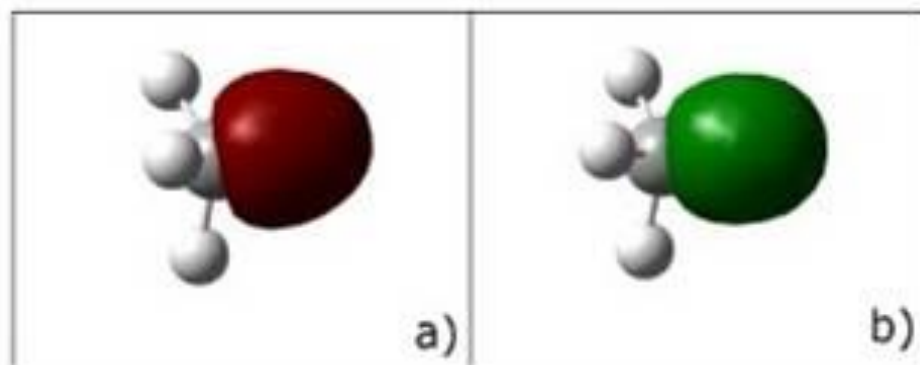
DAFH analysis of CH$_4$

(a) Analysis for C: four essentially degenerate occupation numbers (0.97). Each resembles a CH bond LMO. ['Broken' or free valence from formal splitting of CH$_3$ from H]

(b) Analysis for H: n_1=0.97. Resembles (a). ['Broken' or free valence of H]

DAFH analysis provides an appealing alternative strategy for extracting useful new insights into electronic structure and bonding from correlated wavefunctions by making direct use of the pair density. In general, results are compatible with expectations from modern-VB treatments.

SUMMARY

- SC approach provides highly visual direct insights into electronic rearrangements that accompany molecular bond-breaking and bond-formation processes, especially along the minimum energy paths of organic reactions.

- Straightforward generalization to active spaces of N electrons in M orbitals – SC(N,M).

- CASVB code is available in MOLPRO & MOLCAS.

- Compact SCVB (non-orthogonal CI) calculations can produce useful accuracy for multiple excited states over a wide range of nuclear geometry.

- DAFH analysis provides an appealing alternative strategy for extracting useful new insights from correlated wavefunctions.

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