

CECAM VB/NOCI workshop: Perspective; March 28, 2017.

# Coupled cluster valence bond theory



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# Outline

- 1. Introduction: Valence bond & perfect pairing**
2. Coupled cluster valence bond
3. CCVB with full singles and doubles

# Simplest strong correlation problem: The two-electron bond between atoms A & B

- 2 e's in 2 orbitals wavefunction:

$$|\Psi_{pair}\rangle \propto |(M\alpha)(M\beta)| + t |(M^*\alpha)(M^*\beta)|$$

$M$ : AB bond orbital  
 $M^*$ : AB antibond

- Equivalent VB wavefunction:

$$|\Psi_{pair}\rangle \propto |(A\alpha)(B\beta)| - |(A\beta)(B\alpha)| \\ \propto \mathcal{H} \{ AB(\alpha\beta - \beta\alpha) \}$$

$A, B$  nonorthogonal:  
Can vary from  
molecular to atomic

- Mixing angle  $\Rightarrow$  correlation strength:

$$A = M \cos(\theta/2) + M^* \sin(\theta/2)$$

$$B = M \cos(\theta/2) - M^* \sin(\theta/2)$$

## Perfect pairing (GVB-PP)

- Antisymmetrized product of 2-electron singlet functions

$$G_i \propto |(A_i\alpha)(B_i\beta)| - |(A_i\beta)(B_i\alpha)|$$

$$G_i \propto |(M_i\alpha)(M_i\beta)| + t_i |(M_i^*\alpha)(M_i^*\beta)|$$

$$\Psi_{PP} \propto \mathcal{A} \left\{ \prod_i G_i \right\}$$

- Strong orthogonality between pairs. Not within a pair.

$$\langle A_i | A_j \rangle = \langle B_i | B_j \rangle = \delta_{ij}$$

$$\langle A_i | B_j \rangle = s_i \delta_{ij}$$

- Exact for single electron pairs (or isolated pairs)
  - **singlet** coupling **within** each electron pair
  - electronic structure realization of the Lewis picture

# Coupled cluster version of the PP wave function

- Using sets of orthogonal bonding and antibonding orbitals...

$$A_i B_i (\alpha\beta - \beta\alpha) \leftrightarrow M_i \bar{M}_i + t_i M_i^* \bar{M}_i^*$$

- ... PP becomes a highly simplified CCD wave function

$$\Psi_{PP} = N \mathcal{A} \prod_i^{pairs} A_i B_i (\alpha\beta - \beta\alpha) \leftrightarrow \exp(\hat{T}_{PP}) \Phi_0$$

$$\hat{T} = \sum_i t_{i\bar{i}}^{i^* \bar{i}^*} \hat{a}_{i^*}^\dagger \hat{a}_{\bar{i}^*}^\dagger \hat{a}_{\bar{i}} \hat{a}_i$$

- A nice bridge to conventional coupled cluster theory....
  - ... and suggests one path to improving PP is via adding additional classes of cluster operator

## Four-electron systems: Double bond dissociations

- PP fails for 2 (or more) strongly coupled electron pairs
- Two separating pairs can couple to a singlet in two ways:
- PP style: Each pair is a singlet, couples together to a singlet

$$\delta_{s1} = (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)$$

PP-type

- Post-PP: Each pair is a triplet; couples together as a singlet

$$\delta_{s2} \propto \frac{1}{2}(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha) - \alpha\alpha\beta\beta - \beta\beta\alpha\alpha$$

- Triplet-triplet coupling is **omitted** in PP...
  - What is the simplest way to put it back?

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1. Introduction: Valence bond & perfect pairing

## 2. Coupled cluster valence bond

**David W. Small**

JCP 130, 084103 (2009); PCCP 13, 19285 (2011);  
JCTC 10, 2027 (2014); JCP (submitted).

3. CCVB with full singles and doubles

# Coupled cluster valence bond (CCVB) (David Small)

- Reference wave function is perfect pairing (PP).

$$\Phi_0 \equiv \Psi_{PP} = N\mathcal{A} \prod_i^{\text{pairs}} A_i B_i (\alpha\beta - \beta\alpha)$$

all pairs are singlet spin

- CCVB wave function: cluster-like expansion built on PP

$$\Psi_{\leq Q} = \Phi_0 + \sum_{k<l}^{\text{pairs}} t_{kl} \Phi_{(kl)} + \sum_{k<l<m<n}^{\text{pairs}} \left[ t_{kl} t_{mn} \Phi_{(kl)(mn)} + t_{km} t_{ln} \Phi_{(km)(ln)} + t_{kn} t_{lm} \Phi_{(kn)(lm)} \right]$$

means pairs K and L are triplet spin, recoupled to a singlet

- Energy, amplitudes: by projection. Orbitals optimized.

$$E = \langle \Phi_0 | H | \Psi \rangle = \langle \Phi_0 | H | \Phi_0 \rangle + \sum_{k<l}^{\text{pairs}} t_{kl} \langle \Phi_0 | H | \Phi_{(kl)} \rangle$$

$$\langle \Phi_{(kl)} | \hat{H} | \Psi \rangle = E \langle \Phi_{(kl)} | \Psi \rangle$$



# CCVB approximates spin-coupled valence bond (SCVB)

- **SCVB: The ultimate single-particle model....**
  - A **Hartree product of spatial orbitals**,  $\phi_i$ , 1 per electron.
  - A complete **spin coupling function** -- very complicated...
  - Separates any molecule exactly\* into atoms

$$\Psi_{SC-VB} \propto \mathcal{A} \left\{ \left( \prod_i^n \phi_i \right) \Theta_{S,M}^n \right\}$$

- **Challenging (recall yesterday!!) because:**
  - Spatial orbitals are **fully non-orthogonal**
  - Spin-space grows **exponentially** with  $n$ .
  - For  $S = 0$ : 1, 2, 5, 14, 42, ...

CCVB uses pair-orthogonality

CCVB uses only TT coupling

$$Dim = n! / \left[ \left( \frac{1}{2}n \right)! \left( \frac{1}{2}n + 1 \right)! \right]$$

## Properties of CCVB (Dave Small)

- Spin pure
- Correctly separates  $n$  electron pairs\*
- Size-consistent
- Simple/cheap: only  $O(M^2)$  amplitudes
- **Not variational** (empirically variational in practice)
- **Not exact for 2 pairs or more**
- **Not orbital invariant in valence space (multiple minima)**
- **Neglects not only dynamic, but also ionic correlations**

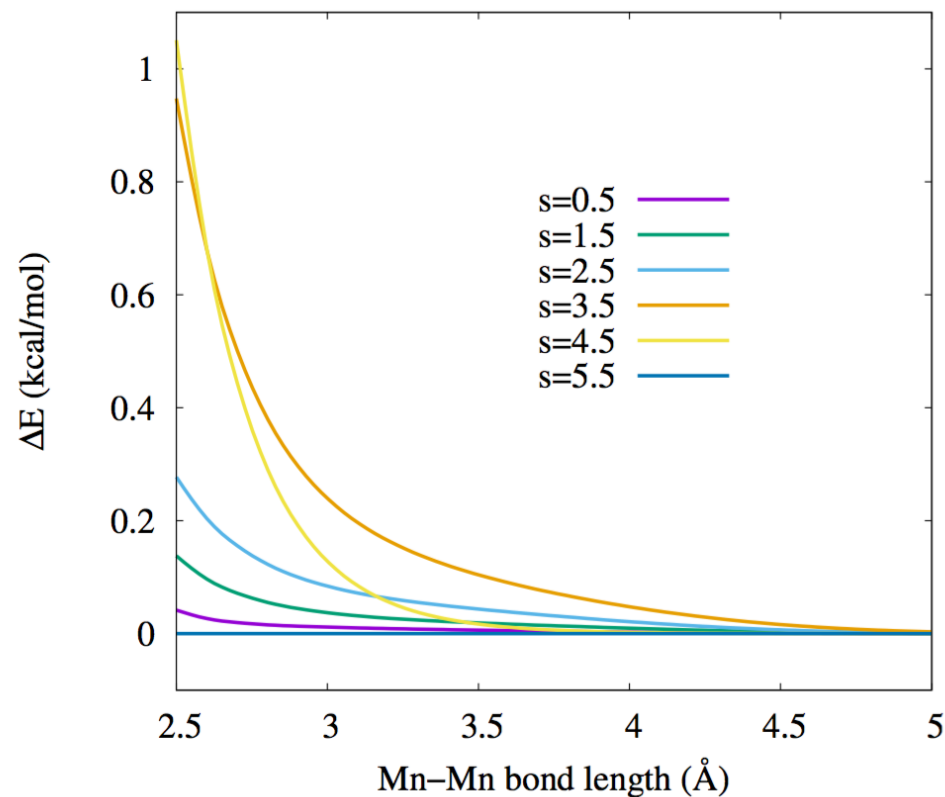
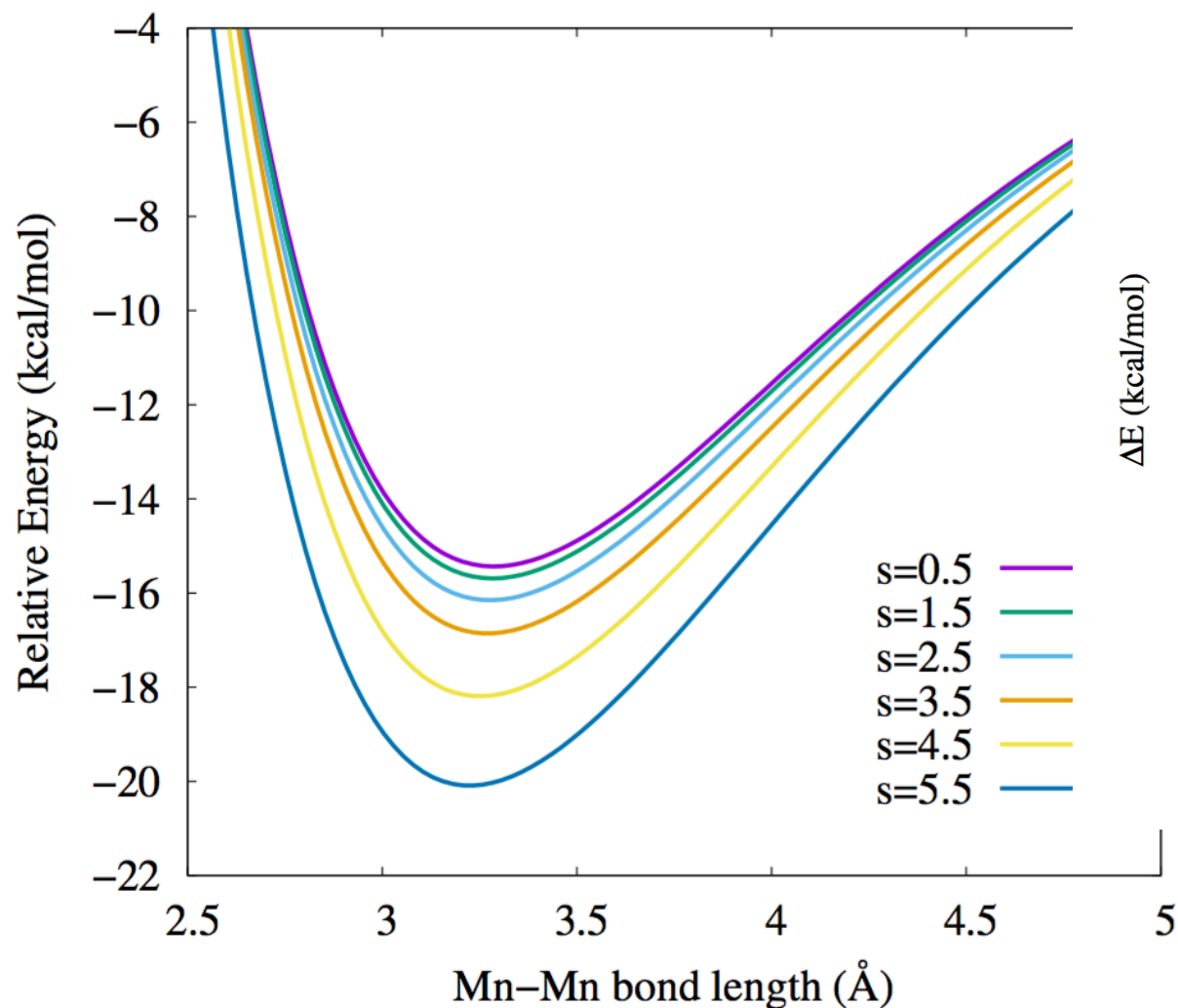
CCVB has the form of PUHF at dissociation...

PUHF not size-consistent

Efficient implementation:  
JCTC 10, 2027 (2014)

# Spin states in ferromagnetic $\text{Mn}_2^+$

$\text{Mn } 4s^2 3d^5$  (sextet);  $\text{Mn}^+ 4s^1 3d^5$  (septet); (11,11) space

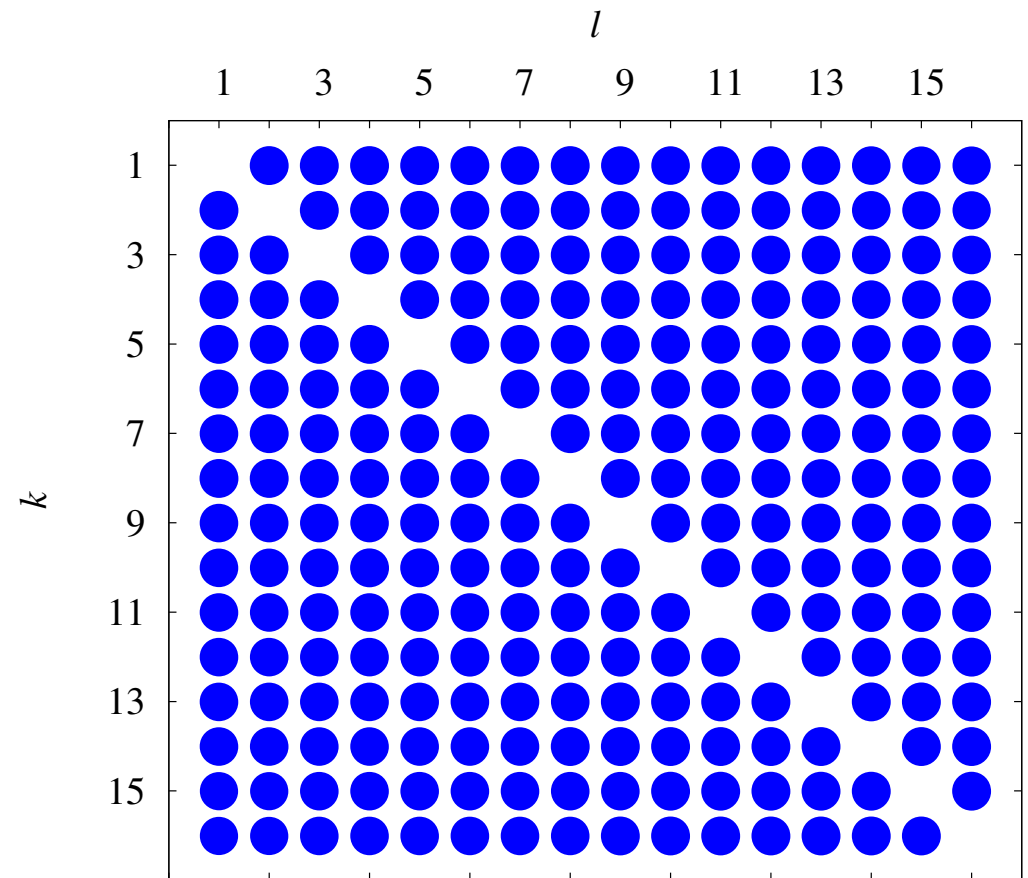
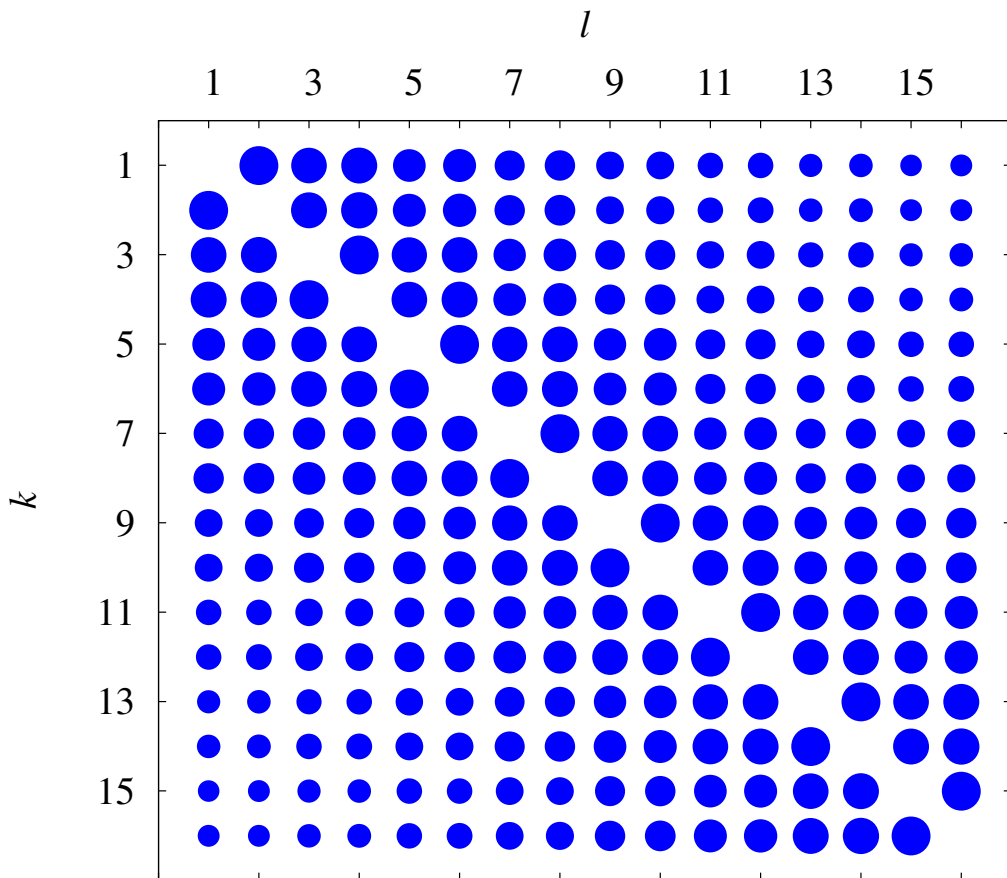


CCVB has small errors  
vs CASSCF

CCVB correctly separates all spin states, while UHF can only separate lowest ( $S=0.5$ ) and highest ( $5.5$ ) correctly



# Non-local strong correlations in polycarbenes (Dave Small)



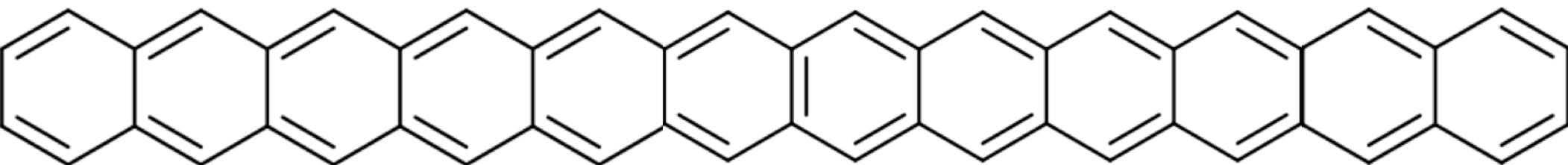
Above:  $t_{kl}$  couplings at  $R = 4 \text{ \AA}$ .  
Large  $t_{kl}$  now include non-local  
carbene-carbene couplings

Above:  $t_{kl}$  couplings at  $R = 5 \text{ \AA}$ .  
Large  $t_{kl}$  across the entire  
system!

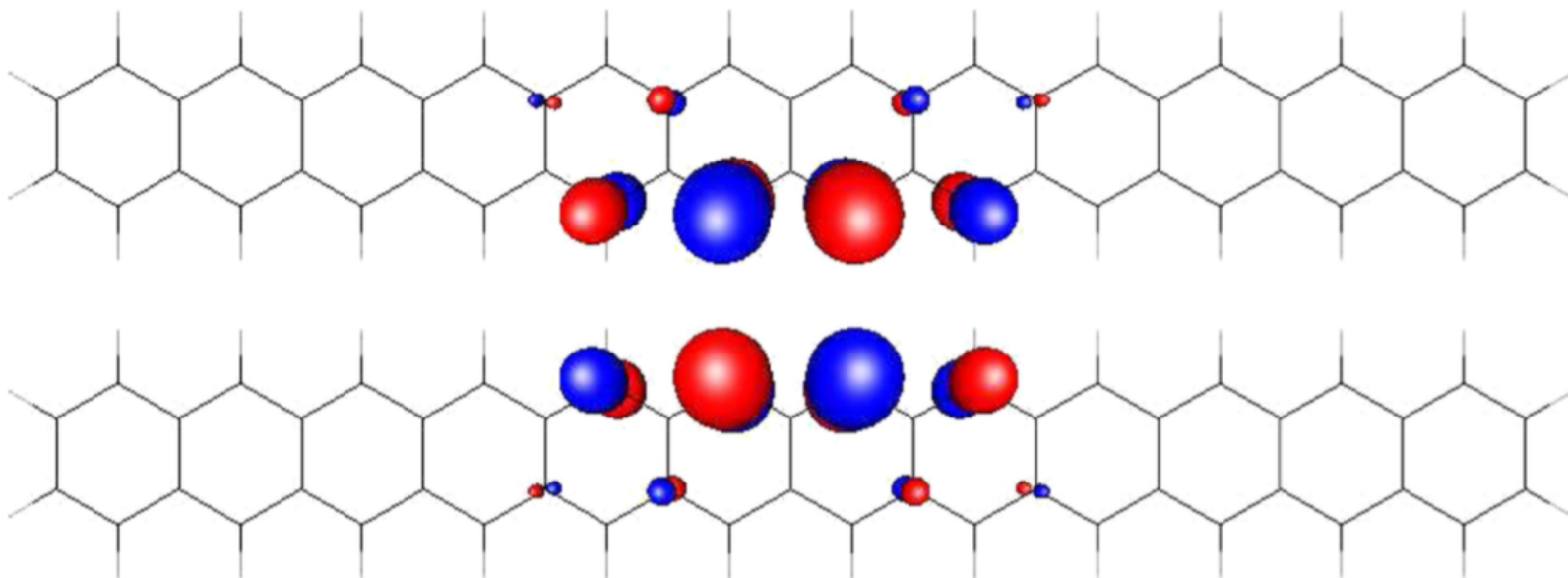
# Acenes: a challenge for CCVB (Dave Small)

- Acenes are have many resonance structures (poorly treated in CCVB) and show emergent strong correlations
  - Can CCVB nonetheless detect strong correlations?

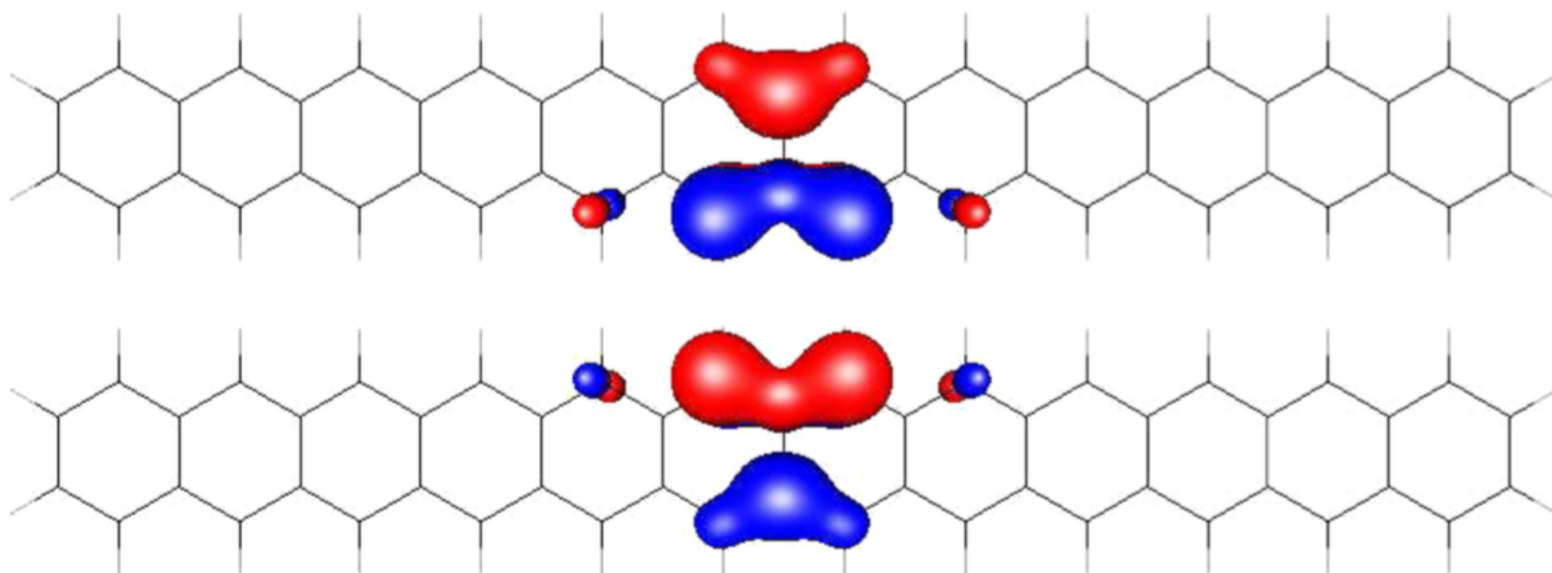
rings	active e's	$\max\{\theta_j\}$ ( $^\circ$ )	$\max\{t_{kl}\}$
4	84	53.1	0.148
6	120	47.6	0.144
8	156	54.7	0.141
12	228	80.6	0.331



One pair shows significant delocalization at  $n=12$



pair 1:  
 $\theta = 80.6^\circ$



pair 2:  
 $\theta = 47.6^\circ$

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**David W. Small; Joonho Lee**

JCP 137, 114103 (2012); JCTC 13, 602 (2017).



# MO form of CCVB wave function (Dave Small)

- Let's introduce a complex doubles operator:

$$\mathbf{T}_{vb} = \mathbf{T}_{PP} + \sum_{\substack{k,l=1 \\ k < l}}^{n_p} t_{kl} (\mathcal{S}_{kl}^{\hat{k}\hat{l}} + i\mathcal{Q}_{kl}^{\hat{k}\hat{l}}),$$

- $\mathbf{T}_{vb}$  is complex, but no extra variables are involved
- CCVB wave function in terms of  $\mathbf{T}_{vb}$ :

$$|\Psi_{\leq Q}\rangle = \mathbf{P}_S (\mathbf{I} + \mathbf{T}_{vb} + \frac{1}{2}\mathbf{T}_{vb}^2) |\Omega_0\rangle.$$

- $\mathbf{Q}$  does not affect the doubles.
- $\mathbf{Q}$  does affect the quadruples:  $\mathbf{P}_S(\mathbf{S}^2 - \mathbf{Q}^2)$ .
- The extension to full doubles is very interesting!
  - Defines a theory we call **CCVB-SD**

CCSD

vs

CCVB-SD

doubles:

$$\hat{\sigma}|\Phi_0\rangle$$

$$\hat{\sigma}|\Phi_0\rangle$$

quadruples:

$$\frac{1}{2}\hat{\sigma}^2|\Phi_0\rangle$$

$$\frac{1}{2}(\hat{\sigma}^2 - P_S \kappa^2)|\Phi_0\rangle$$

cluster operator:

$$T = \hat{\sigma}$$

$$T = \hat{\sigma} - i\hat{\kappa}$$

energy:

$$E = \langle \Phi_0 | e^{-T} H e^T | \Phi_0 \rangle$$

amplitudes:

$$\langle \Phi_{ij}^{ab} | e^{-T} H e^T | \Phi_0 \rangle = 0$$

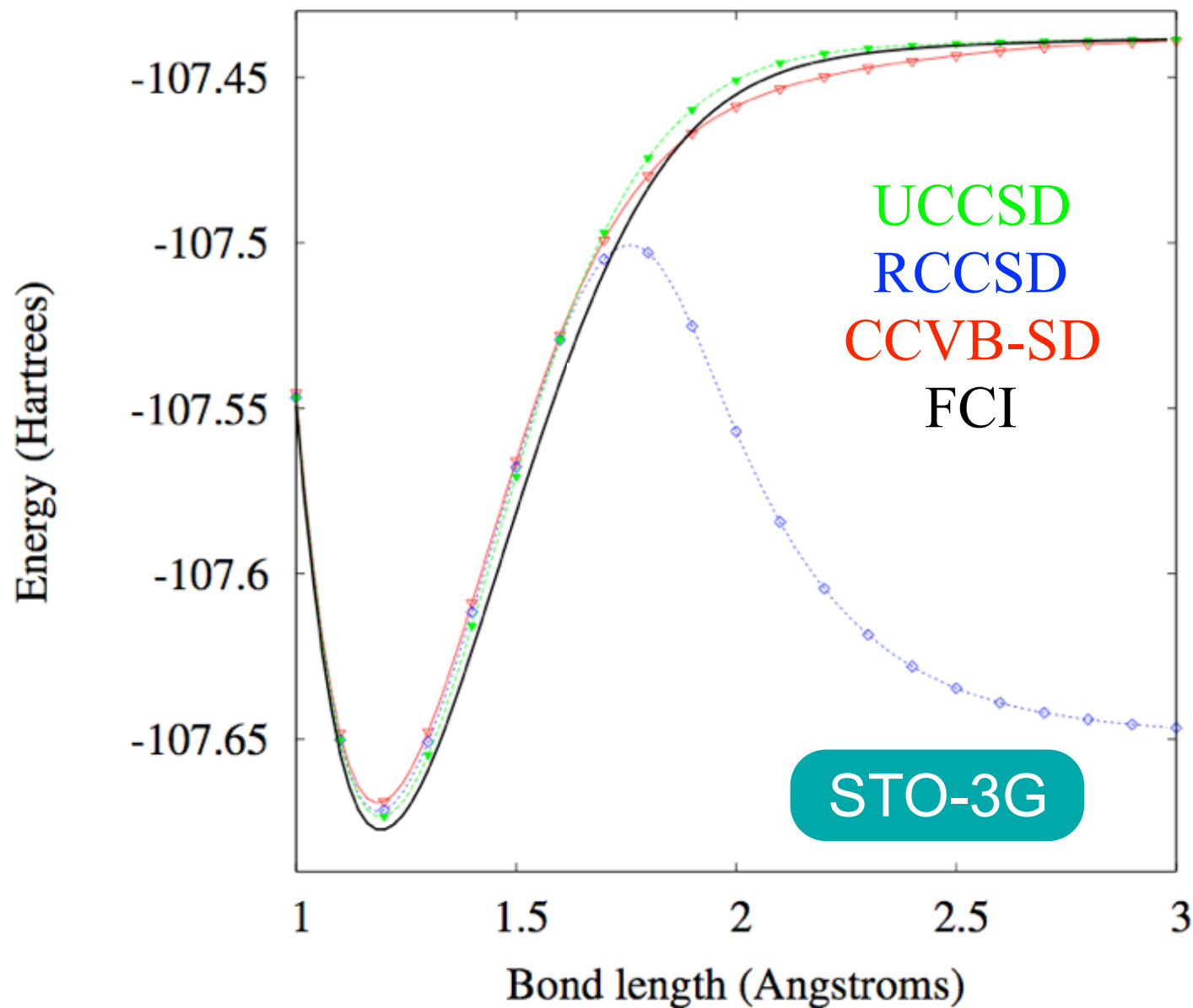
## CCVB-SD vs RCCSD vs CCVB... (Dave Small)

- Our starting points were:
  - **CCVB**: good for strong correlations, but neglects ionic terms, and has problems with multiple orbital solutions
  - **RCCSD**: good for dynamic correlation, is orbital invariant, but has problems with strong correlations.
- CCVB-SD is a fusion of CCVB with RCCSD:
  - Size-extensive (CCVB and RCCSD)
  - Exact for pairs of electrons (RCCSD)
  - Dissociates exactly in a minimal basis (CCVB)

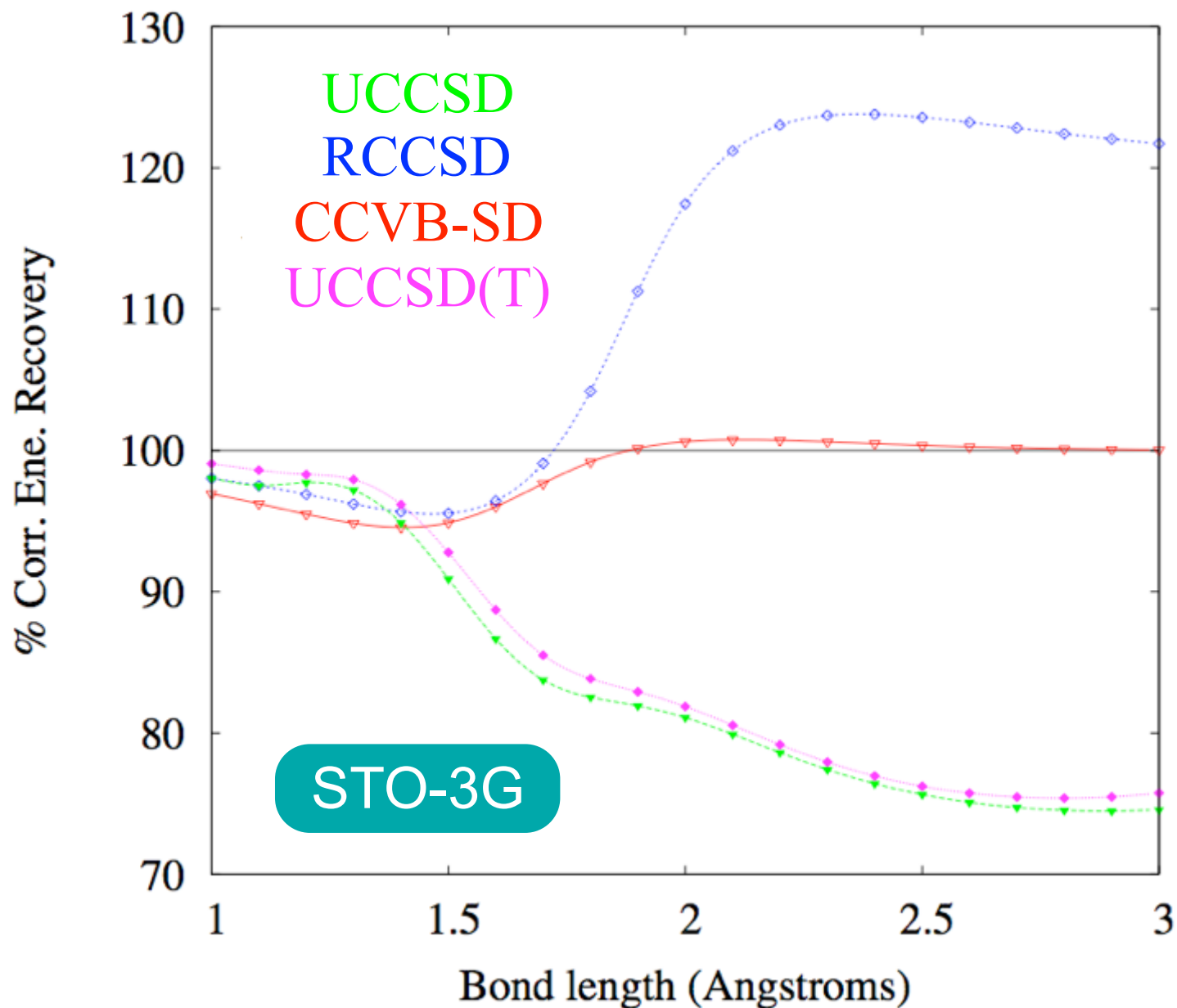
D.W. Small & MHG, JCP 137, 114103 (2012)

J. Lee, D.W. Small, E. Epifanovsky & MHG, JCTC 13, 602 (2017)

# Minimum basis N<sub>2</sub> (Dave Small)



# % correlation recovered for N<sub>2</sub> (Dave Small)

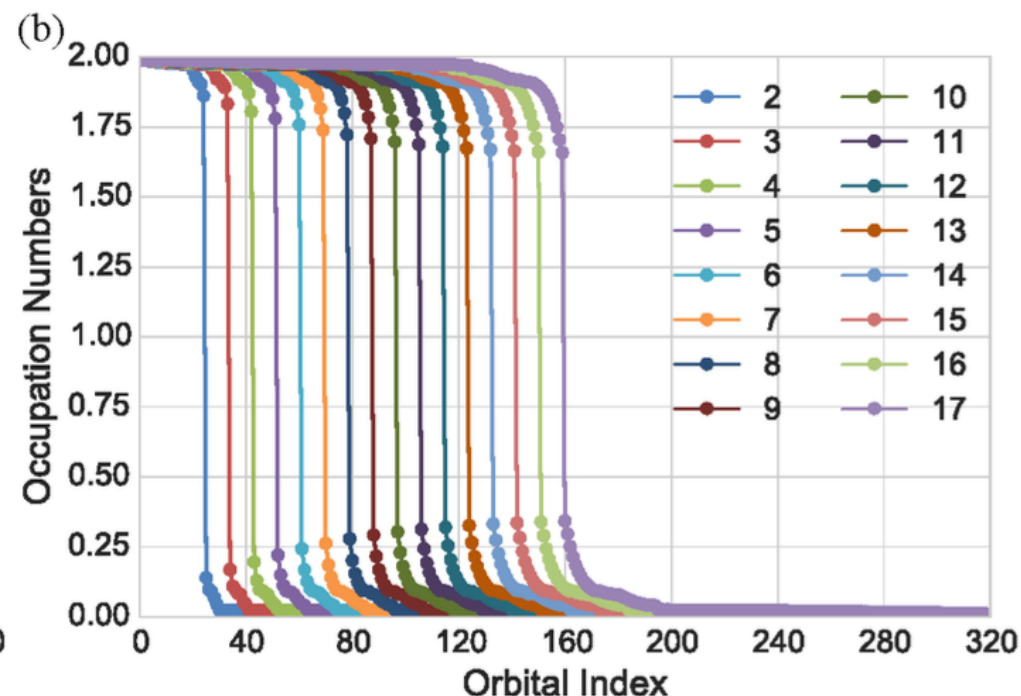
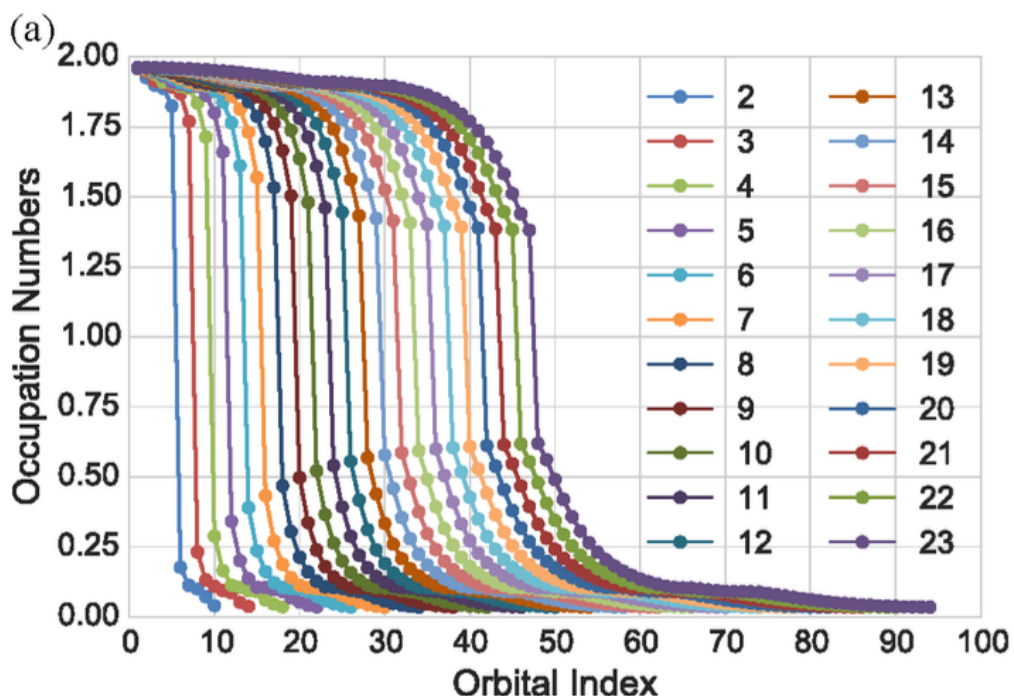


# CCVB-SD for the acenes (Joonho Lee)

The first reported S+D method that gives valid results....

- Only pi electrons correlated

- Full valence correlation



- Results for small pi spaces agree well with DMRG
- Full valence results show interesting suppression of the onset of strong correlations. Up to 318 electrons in 318 orbitals.

## Summary and future directions

- CCVB is a tractable VB theory for strong spin correlations.
  - A large-scale implementation is complete.
  - Open shell systems can also be handled.
- CCVB has some (VB-ish) issues. Not a true black box.
  - Ionic terms, multiple Lewis structures, orbital optimization
- There is a bridge between CCVB and CC theory.
  - In CC form, CCVB uses a complex doubles operator
  - There is a corresponding CCVB-SD extension for CCSD.
- There are interesting future challenges
  - Dynamic correlation; 3-pair correlations; ionic correlations!



# Acknowledgements



- Co-workers:
  - **Dr. David Small, Joonho Lee**

- Funding:
  - **US DOE**



- Software: Partly available (more coming!) in:
  - **Q-Chem:** [www.q-chem.com](http://www.q-chem.com)

