Quantum Monte Carlo backflow calculations of benzene dimers

Kathleen Schwarz*, Cyrus Umrigar, Richard Hennig*****

***Cornell University Department of Chemistry, **Cornell University Department of Physics, ***Cornell University Department of Materials Science and Engineering**

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Trial wave functions

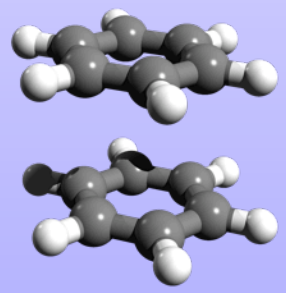
- How does backflow compare with other nodal improvement methods (orbital optimization, multideterminant expansion) for benzene energies?

Benzene dimers

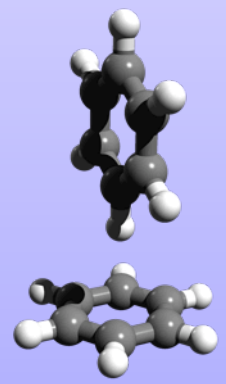
- How does backflow change the binding energy of benzene dimer?
- For the geometries that we consider, what is the lowest energy benzene dimer geometry?

The Benzene Dimer

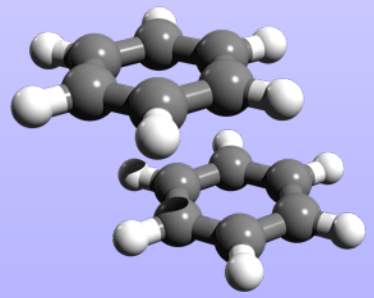
- Motivation: Prototypical system for weak π-π interactions
- Problem: Computationally expensive methods and large basis sets needed to accurately describe weak van der Waals interactions
- Previous QMC and quantum chemical calculations give a range of energies and ground state geometries



Face to face



T-shaped



Parallel displaced

Previous calculations

Binding energies [kcal/mol]

Method	Authors	Face to Face	Parallel Displaced	T-Shaped
CCSD(T)	Park & Lee 2006		3.03	2.67
	Tsuzuki et al. 2002	1.48*	2.48	2.46
	Sinnokrot et al. 2004	1.81	2.78**	2.74
	Hobza et al. 1996		2.01	2.17
	Jurecka et al. 2006		2.73	2.74
SAPT	Podeszwa et al. 2006	2.42	2.74	
DMC	Sorella et al. 2007	0.5	2.2(3)	
	Diedrich et al. 2005		3.6(4)	3.0(4)
	Korth et al. 2008		1.7(4)	3.8(4)
Experiment	Grover et al. 1987			2.4(4)*
	Krause et al. 1991			1.6(4)*

*Calculations report D_e experiments report D_o. Park & Lee calculate a zpe of -0.3 kcal/mol for the T-Shaped dimer, and -0.2 kcal/mol for the PD geometry.

** darker blue color indicates MP2 geometries

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- Small binding energies
- Computationally demanding calculations
- Unclear which method is most accurate

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Calculation Details

Parameters of Slater Trial Wavefunction

- B3LYP orbitals from Gaussian03
- Hartree-Fock pseudopotential and triple-zeta basis [Burkatzki, Filippi,Dolg]
- Geometries from Tsuzuki et al.

Quantum Monte Carlo Calculations

- CASINO QMC code [Needs, Towler et al.]
- Variance minimization of Jastrow and backflow parameters
- Select optimal cutoffs from single benzene

Jastrow [a.u.]		VMC [Ha]	
e-n	e-e	Energy	Variance
5	4	-75.083(5)	1.37(2)
12	9	-75.203(3)	1.147(9)

- Casula “tmoves” scheme used for CASINO DMC calculations

Wavefunction Benchmarking

CASINO vs. CHAMP

- Single benzene molecule
- Both have optimized Jastrow factors
- Hartree Fock orbitals
    - CASINO orbitals from Gaussian
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no tmoves	-37.637(2) var=0.431(6)	-37.7076(8)	-37.6342(6) var = 0.507	-37.711(1)
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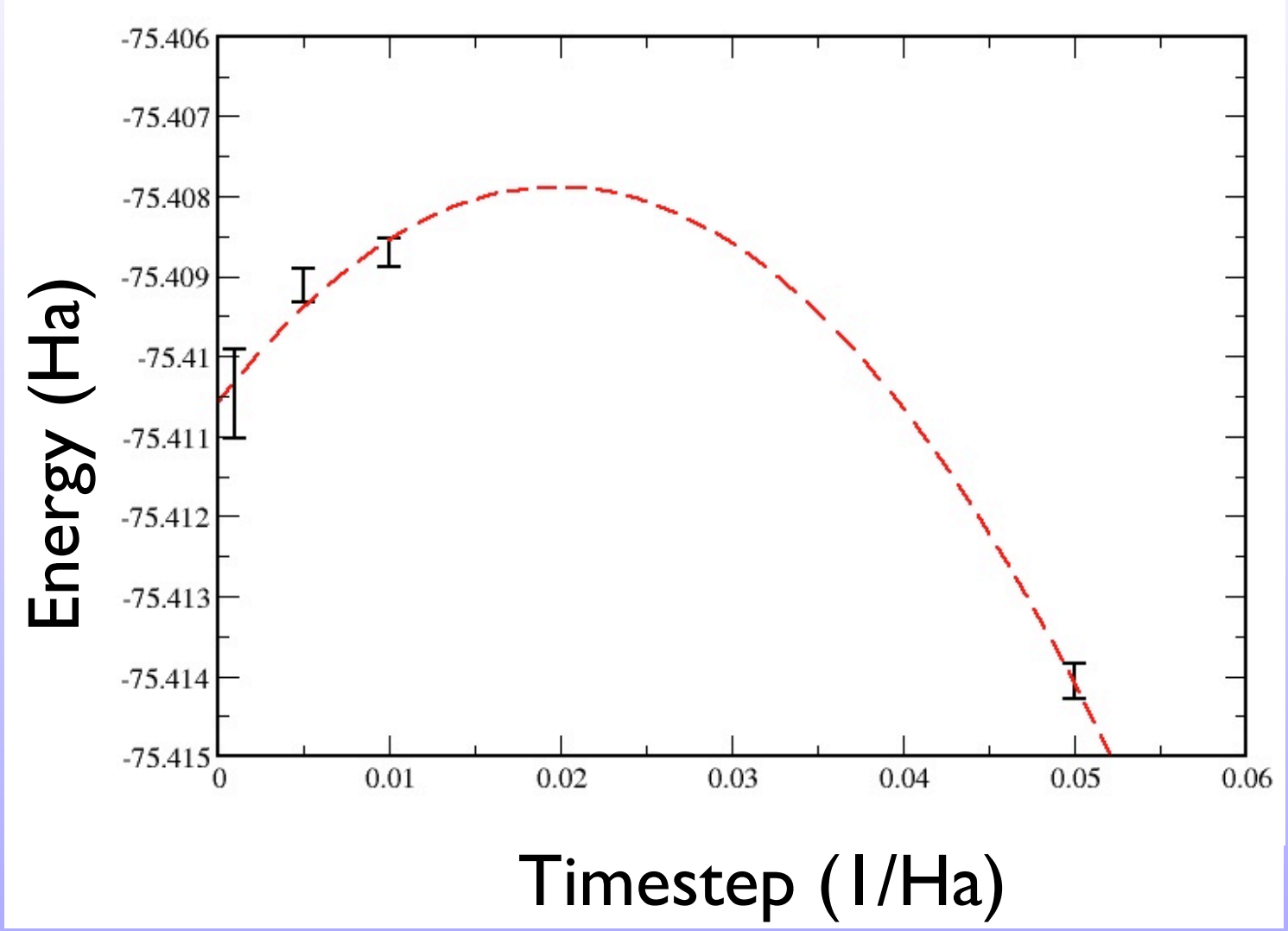
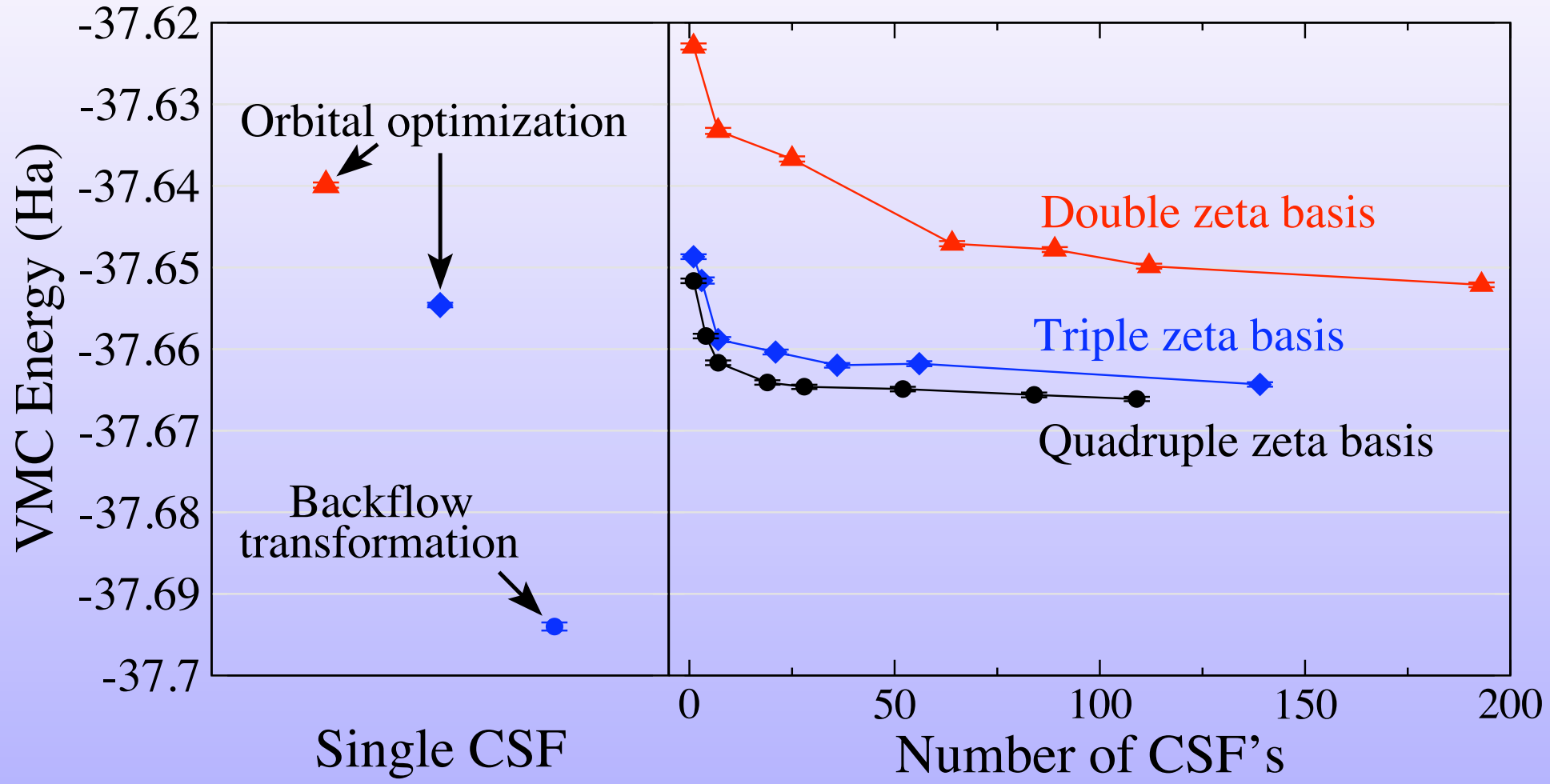
DMC timestep convergence (Slater Jastrow)



We expect a timestep of 0.01 1/Ha to give binding energies better than 1 mHa

Trial wavefunction optimization (single benzene)



Backflow most efficiently improves the benzene VMC energy

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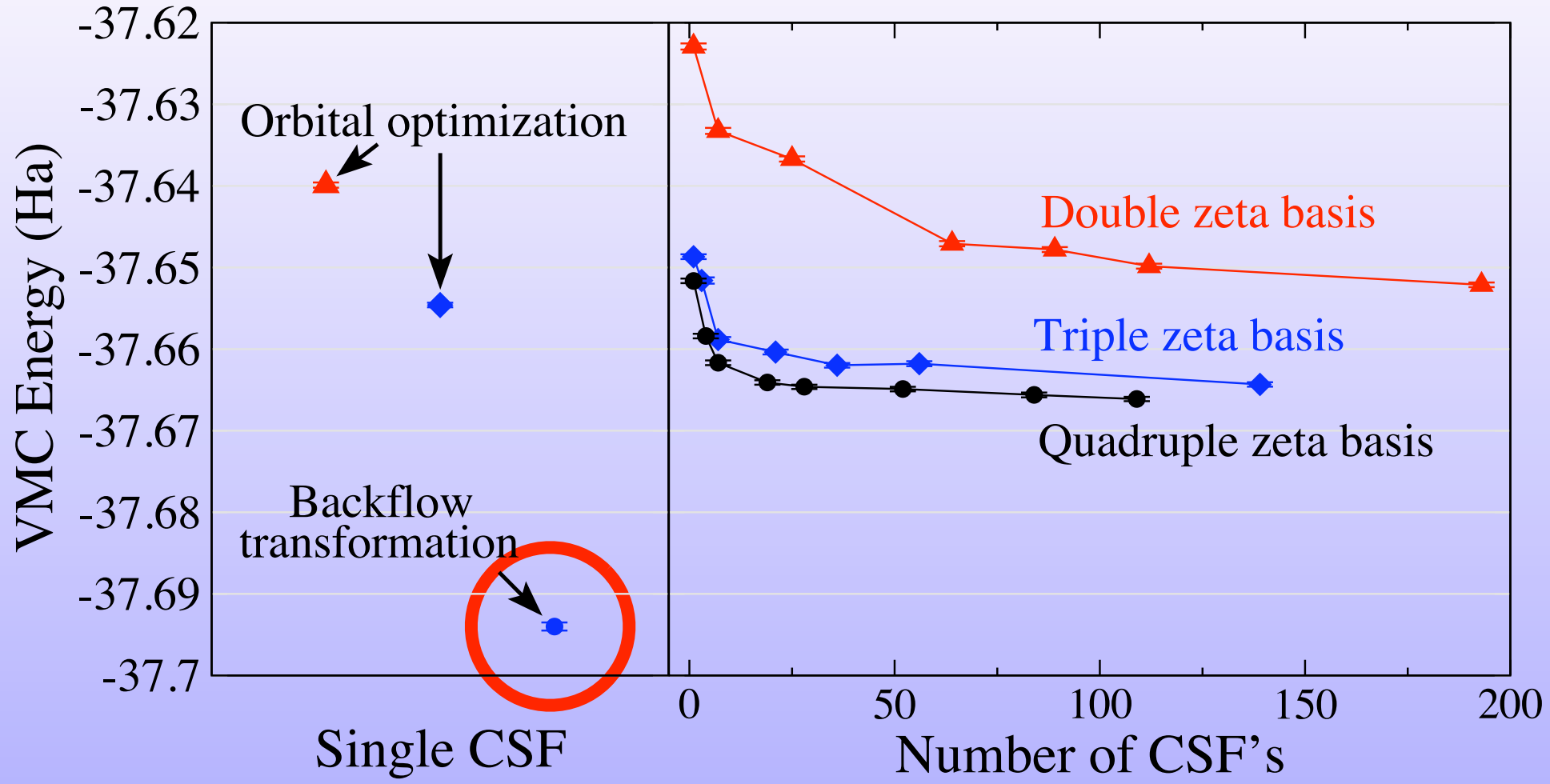
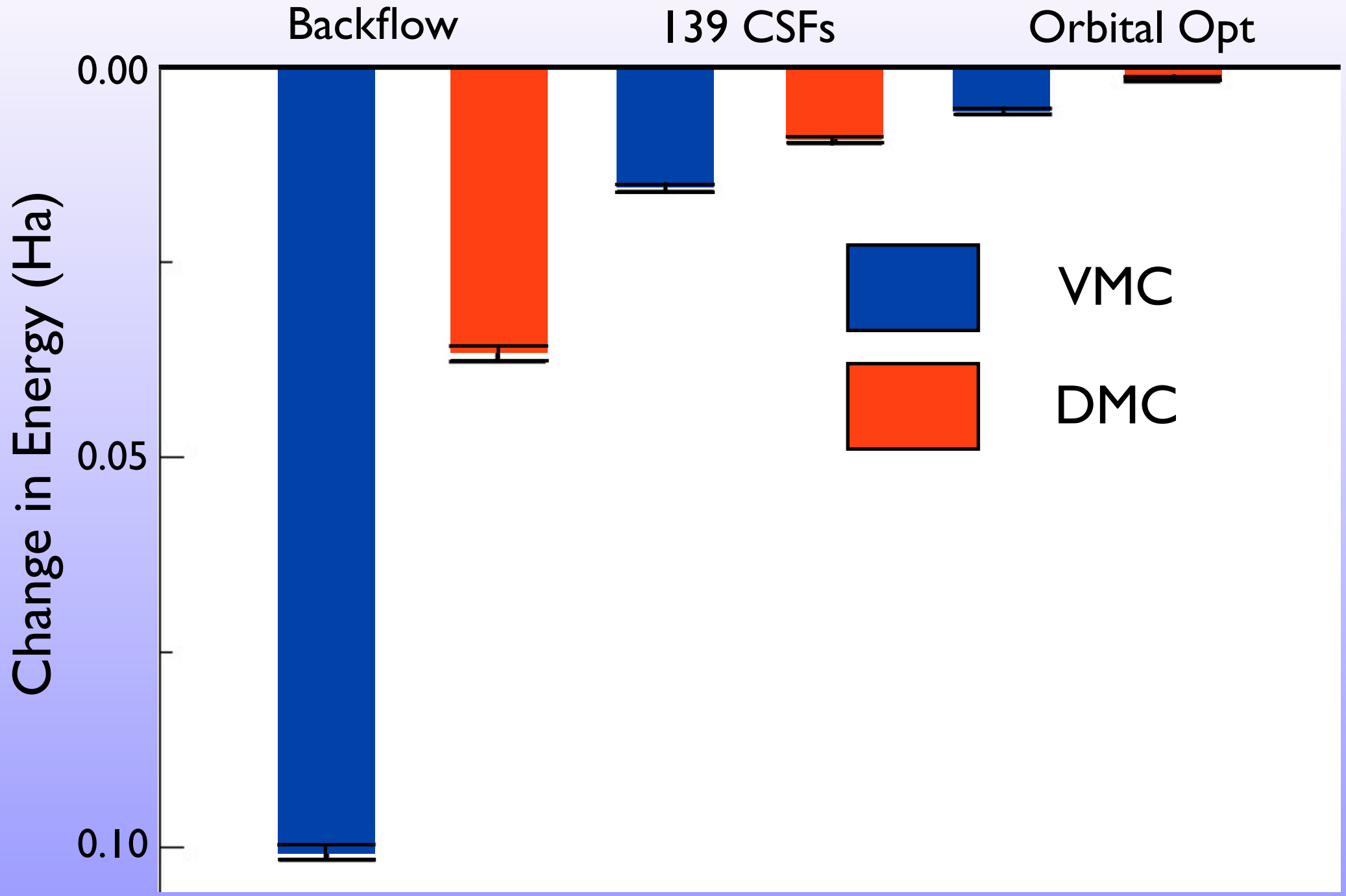


Backflow most efficiently improves the benzene VMC energy

Energy improvement from a Slater Jastrow wavefunction



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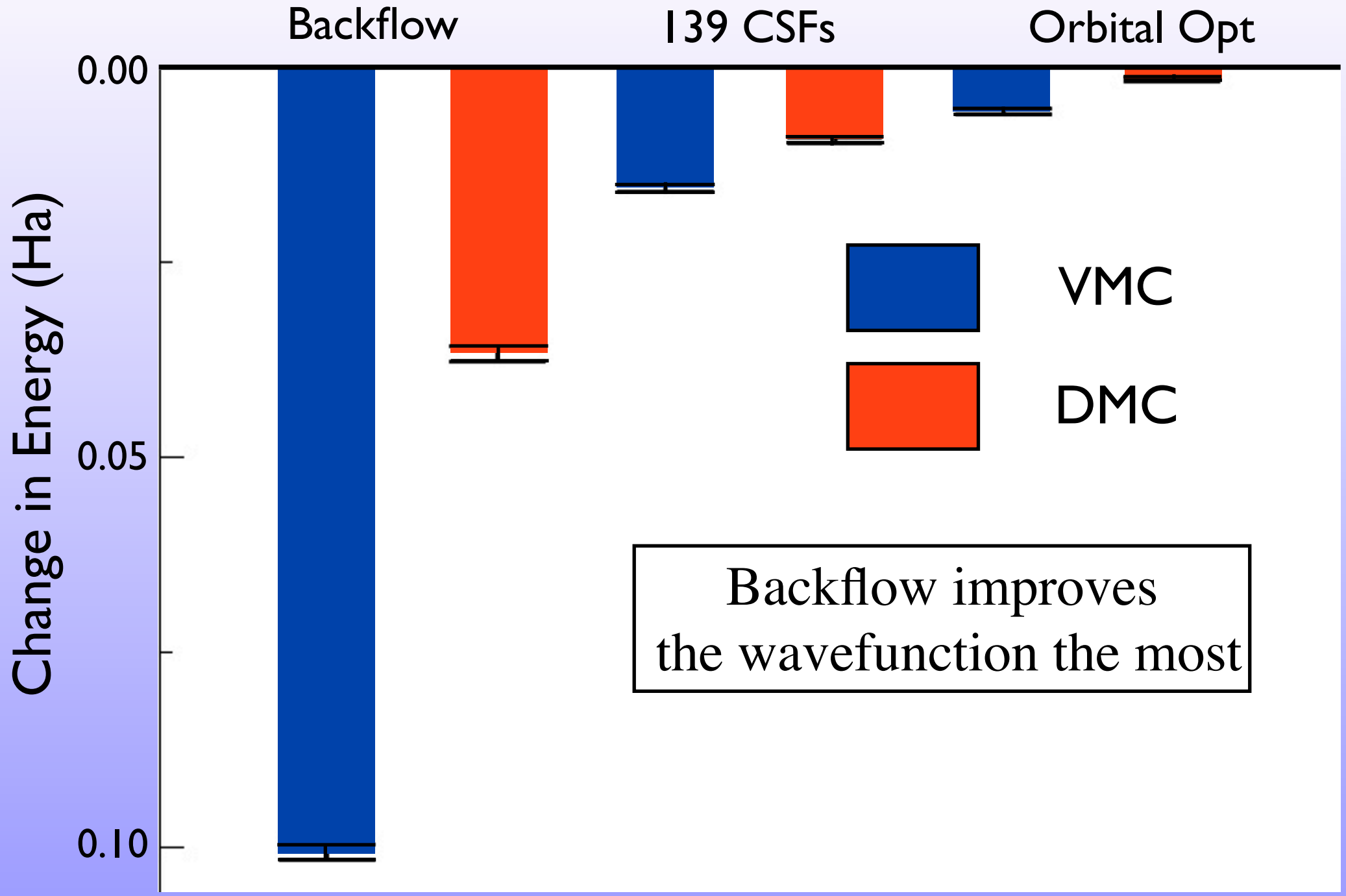
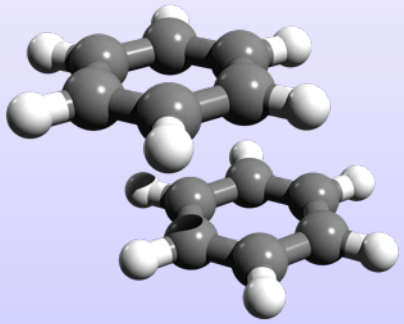
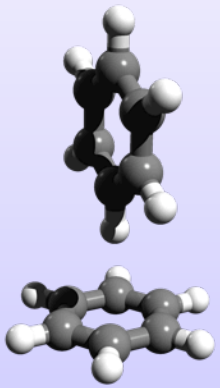


DMC benzene dimerization energies

Trial Wavefunction	 parallel displaced	 T-shaped
Slater-Jastrow	1.6(3) kcal/mol	2.8(4) kcal/mol
Slater-Jastrow-Backflow	3.1(6) kcal/mol	2.8(7) kcal/mol

DMC benzene dimerization energies

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	Our results: SJ		1.6(3)	2.8(4)
	Our results: SJB		3.1(6)	2.8(7)
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Conclusions

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Computational resources provided by CCNI and NCSA

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Trial wave functions

- Backflow more efficient than a multi-determinant expansion or orbital optimization in improving the wavefunction

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