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 $\pi-\pi$ 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]

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

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<th>Jastrow [a.u.]</th>
<th>VMC [Ha]</th>
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<tr>
<td>e-n</td>
<td>e-e</td>
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<tr>
<td>5</td>
<td>4</td>
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<td>12</td>
<td>9</td>
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- Casula “t mover” 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
  • CHAMP orbitals from Gamess
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Trial wavefunction optimization (single benzene)

Backflow most efficiently improves the benzene VMC energy
Trial wavefunction optimization (single benzene)

-37.62
-37.63
-37.64
-37.65
-37.66
-37.67
-37.68
-37.69
-37.7

VMC Energy (Ha)

Orbital optimization

Double zeta basis

Triple zeta basis

Quadruple zeta basis

Backflow transformation

Single CSF

Number of CSF’s

0
50
100
150
200

Backflow most efficiently improves the benzene VMC energy
Energy improvement from a Slater Jastrow wavefunction

Change in Energy (Ha)

- Backflow
- 139 CSFs
- Orbital Opt

*VMC*  
*DMC*
Energy improvement from a Slater Jastrow wavefunction

Backflow improves the wavefunction the most

VMC

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Orbital Opt

DMC

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

email contact:  kas382@cornell.edu

Conclusions
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The Benzene Dimer
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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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