Geminal wavefunctions: Looking for size extensivity beyond Slater-Jastrow

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Quantum Monte-Carlo

1. Use VMC to generate a trial wavefunction.
2. Run a DMC calculation on this trial wavefunction in the fixed-node approximation.

Accuracy

Improving the accuracy of DMC means improving the nodal surface of the trial wavefunction.

This is controlled by the anti-symmetric part of the wavefunction.

Beyond Slater determinants?

- Backflow
- Multi-determinant expansion
- Geminal and Pfaffian wavefunctions

Geminals

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Idea

Can we build correlation into the orbitals?

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Can we build correlation into the orbitals?

This is where multi-electron orbitals come in. This talk will focus on orbitals containing two electrons of opposite spins, also called bi-orbitals or geminals.

$$\{\Phi_1(\mathbf{x}, \mathbf{y}), \Phi_2(\mathbf{x}, \mathbf{y}) \ldots\}$$

Geminal Parametrization

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Assume no spin-polarization, and each bi-orbital contains an up-spin electron $\mathbf{x}$ and a down-spin electron $\mathbf{y}$.

$$\Phi(\mathbf{x}, \mathbf{y}) = \sum_{i,j} g_{ij} \cdot \phi_i(\mathbf{x})\phi_j(\mathbf{y})$$

$$\Phi^\dagger = \sum_{i,j} g_{ij} \cdot b_i^\dagger \bar{b}_j^\dagger$$

An Example: H_4

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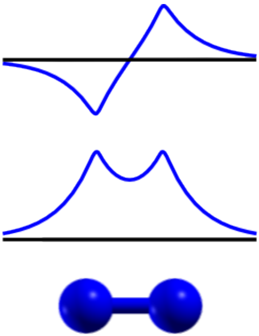

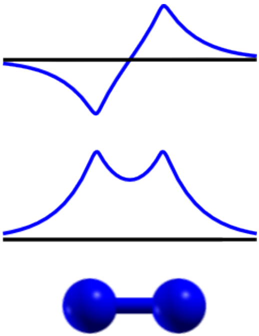

H_4 geminal basis states

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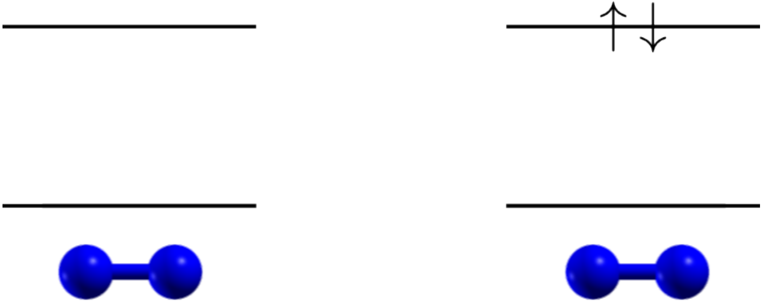
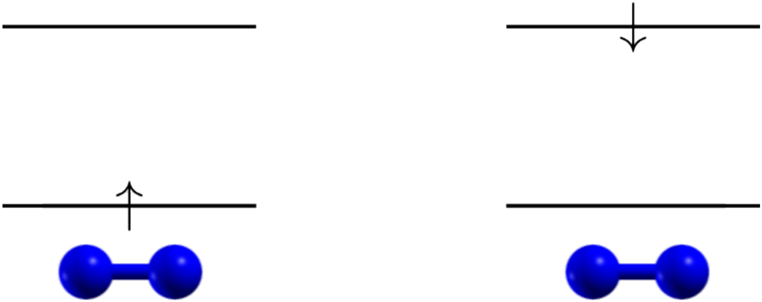


H_4 geminal basis states



H_4 geminal basis states

From bi-orbitals to wavefunctions

$$
\begin{aligned}
|\Phi\rangle \;=\; & a\left(\left|\begin{array}{cc} - & - \\ \uparrow\downarrow & - \end{array}\right\rangle + \left|\begin{array}{cc} - & - \\ - & \uparrow\downarrow \end{array}\right\rangle\right) \\
& + b\left(\left|\begin{array}{cc} \uparrow\downarrow & - \\ - & - \end{array}\right\rangle + \left|\begin{array}{cc} - & \uparrow\downarrow \\ - & - \end{array}\right\rangle\right)
\end{aligned}
$$

From bi-orbitals to wavefunctions

$$
\begin{aligned}
|\Phi\rangle &= a\left(\left|\begin{matrix} - & - \\ \upharpoonleft\!\downharpoonright & - \end{matrix}\right\rangle + \left|\begin{matrix} - & - \\ - & \upharpoonleft\!\downharpoonright \end{matrix}\right\rangle\right) \\
&\quad + b\left(\left|\begin{matrix} \upharpoonleft\!\downharpoonright & - \\ - & - \end{matrix}\right\rangle + \left|\begin{matrix} - & \upharpoonleft\!\downharpoonright \\ - & - \end{matrix}\right\rangle\right)
\end{aligned}
$$

$$
{\Phi^{\dagger}}^{2}|0\rangle =
$$

From bi-orbitals to wavefunctions

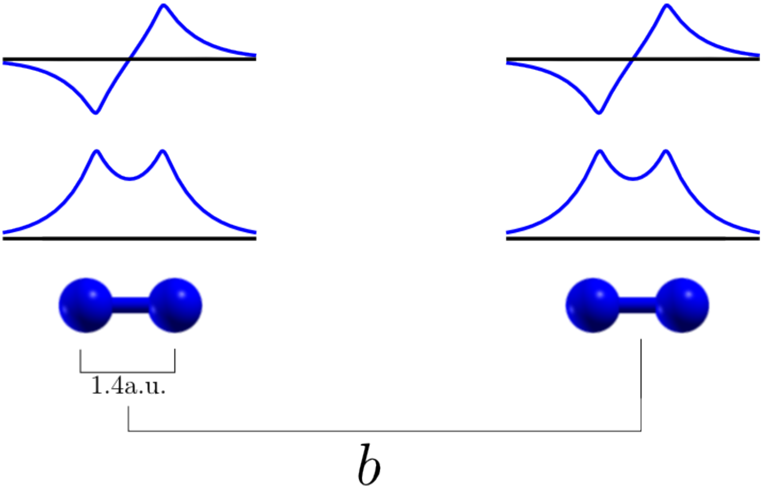
$$
\begin{aligned}
|\Phi\rangle &= a\left(\left| \begin{array}{cc} \text{—} & \text{—} \\ \uparrow\downarrow & \text{—} \end{array} \right\rangle + \left| \begin{array}{cc} \text{—} & \text{—} \\ \text{—} & \uparrow\downarrow \end{array} \right\rangle \right) \\
&\quad + b\left(\left| \begin{array}{cc} \uparrow\downarrow & \text{—} \\ \text{—} & \text{—} \end{array} \right\rangle + \left| \begin{array}{cc} \text{—} & \uparrow\downarrow \\ \text{—} & \text{—} \end{array} \right\rangle \right)
\end{aligned}
$$

$$
{\Phi^{\dagger}}^{2}|0\rangle = a^2 \left| \begin{array}{cc} \text{—} & \text{—} \\ \uparrow\downarrow & \uparrow\downarrow \end{array} \right\rangle + b^2 \left| \begin{array}{cc} \uparrow\downarrow & \uparrow\downarrow \\ \text{—} & \text{—} \end{array} \right\rangle + \ldots
$$

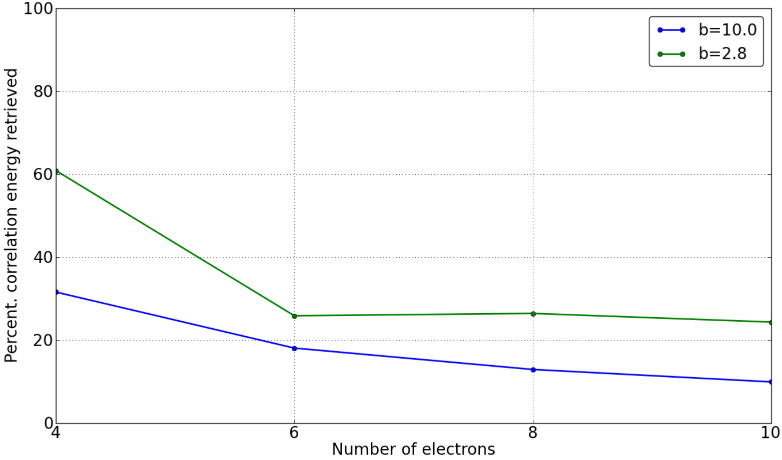
From bi-orbitals to wavefunctions

$$
\begin{aligned}
\Phi^{\dagger 2}\left|0\right\rangle \;=\; & a^2 \left| \begin{array}{cc} - & - \\ \uparrow\!\downarrow & \uparrow\!\downarrow \end{array} \right\rangle + b^2 \left| \begin{array}{cc} \uparrow\!\downarrow & \uparrow\!\downarrow \\ - & - \end{array} \right\rangle \\
& + ab \cdot \left(\left| \begin{array}{cc} \uparrow\!\downarrow & - \\ - & \uparrow\!\downarrow \end{array} \right\rangle + \left| \begin{array}{cc} - & \uparrow\!\downarrow \\ \uparrow\!\downarrow & - \end{array} \right\rangle \right. \\
& \left. + \left| \begin{array}{cc} \uparrow\!\downarrow & - \\ \uparrow\!\downarrow & - \end{array} \right\rangle + \left| \begin{array}{cc} - & \uparrow\!\downarrow \\ - & \uparrow\!\downarrow \end{array} \right\rangle \right)
\end{aligned}
$$

Test system: H_{2x}



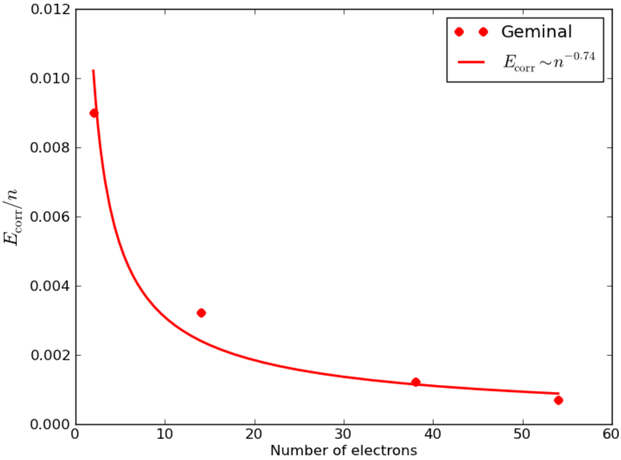
H_{2x} Results



100
80
60
40
20
0
4
6
8
10
Percent. correlation energy retrieved
Number of electrons
b=10.0
b=2.8

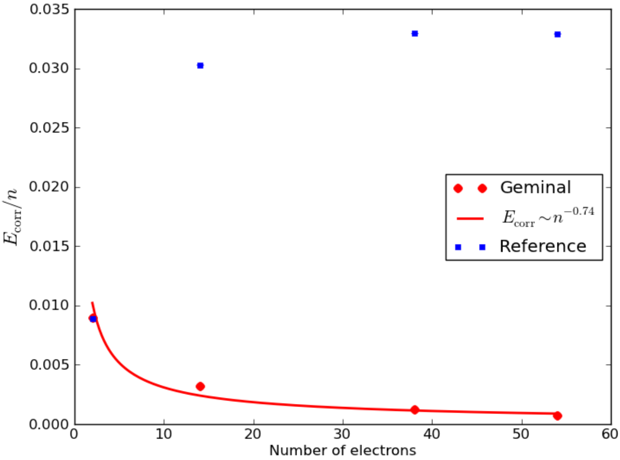
HEG Results

Homogeneous electron gas, $r_s = 2\ a_0$.



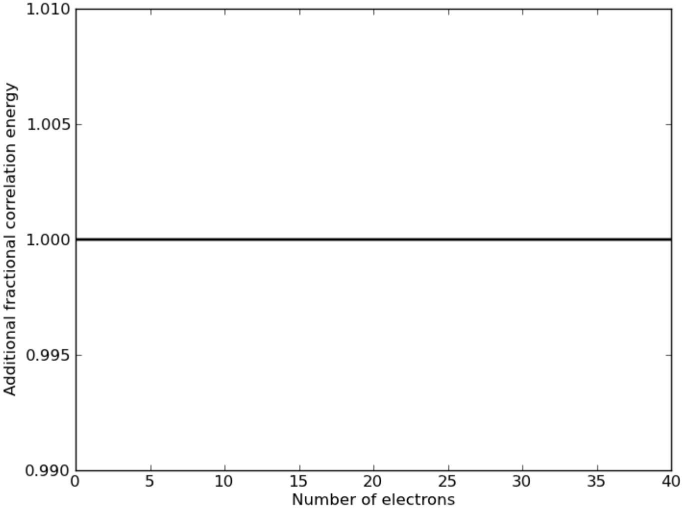
HEG Results

Homogeneous electron gas, $r_s = 2\ a_0$.



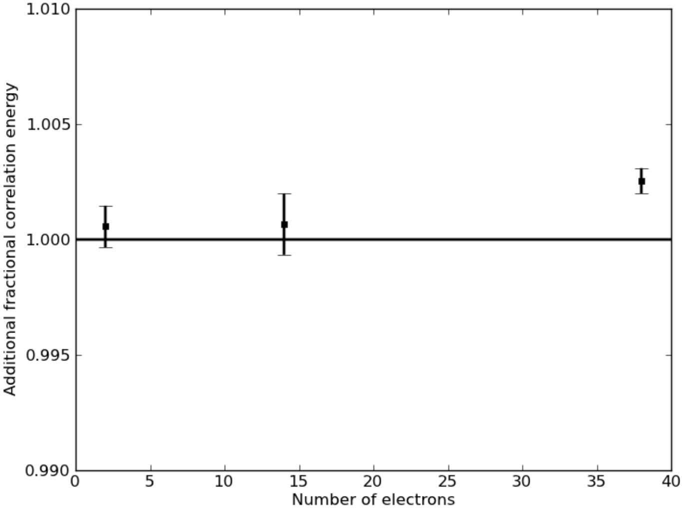
HEG Results: Geminal-Jastrow in DMC

Geminal-Jastrow vs. Slater-Jastrow:



HEG Results: Geminal-Jastrow in DMC

Geminal-Jastrow vs. Slater-Jastrow:



Multi-geminals?

Additional freedom can be introduced by introducing additional geminals.

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For example, for a four electron wavefunction:

$$|\Psi\rangle = {\Phi_1^\dagger}^2 |0\rangle + {\Phi_2^\dagger}^2 |0\rangle + \ldots$$

Decoupling excitations

$$
\begin{aligned}
|\Phi_1\rangle \;=\; & {\color{blue} 0 \left| \begin{array}{cc} — & — \\ \uparrow\downarrow & — \end{array} \right\rangle} + a \left| \begin{array}{cc} — & — \\ — & \uparrow\downarrow \end{array} \right\rangle \\
& + b \left| \begin{array}{cc} \uparrow\downarrow & — \\ — & — \end{array} \right\rangle + c \left| \begin{array}{cc} — & \uparrow\downarrow \\ — & — \end{array} \right\rangle
\end{aligned}
$$

Decoupling excitations

$$|\Phi_1\rangle = a\left|\begin{array}{cc} \text{—} & \text{—} \\ \text{—} & \upharpoonleft\!\downarrow \end{array}\right\rangle + b\left|\begin{array}{cc} \upharpoonleft\!\downarrow & \text{—} \\ \text{—} & \text{—} \end{array}\right\rangle + c\left|\begin{array}{cc} \text{—} & \upharpoonleft\!\downarrow \\ \text{—} & \text{—} \end{array}\right\rangle$$

Decoupling excitations

$$|\Phi_1\rangle = a\left|\begin{matrix} - & - \\ - & \upharpoonleft\!\downharpoonright \end{matrix}\right\rangle + b\left|\begin{matrix} \upharpoonleft\!\downharpoonright & - \\ - & - \end{matrix}\right\rangle + c\left|\begin{matrix} - & \upharpoonleft\!\downharpoonright \\ - & - \end{matrix}\right\rangle$$

$$\begin{aligned} {\Phi_1^\dagger}^2|0\rangle &= ab\left|\begin{matrix} \upharpoonleft\!\downharpoonright & - \\ - & \upharpoonleft\!\downharpoonright \end{matrix}\right\rangle + ac\left|\begin{matrix} - & \upharpoonleft\!\downharpoonright \\ - & \upharpoonleft\!\downharpoonright \end{matrix}\right\rangle \\ &+ bc\left|\begin{matrix} \upharpoonleft\!\downharpoonright & \upharpoonleft\!\downharpoonright \\ - & - \end{matrix}\right\rangle \end{aligned}$$

Multi-geminal wavefunction for H_4

$$|\Psi\rangle = |HF\rangle + \Phi_1^{\dagger\,2}|0\rangle + \Phi_2^{\dagger\,2}|0\rangle$$

Multi-geminal wavefunction for H_4

$$
\begin{aligned}
|\Psi\rangle \;=\; |HF\rangle &+ ab \cdot \left(\left| \begin{array}{cc} \upharpoonleft\!\downharpoonright & - \\ - & \upharpoonleft\!\downharpoonright \end{array} \right\rangle + \left| \begin{array}{cc} - & \upharpoonleft\!\downharpoonright \\ \upharpoonleft\!\downharpoonright & - \end{array} \right\rangle \right) \\
&+ ac \cdot \left(\left| \begin{array}{cc} - & \upharpoonleft\!\downharpoonright \\ - & \upharpoonleft\!\downharpoonright \end{array} \right\rangle + \left| \begin{array}{cc} \upharpoonleft\!\downharpoonright & - \\ \upharpoonleft\!\downharpoonright & - \end{array} \right\rangle \right) \\
&+ 2bc \left| \begin{array}{cc} \upharpoonleft\!\downharpoonright & \upharpoonleft\!\downharpoonright \\ - & - \end{array} \right\rangle
\end{aligned}
$$

Multi-geminal wavefunction

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For a non-spin polarised system with $2N$ electrons:

$$|\Psi\rangle = |HF\rangle + \sum_{\substack{a \,\in\, \text{up electrons} \\ b \,\in\, \text{down electrons}}} a_{ab} \cdot {\Phi^{\dagger}_{ab}}^{N} |0\rangle$$

Multi-geminal wavefunction

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$$|\Psi\rangle = |HF\rangle + \sum_{\substack{a \;\in\; \text{up electrons} \\ b \;\in\; \text{down electrons}}} a_{ab} \cdot {\Phi^{\dagger}_{ab}}^{N} |0\rangle$$

where

$$\Phi^{\dagger}_{ab} = \sum_{i,j} g_{ij} \cdot b^{\dagger}_{i} \bar{b}^{\dagger}_{j}$$

where $g_{ij} = 0$ if $i = a$ or $j = b$.

Multi-geminal results

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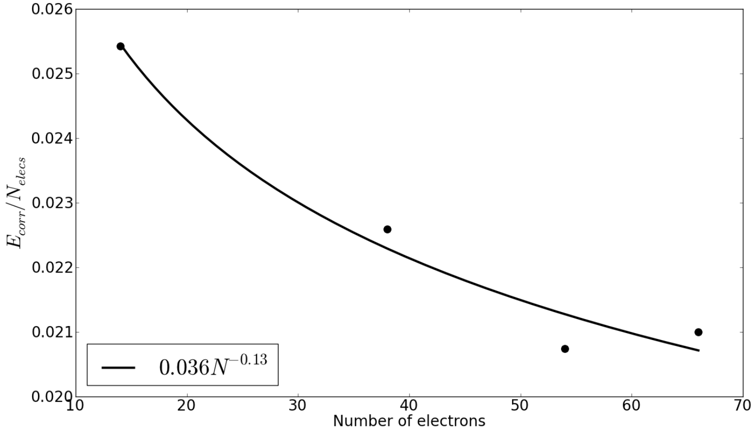
Homogeneous electron gas, $r_s = 2\ a_0$.



Remaining questions

1. How good is the Multi-Geminal-Jastrow wavefunction in DMC?

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2. Is it any better than a multi-determinant expansion?

Conclusions

- Single geminal wavefunctions give poor energies, both at VMC and DMC level.

Conclusions

- Single geminal wavefunctions give poor energies, both at VMC and DMC level.
- The multi-geminal wavefunction presented here might be promising.

References

Geminal wavefunctions with Jastrow correlation: a first application to atoms
M. Casula and S. Sorella, J. Chem. Phys. 119, 6500 (2003)

Generalized Pairing Wave Functions and Nodal Properties for Electronic Structure Quantum Monte Carlo
Michael Bajdich (PhD thesis) - available online.

Thank you for your attention!