Diffusion Monte-Carlo, nodal surfaces and pairing functions

Variational principle for Fermions

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Subject to. . .

Ψ must remain anti-symmetric.

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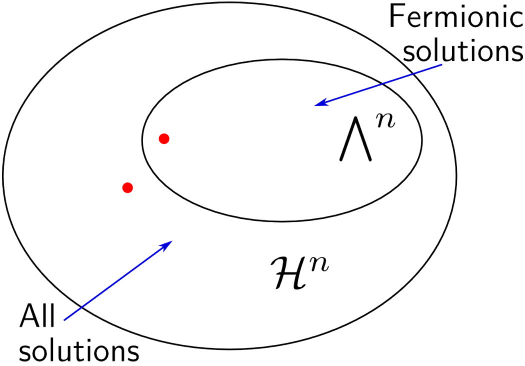
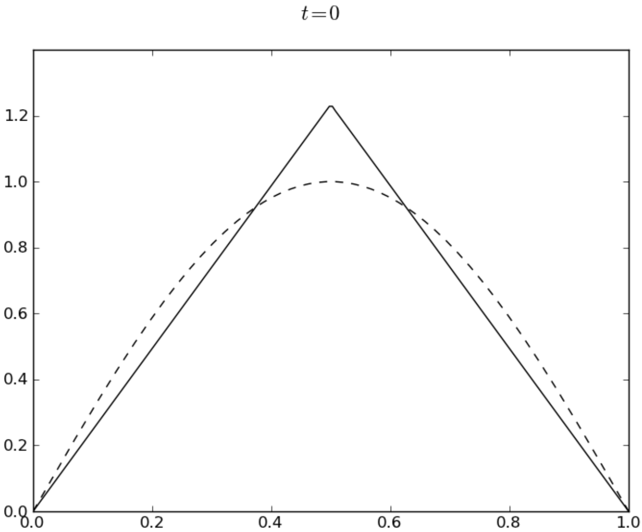


Diffusion Monte-Carlo

$$\lim_{t\to\infty}\left(\exp^{-\hat{H}t}\Psi_T\right)=\Psi_0$$

where Ψ_T is *any* n-electron wavefunction and Ψ_0 is the wavefunction that minimizes the energy in $\mathcal{H}^n$.

DMC for the particle in a box



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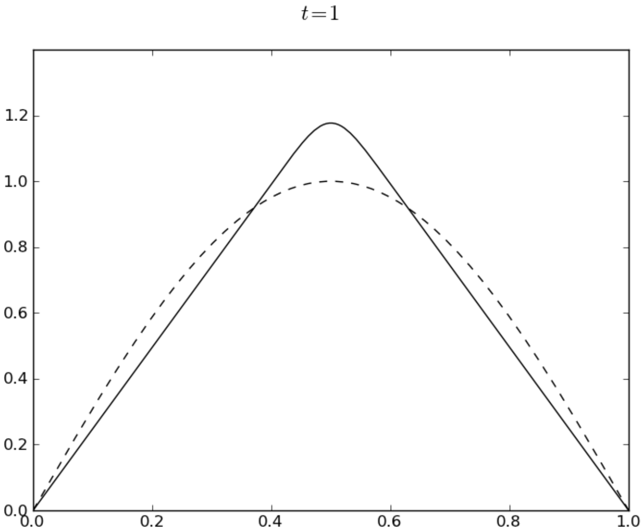

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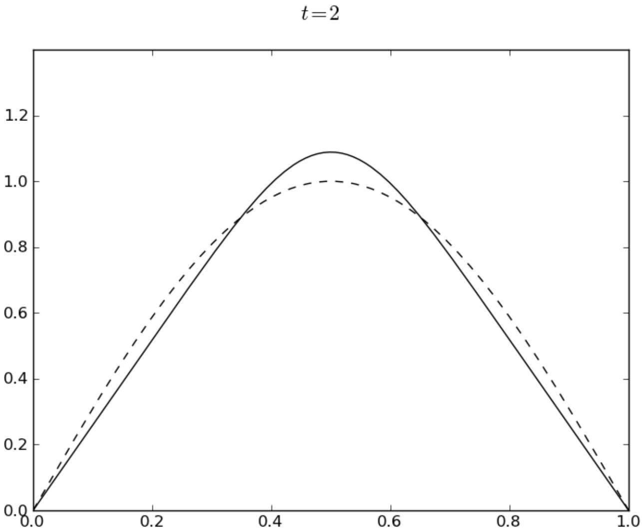

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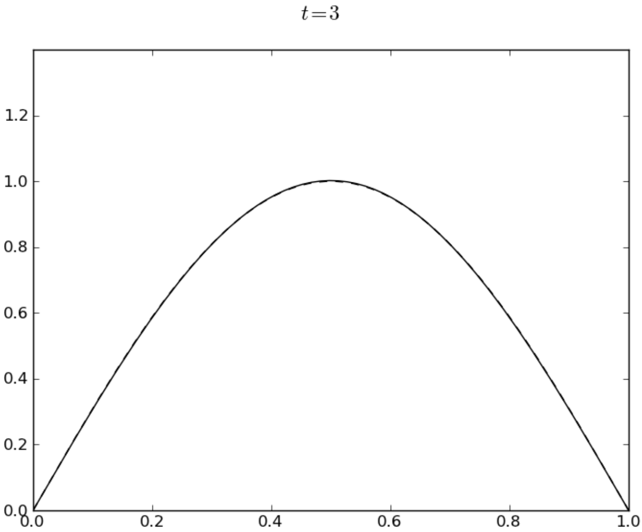
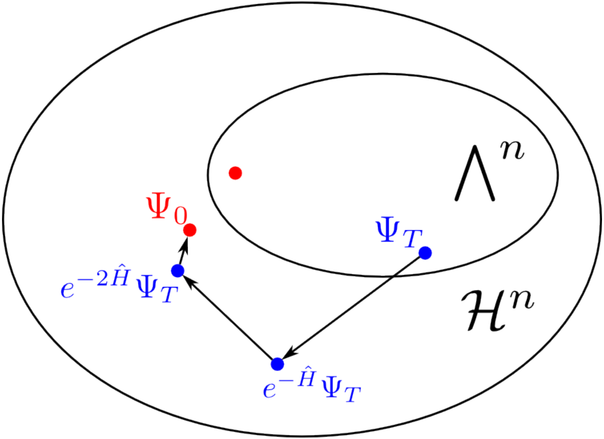


Fermion sign problem

Repeated application of $\exp^{-\hat{H}}$ will eventually give the lowest-energy eigenfunction in $\mathcal{H}^n$.



Nodal surface

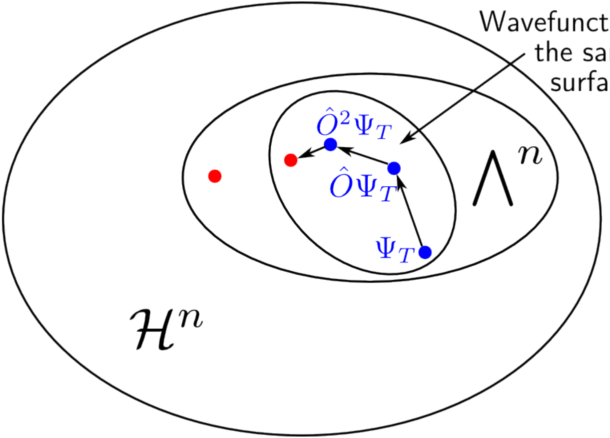
The Hamiltonian operator acts in the same manner on all particles.

Ensuring that the wavefunction is 0 when any two electrons coincide is sufficient to guarantee anti-symmetry.

The locus of points on which the wavefunction is 0 is called the nodal surface.

Fixed node approximation

DMC within the fixed-node approximation allows the optimization of a trial wavefunction without changing the nodal surface.



Wavefunctions with the same nodal surface as Ψ_T

Trial functions

Traditionally, the Slater-Jastrow wavefunction is used as a trial wavefunction:

$$\Psi_T = e^J D$$

where e^J is positive everywhere and D is the Hartree-Fock wavefunction for the system.

New trial wavefunctions?

The nodal surface of the trial wavefunction can be improved by replacing the Slater determinant with some more complex anti-symmetric function Ψ_A:

$$\Psi_T = e^J \Psi_A$$

But what functional form can we use for Ψ_A?

Beyond one-electron orbitals

Electrons in the real world do not exists in one-electron orbitals. Could we build two-electron orbitals?

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$$\Phi(\mathbf{r},\bar{\mathbf{r}}) = \sum_{i,j} g_{ij}\phi_i(\mathbf{r})\phi_j(\bar{\mathbf{r}})$$

These two-electron orbitals are called geminals in the litterature.

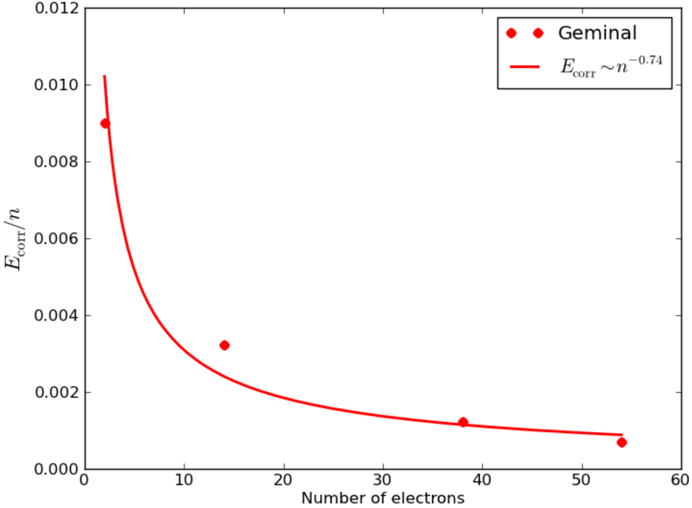
From orbitals to wavefunction

$$\Psi_A = \hat{\mathcal{A}}\left[\Phi(\mathbf{r}_1, \bar{\mathbf{r}}_1)\Phi(\mathbf{r}_2, \bar{\mathbf{r}}_2)\ldots\Phi(\mathbf{r}_n, \bar{\mathbf{r}}_n)\right]$$

From orbitals to wavefunction

$$
\begin{aligned}
\Psi_A &= \hat{\mathcal{A}}\left[\Phi(\mathbf{r}_1, \bar{\mathbf{r}}_1)\Phi(\mathbf{r}_2, \bar{\mathbf{r}}_2)\ldots\Phi(\mathbf{r}_n, \bar{\mathbf{r}}_n)\right] \\
\Psi_A &= \begin{vmatrix}
\Phi(\mathbf{r}_1, \bar{\mathbf{r}}_1) & \Phi(\mathbf{r}_1, \bar{\mathbf{r}}_2) & \cdots & \Phi(\mathbf{r}_1, \bar{\mathbf{r}}_N) \\
\Phi(\mathbf{r}_2, \bar{\mathbf{r}}_1) & \Phi(\mathbf{r}_2, \bar{\mathbf{r}}_2) & \cdots & \Phi(\mathbf{r}_2, \bar{\mathbf{r}}_N) \\
\vdots & \vdots & \ddots & \vdots \\
\Phi(\mathbf{r}_N, \bar{\mathbf{r}}_1) & \Phi(\mathbf{r}_N, \bar{\mathbf{r}}_2) & \cdots & \Phi(\mathbf{r}_N, \bar{\mathbf{r}}_N)
\end{vmatrix}
\end{aligned}
$$

Results - Geminals alone



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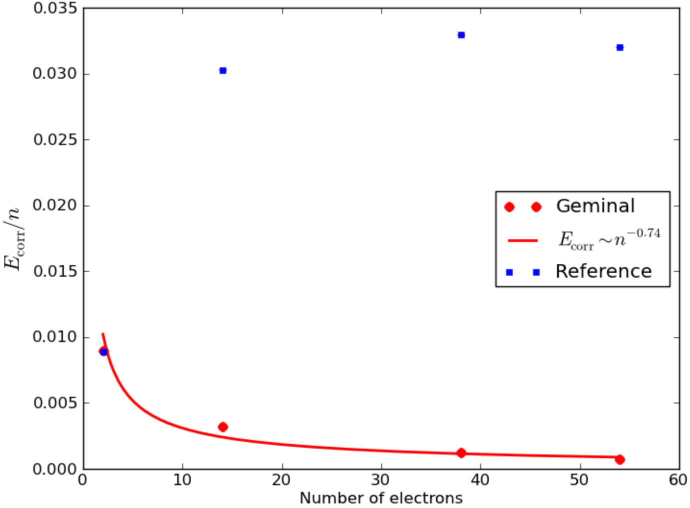
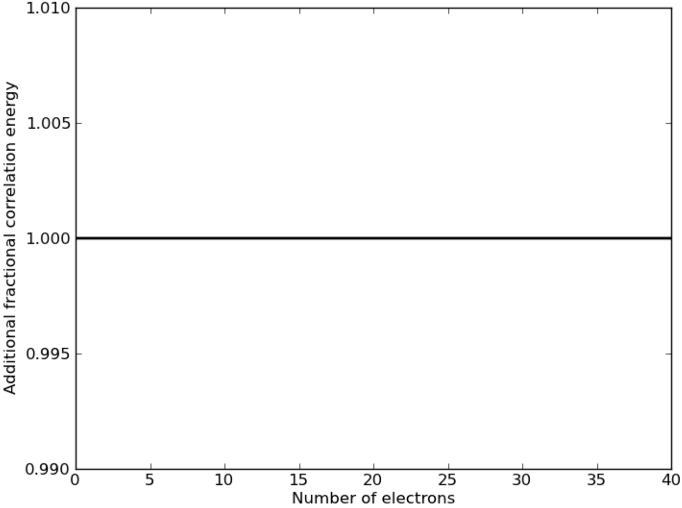
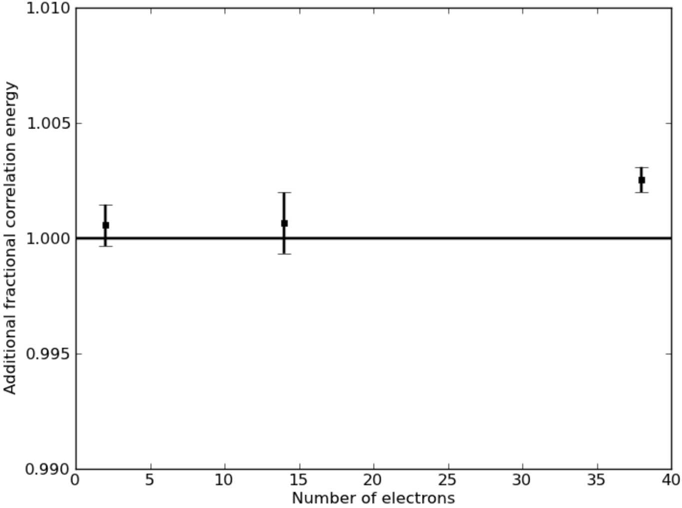


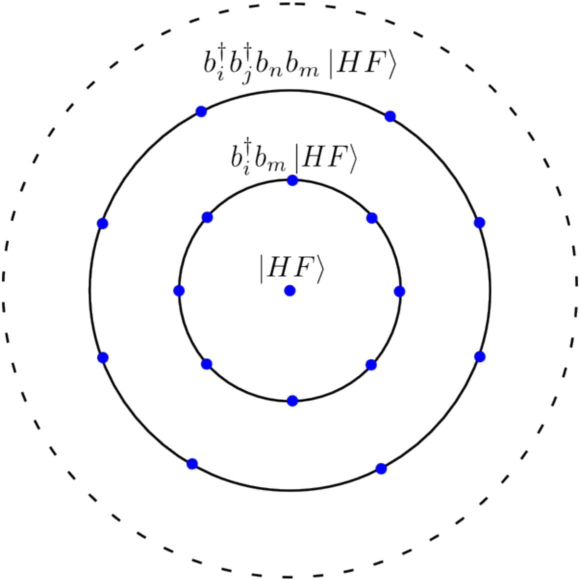
Results - Geminals in DMC



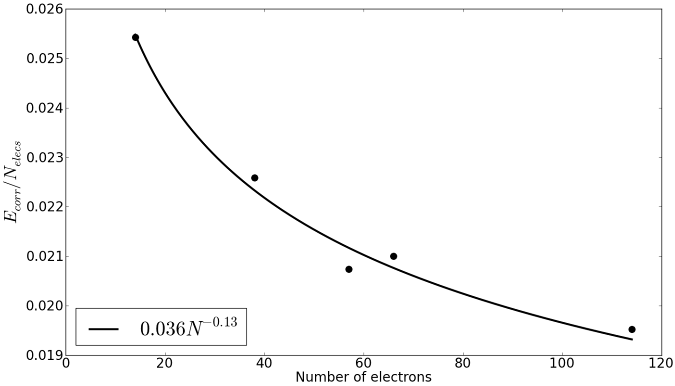
Results - Geminals in DMC



The shape of $\bigwedge^n$



Multi-geminals?



Conclusions

- The nodal surface of the trial wavefunction controls the ultimate accuracy of a DMC calculation.
- Single geminals scale very poorly in bulk systems.
- Sums of geminals may be an (expensive) answer?

References

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

Thank you for listening!