Topology of fermion nodes and pfaffian pairing wavefunctions

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Electronic structure QMC and the fixed-node approximation: the key (only) fundamental approximation

QMC: $\psi_0 = \lim_{\tau \to \infty} \exp(-\tau H) \psi_T$  
$H$ : interacting electrons+ions

Recast as diffusion MC (DMC)  
$f(R, t+\tau) = \int G^*(R, R', \tau)f(R', t)dR'$

with importance sampling:  
$f(R, t \to \infty) = \psi_{\text{Trial}}(R) \phi_{\text{ground}}(R)$

Fermion sign problem -> Fixed-node approximation: $f(R, t) > 0$
(continuous space, boundary replaces antisymmetry)

Fermion node: $\phi(r_1, r_2, ..., r_N) = 0$ (3N-1)-dimen. hypersurface

Exact node -> exact energy in polynomial time

The exact node, in general: an intractable multi-D problem ??? (Will see...)

Anyway, how well does the FN DMC method work?
Example of a fixed-node DMC calculation of a difficult system: FeO solid
“Plain vanilla” FN DMC -> 90-95 % of $E_{corr}$

- FeO ground state: B1 structure, antiferromagnetic insulator
- DFT: wrong structure (B8) and wrong electronic state (metal)

FNDMC:  - Ne-core relativistic pseudopotentials for Fe
- 16 FeO supercell, 352 valence e-
- GGA/HF orbs, $\psi_T = \det^{\uparrow}[\phi_\alpha]\det^{\downarrow}[\phi_\beta]\exp[\sum_{i,j,I} U_{corr}(r_{ij}, r_{il}, r_{jl})]$

Cohesive energy [eV]:

<table>
<thead>
<tr>
<th>Method</th>
<th>LDA</th>
<th>HF</th>
<th>B3LYP</th>
<th>DMC</th>
<th>Exper.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11.7</td>
<td>5.9</td>
<td>7.9</td>
<td>9.47(4)</td>
<td>~9.7</td>
</tr>
</tbody>
</table>

Gap [eV]:

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<th>DMC</th>
<th>Exper.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>10.2</td>
<td>3.4</td>
<td>2.8(4)</td>
<td>~ 2.2</td>
</tr>
</tbody>
</table>

DMC transition B1->B8 pressure 70(5) GPa, Exper. ~70-100GPa!
Beyond the fixed-node approximation: How much do we know about fermion nodes?

\[ \phi(r_1, r_2, ..., r_N) = 0 \rightarrow \text{(DN-1)-dim. smooth manifold divides the space into cells/domains with constant wf. sign ("+") or "-" )} \]

- 1D systems, ground state node known exactly: \( N! \) domains
- 3D, special cases of 2e,3e atoms known exactly: 2 domains, eg,

He atom triplet \( ^3S[1s2s] \): the exact node is 5D hyperboloid in 6D quartet \( ^4S[2p^3] \): the exact node is \( r_1 \cdot (r_2 \times r_3) = 0 \)

**Tiling property for nondegenerate ground states (Ceperley '92):**

Let \( G(R_0) \rightarrow \text{nodal cell/domain around } R_0 \)

**Can show that** \( \sum_P P[G(R_0)] = \text{whole configuration space} \)

**However, it does not say how many domains are there ???**
But that is the key question: the nodal topology!
Focus on fermion nodes: some history in mathematics and...
what do we want to know?

Interest in nodes of eigenstates goes back to D. Hilbert. Later Courant proved some properties of one-particle eigenstates (n-th excited state has n or less nodal domains). However, that is too weak for what we need for many-body systems:

- nodal topologies, ie, number of nodal cells/domains
- accurate nodal shapes? how complicated are they?
- nodes <-> types of wavefunctions?
- nodes <-> physical effects?
Conjecture: for $d >1$ ground states have only two nodal cells, one “+” and one “-”

Numerical proof: 200 noninteracting fermions in 2/3D (Ceperley '92):

For a given $\phi(R)$ find a point such that triple exchanges connect all the particles into a single cluster: then there are only two nodal cells

(Why ? Connected cluster of triple exchanges exhausts all even/odd permutations + tiling property $\rightarrow$ no space left)

Conjecture unproven even for noninteracting particles!!!
Sketch of a proof of two nodal cells for spin-polarized noninteracting 2D harmonic fermions of any size:

**Step 1 -> Wavefunction factorization**

Place fermions on a Pascal-like triangle

\[ M \text{ lines } \rightarrow N_M = \frac{(M+1)(M+2)}{2} \text{ fermions (closed shell)} \]

Wavefunction factorizes by “lines of particles”:

\[
\psi_M(1, \ldots, N_M) = C_{\text{gauss}} \det [1, x, y, x^2, xy, y^2, \ldots] =
\]

\[
= \psi_{M-1}(1, \ldots, N_M/I_{\xi_1}) \prod_{i,j \in I_{\xi_1}} (y_j - y_i) \prod_{1 < k \leq M} (\xi_k - \xi_1)^{n_k}
\]

Factorizable along vertical, horizontal or diagonal lines, recursive.
Explicit proof of two nodal cells for spin-polarized harmonic fermions: Step 2 -> Induction

Therefore all particles connected, any size. Q.E.D.
The key points of the proof generalize to other paradigmatic models and arbitrary $d>1$

True for any model which transforms to homog. polynomials!

- fermions in a periodic box 
  2D, 3D
  
  $\phi_{nm}(x, y) = e^{i(nx+my)} = z^n w^m$

- fermions on a sphere surface

  $Y_{lm}(\theta, \phi) = (\cos \theta)^n (\sin \theta e^{i\phi})^m$

- fermions in a box

  $\phi_{nm}(x, y) = \sin(x)\sin(y) U_{n-1}(p) U_{m-1}(q)$

  homeomorphic variable map: $p = \cos(x)$, $q = \cos(y)$  $\rightarrow$  $p^m q^n$

Works for any $d>1$: factorization along lines, planes, hyperplanes!
Two nodal cells theorem. Consider a spin-polarized system with a closed-shell ground state given by a Slater determinant times an arbitrary prefactor (which does not affect the nodes)

$$\psi_{\text{exact}} = C(1,\ldots,N) \det\{\phi_i(j)\}$$

Let the Slater matrix elements be monomials of positions or their homeomorphic maps in $d>1$.

Then the wavefunction has only two nodal cells.

Can be generalized to some open shells, to nonpolynomial cases such as HF wavefunctions of atomic states, etc.
For noninteracting/HF systems adding another spin channel or imposing additional symmetries generate more nodal cells.

Unpolarized noninteracting/HF systems: $2 \times 2 = 4$ nodal cells!!!
- $\psi_{HF} = \det \{ \phi_\alpha \} \det \{ \phi_\beta \}$
- in general, imposing symmetries generates more nodal cells: the lowest quartet of $S$ symmetry $^4S(1s^2s^3s)$ has six nodal cells.

What happens when interactions are switched on?

“Nodal/topological degeneracy” is lifted and multiple nodal cells fuse into the minimal two again!

First time showed on the case of Be atom, Bressanini et al '03
Sketch the proof idea on a singlet of interacting harmonic fermions using the BCS wave function

Example: 6 harmonic 2D fermions in the singlet ground state. Rotation by $\pi$ exchanges particles in each spin channel: positioned on HF node

$$\psi_{HF} = det^\dagger[\psi_n(i)] det^\dagger[\psi_n(j)] =$$

$$= det[\sum_n^N \psi_n^\dagger(i) \psi_n^\dagger(j)] = det[\phi_{HF}^\dagger(i, j)] = 0$$

BCS pair orbital -> add correlations:

$$\phi_{BCS}^{\dagger\dagger}(i, j) = \phi_{HF}^{\dagger\dagger}(i, j) + \alpha \phi_{corr}^{\dagger\dagger}(i, j)$$

virtuals from the first unoccupied subshell

$$\psi_{BCS} = det\{\phi_{BCS}^{\dagger\dagger}(i, j)\} = \alpha r_a r_b \cos(\phi)[2(r_a r_b \cos(\phi))^2 - r_a^2 - r_b^2] \neq 0$$

BCS wavefunction is nonvanishing for arbitrary weak interaction!
Effect of correlation in homogeneous electron gas: singlet pair of e- winds around the box without crossing the node

\[ r_i \uparrow = r_{i+5} \downarrow + \text{offset}, \quad i = 1, \ldots, 5 \]

HF crosses the node multiple times, BCS does not (supercond.)
The same is true for the nodes of temperature/imaginary time density matrix

Analogous argument applies to temperature density matrix

\[ \rho(R, R', \beta) = \sum_\alpha \exp[-\beta E_\alpha] \psi^*_\alpha(R) \psi_\alpha(R') \]

fix \( R', \beta \) -> nodes/cells in the \( R \) subspace

High (classical) temperature: \( \rho(R, R', \beta) = C_N \det\{\exp[-(r_i - r'_j)^2/2 \beta]\} \)

enables to prove that \( R \) and \( R' \) subspaces have only two nodal cells. Stunning: sum over the whole spectrum!!!
L.M. PRL, 96, 240402; cond-mat/0605550

The next problem: more efficient description of nodal shapes. Calls for better description of correlation -> pfaffians ...
Let us recall what is pfaffian: signed sum of all distinct pair partitions (Pfaff, Cayley ~ 1850)

\[
pf[a_{ij}] = \sum_{P} (-1)^{P} a_{i_1,j_1} \ldots a_{i_N,j_N}, \quad i_k < j_k, \quad k=1, \ldots, N
\]

Example: pfaffian of a skew-symmetric matrix

\[
\begin{bmatrix}
0 & a_{12} & a_{13} & a_{14} \\
-a_{12} & 0 & a_{23} & a_{24} \\
-a_{13} & -a_{23} & 0 & a_{34} \\
-a_{14} & -a_{24} & -a_{34} & 0
\end{bmatrix}
\]

\[
pf = a_{12}a_{34} - a_{13}a_{24} + a_{14}a_{23}
\]

Signs:

\[
\begin{array}{cccc}
1 & 2 & 3 & 4 \\
\hline
+ & - & +
\end{array}
\]
Relations of pfaffians and determinants

Pfaffian is easy to evaluate in $O(n^3)$ time

• For any square matrix $B$ (nxn)

$$\det(B) = (-1)^{n(n-1)/2} pf \begin{bmatrix} 0 & B \\ -B^T & 0 \end{bmatrix}$$

• For any skew-symmetric matrix $A$ (2nx2n)

$$\det(A) = \left[ pf(A) \right]^2$$

• Any determinant can be written as pfaffian but not vice versa: pfaffian is more general, determinant is a special case

Algebra similar to determinants: pfaffian can be expanded in minors, evaluated by Gauss-like elimination directly, etc.
Pfaffian is useful: the simplest antisymmetric wavefunction constructed from a pair spinorbital

Pair orbital + antisymmetry -> pfaffian*

\[
\psi_{PF} = A \left[ \phi(x_1, x_2) \phi(x_3, x_4) \ldots \right] = pf[\phi(x_i, x_j)]
\]

\[
i, j = 1, \ldots, 2N
\]

\[
\phi(x_i, x_j) = \phi^{\uparrow \downarrow}(r_i, r_j)(\uparrow \downarrow - \downarrow \uparrow) + \chi^{\uparrow \uparrow}(r_i, r_j)(\uparrow \uparrow) + \chi^{\downarrow \downarrow}(r_i, r_j)(\downarrow \downarrow) + \chi^{\uparrow \downarrow}(r_i, r_j)(\uparrow \downarrow + \downarrow \uparrow)
\]

\[\uparrow\]
symmetric/singlet

\[\downarrow\]
antisymmetric/triplet

* L'Huillier et al, ~ '89 (and others before)
Pfaffian wavefunctions with both singlet and triplet pairs (beyond BCS!) -> all spin states treated consistently: simple, elegant

\[
\psi_{PF} = pf \begin{bmatrix}
\chi^{\uparrow\uparrow} & \phi^{\uparrow\downarrow} & \psi^{\uparrow}
-\phi^{\uparrow\downarrow T} & \chi^{\downarrow\downarrow} & \psi^{\downarrow}
-\psi^{\uparrow T} & -\psi^{\downarrow T} & 0
\end{bmatrix} \times \exp[U_{corr}]
\]

- pairing orbitals expanded in one-particle basis
  \[
  \phi(i, j) = \sum_{\alpha \geq \beta} a_{\alpha \beta} [h_\alpha(i) h_\beta(j) + h_\beta(i) h_\alpha(j)]
  \]
  \[
  \chi(i, j) = \sum_{\alpha > \beta} b_{\alpha \beta} [h_\alpha(i) h_\beta(j) - h_\beta(i) h_\alpha(j)]
  \]
- unpaired
  \[
  \psi(i) = \sum_\alpha c_\alpha h_\alpha(i)
  \]
- expansion coefficients and the Jastrow correlation optimized
DMC correlation energies of atoms, dimers
Pfaffians: more accurate and systematic than HF
while scalable (unlike CI)
Expansions in many pfaffians for first row atoms: FNDMC ~ 98 % of correlation with a few pfaffians

Table of correlation energies [%] recovered: MPF vs CI nodes

<table>
<thead>
<tr>
<th>WF</th>
<th>n</th>
<th>C</th>
<th>n</th>
<th>N</th>
<th>n</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMC/MPF</td>
<td>3</td>
<td>98.9</td>
<td>5</td>
<td>98.4</td>
<td>11</td>
<td>97.2</td>
</tr>
<tr>
<td>DMC/CI</td>
<td>98</td>
<td>99.3</td>
<td>85</td>
<td>98.9</td>
<td>136</td>
<td>98.4</td>
</tr>
</tbody>
</table>

- further generalizations: pairing with backflow coordinates, independent pairs, etc (M. Bajdich et al, PRL 96, 130201 (2006))

Pfaffians describe nodes more efficiently
Nodes of different WFs (%E_corr in DMC):
- oxygen atom wavefunction scanned by 2e- singlet
  (projection into 3D -> node subset)

- HF (94.0(2)%)  
- MPF (97.4(1)%)  
- CI (99.8(3)%)

[Diagram showing wavefunction scans for HF, MPF, and CI]
Nodal topology change from correlation: nitrogen dimer

\[ \pi_x, \pi_y \rightarrow \text{planar like surfaces} \]

\[ \{ \sigma_g, \sigma_u, \sigma_g \} \cup \{ \pi_x, \pi_y \} \rightarrow \text{distorted planar surfaces} \]
Nodes in quantum Hall states

$H$ with broken time-reversal invariance $\rightarrow$ inherently complex wavefunction $\rightarrow$ define the nodes for real and imaginary parts (or, in special cases, phase times a real)

- use exact adiabatic mapping to “1D”-like model (Bergholtz et al, Horsdal et al) $\rightarrow$ enough to understand that the nodes of both real and imaginary parts are essentially 1D (LLL integer QHE, Laughlin states)

- easy to see on the simplest case of three electrons: wavefunction is a symmetric phase times 1D w.f. depending on radii only:

$$\psi(z_1, z_2, z_3) = \exp(i \sum_i \phi_i) \psi_{1D}^{\text{real}}(r_1, r_2, r_3); \quad |z_i| = r_i$$

triple exchange $\rightarrow$ basically a rotation of three particle on a circle
Summary

- explicit proof of two nodal cells for d>1 and arbitrary size with rather general conditions: fundamental property of closed-shell fermionic ground states

- pfaffian: compact wavefunction, has the right topology; still, nodes more subtle: ~ 5 % of correlation energy;

- fermion nodes: another example of importance of quantum geometry and topology for electronic structure
What if matrix elements are not monomials? Atomic states (different radial factors for subshells): Proof of two cells for nonint. and HF wavefunctions

- Position subshells of electrons onto spherical surfaces:

$$\Psi_{HF} = \Psi_{1s} \Psi_{2s2p^3} \Psi_{3s3p^3 d^5} \ldots$$

- Exchanges between the subshells: simple numerical proof up to size $^{15}S(1s2s2p^33s3p^33d^5)$ and beyond (n=4 subshell)
Observations from comparison of HF and “exact” (CI) nodes

- the two nodal cells for Coulomb interactions as well

- the nodal openings have very fine structure: ~ 5% of E_corr

- although topologically incorrect, away from openings the HF nodes unexpectedly close to exact
Two nodal cells: generic property, possible exceptions
The exact shape of the node?

Topology of nodes for closed-shell gr. states is surprisingly simple:

The ground state node bisects the configuration space
(the most favorable way to satisfy the antisymmetry)

Possible exceptions/caveats:
- nonlocal or singular interactions
- imposing symmetries or boundaries
- degeneracies

The next problem: the exact nodal shape is difficult to get!
The key: better description of correlations -> pfaffians
Correlation in the BCS wavefunction is enough to fuse the noninteracting four cells into the minimal two

Arbitrary size: position the particles on HF node (wf. is rotationally invariant)

HF pairing (sum over occupieds, linear dependence in Sl. dets)
\[ \psi_{HF} = \det[\phi_{HF}(i, j)] = \det[\sum_n \psi_n(i)\psi_n(j)] = \det[\psi_n(i)]\det[\psi_n(j)] = 0 \]

BCS pairing (sum over occupieds and virtuals, eliminate lin. dep.)
\[ \phi(i, j) = \phi_{HF}(i, j) + \phi_{corr}(i, j) \]
\[ \psi_{BCS} = \det[\phi_{BCS}(i, j)] \neq \det[\psi_{nm}(i)]\det[\psi_{nm}(j)] \rightarrow \psi_{BCS} \neq 0 \]