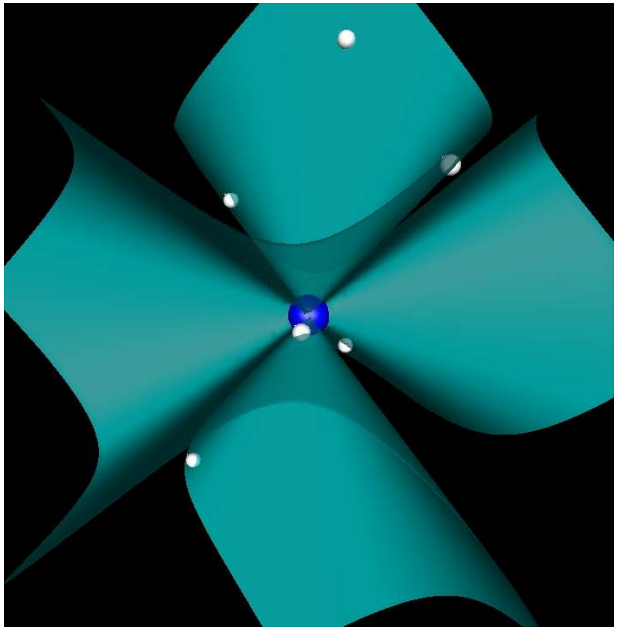
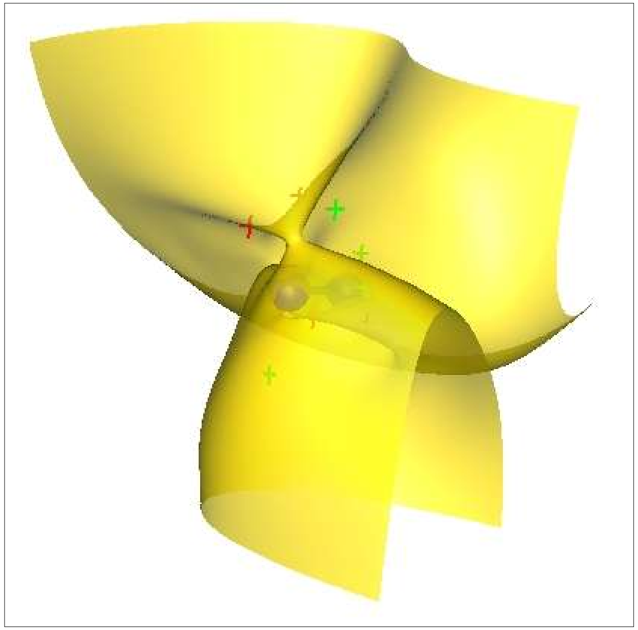
Topology of fermion nodes and pfaffian pairing wavefunctions





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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) with importance sampling:

$$f(\boldsymbol{R}, t+\tau) = \int G^*(\boldsymbol{R}, \boldsymbol{R}', \tau) f(\boldsymbol{R}', t)\, d\boldsymbol{R}'$$
$$f(\boldsymbol{R}, t\to\infty) = \psi_{Trial}(\boldsymbol{R})\phi_{ground}(\boldsymbol{R})$$

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

Fermion node: $\phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) = 0$ **(3N-1)-dimen. hypersurface**

Exact node -> exact energy in polynomial time

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

NC STATE UNIVERSITY **Anyway, how well does the FN DMC method work ?**

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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, $\psi_T = det^{\uparrow}[\phi_\alpha] det^{\downarrow}[\phi_\beta] \exp[\sum_{i,j,I} U_{corr}(r_{ij}, r_{iI}, r_{jI})]$

Cohesive energy[eV]:

LDA	HF	B3LYP	DMC	Exper.
11.7	5.9	7.9	9.47(4)	~9.7

Gap [eV]:

LDA	HF	B3LYP	DMC	Exper.
0	10.2	3.4	2.8(4)	~ 2.2

DMC transition B1->B8 pressure 70(5) GPa, Exper. ~70-100GPa !

Beyond the fixed-node approximation: How much do we know about fermion nodes ?

$\phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) = 0$ -> (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 $\boldsymbol{r}_1 \cdot (\boldsymbol{r}_2 \times \boldsymbol{r}_3) = 0$

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

Let $G(R_0) \rightarrow nodal\, cell/domain\, around\, R_0$ $\qquad P \rightarrow particle\, permutation$

Can show that $\sum_P P[G(R_0)] \;=\; whole\, configuration\, space$

However, it does not say **how many domains are there ???**
But that is the key question: the nodal topology!

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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 ?

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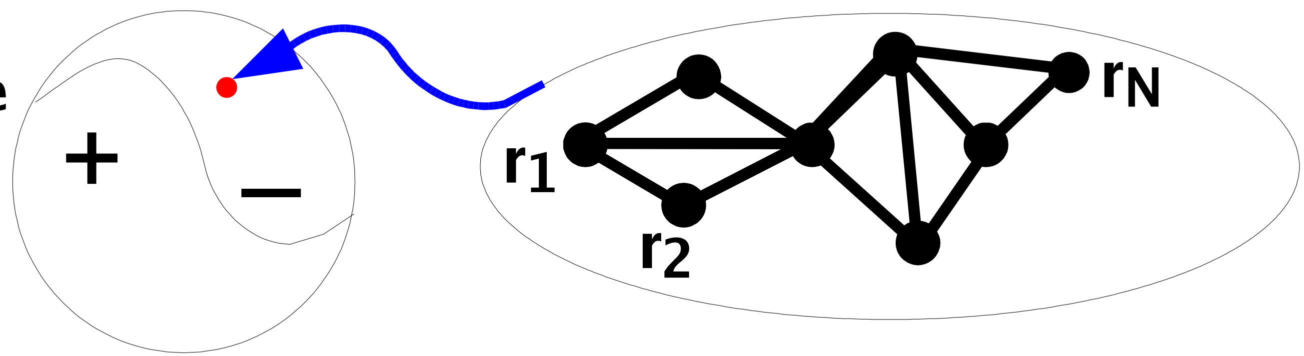
Conjecture: for d >1 ground states have only two nodal cells, one "+" and one "-"

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

All-particle configuration space



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

Conjecture unproven even for noninteracting particles!!!

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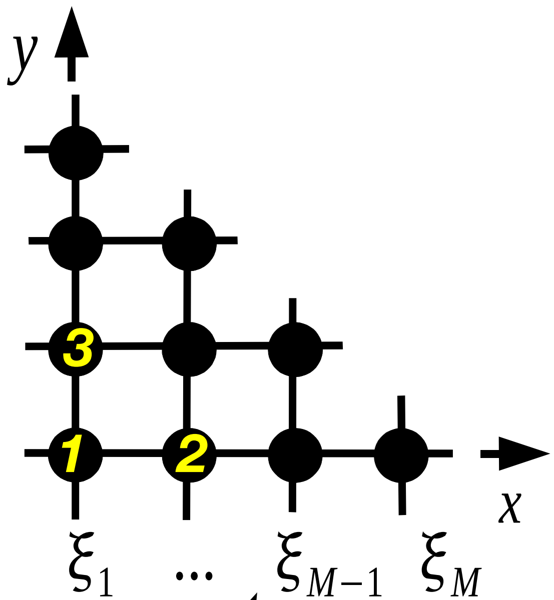
Skecth of a proof of two nodal cells for spin-polarized noninteracting 2D harmonic fermions of any size: Step 1 -> Wavefunction factorization

Place fermions on a Pascal-like triangle



M **lines ->** $N_M=(M+1)(M+2)/2$ **fermions (closed shell)**

Wavefunction factorizes by "lines of particles":

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

$$=\psi_{M-1}(1,...,N_M/I_{\xi_1})\prod_{i<j}^{i,j\in I_{\xi_1}}(y_j-y_i)\prod_{1<k\le M}(\xi_k-\xi_1)^{n_k}$$

particle coords

lines coords

Factorizable along vertical, horizontal or diagonal lines, recursive.

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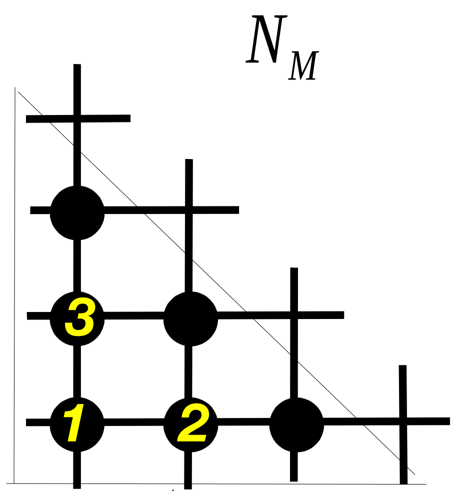
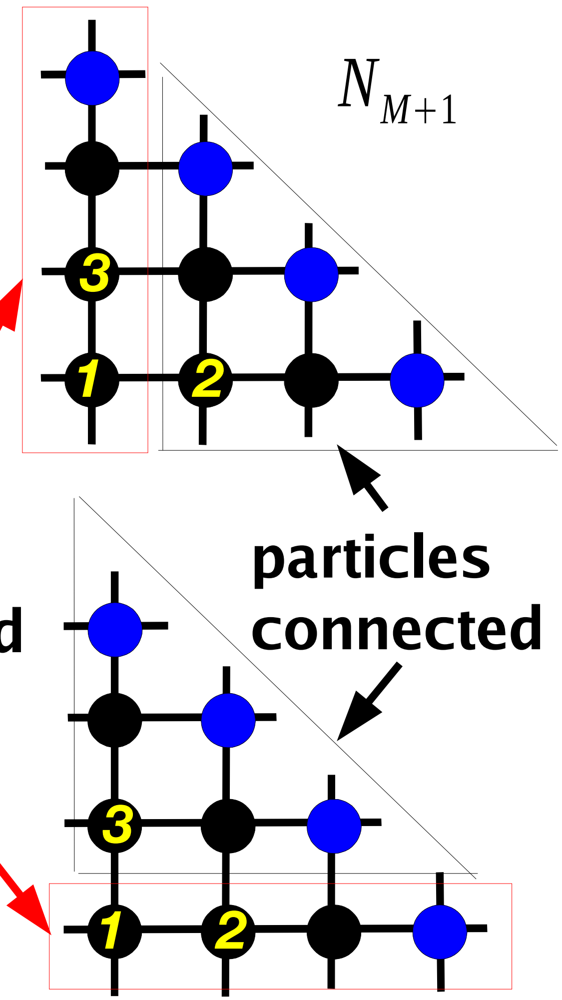
Explicit proof of two nodal cells for spin-polarized harmonic fermions: Step 2 -> Induction



assume particles connected by exchanges

$M \to M+1$

"lines" factorized out



particles connected

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** $\phi_{nm}(x,y) = e^{i(nx+my)} = z^n w^m$
  2D, 3D

- **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: $p = \cos(x),\ \ q = \cos(y) \quad \rightarrow \quad p^m q^n$

Works for any d>1: factorization along lines, planes, hyperplanes!

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Two nodal cells theorem: generic (and fundamental) property of fermionic ground states of many models

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)

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

Let the Slater matrix elements be monomials $x_i^n y_i^m z_i^l \ldots$ 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.

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For noninteracting/HF systems adding another spin channel or imposing additional symmetries generate more nodal cells

Unpolarized nonintenracting/HF systems: 2*2=4 nodal cells!!!

-> product of two independent Slater determinants

$$\psi_{HF} = det^{\uparrow}\{\phi_{\alpha}\} det^{\downarrow}\{\phi_{\beta}\}$$

- in general, imposing symmetries generates more nodal cells:

the lowest quartet of S symmetry $^4S(1s2s3s)$ 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 etal '03

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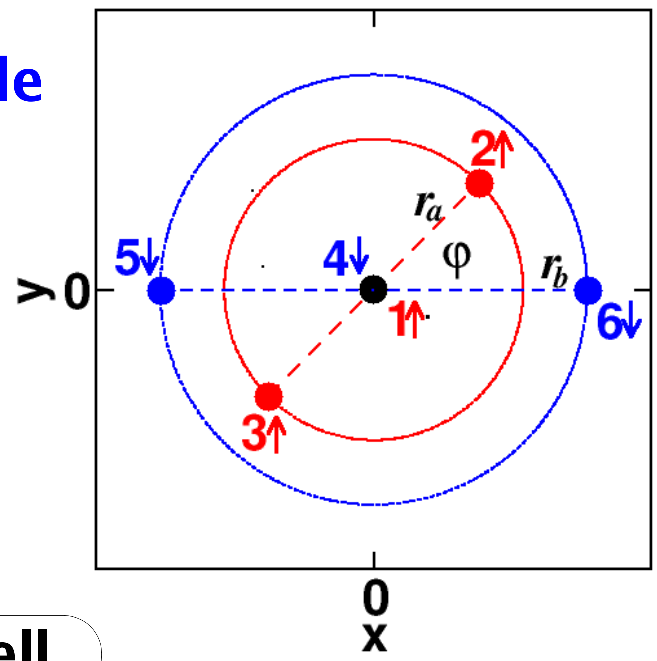
Sketch the proof idea on a singlet of *interacting* harmonic fermions using the BCS wave function

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



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

BCS pair orbital -> add correlations:

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

virtuals from the first unoccupied subshell

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

BCS wavefunction is nonvanishing for arbitrary weak interaction!

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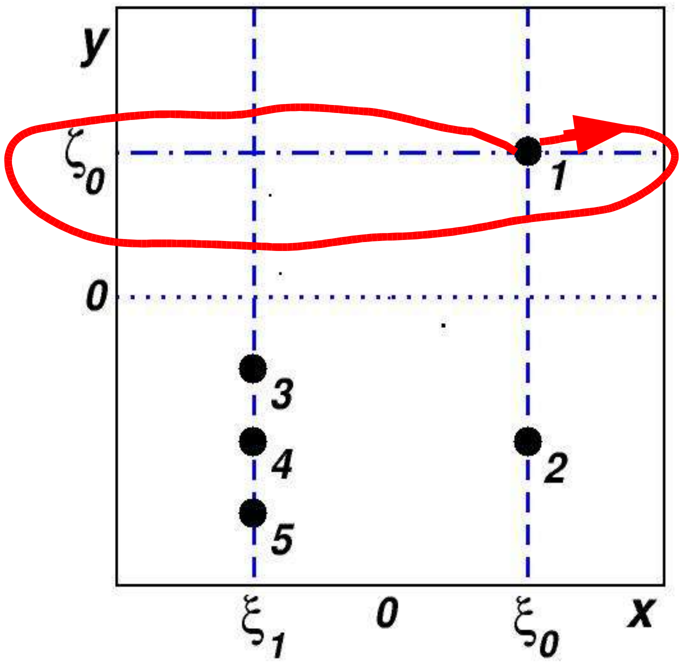
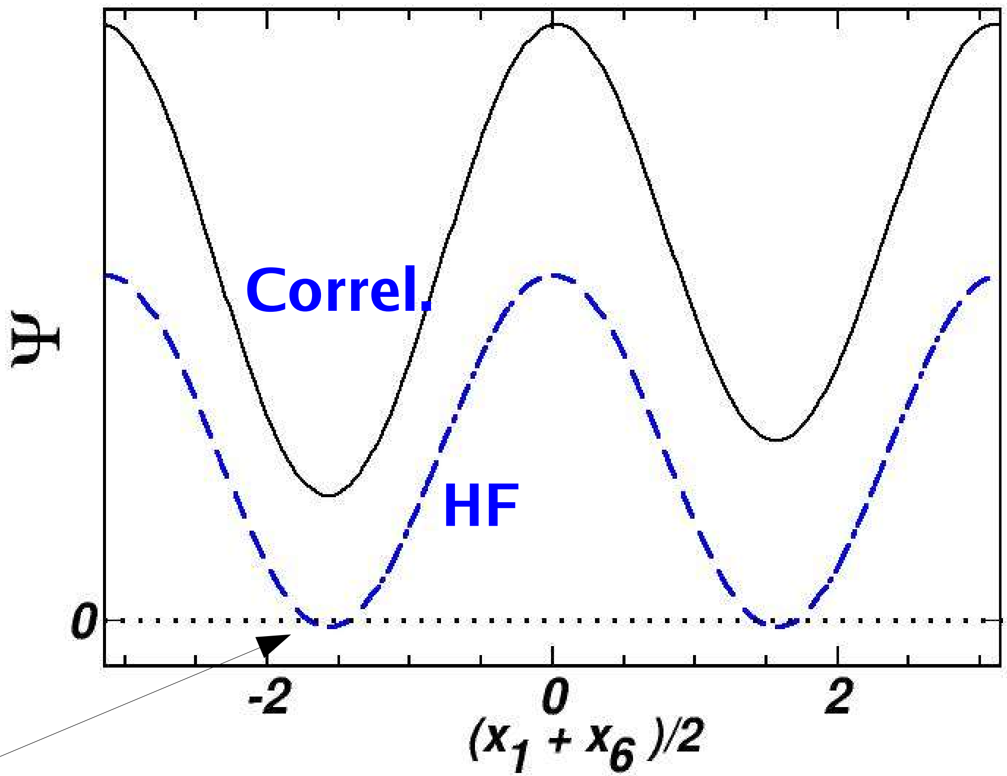
Effect of correlation in homogeneous electron gas: singlet pair of e- winds around the box without crossing the node

$$r_i\uparrow = r_{i+5}\downarrow + offset, \quad i=1,\dots,5$$



Wavefunction along the winding path



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',β -> 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 ...

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Let us recall what is pfaffian: signed sum of all distinct pair partitions (Pfaff, Cayley ~ 1850)

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

Example: pfaffian of a skew-symmetric matrix

$$pf \begin{bmatrix} 0 & a_{12} & a_{13} & a_{14} \\ -a_{12} & 0 & a_{23} & a_{24} \\ -a_{13} & -a_{23} & 0 & a_{34} \\ -a_{14} & -a_{24} & -a_{34} & 0 \end{bmatrix} = a_{12}a_{34} - a_{13}a_{24} + a_{14}a_{23}$$

Signs: + - +

1 2 3 4 1 2 3 4 1 2 3 4

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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)**

$$det(A) = [pf(A)]^2$$

- **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.

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Pfaffian is useful: the simplest antisymmetric wavefunction constructed from a pair spinorbital

Pair orbital + antisymmetry -> pfaffian*

$$\psi_{PF} = A[\phi(x_1, x_2)\phi(x_3, x_4)\ldots] = pf[\phi(x_i, x_j)] \qquad i, j = 1, \ldots, 2N$$

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

symmetric/singlet **antisymmetric/triplet**

*** L'Huillier et al, ~ '89 (and others before)**

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Pfaffian wavefunctions with both singlet and triplet pairs (beyond BCS!) -> all spin states treated consistently: simple, elegant

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

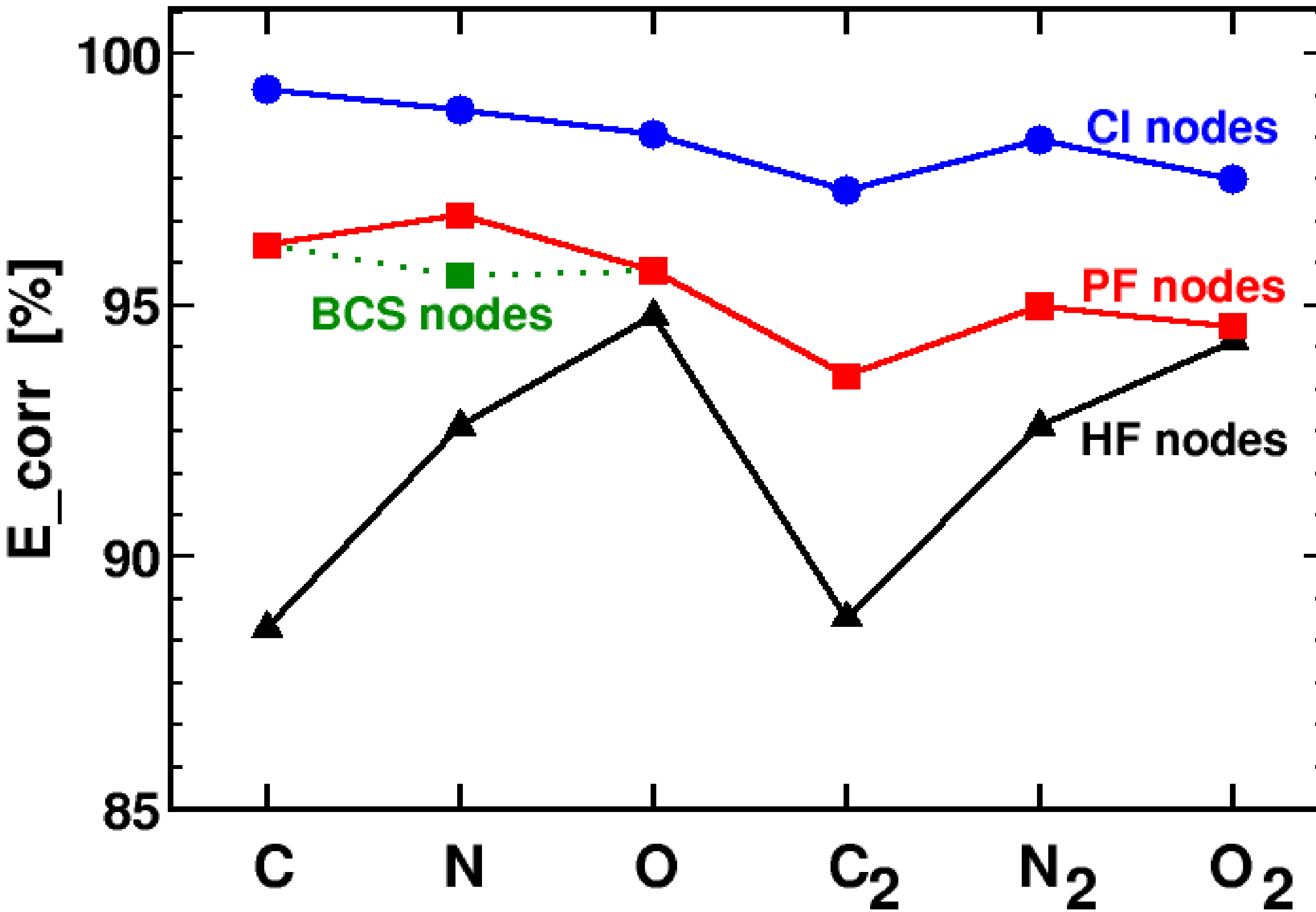
- pairing orbitals expanded in one-particle basis

$$\phi(i,j)=\sum_{\alpha\geq\beta}a_{\alpha\beta}[h_\alpha(i)h_\beta(j)+h_\beta(i)h_\alpha(j)]$$
$$\chi(i,j)=\sum_{\alpha>\beta}b_{\alpha\beta}[h_\alpha(i)h_\beta(j)-h_\beta(i)h_\alpha(j)]$$

- **unpaired** $\psi(i)=\sum_\alpha c_\alpha h_\alpha(i)$

- **expansion coefficients and the Jastrow correlation optimized (M. Bajdich, L.M. et al, PRL 96, 130201 (2006))**

DMC correlation energies of atoms, dimers Pfaffians: more accurate and systematic than HF while scalable (unlike CI)



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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

n= # of pfs/dets

WF	n	C	n	N	n	O
DMC/MPF	3	98.9	5	98.4	11	97.2
DMC/CI	98	99.3	85	98.9	136	98.4

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

Pfaffians describe nodes more efficiently

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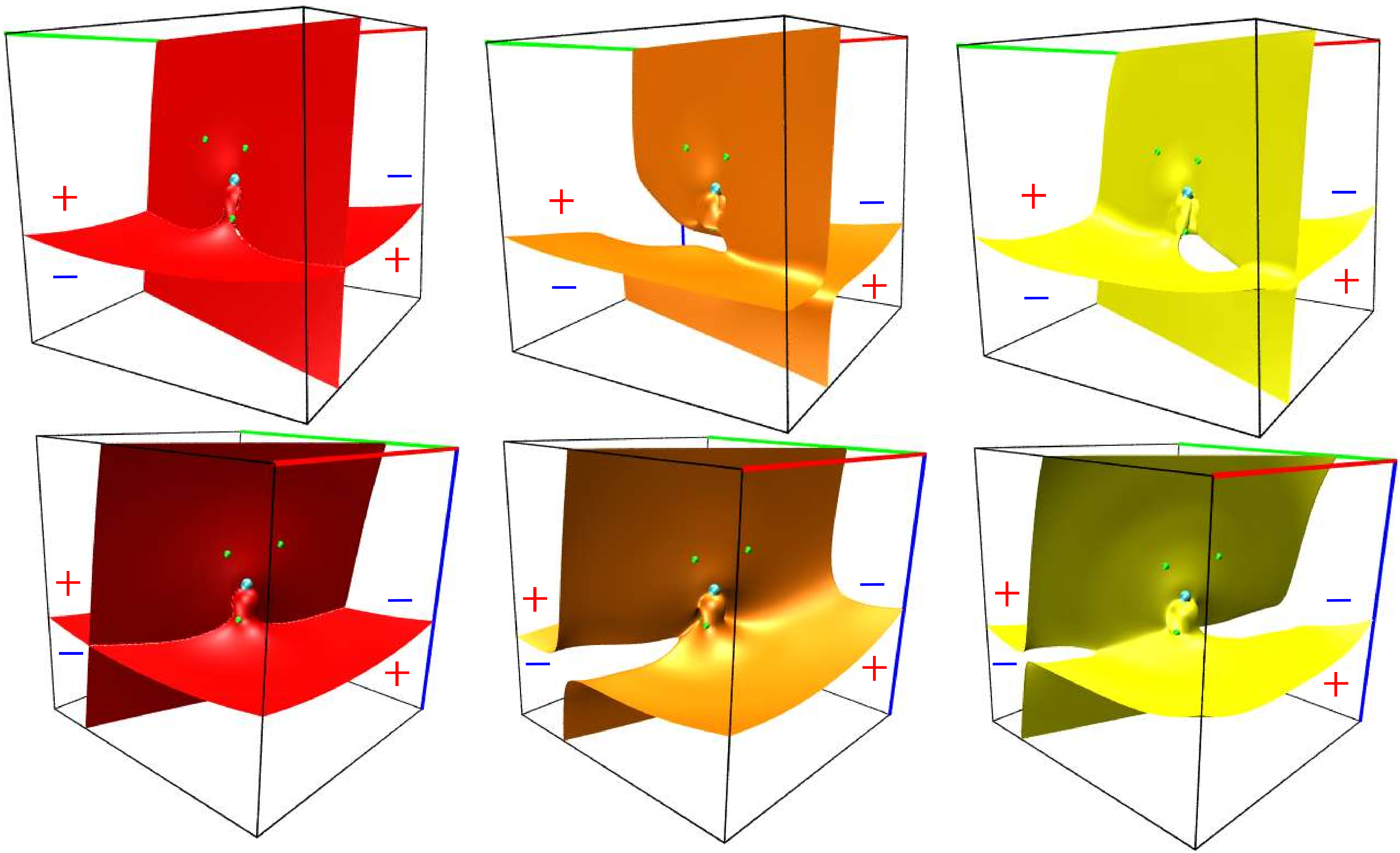
Nodes of different WFs (%E_corr in DMC): oxygen atom wavefunction scanned by 2e- singlet (projection into 3D -> node subset)

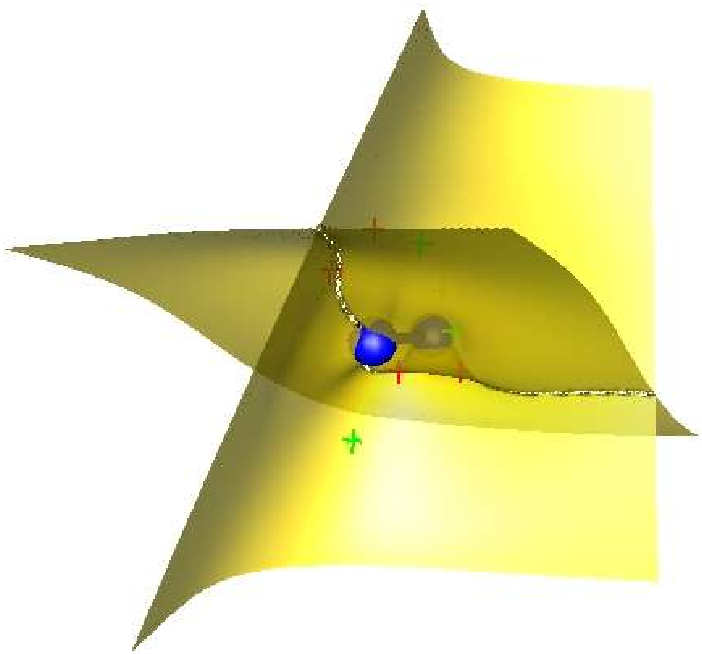
HF (94.0(2)%) **MPF** (97.4(1)%) **CI** (99.8(3)%)



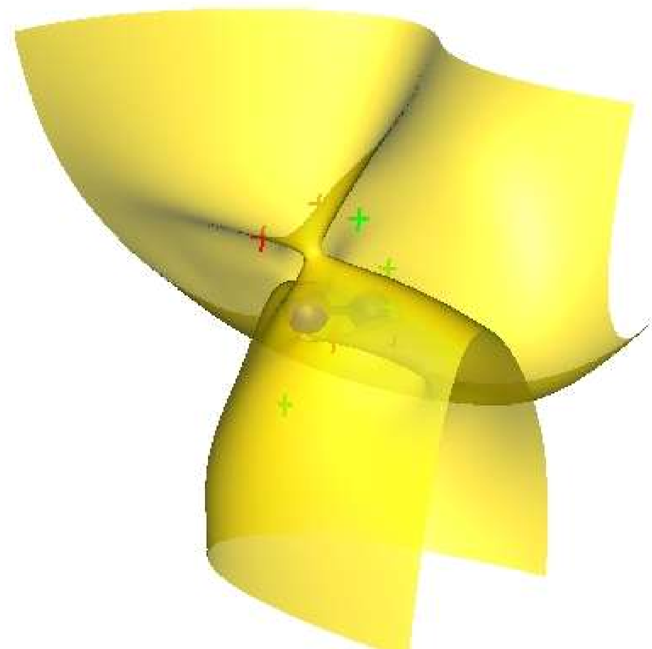
Nodal topology change from correlation: nitrogen dimer

$$\pi_x, \pi_y \rightarrow planar\ like\ surfaces$$

$$\{\sigma_g, \sigma_u, \sigma_g\} \cup \{\pi_x, \pi_y\} \rightarrow distorted\ planar\ surfaces$$



HF node
4 cells



Correlated node
2 cells

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Nodes in quantum Hall states

H **with broken time-reversal invariance -> inherently complex wavefunction -> 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) -> 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:

$$\psi(z_{1,} z_{2,} z_3) = \exp(i q \sum_i \phi_i) \psi_{1D}^{real}(r_1, r_{2,} r_3); \quad |z_i| = r_i$$

triple exchange -> basically a rotation of three particle on a circle

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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

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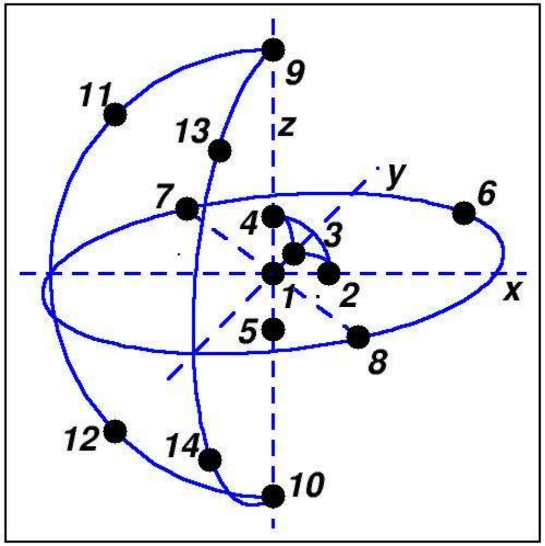
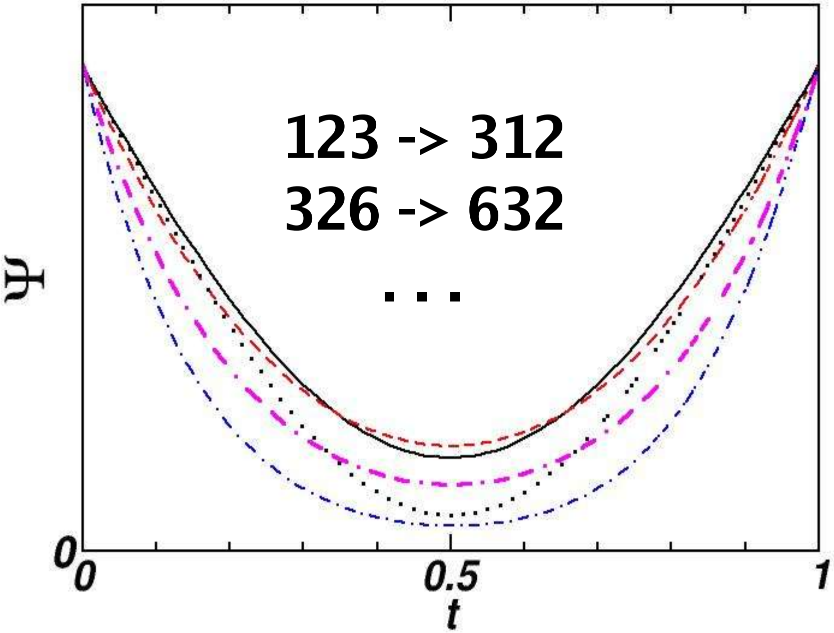
What if matrix elements are not monomials ? Atomic states (different radial factors for subshells): Proof of two cells for nonint. and HF wavefunctions

- position subshells of electrons onto spherical surfaces:

$$\psi_{HF} = \psi_{1s}\psi_{2s2p^3}\psi_{3s3p^3d^5}\cdots$$

- exchanges between the subshells: simple numerical proof up to size $^{15}S(1s2s2p^3 3s3p^3 3d^5)$ and beyond (n=4 subshell)





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Observations from comparison of HF and “exact” (CI) nodes

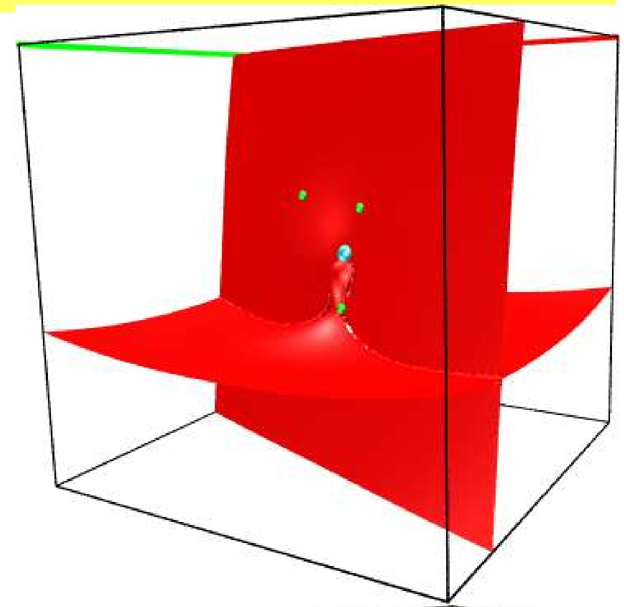
- the two nodal cells for Coulomb interactions as well

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

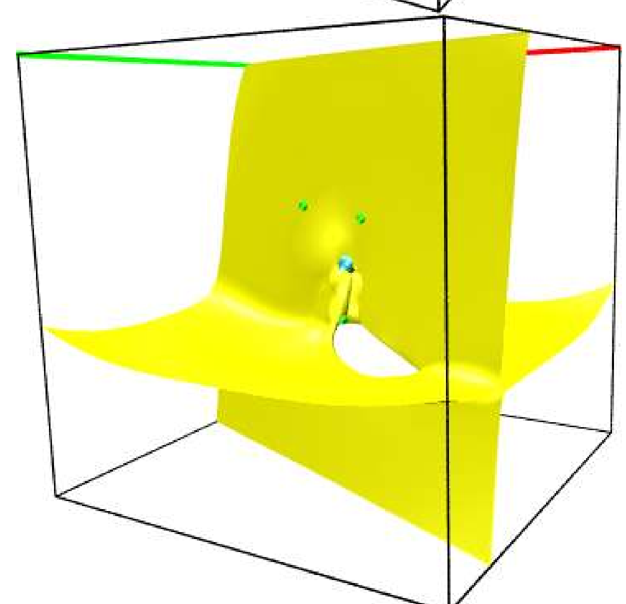
-

- although topologically incorrect, away from openings the HF nodes unexpectedly close to exact

HF



CI



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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

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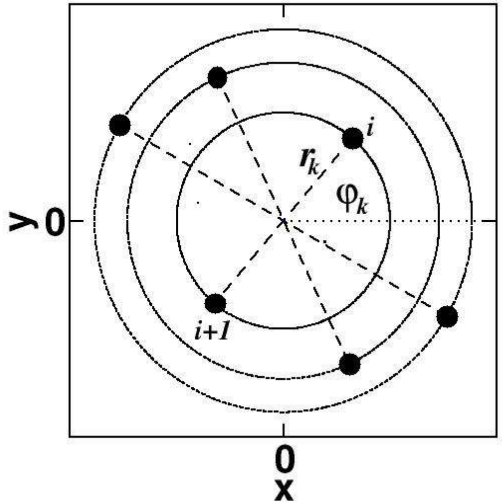
Correlation in the BCS wavefunction is enough to fuse the noninteracting four cells into the minimal two

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.)

$$\phi(i,j) = \phi_{HF}(i,j) + \phi_{corr}(i,j)$$

$$\psi_{BCS} = det[\phi_{BCS}(i,j)] \neq det[\psi_{nm}(i)] det[\psi_{nm}(j)] \quad \rightarrow \quad \psi_{BCS} \neq 0$$

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