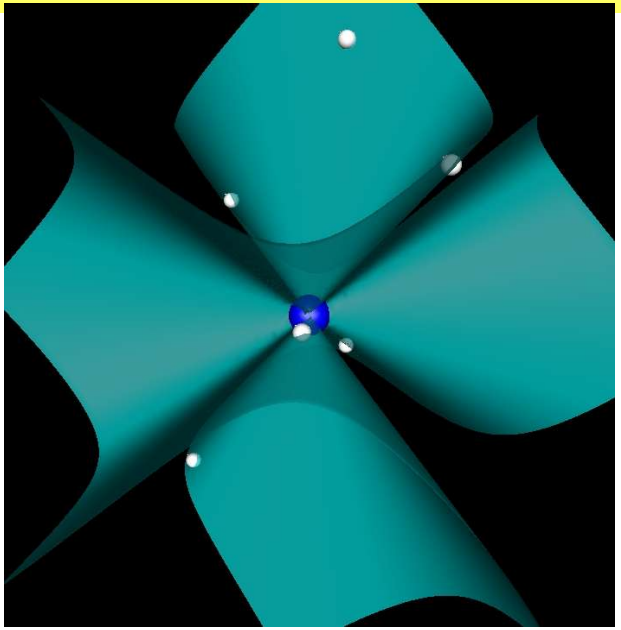
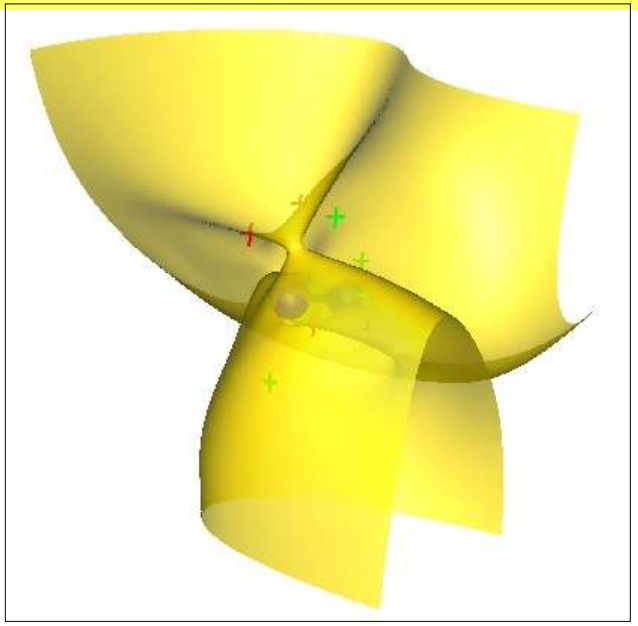
# Fixed-node methods and geminal nodes (or Topology of fermion nodes and pairing wavefunctions)



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Urbana, July 2007


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# Hmmm, fermion nodes

Fermion nodes is a challenging, rather advanced topic. Why ?

- essentially the only key approximation for QMC to scale as a low-order polynomial in the number of particles

- different ideas, tools and language from typical electronic structure

- seem hopelessly complicated, difficult to improve, unsolved problem

but

- recently, some progress in understanding the properties of f.n.

- a few ideas and successes how to improve the nodes of wavefunctions

- perhaps even fundamental connections with physical properties


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# Outline of this talk

- fermion sign problem and fixed-node approximation, toy model

- beyond fixed-node approximation: accuracy!

- properties of fermion nodes

- fermion nodes and nodal cells: importance of topology

- two-nodal cells of generic fermionic ground states

- single-particle vs pairing orbital wavefunctions

- relevance of pfaffians and their properties

- pfaffian calculations



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# DMC method in a nutshell

**DMC is a stochastic realization of projection of the (ground) state in imaginary time (projection parameter)**

$$\psi(\boldsymbol{R},t)=\exp(-tH)\psi_T(\boldsymbol{R})$$

$$-\partial_t\psi(\boldsymbol{R},t)=H\psi(\boldsymbol{R},t)$$

$$\psi(\boldsymbol{R},t+\tau)=\int G(\boldsymbol{R},\boldsymbol{R}',\tau)\psi(\boldsymbol{R}',t)d\boldsymbol{R}'$$

**Wave function can be sampled and the equation solved by interpreting the Green's functions as a transition probability density: simulation of an equivalent stochastic process -> essentially an exact mapping**



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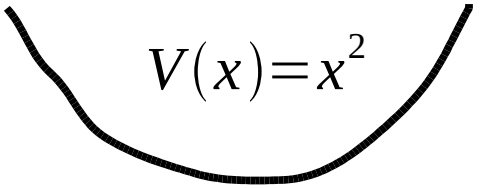
# Toy model: 1D harmonic oscillator

$$H = T + V(x)$$



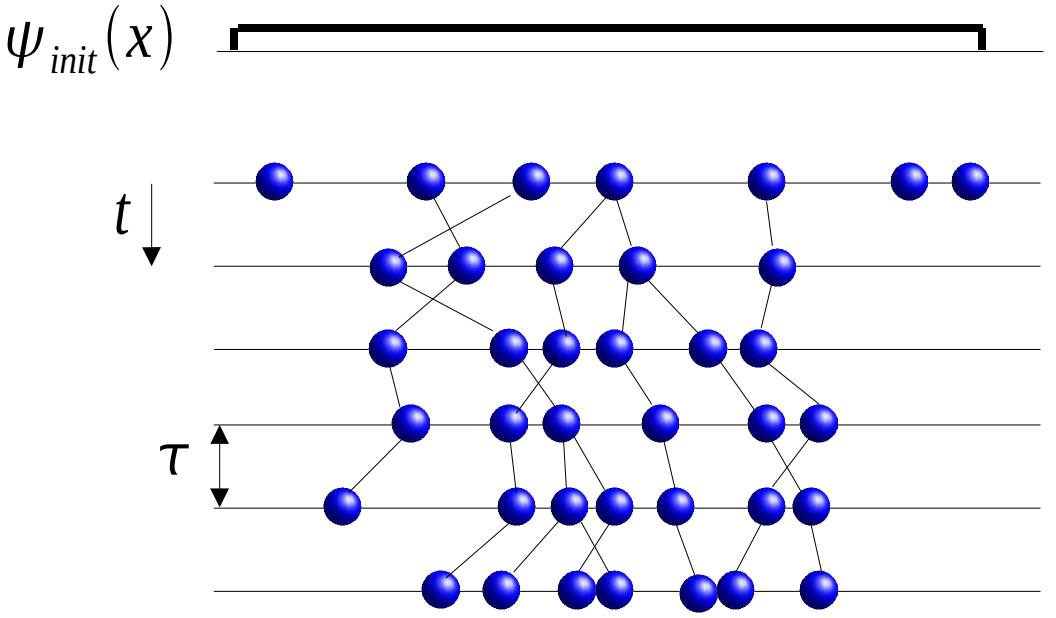

**Propagator**

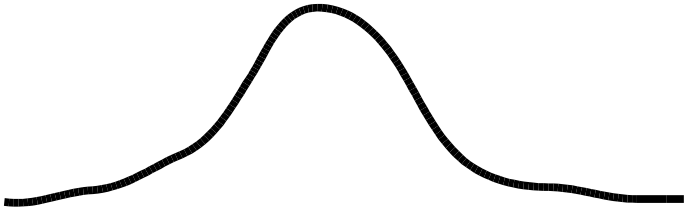
$$G(x,x',\tau)$$

$$\downarrow$$

$$C e^{-(x-x')^2/2\tau} \cdot e^{-(V(x)-E_T)\tau}$$

**diffusion** **renorm**



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# But wavefunctions is both + and -: statistics suffers from the fermion sign problem

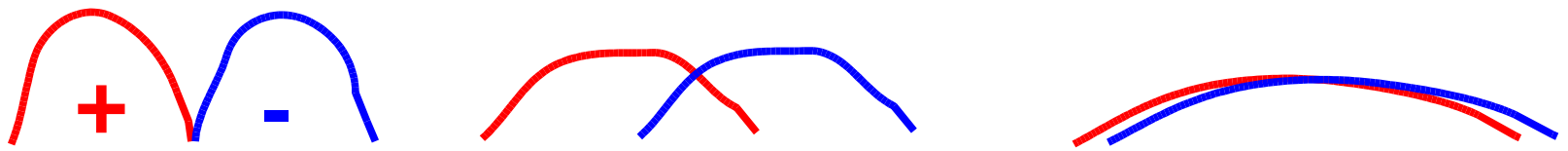
**Naïve approach for fermionic wave functions: decompose to + and -**

$$\psi_T(\boldsymbol{R}) = \psi_T^+(\boldsymbol{R}) - \psi_T^-(\boldsymbol{R})$$

$$-\partial_t \psi^+(\boldsymbol{R},t) = H\psi^+(\boldsymbol{R},t)$$

$$-\partial_t \psi^-(\boldsymbol{R},t) = H\psi^-(\boldsymbol{R},t)$$

**Unfortunately, + and - components converge independently to the lowest energy solution (which is bosonic) because Schr. eq. is linear!**




$$\lim_{t\to\infty} \psi^+(\boldsymbol{R},t) - \lim_{t\to\infty} \psi^-(\boldsymbol{R},t) \propto \exp\left[-(E_{Fermi} - E_{Boson})t\right]$$

**Fermion "signal" decays exponentially quickly into a bosonic "noise"**



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# Importance sampling and fixed-node diffusion Monte Carlo (FNDMC)

$$f(\boldsymbol{R},t+\tau)=\int G^{*}(\boldsymbol{R},\boldsymbol{R}',\tau)f(\boldsymbol{R}',t)\,d\boldsymbol{R}'$$

$$f(\boldsymbol{R},t)=\psi_T(\boldsymbol{R})\phi(\boldsymbol{R},t), \qquad \psi_T=\psi_{HF}e^{U_{corr}}=det\{\phi_\alpha\}det\{\phi_\beta\}e^{U_{corr}}$$

$$f(\boldsymbol{R},t\to\infty)\ \propto\ \psi_T(\boldsymbol{R})\phi_{ground}(\boldsymbol{R}) \qquad G^{*}(\boldsymbol{R},\boldsymbol{R}',\tau)=\frac{\langle \boldsymbol{R}|\exp(-\tau H)|\boldsymbol{R}'\rangle}{\psi_T(\boldsymbol{R}')\psi_T^{-1}(\boldsymbol{R})}$$

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

**Fixed-node (FN) approximation:** $f(\boldsymbol{R},t)>0$

- antisymmetry (nonlocal) replaced by a boundary (local)
- exact node implies recovering exact energy (in polynomial time)

**Accuracy quite high: energy differences within a few % of experiment**



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# Fermion node toy model: excited state of harmonic oscillator

$$H = T + V(x)$$

$V(x) = x^2$

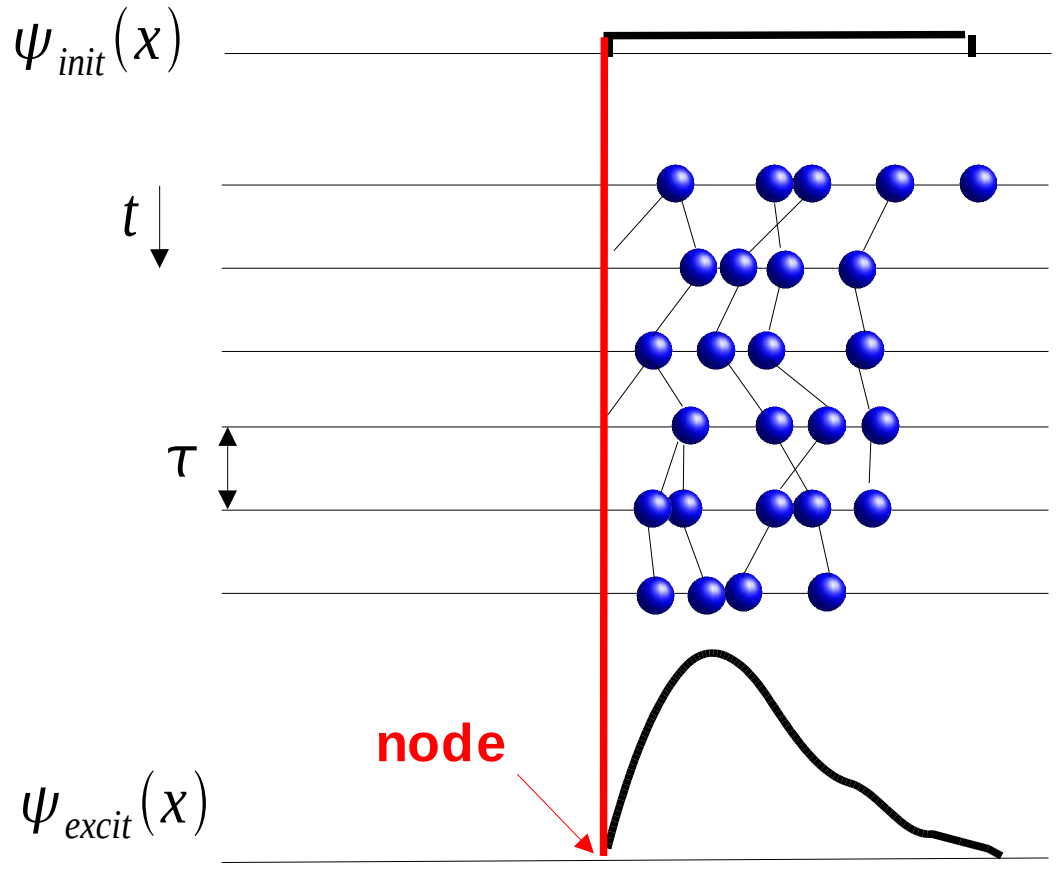
**Propagator**

$G(x, x', \tau)$

$$C e^{-(x-x')^2/2\tau} \cdot e^{-(V(x)-E_T)\tau}$$

**diffusion** **renorm**

**+ boundary condition (evaluate trial function)**




**Assuming you know where the node is!**



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# Propagator with importance sampling using a trial function

$$f(\boldsymbol{R},t+\tau)=\int G^{*}(\boldsymbol{R},\boldsymbol{R}',\tau)f(\boldsymbol{R}',t)\,d\boldsymbol{R}'$$

**Propagator** $$G^{*}(\boldsymbol{R},\boldsymbol{R}',\tau)=\frac{\langle \boldsymbol{R}|\exp(-\tau H)|\boldsymbol{R}'\rangle}{\psi_T(\boldsymbol{R}')\psi_T^{-1}(\boldsymbol{R})}$$

**drift term**

**...which for a small time slice tau is**

$$G(R,R',\tau)=C\exp[-(R-R'-\tau\nabla\ln\psi_T(R'))^2/2\tau]\times$$
$$\times\exp[-(E_L(R)+E_L(R')-2E_T)\tau/2]+O(\tau^3)$$

**where** $E_L(R)=[H\psi_T(R)]/\psi_T(R)$ **is the local energy**

**- node naturally enforced by divergence of the drift at the node**



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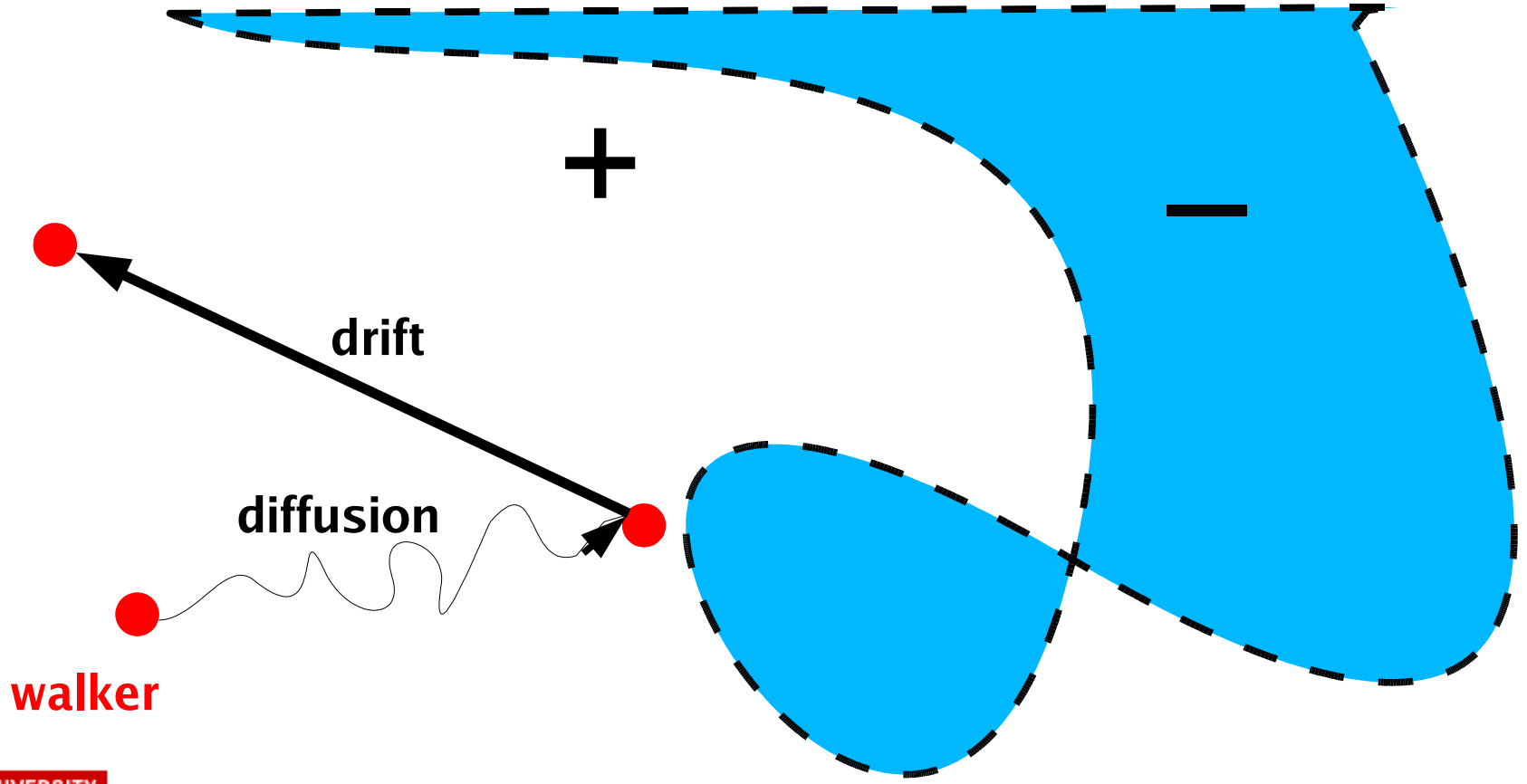
# Role of drift in the fixed-node DMC walker evolution: pushes away from the node

**drift:** $\tau \nabla \ln \psi_T(R)$

**diverges at the node** $R \to node: \quad \tau \nabla \ln \psi_T(R) \to \infty$



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# Fixed-node approximation (assumes that reasonably accurate nodes can be constructed)

- bosonization of the fermionic problem

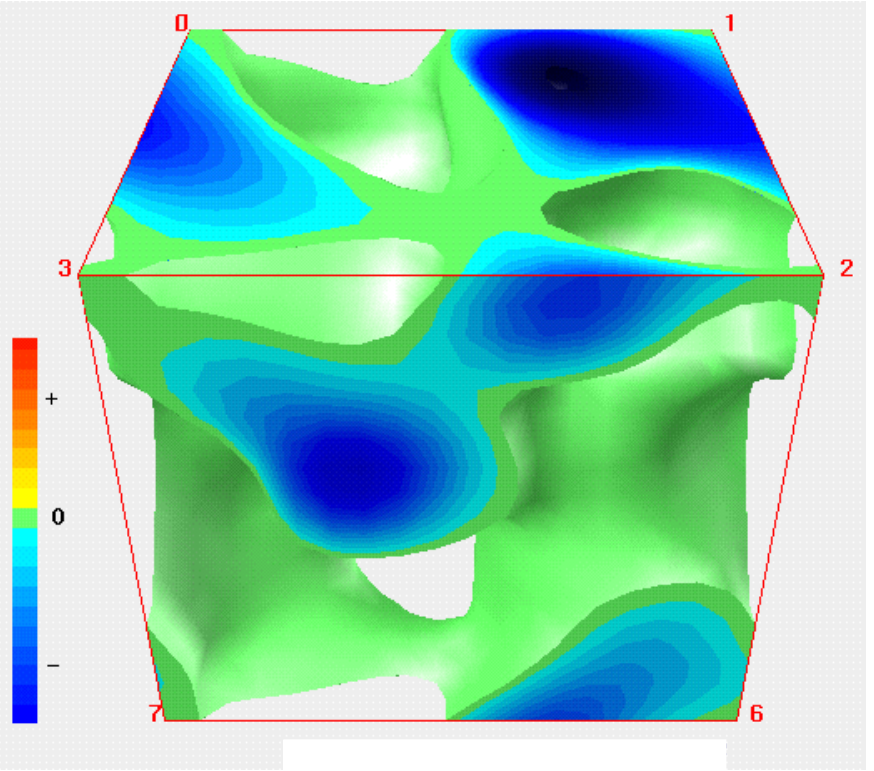
- important (funadmental) approximation:

  antisymmetry -> boundary condition
  (nonlocal) (local)

- fermion node is (3N-1)-dim hyper - surface:

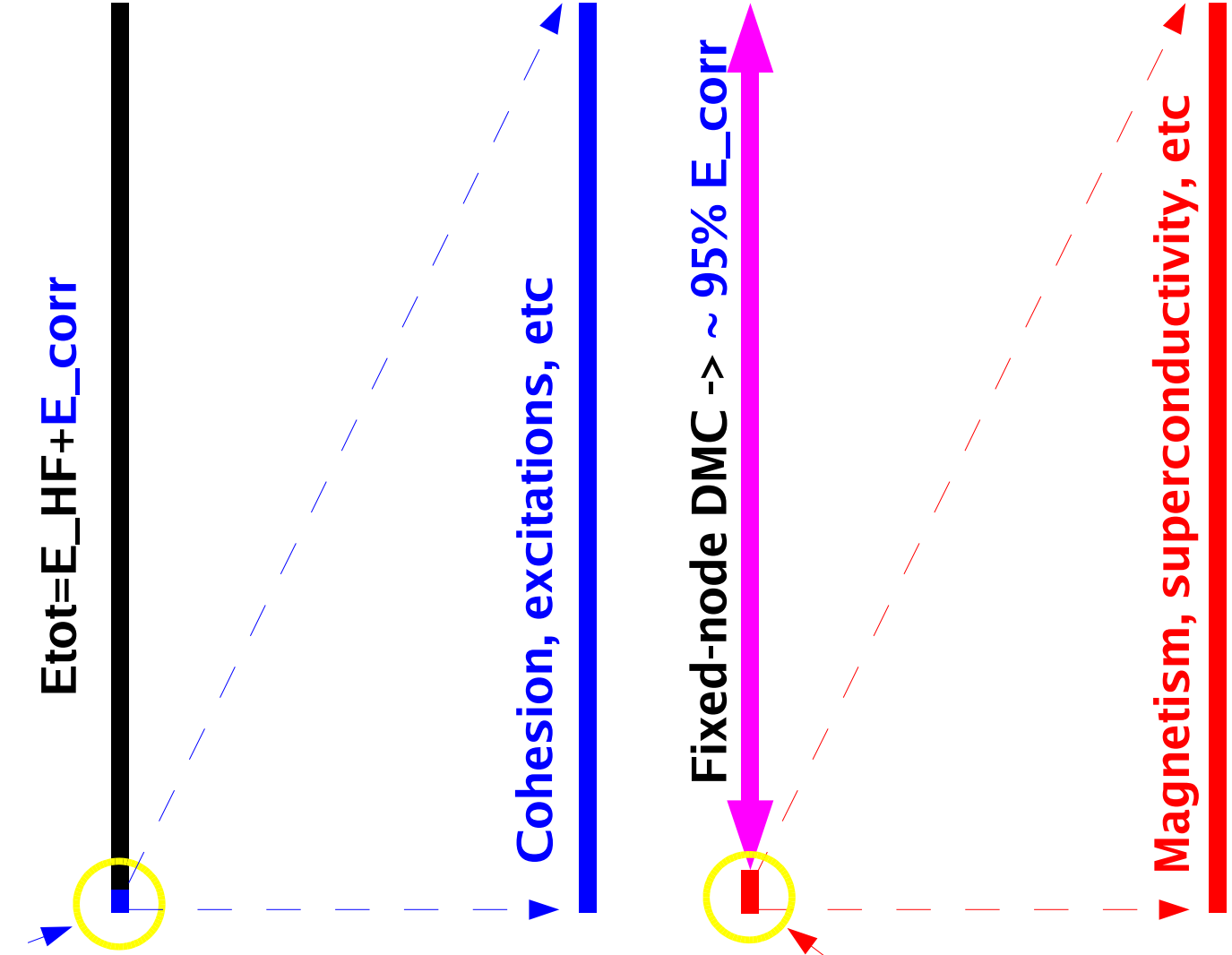
  - easy to enforce (check the sign of the determinant)

  - difficult to parametrize with arbitrary accuracy (more on that later)




Green surface: 3D cut of 59-dimensional fermion node hypersurface

# Beyond the fixed-node DMC: higher accuracy needed for magnetism, superconductivity, etc




E_corr = ~3% Etot

- FN error: ~5% Ecorr
- agree with exper: ~ 1-2%

Methods which work here ??? (beyond the fixed-node ...)



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# Fermion node: manifold of configurations for which the wave function vanishes
# Key approximation in quantum Monte Carlo

QMC solves the Schrodinger eq.

$$f(\boldsymbol{R}, t+\tau) = \int G^{*}(\boldsymbol{R}, \boldsymbol{R}', \tau) f(\boldsymbol{R}', t)\, d\boldsymbol{R}'$$

$$f(\boldsymbol{R}, t \to \infty) = \psi_{Trial}(\boldsymbol{R})\, \phi_{ground}(\boldsymbol{R})$$

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

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

Exact node -> exact energy in polynomial time

Find the exact node, in general: difficult multi-D many-body problem!



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# Antisymmetry/fermion sign problem and fixed-node approximation: strategies to deal with the nodes

”Sample-it-out”:
- nodal realease (Ceperley '80s)
- walker pairing algorithms (Kalos '90s)
- transform into another space (Hubbard -Stratonovitch) ...

“Capture the nodes/physics”:
- more sophisticated wavefunctions
- backflow
- pair orbitals, pfaffians, ...

“Understand the nodes”:
- general properties
- cases of exact nodes (special)
- way to describe, simplify
- new insights, something more fundamental (?)


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# Focus on fermion nodes: How much do we know ?

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

**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!
Also, we want to know:

- accurate nodal shapes ? how complicated are they ?
- nodes <-> types of wavefunctions ?
- nodes <-> physical effects ?


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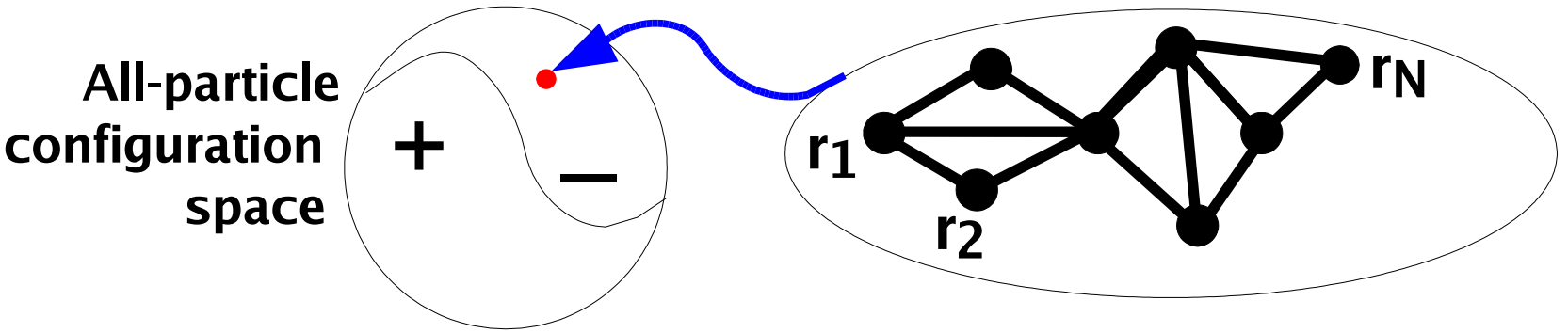
# Conjecture: for d >1 ground states have only two nodal cells, one "+" and one "-"

**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**




**(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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# Explicit 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)**

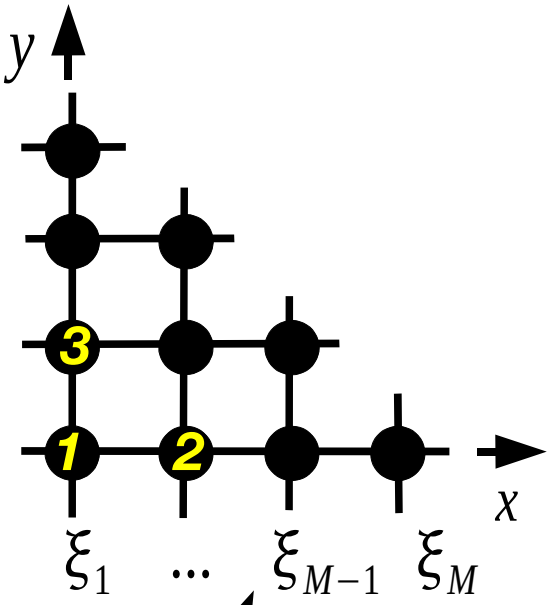
**Wavefunction factorizes by "lines of particles":**

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

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

particle coords

lines coords




**Factorizable along vertical, horizontal or diagonal lines, recursive.**



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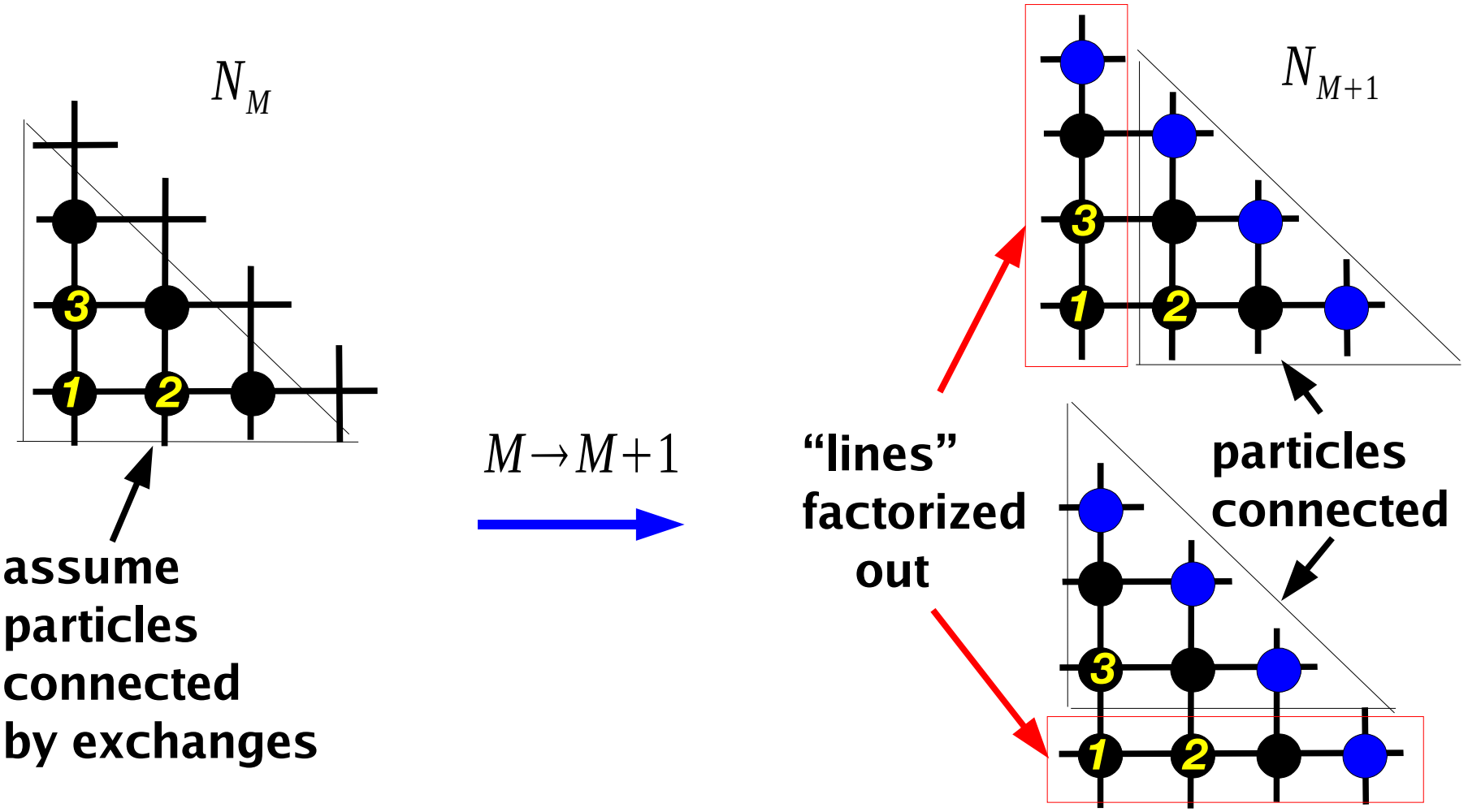
# Explicit proof of two nodal cells for spin-polarized harmonic fermions: Step 2 -> Induction




**Therefore all particles connected, any size. Q.E.D.**



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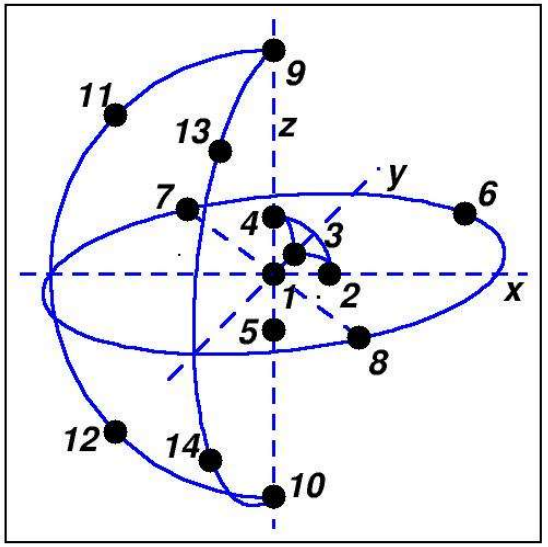
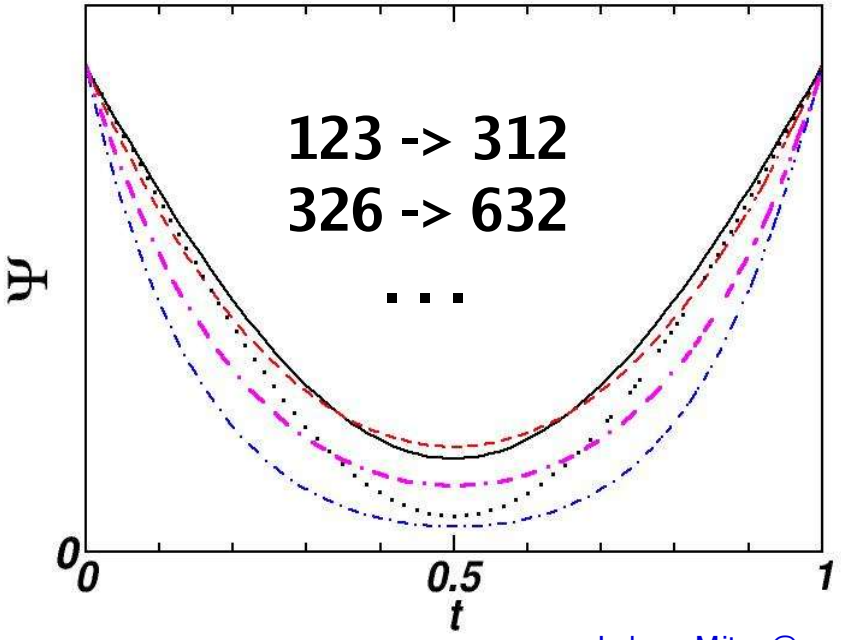
# What if matrix elements are not monomials ? Atomic states (different radial factors for subshells): Proof of two cells for nonint. and HF wavefunctions

- 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 $^{15}S(1s2s2p^33s3p^33d^5)$ and beyond (n=4 subshell)



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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 $^4$S(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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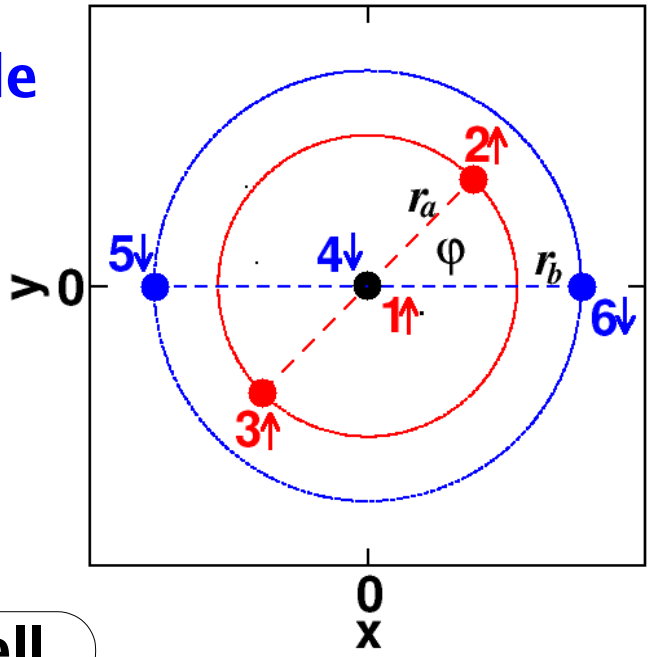
# Sketch the proof idea on a singlet of *interacting* harmonic fermions using the BCS wave function

**Example: 6 harmonic 2D fermions in the singlet ground state.**
**Rotation by $\pi$ 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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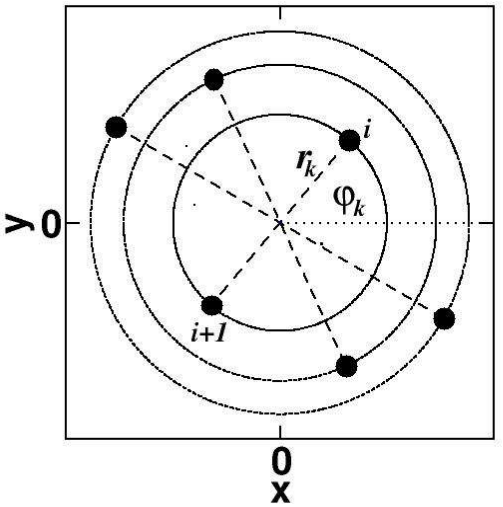
# Correlation in the BCS wavefunction is enough to fuse the noninteracting four cells into the minimal two

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




**HF pairing (sum over occupieds, linear dependence in Sl. dets)**

$$\psi_{HF}=det[\psi_n(i)]det[\psi_n(j)]=det[\sum_{n\le N}\psi_n(i)\psi_n(j)]=det[\phi_{HF}(i,j)]=0$$

**BCS pairing (sum over occupieds and virtuals, eliminate lin. dep.)**

$$\phi_{BCS}(i,j)=\phi_{HF}(i,j)+\alpha\sum_{n,m>N}c_{nm}\psi_n(i)\psi_m(j)$$

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



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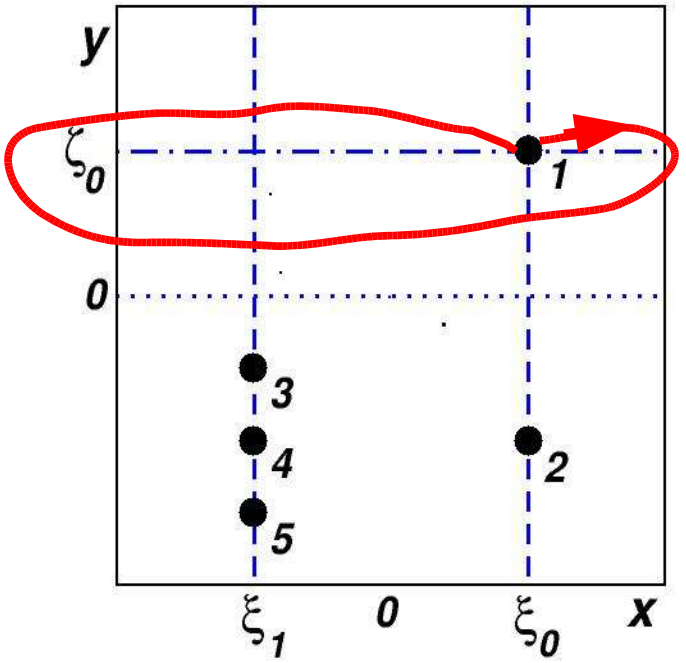
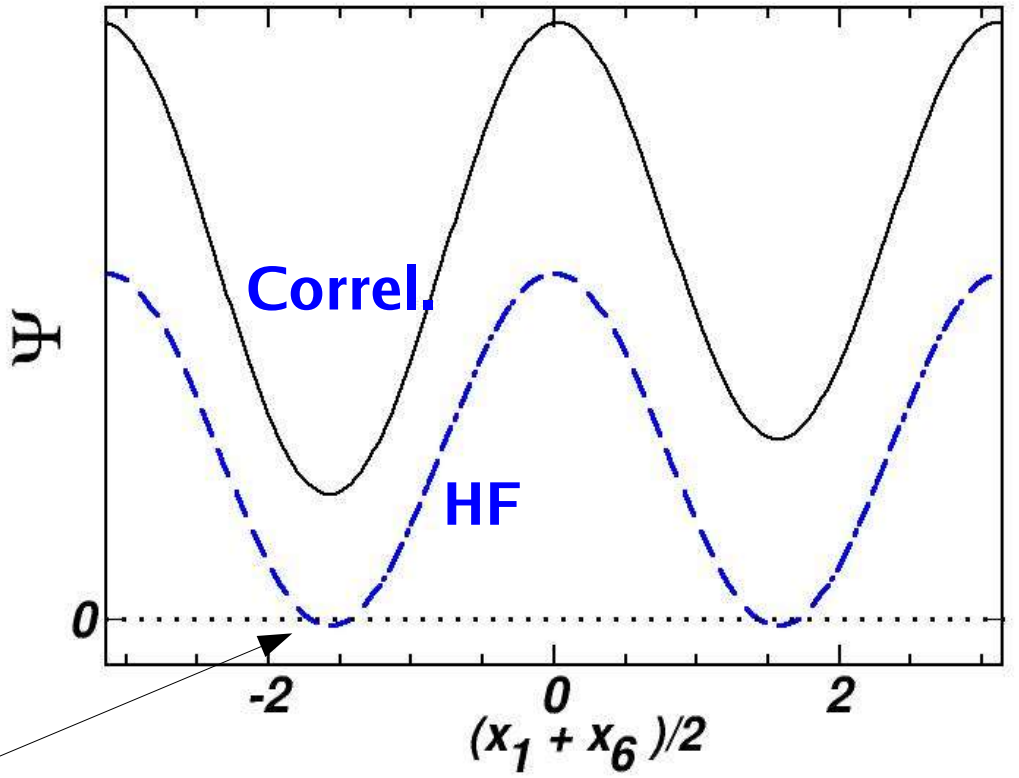
# Effect of correlation in homogeneous electron gas: singlet pair of e- winds around the box without crossing the node

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




Wavefunction along the winding path




HF crosses the node multiple times, BCS does not (supercond.)



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## 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 correlations -> pfaffians ...**


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# Let us introduce a 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**

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

**Signs:** + - +




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# Relations of pfaffians and determinants

- 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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# Why is pfaffian useful ?
# The simplest antisymmetric wavefunction constructed from pair spinorbital!

**One-particle orbitals + antisymmetry -> Slater determinant/HF**

$$\psi_{HF}=A[h_1(x_1)h_2(x_2)...] = det[h_k(x_i)] \qquad x_i=(r_i,\sigma_i) \qquad i,k=1,...,N$$

**Pair orbital + antisymmetry -> pfaffian !!!**

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

**Note: in the simplest case only one pair (spin)orbital**

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

**symmetric/singlet** **antisymmetric/triplet**



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# Pfaffian special cases: for example, Bardeen-Cooper-Schrieffer (BCS) wavefunction

**Antisymmetized product of singlet pair orbitals** $\phi^{\uparrow\downarrow}(i,j)$

$$\psi_{BCS}=A[\phi(i,j)]=det[\phi(i,j)]$$

**- supeconductivity, BEC; Casula, Sorella etal '04 for atoms**

**Problem with spin-polarized cases:** $N^{\downarrow}=n$ **while** $N^{\uparrow}=n+m$

$$\psi_{BCS}=A[\phi(1,n)...\phi(n,2n)\times h_1(2n+1)...h_m(2n+m)]$$

**where** $h_k(i)$ **are one-particle orbitals**

**- fully spin-polarized state trivially recovers Hartree-Fock, pair correlations gone :-(**

$$\psi_{BCS}=A[h_k(i)]=det[h_k(i)]=\psi_{HF}$$



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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, 2006)


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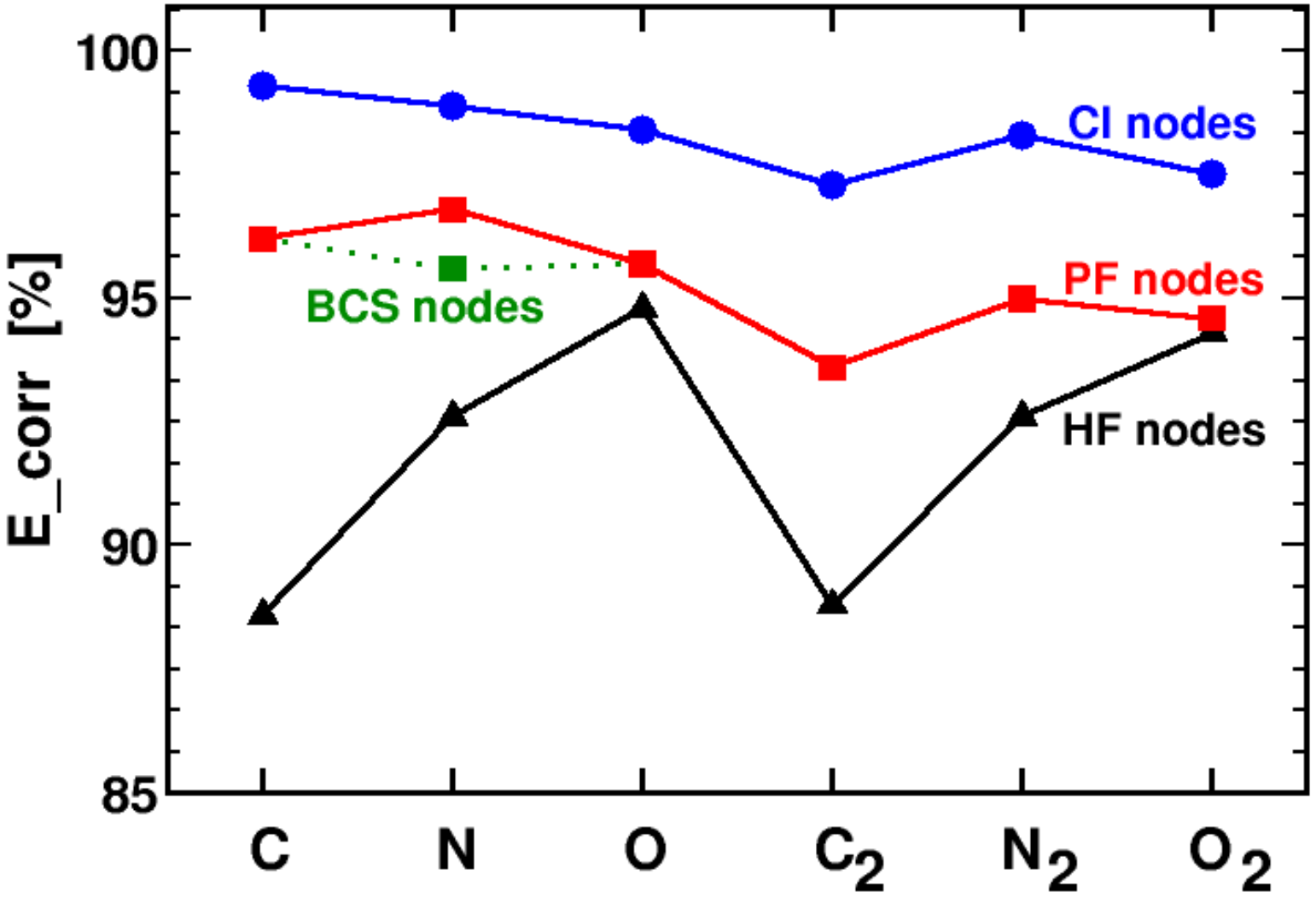
# DMC correlation energies of atoms, dimers
# Pfaffians: more accurate and systematic than HF while scalable (unlike CI)



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# Expansions in multiple 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 (talk by M. Bajdich, V21.11 )

**Pfaffians describe nodes more efficiently**



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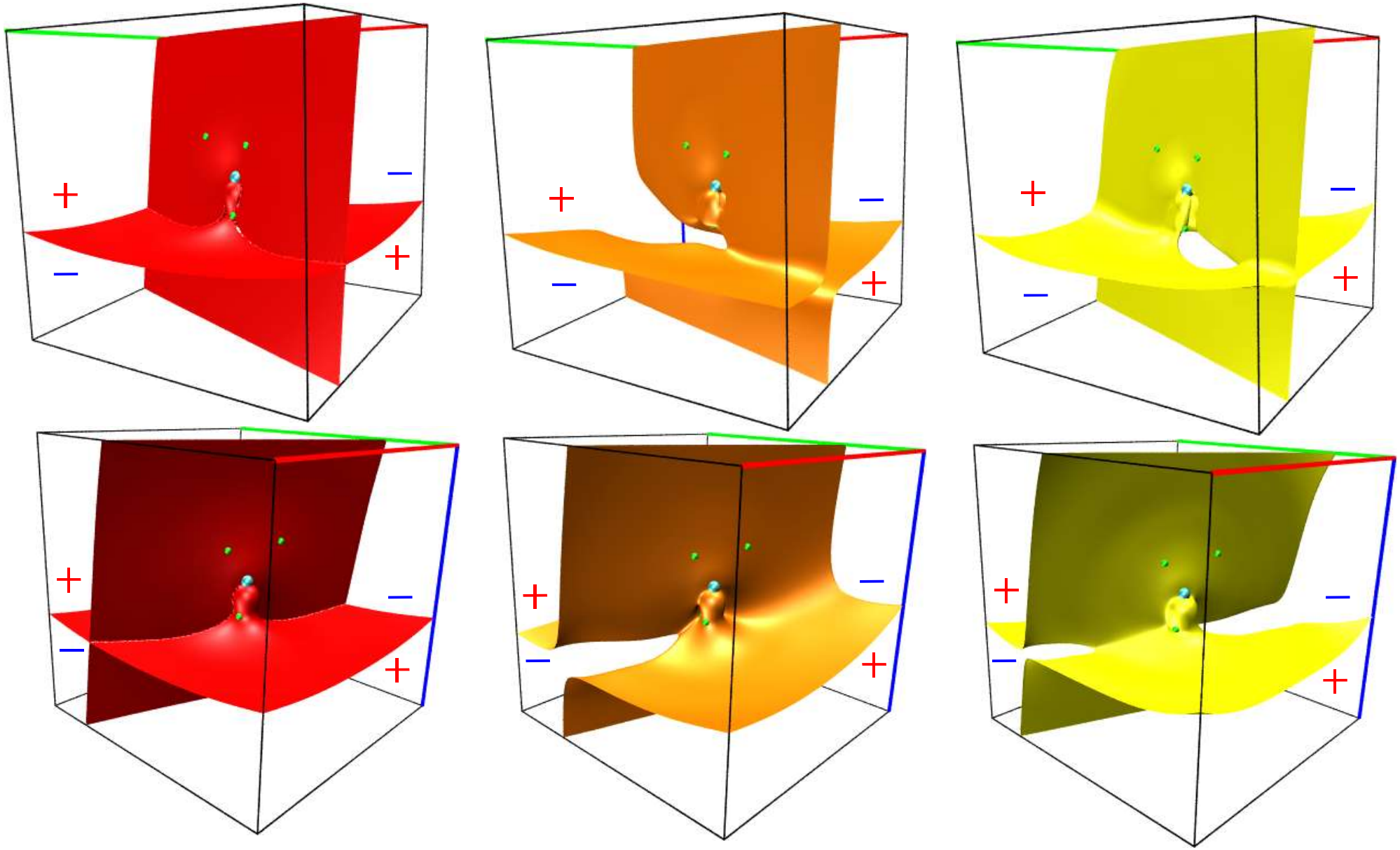
# Nodes of different WFs (%E_corr in DMC): oxygen atom wavefunction scanned by 2e- singlet (projection into 3D -> node subset)

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



# Summary

- fixed-node approximation: in most cases the most accurate and practical electronic structure method around; to reach beyond one needs to understand the properties of nodes

- explicit proof of two nodal cells for d>1 and for any size: fundamental property of fermionic ground states

- antisymmetrized pair spinorbital wavefunction: pfaffian

- nodal shapes subtle: ~ 5 % of correlation energy;
  pfaffian: compact, has the right topology

- fermion nodes: another example of importance of quantum geometry and topology for electronic structure



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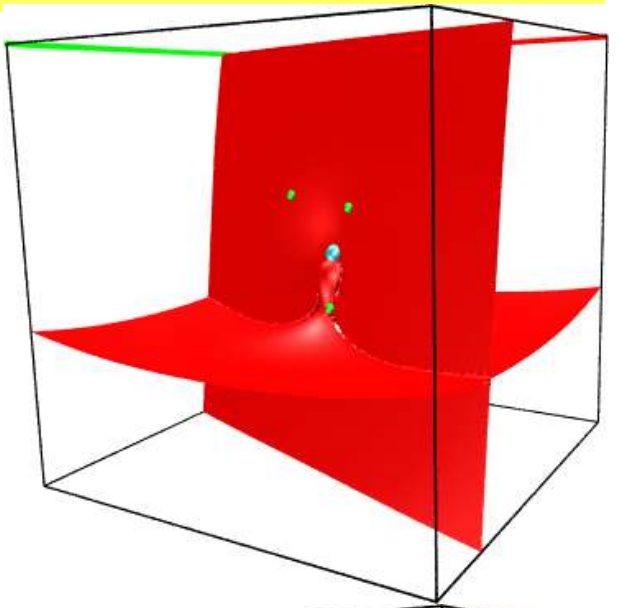
# Observations from comparison of HF and "exact" (CI) nodes

- 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