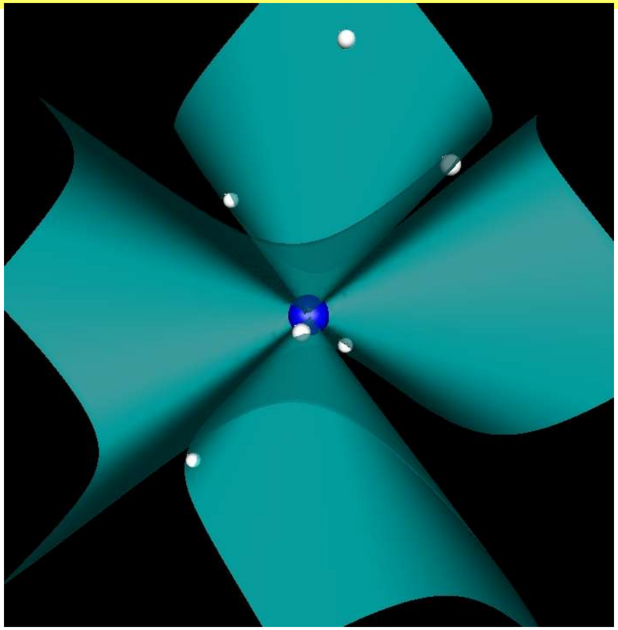
Structure of fermion nodes and pfaffian pairing wavefunctions



Michal Bajdich, Lucas Wagner, G. Drobny
Kevin Schmidt (ASU), Lubos Mitas
North Carolina State University

Towler Institute,, Tuscany, Italy, July 2006

NC STATE UNIVERSITY

Lubos_Mitas@ncsu.edu

Solving many-particle Schrodinger equation by fixed-node diffusion Monte Carlo (FNDMC)

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

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

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

$$\lim_{\tau\to\infty} f(\mathbf{R},\tau)\ \propto\ \psi_T(\mathbf{R})\phi_{ground}(\mathbf{R})$$

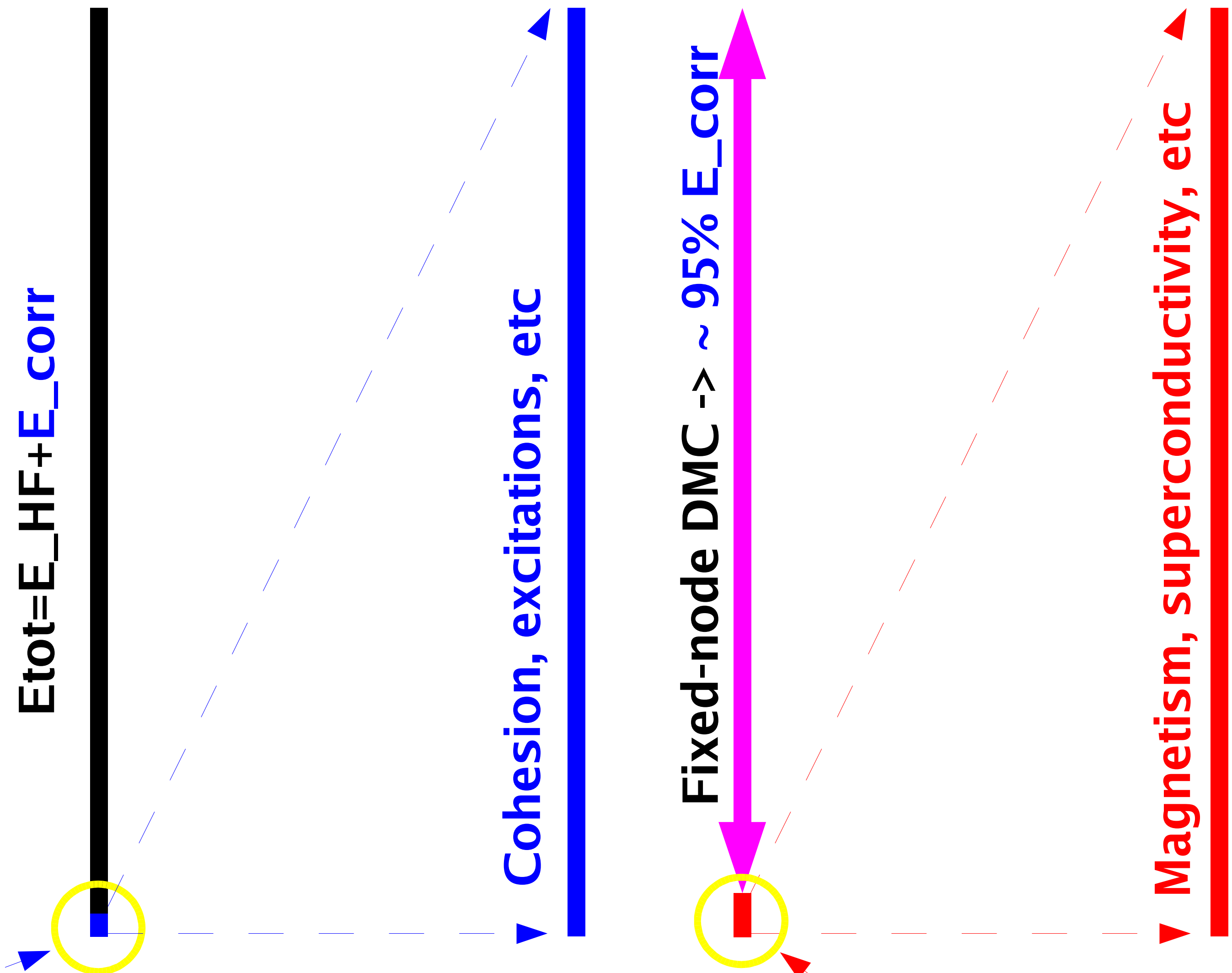
Fermion node: defined as $\phi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=0$

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

Antisymmetry (nonlocal) replaced by a boundary (local)

Lubos_Mitas@ncsu.edu

Experience with the fixed-node DMC: applicable to tens/hundreds of valence electrons – but ...



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

E_corr = ~3% Etot

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

Lubos_Mitas@ncsu.edu

Fermion node: manifold of configurations for which the wave function vanishes
The (only) approximation in quantum Monte Carlo

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

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

The Schrodinger eq.

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

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

Exact node -> exact energy in polynomial time

Exact nodes:
- in 1D, particle concidence points
- in 3D known for a few 2e and 3e states

In general, high-dimensional problem influenced by many-body effects and interactions

NC STATE UNIVERSITY

Lubos_Mitas@ncsu.edu

Antisymmetry/fermion sign problem: various ideas how 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 physics (the nodes will follow)":
- more elaborate wavefunctions
- backflow
- pair orbitals, pfaffians, ...

"Understand the nodes":
- general properties
- new insights, more fundamental issue (?)

Key questions:
- correct topology, ie, number of nodal cells
- correct shape

Lubos_Mitas@ncsu.edu

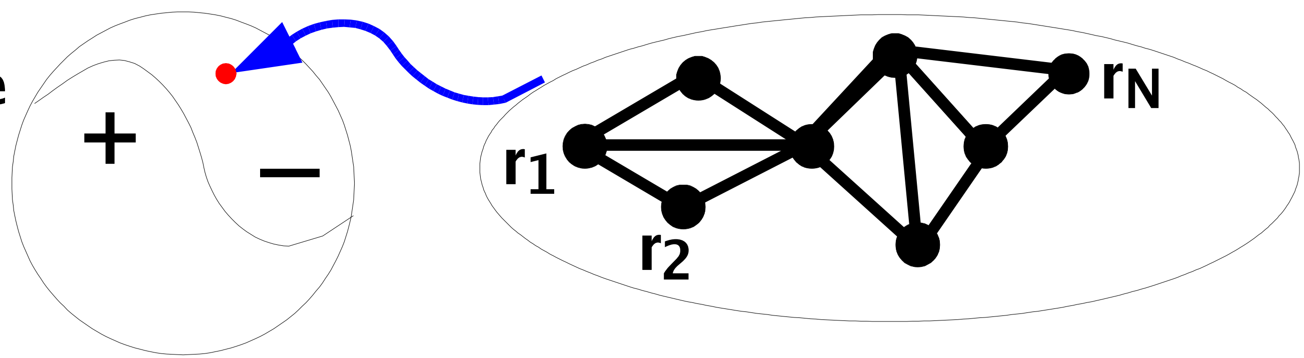
Topology of a few-electron exact nodes, numerical studies -> Conjecture: for d >1 ground states have only two nodal cells, one "+" and one "-"

So far unproven even for noninteracting systems !

Tool to demonstrate some $\psi(R)$ has only two cells (Ceperley '92, numerical proofs up to 200 noninteracting fermions):

Find a point such that triple exchanges connect all the particles into a single cluster: then there are only two nodal cells

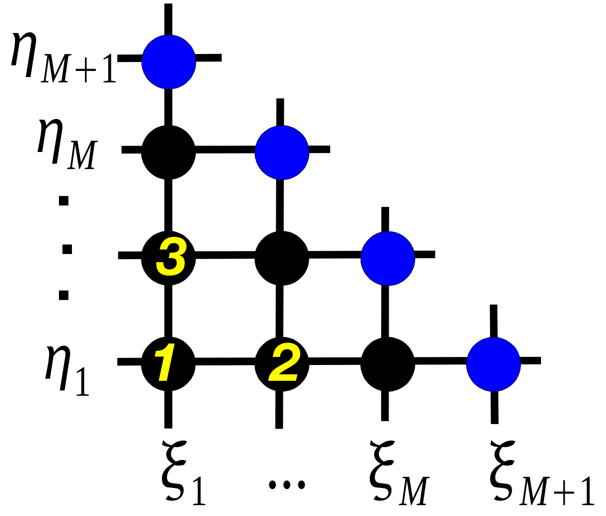
All-particle configuration space



Lubos_Mitas@ncsu.edu

Explicit proof of two nodal cells for spin-polarized noninteracting system for any size (Idea illustrated for 2D harmonic fermions)

Place fermions in a Pascal-like triangle



M **lines ->** $N_M = (M+1)(M+2)/2$ **particles**

The wavefunction:

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

Evaluated explicitly by recursion:
factorizing out "lines of particles"

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

By induction: if N_M **particles are connected, then also** N_{M+1} **. QED.**

Lubos_Mitas@ncsu.edu

The key points of the proof:
a) Slater matrix elements are multivariate monomials
b) configuration enables to factorize the determinant

The factorization enables to explicitly show that the particles are connected

Any model which transforms to homogeneous polynomials!

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

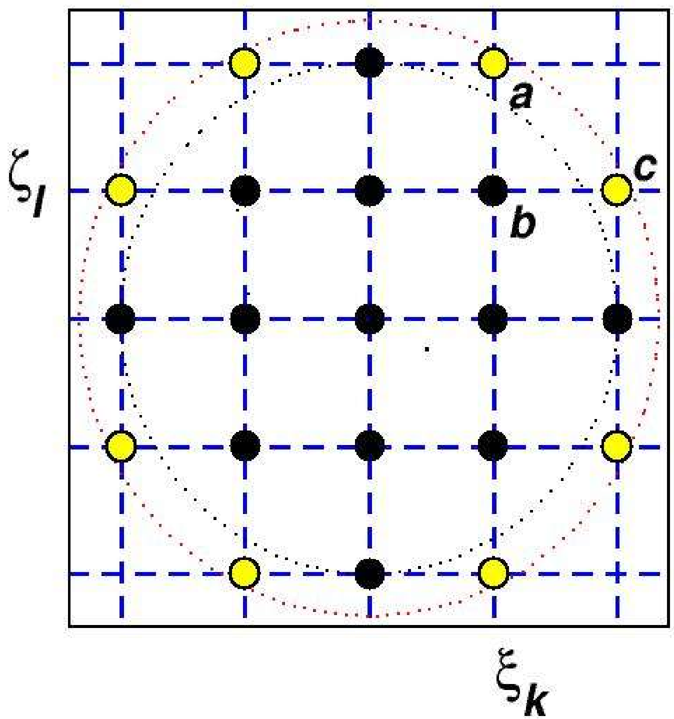
- **fermions on a spherical surface** $$Y_{lm}(\theta,\phi)=(\cos\theta)^n(\sin\theta\, e^{i\phi})^m$$

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

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

Lubos_Mitas@ncsu.edu

2D periodic fermions: similar factorization
3D or higher: the same idea



- particles on the line $x = \xi_k$

$$\psi_{1D}(\ldots, i_l^{(k)}, \ldots, i_m^{(k)}, \ldots) = \prod_{l<m} \sin(\zeta_{lm}/2)$$

- complete wavefunction

$$\psi(1,\ldots,N) = \prod_{k=0}^{M} \left[\psi_{1D}(I_k) \prod_{j<k} \sin^{n_j}(\xi_{jk}/2) \right]$$

- induction step: particles a,b,c connected

Factorization works for any d>1 (!!!): lines, planes, hyperplanes

Lubos_Mitas@ncsu.edu

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.

Then the wavefunction has only two nodal cells.

With some effort can be generalized to some open shells.

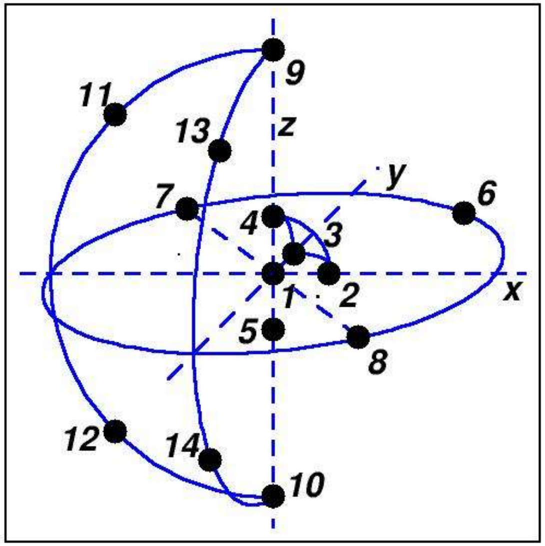
Lubos_Mitas@ncsu.edu

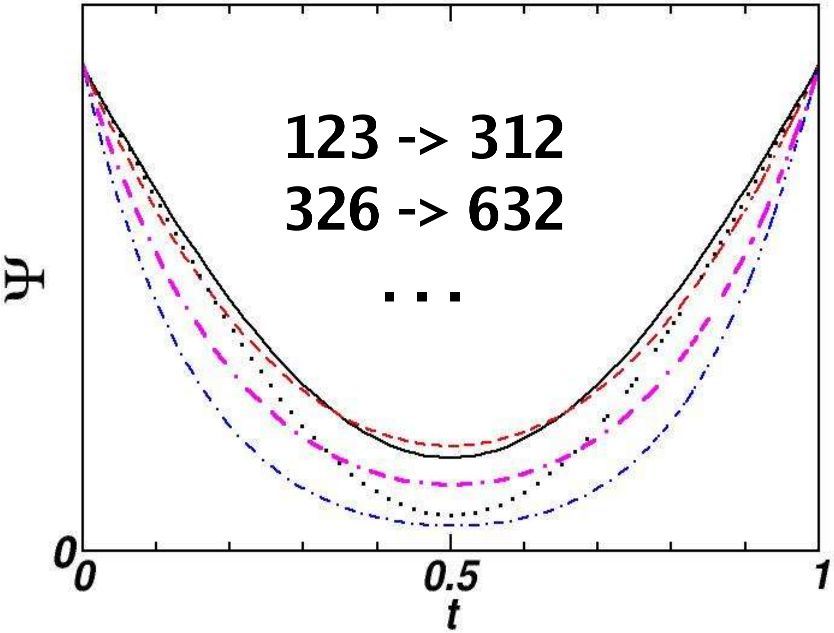
What if matrix elements are not monomials ? Atomic states (different radial orbitals for subshells): Proof of two cells for nonint. and HF wavefunctions

- position subshells of electrons onto spherical surfaces: explicit factorization

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

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





Lubos_Mitas@ncsu.edu

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!

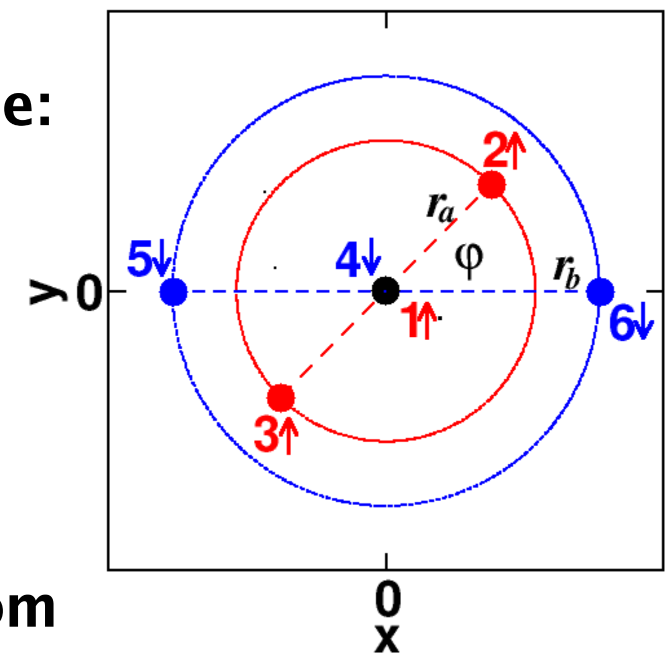
First time showed on Be atom, Bressanini etal '03

Lubos_Mitas@ncsu.edu

Illustrate the general proof idea on a singlet of *interacting* harmonic fermions with BCS as variational wave function

Consider 6 harmonic 2D fermions in the singlet ground state. Rotation by π exchanges two particles in each spin channel, they lie on HF node:

$$\psi_{HF}=0$$



Describe the correlation using the BCS wavefunction:

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

pairing function includes the virtuals from the first unoccupied subshell

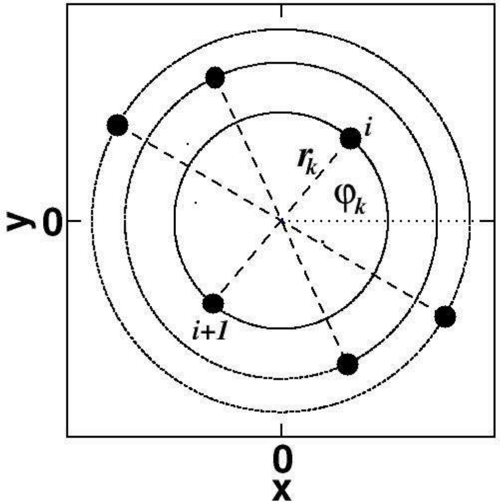
$$\psi_{BCS}=det\{\phi(i,j)\}=\alpha\, r_a r_b \cos(\phi)[2(r_a r_b \cos(\phi))^2-r_a^2-r_b^2]\neq 0$$

Nonvanishing for arbitrarily weak interaction!

Lubos_Mitas@ncsu.edu

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.)

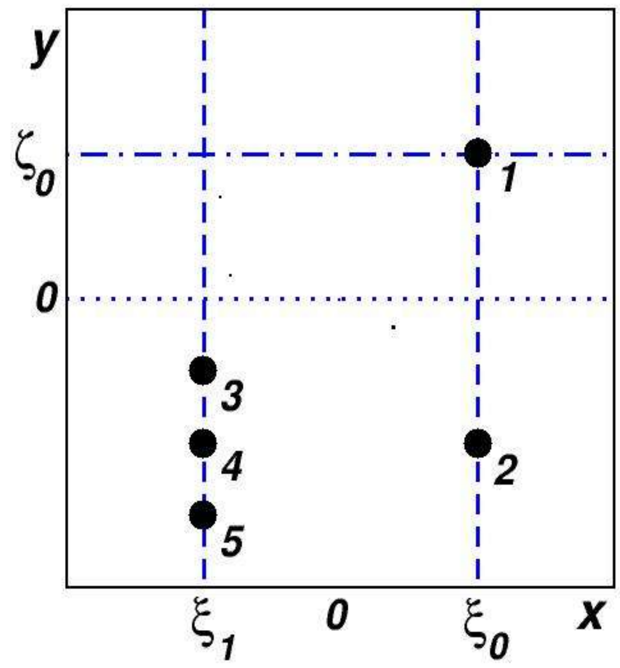
$$\phi(i,j) = \phi_{HF}(i,j) + \phi_{corr}(i,j)$$

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

Lubos_Mitas@ncsu.edu

Homogeneous electron gas: the spin-up and -down subspaces are interconnected as well; other interacting models

$$r_1\uparrow = r_6\downarrow,\ \ r_2\uparrow = r_7\downarrow, \ldots, r_5\uparrow = r_{10}\downarrow$$



Translation by L/2 in y direction exchanges

$$r_1\uparrow \longleftrightarrow r_2\uparrow \qquad r_5\downarrow \longleftrightarrow r_6\downarrow$$

Translational invariance implies that the wavefunction is constant

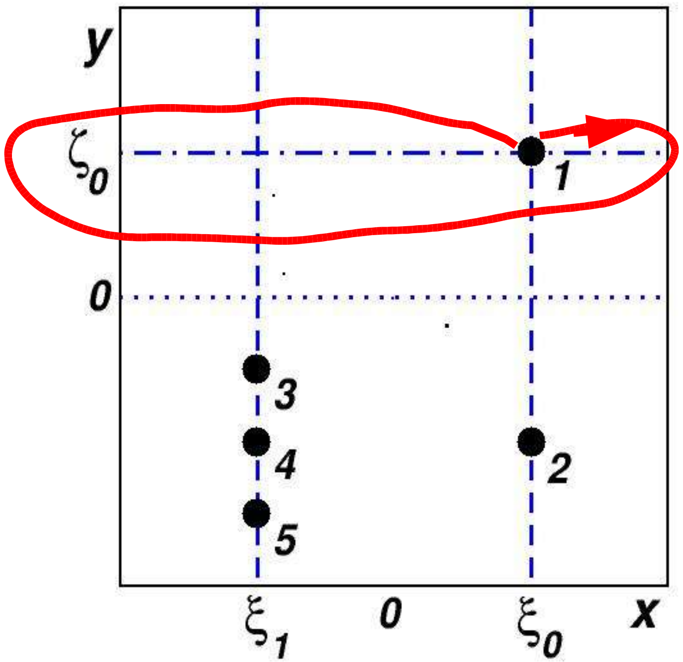
$$\boxed{\begin{gathered}\psi_{HF} = 0\\ \psi_{BCS} \neq 0\end{gathered}}$$

Other interacting models: similar construction

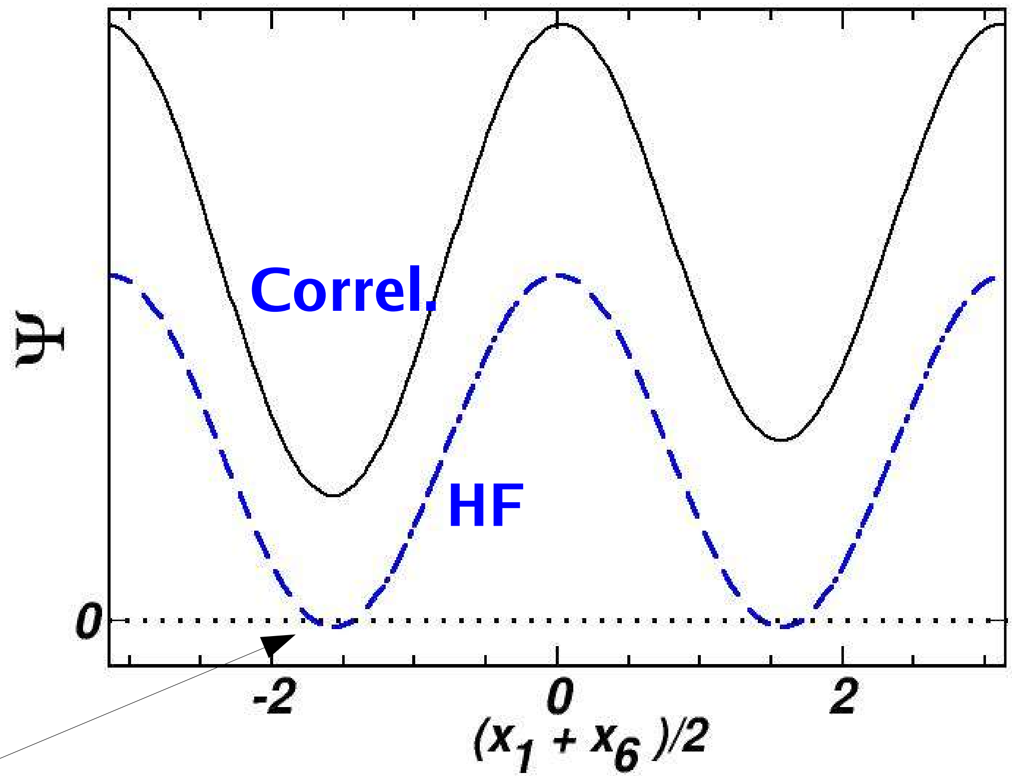
Lubos_Mitas@ncsu.edu

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.)

Lubos_Mitas@ncsu.edu

The same applies to 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**

At high (classical) temperatures

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

It is not too difficult to prove that at classical temperatures R and R' subspaces have only two nodal cells: it is stunning since there is a summation over the whole spectrum!

PRL, 96, 240402 /cond-mat/0601485 (the basic ideas)
cond-mat/0605550 (all the models, density matrix)

Lubos_Mitas@ncsu.edu

Two nodal cells: generic property, possible counterexamples
Also, how about the exact shape of the node ?

Topology of the nodes closed-shell ground states is surprisingly simple:

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

Possible exceptions:

- nonlocal interactions, strong interactions
- impose more symmetries or boundaries
- large degeneracies

But the exact shape very difficult to get

- **mostly through wavefunction improvement methods**

Lubos_Mitas@ncsu.edu

Beyond sing particle ornitals: singlet pair orbital Bardeen-Cooper-Schrieffer (BCS) wavefunction

- used to describe supeconductivity or BEC, Sorella et al for electronic structure, '04

  antisymmetized product of singlet pair orbitals $\phi(i,j)$

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

- spin-polarized case: $N^{\downarrow} = n$ while $N^{\uparrow} = n + o$

$$\psi_{BCS} = A[\phi(1,n)\ldots\phi(n,2n) \times h_1(2n+1)\ldots h_o(2n+o)]$$

where $h_k(i)$ are one-particle orbitals (usually HF)

- fully spin-polarized state trivially recovers Hartree-Fock

$$\psi_{BCS} = A[h_i(j)] = det[h_i(j)] = \psi_{HF}$$

Lubos_Mitas@ncsu.edu

Beyond Slater determinants: pfaffian pairing wavefunctions contain both singlet and triplet pairs -> all spin states treated consistently

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

- 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 with respect to energy

Lubos_Mitas@ncsu.edu

Algebra of Determinants vs Pfaffians

Determinant

- signed sum of all antisymmetric permutations of rows/collums
- square matrix N×N
- for N=2

$$det\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = a_{11}a_{22} - a_{21}a_{12}$$

- expansion by minors
- for any square matrix B

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

Pfaffian

- signed sum of all antisymmetric perm. of pairs of elements
- skew-symmetric matrix (N=2n)

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

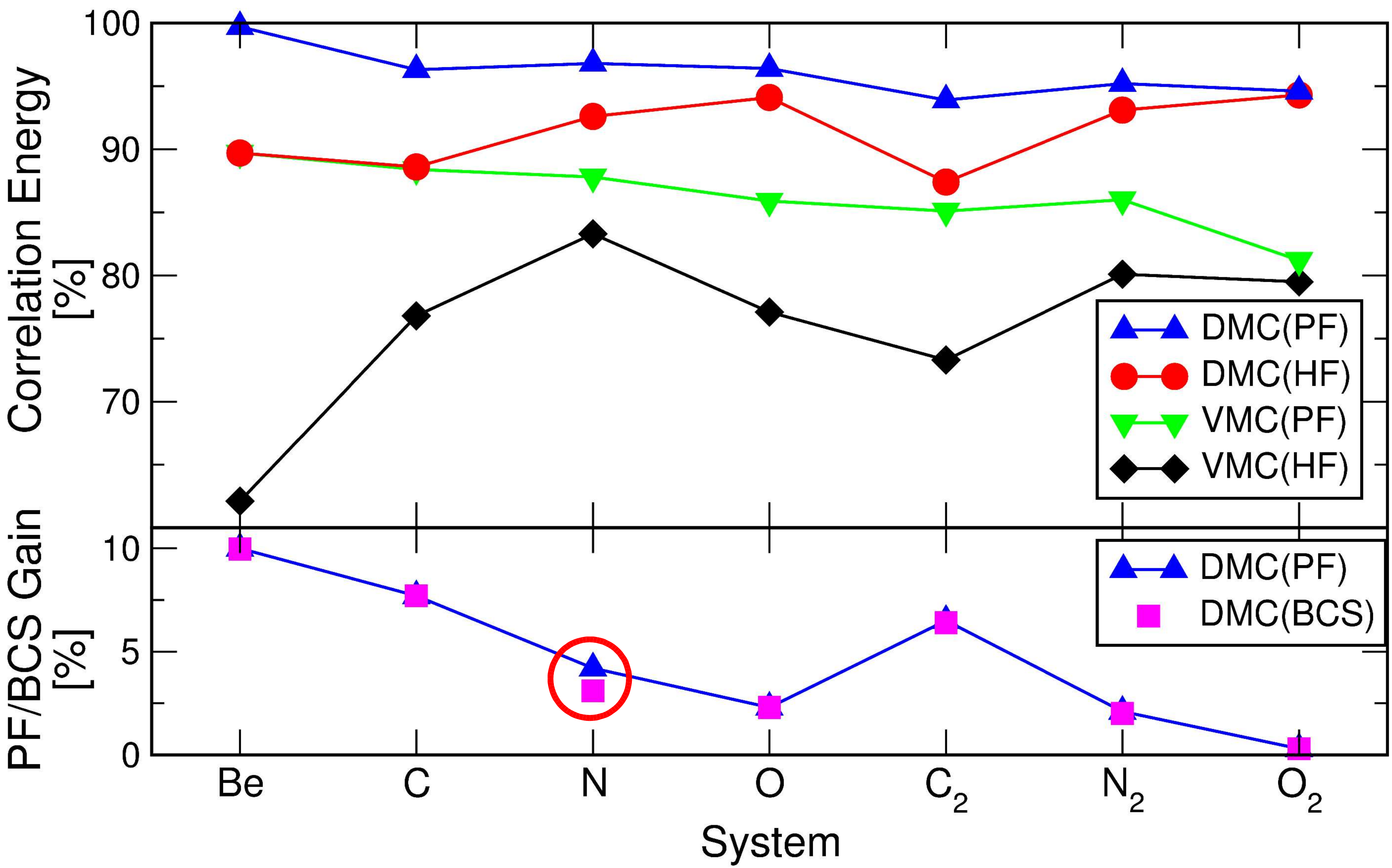
$$= [a_{12}a_{34} - a_{13}a_{24} + a_{14}a_{23}]$$

- expansion by pfaffian minors
- for any skew-symetric matrix *A*

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

Lubos_Mitas@ncsu.edu

Correlation energies of first row atoms and dimers
Correlation from singlet vs triplet pairing



Multi-pfaffian wavefunctions for first row atoms: FNDMC ~98-99 % of correlation with a few pfaffians!

Table of % of correlation energies recovered for CI vs MPF w.f.
- n denotes the number of dets/pfs in the expansion

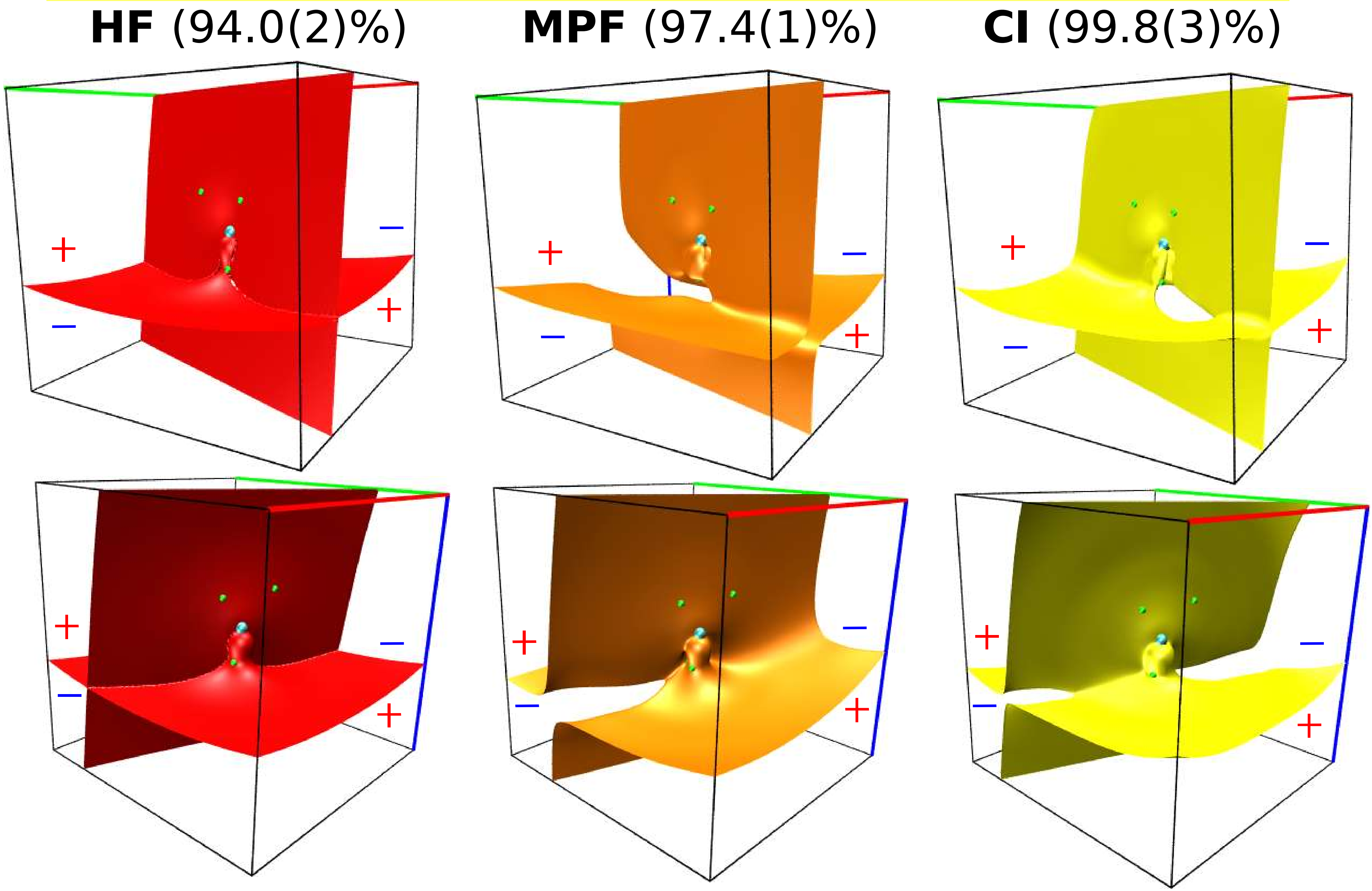
WF	n	C	n	N	n	O
VMC(MPF)	3	92.3(1)	5	90.6(1)	11	92.6(3)
VMC(CI)	98	89.7(4)	85	91.9(2)	136	89.7(4)
DMC(MPF)	3	98.9(2)	5	98.4(1)	11	97.2(1)
DMC(CI)	98	99.3(3)	85	98.9(2)	136	98.4(2)

- number of pfaffians n
- **- subject to symmetry constraints**
- **- in principle all distinct pairs could be included**

M. Bajdich et al, PRL 96, 130201 (2006)

Lubos_Mitas@ncsu.edu

3D scan of the oxygen atom node by 2e- singlet: Topologies of different wfs (fixed-node DMC Ecorr)



Observations from comparison of HF and "exact" nodes

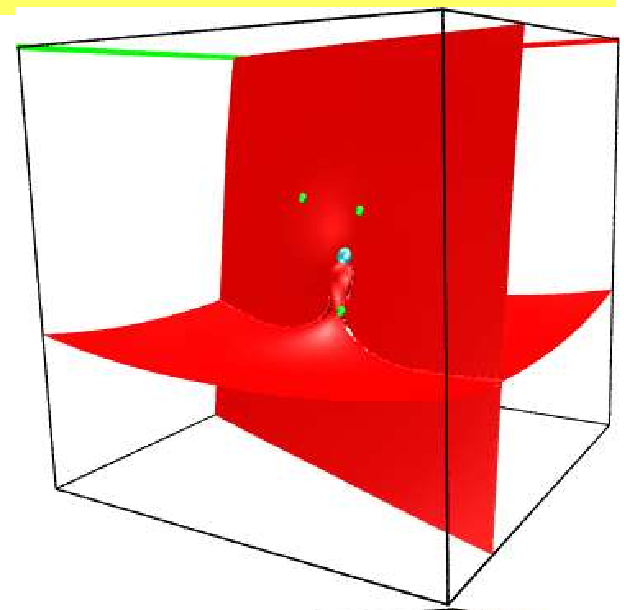
- the two nodal cells for Coulomb interactions as well

- the nodal openings have rather fine structure

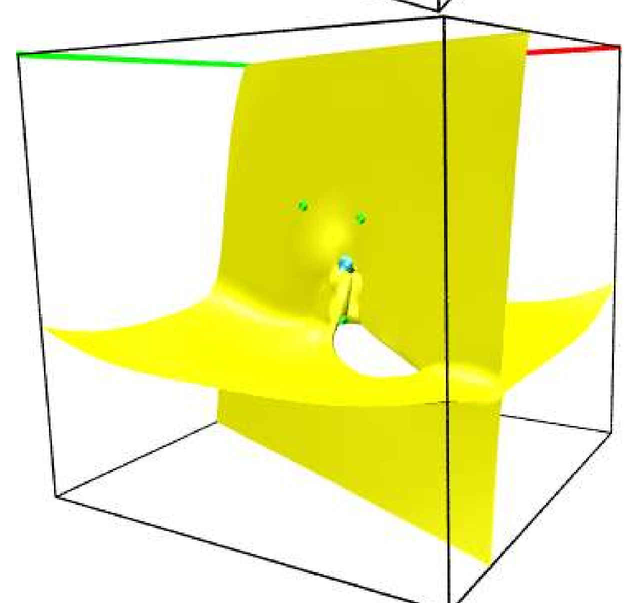
- openings are important -> ~ 5% of the correlation energy

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

HF



CI



Summary

- **explicit proof** that, in general, fermionic ground states and density matrices have **two nodal cells for d>1** and for any size - **fundamental property of fermionic systems**

- **nodal openings** in correlated wave functions and **exact nodal shape important**: **5 % of correlation energy**, necessary condition for superconductivity; pfaffians pairing wfs very efficient

- **counterexamples:** multiple cells can be genuine, eg, from singular or nonlocal interactions, boundary conditions, possibly by large degeneracies, etc

- fermion nodes: another example of importance of **quantum geometry (field theory) and topology** for electronic structure

Lubos_Mitas@ncsu.edu