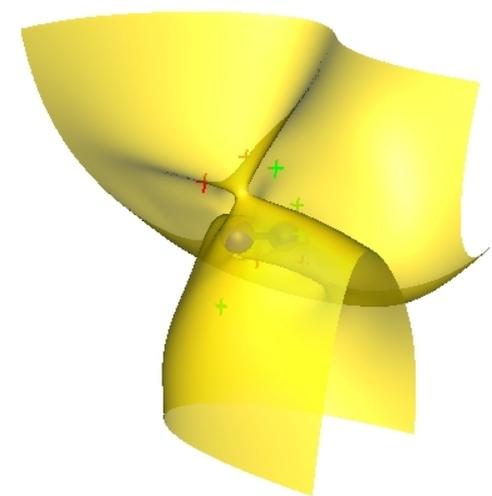
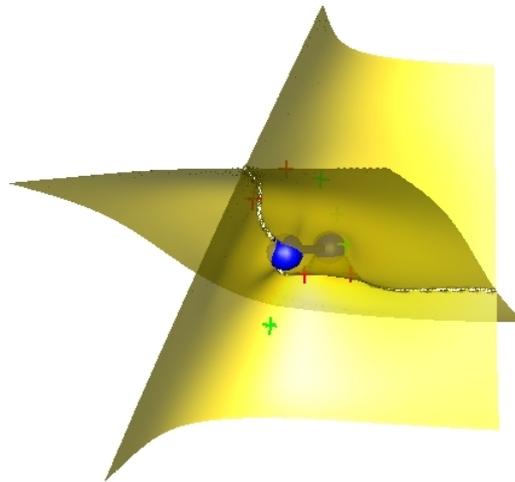
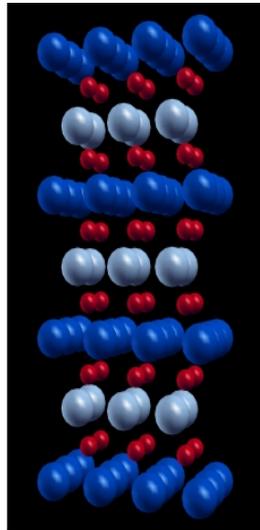
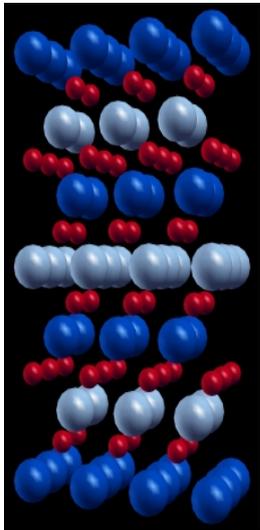


Electronic structure quantum Monte Carlo: pfaffians and many-body nodes of ground and excited states



Jindrich Kolorenc (von Humboldt Fellow), U. Hamburg

Michal Bajdich, ORNL

Lubos Mitas, **North Carolina State University and KITP**

KITP, Santa Barbara, October '09

Diffusion Monte Carlo for stationary Schrodinger equation in continuous space

QMC: $\phi_0 = \lim_{\tau \rightarrow \infty} \exp(-\tau H) \psi_{Trial}$



Recast as integral Sch. eq. :
with importance sampling

$$f(\mathbf{R}, t + \tau) = \int G(\mathbf{R}, \mathbf{R}', \tau) f(\mathbf{R}', t) d\mathbf{R}'$$
$$f(\mathbf{R}, t \rightarrow \infty) = \psi_{Trial}(\mathbf{R}) \phi_0(\mathbf{R})$$

Solved by simulation of an equivalent, diffusion-like stochastic process
- wavefunction is sampled by **points in 3N-dim space** (“random walkers”)

wavefunction \leftrightarrow spatial density of random walkers

“basis” is a set of walkers/delta-functions, ie, eigenstates of R

- walkers evolve according to the propagator G (transition probability)
- limit $\tau \rightarrow \infty$ by iteration \rightarrow diffusion Monte Carlo (DMC) method

H : electrons+ions, or (almost) any other system/interactions

The fixed-node approximation: the key (and basically the only) approximation

Exact mapping onto a statistical solution but fermion sign problem!

Adopt the fixed-node (FN) approximation: $f(\mathbf{R}, t) = \phi_0(\mathbf{R}) \psi_{Trial}(\mathbf{R}) > 0$

Continuous space: boundary(local) replaces antisymmetry(nonlocal)

Fermion node: $\phi(\mathbf{R}) = \phi(r_1, r_2, \dots, r_N) = 0$ **(3N-1)-dim. hypersurface**

Exact node \rightarrow exact solution in polynomial time

The exact node, in general: a difficult (intractable?) multi-D problem

Anyway, how well does the FNDMC method work? \rightarrow basics

QMC calculations: basic steps

- Hamiltonian:**
- e-e interactions
 - valence e- only, using pseudopots/ECPs
 - size: up to a few hundreds valence e-

Explicitly correlated **trial wavefunction** of Slater-Jastrow type:

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

(more sophisticated: BCS, pfaffians, backflow,..., later)

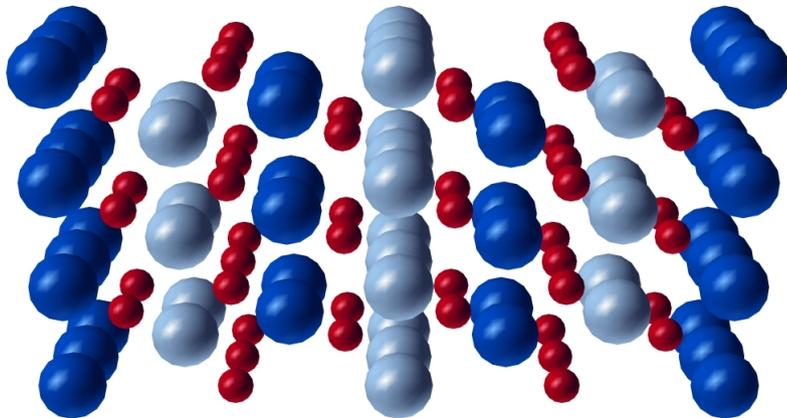
- Orbitals:**
- from HF, DFT, hybrid DFT, possibly CI, etc

- Solids:**
- supercells
 - finite size corrections

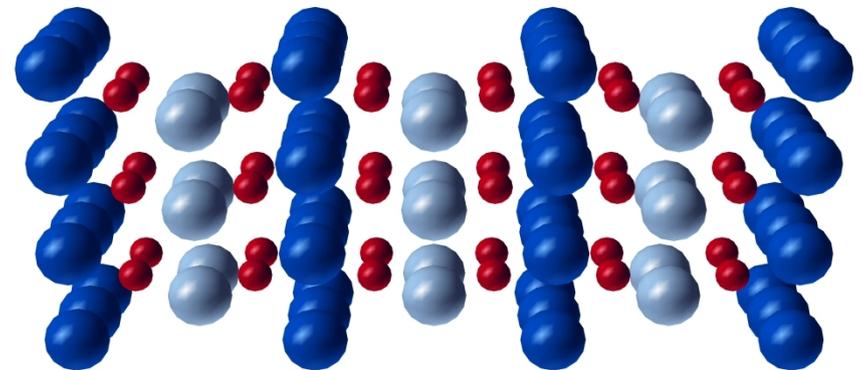
FeO solid at high pressures

- **large e-e correlations, difficult:** competition of Coulomb, exchange, correlation and crystal-field effects; important **high-pressure physics** (Earth interior, for example)
- mainstream Density Functional Theories (DFT) predict: **wrong** equilibrium structure; and for the correct structure predict a **metal instead of a large-gap insulator**

B1/AFII (equil.)

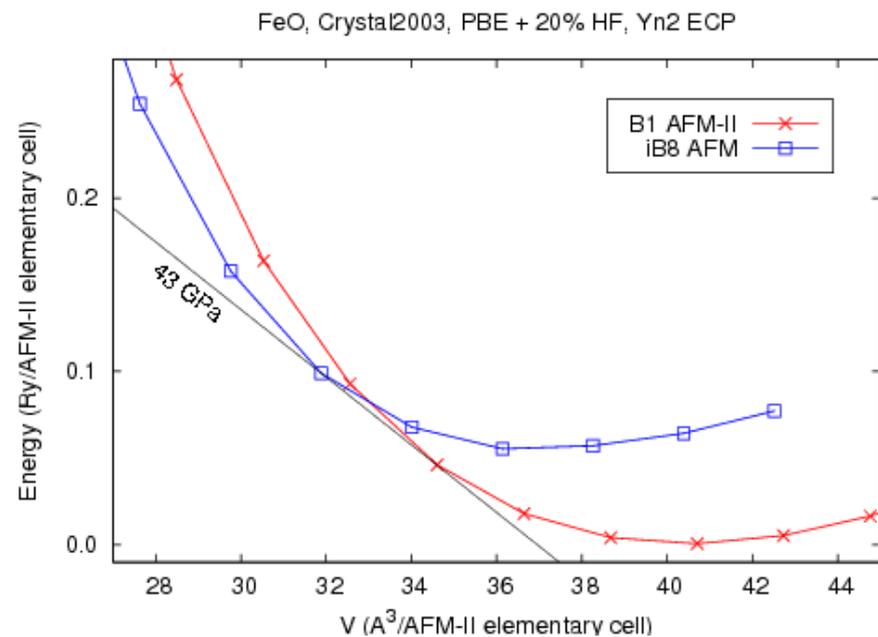
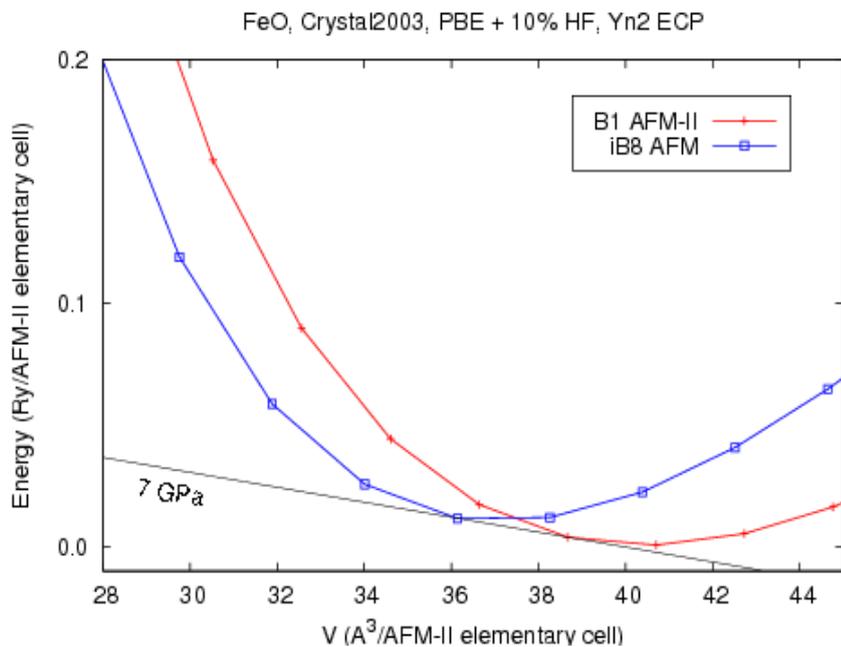


iB8/AFII



FeO solid at high pressures DFT with HF mixing

In order to reconcile theory with experiment one needs Hubbard U or, alternatively, mixing of an exact exchange into the effective Hamiltonian: non-variational, certain arbitrariness

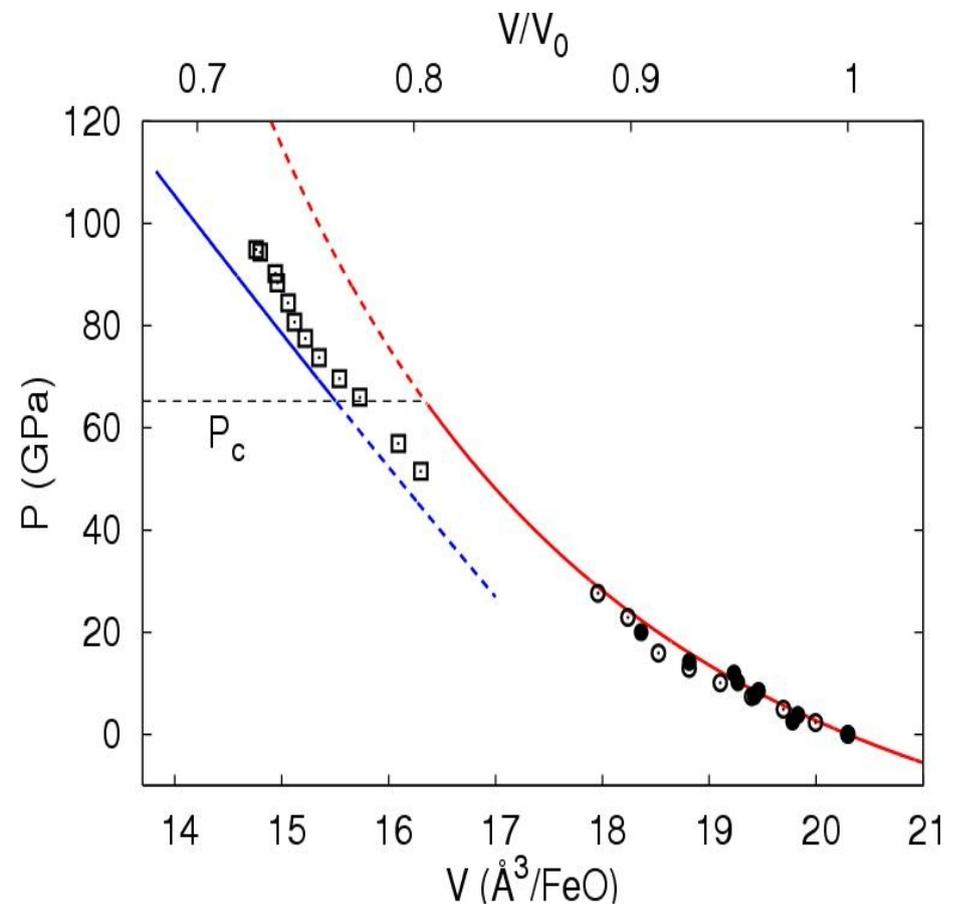
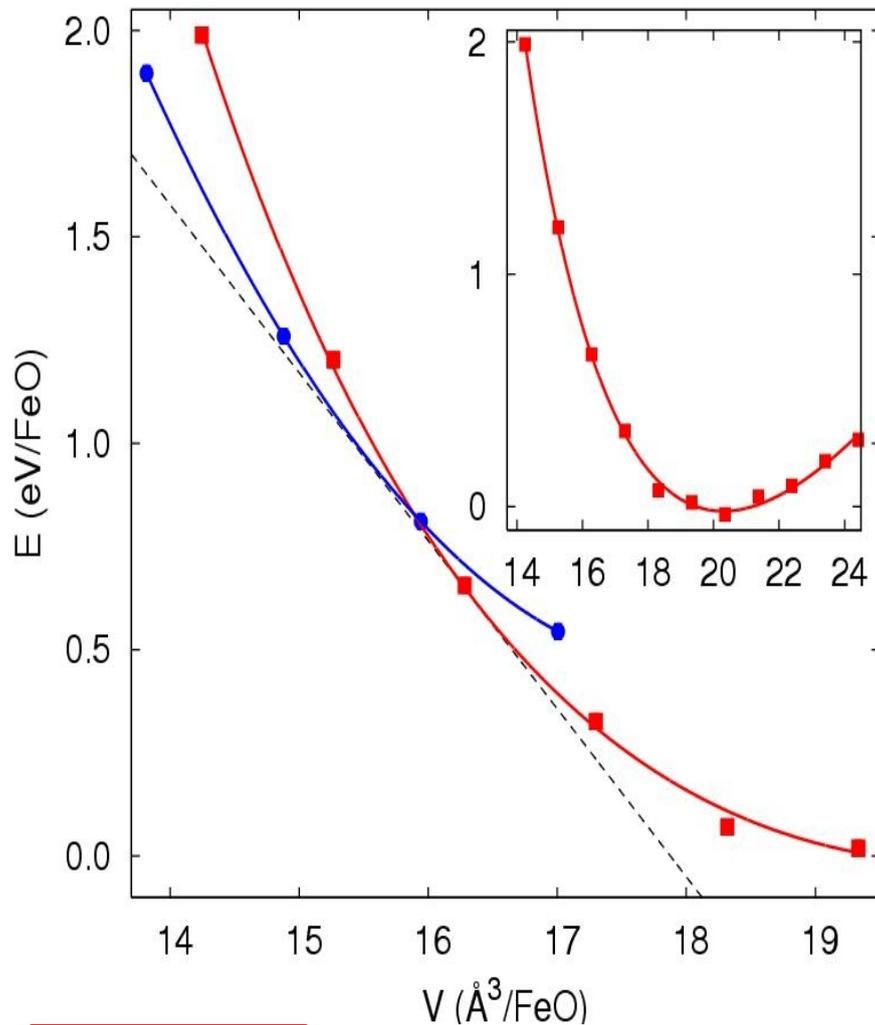


Comparisons of the FeO solid equilibrium parameters

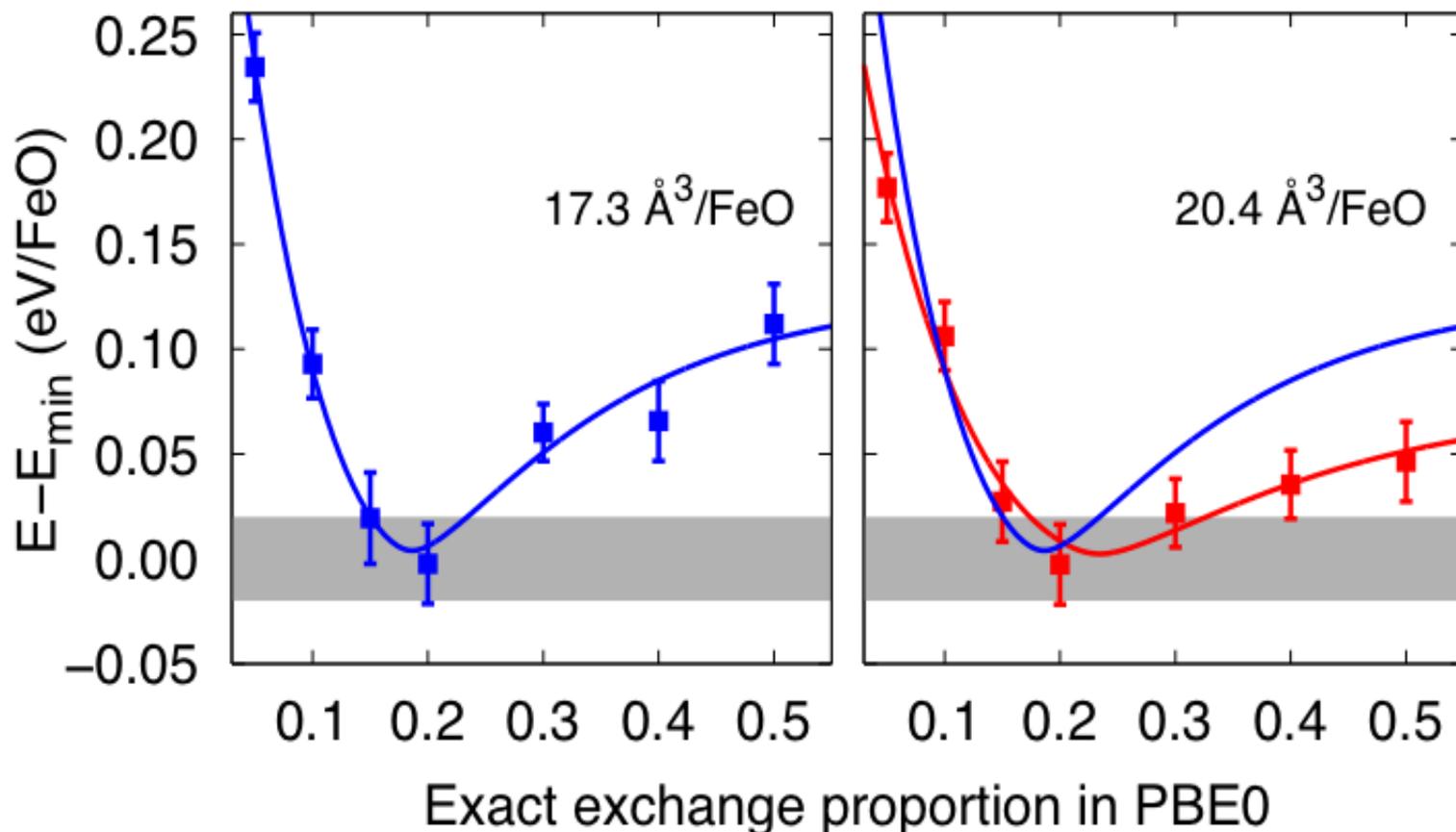
	DFT/PBE	FNDMC	Exp.(FeO _{1-x})
iB8-B1/AFMII [eV]	- 0.2	0.5 (1)	>0
Cohesion [eV]	~ 11	9.7 (1)	9.7(2)
a ₀ [Å]	4.28	4.32	4.33
K ₀ [GPa]	180	170(10)	152(10)
Opt. gap [eV]	~ 0 (metal)	2.8(3) eV	~ 2.4 eV

FeO solid at high pressures

QMC shows transition at ~ 65 GPa (Exper. 70-100)



Orbitals from hybrid PBE0 functional
Optimal weight of the Fock exchange found by
minimization of the fixed-node DMC energy



HF weight → d-p hybridization: HF “ionic” vs DFT “covalent”

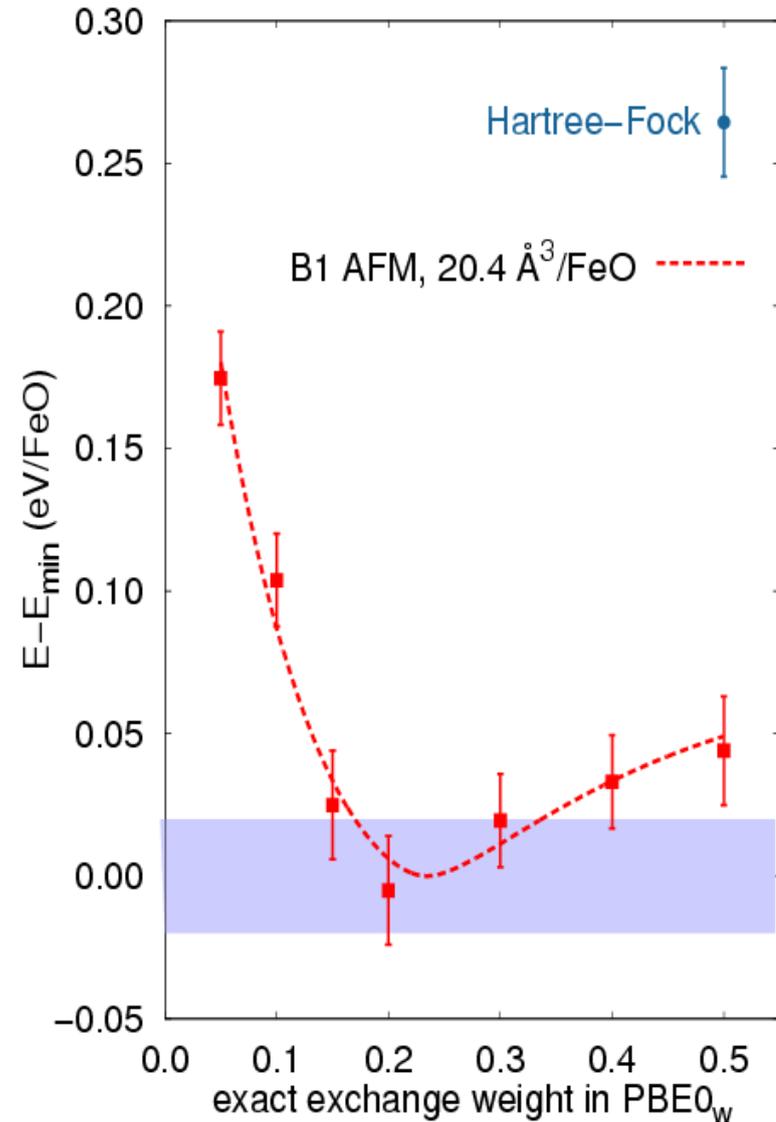
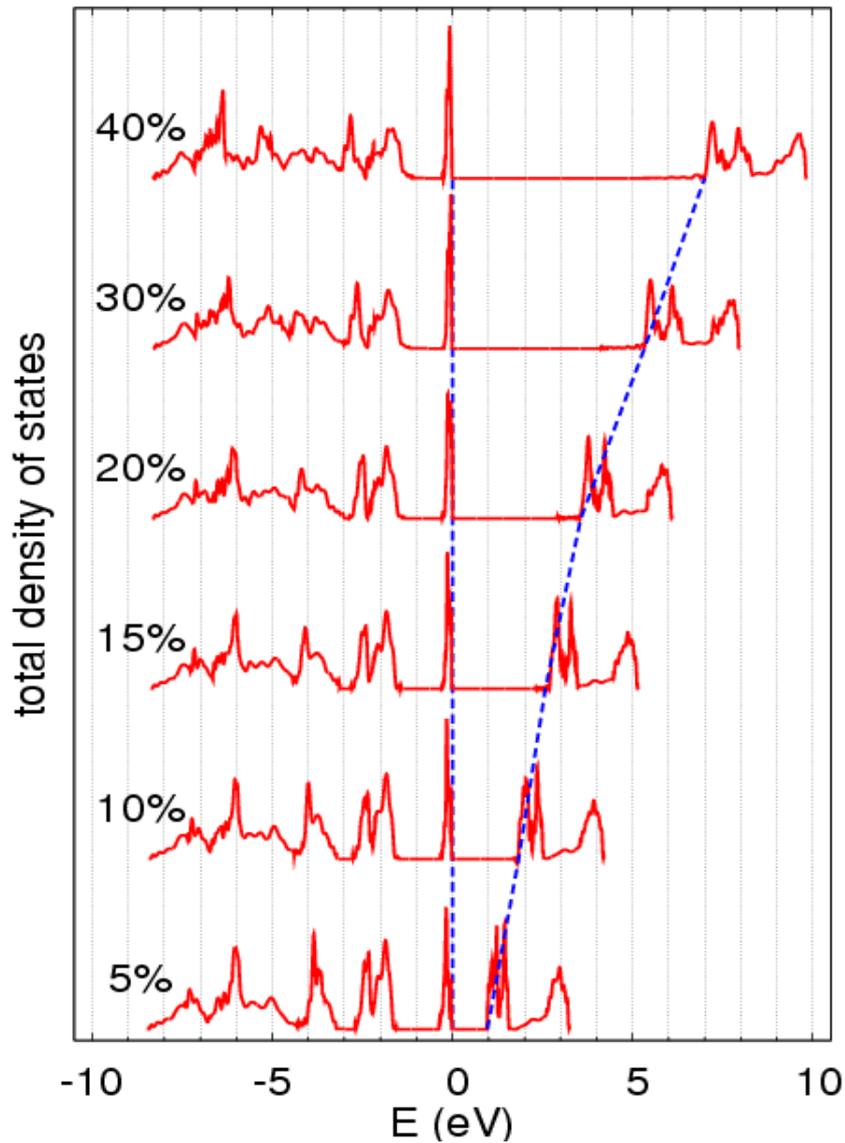
Note: variational FNDMC optimization of the DFT functional!

QMC byproduct: construction of optimal effective Hamiltonians (one-body or beyond)

The mixing of exact exchange into the effective one-particle (DFT) Hamiltonian is useful and clearly justified:

- variationally optimized fixed-node DMC energy
- **orbitals beyond HF**, closer in spirit to correlated orbitals, (since most of the correlation is included: all the bosonic correlations, cusps, etc, captured **exactly**)
- points out towards a more general idea/tool: **variational space** includes not only wavefunction but also effective Hamiltonian (more efficient and faster generation of accurate nodes)

Enables also to look back at the (corrected) one-particle picture, eg, density of states, gap, etc



Large-scale QMC calculations: performance and cost

- FNDMC:**
- Ne-core relativistic ECPs for Fe
 - orbitals: HF, hybrid DFT
 - size: 8 and 16 FeO supercells, up to **352 valence e-**
 - finite size corrections

Explicitly correlated trial wavefunction of Slater-Jastrow type:

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

Scaling as $\sim N^2$ - N^3 , parallel scalability

**Computational cost: typical run 10,000 - 30,000 hours
(2-3 orders of magnitude slower than a typical DFT run)**

Correlation energy ($E_{HF} - E_{exact}$) recovered: $\sim 90 - 95 \%$

FeO calculations illustrate a few key points about QMC

Practical:

- systems with hundreds of electrons are feasible
- agreement with experiment within few %
- the simplest, “plain vanilla” FNQMC -> single-determinant nodes!

Principal:

- note: no ad hoc parameters, no Hubbard U or Stoner J, etc: applicable to solids, nanosystems, BEC-BCS condensates ...
- 90-95 % of correlation is “bosonic”-like (within nodal domains), efficiently captured by algebraically scaling methods
- fixed-node approx. is the only key issue: 5-10% of correlation → enough accuracy for cohesion, gaps, optical excitations, etc
- 5-10% still important: magnetic effects, superconductivity, etc

Beyond the fixed-node approximation: fermion nodes

What do we need and want to know ?

$$\phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = 0 \rightarrow (DN-1)\text{-dim. smooth hypersurface}$$

It divides the space into domains with constant wf. sign (“+” and “-”)

Interest in nodes goes back to D. Hilbert and L. Courant (eg, n-th exc. state has n or less nodal domains). However, ... we need (much) more:

- nodal topologies, ie, number of nodal cells/domains → important for correct sampling of the configuration space
- accurate nodal shapes ? how complicated are they ? → affects the accuracy of the fixed-node energies
- nodes ↔ types of wavefunctions ?
- nodes ↔ physical effects ?

Topology of fermion nodes: how many domains are there ?

- 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 $r_1 \cdot (r_2 \times r_3) = 0$

Recent proof (L.M. PRL, 96, 240402; cond-mat/0605550)L.M.) that **ground states have the minimal number of two nodal domains:**

Two nodal cells theorem. Consider a spin-polarized a closed-shell ground state given by a Slater determinant

$$\psi_{exact} = C_{symm} (1, \dots, N) \det \{ \phi_i(j) \}; \quad C_{symm} \geq 0$$

Let the Slater matrix elements be monomials $x_i^n y_i^m z_i^l \dots$ of positions or their homeomorphic maps in $d > 1$.

Then the wavefunction has only two nodal cells for any $d > 1$.

Covers many models: homog. gas, fermions on sphere, atoms, ...

**For noninteracting/HF systems with both spin channel occupied -> more nodal cells.
Interactions -> minimal number of two cells again!**

Unpolarized noninteracting/HF systems: $2*2=4$ nodal cells!!!
-> product of two independent Slater determinants

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

What happens when interactions are switched on ?

**“Nodal domain degeneracy” is lifted → topology change
→ multiple nodal cells fuse into the minimal two again!**

**Bosonic ground states -> global/all-electron S-waves
Fermionic ground states -> global/all-electron “P-waves” !**

Fundamental and generic property of fermions!

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 $R', \beta \rightarrow$ 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

H. Monkhorst: “So what you are saying is that nodes are simple!”
Topology: yes! Shapes: no! \rightarrow better wavefunctions crucial ...

The simplest case of a nodal topology change from interactions/correlations: three e- in Coulomb pot.

Consider three electrons in Coulomb potential, in the lowest quartet (all spins up) of S symmetry and even parity state

Noninteracting Hamiltonian has two degenerate states:

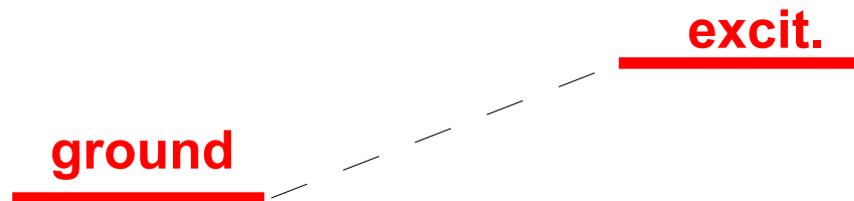
$$\psi_I = \det[1s, 2s, 3s]$$

$$\psi_{II} = \det[1s, 2p_x, 3p_x] + x \rightarrow y + y \rightarrow z$$

non-interacting

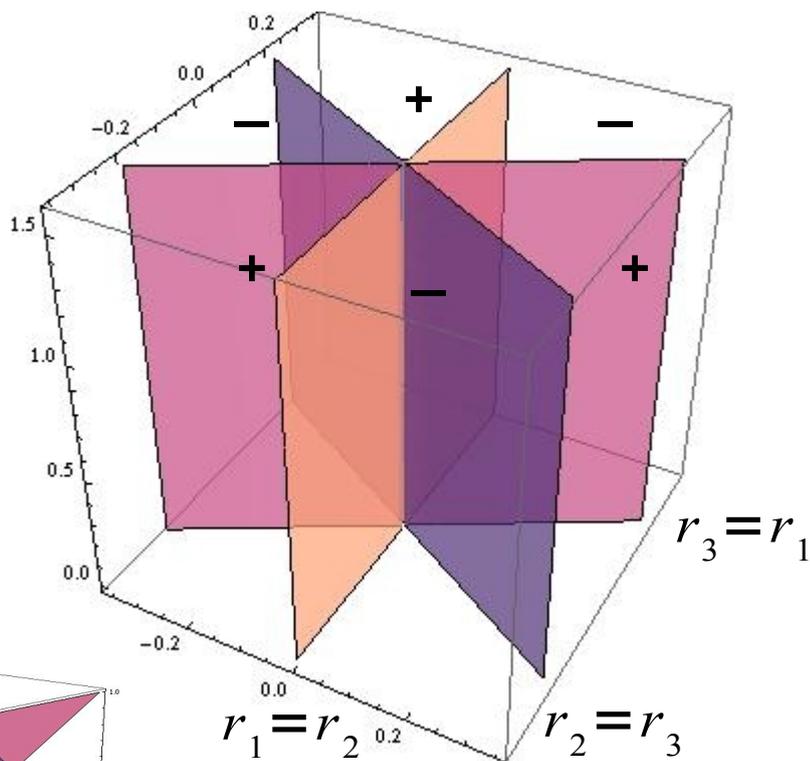


Interaction -> states split (already in HF)



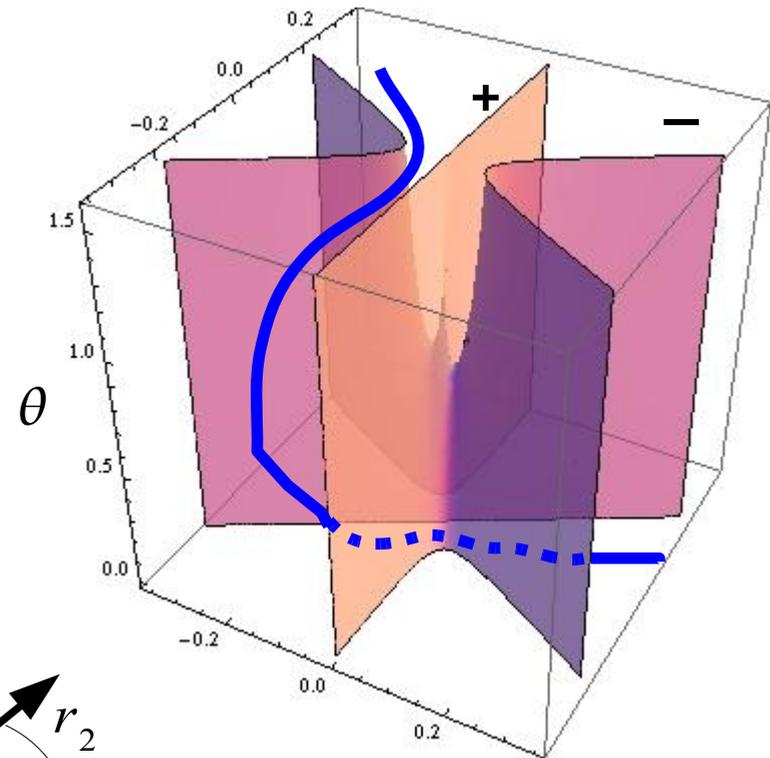
$^4S(1s2s3s)$ HF node: $(r_1 - r_2)(r_2 - r_3)(r_3 - r_1) = 0 \rightarrow 6$ domains (quasi 1D!)

Nodal topology change from interactions/correlation ("triplet pairings": tiny but nonzero effect)



HF node

6 cells



**Pfaffian (or expansion
in dets) → corr. node**

2 cells

Pfaffian: signed sum of all distinct pair partitions of permutations (Pfaff, Cayley ~ 1850) -> the simplest antisymm. pair spinorbital wavefunction

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

Pair orbital $\phi(x_1, x_2)$ + antisymmetry -> pfaffian*

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

- determinant is a special case of pfaffian (**pfaffian is more general**)
- pfaffian algebra similar to determinants (minors, etc)
- ψ_{HF} is a special case of ψ_{PF}

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

symmetric/singlet **antisymmetric/triplet**

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 (geminals) expanded in one-particle basis

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

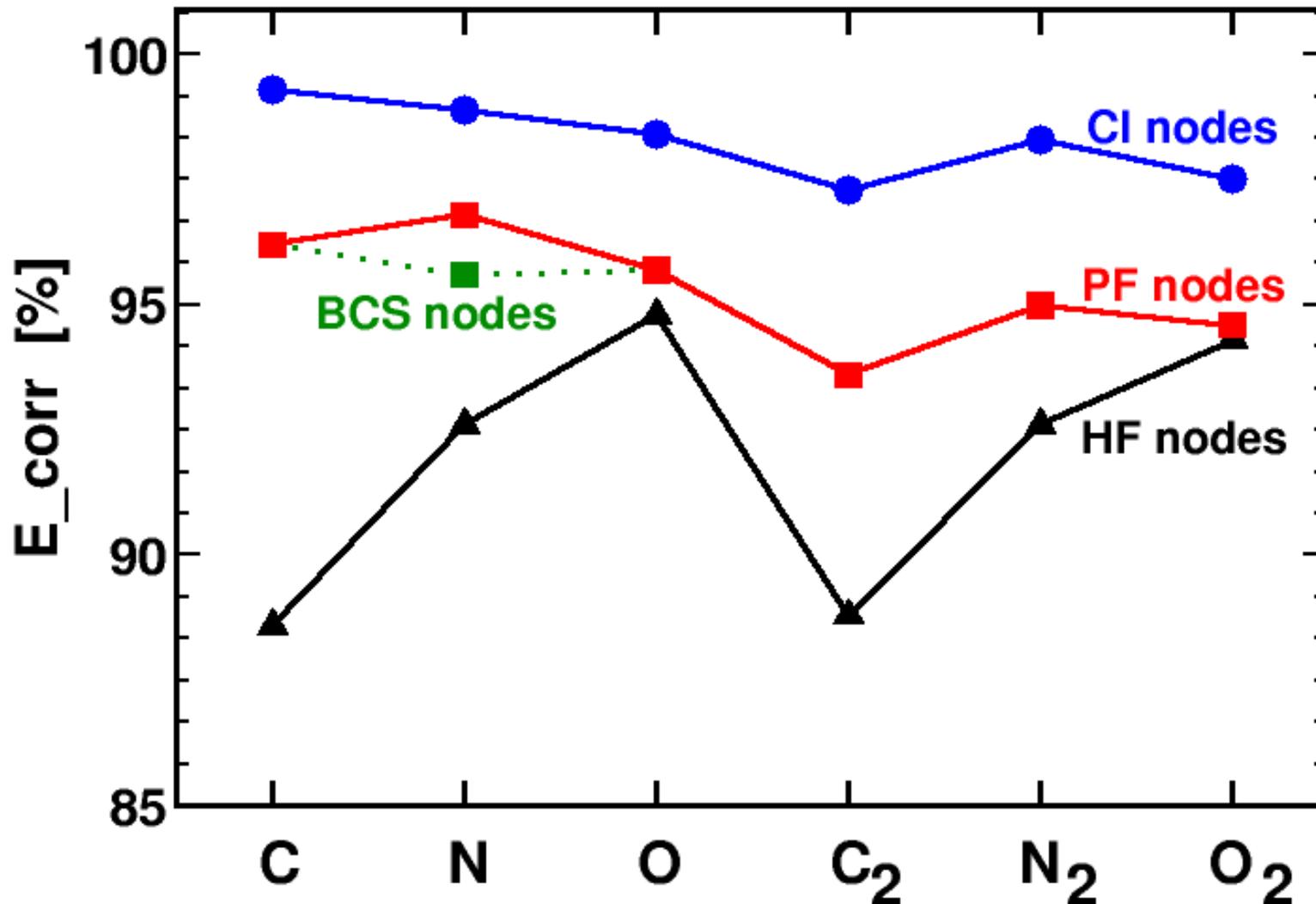
- unpaired

$$\psi(i) = \sum_{\alpha} c_{\alpha} h_{\alpha}(i)$$

BCS wf. for 2N-particle singlet is a special case: $\psi_{BCS} = \det[\phi^{\uparrow\downarrow}]$

Pairing wavefunctions enable to get the correct nodal topologies ...

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

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))

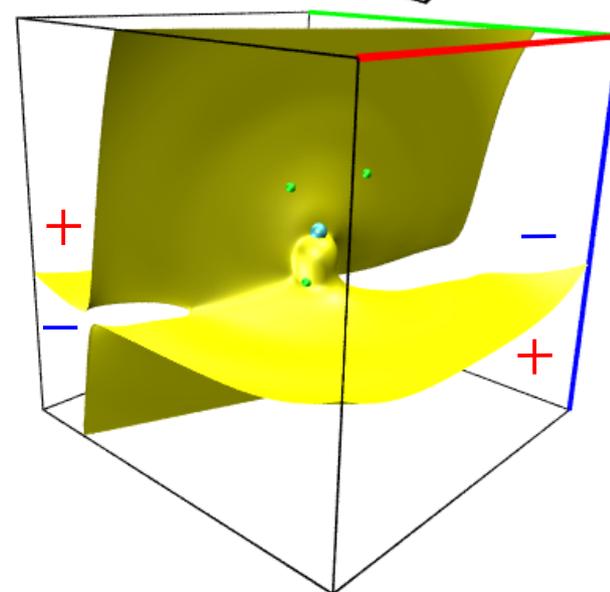
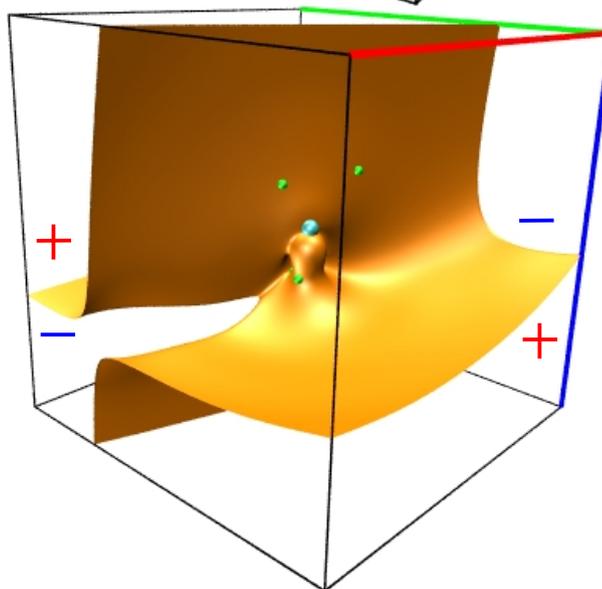
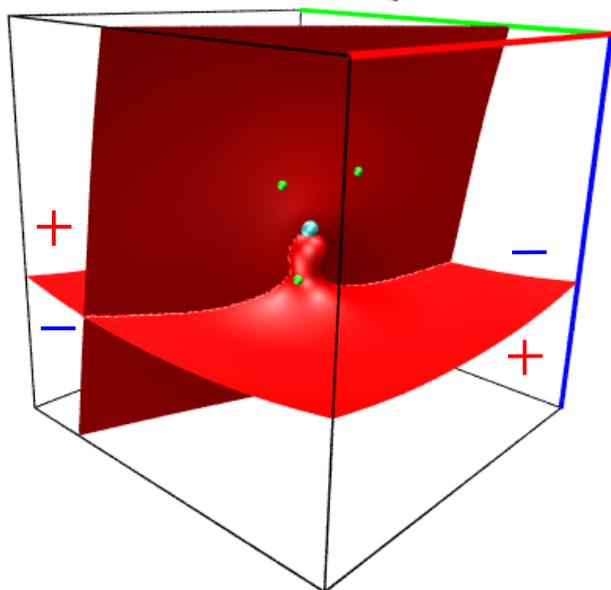
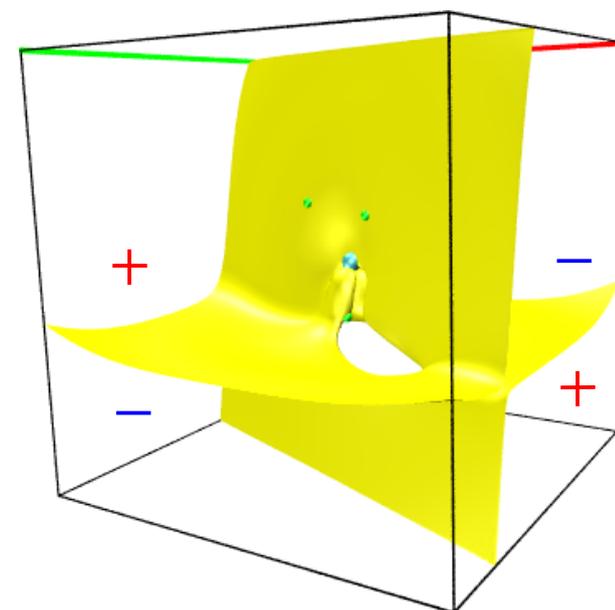
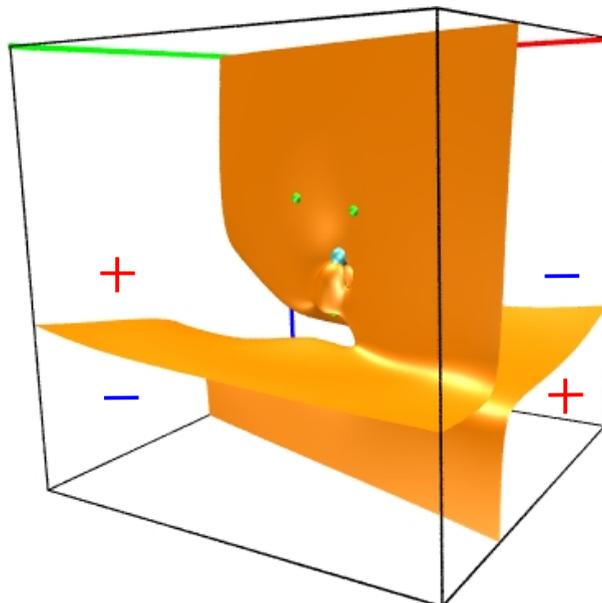
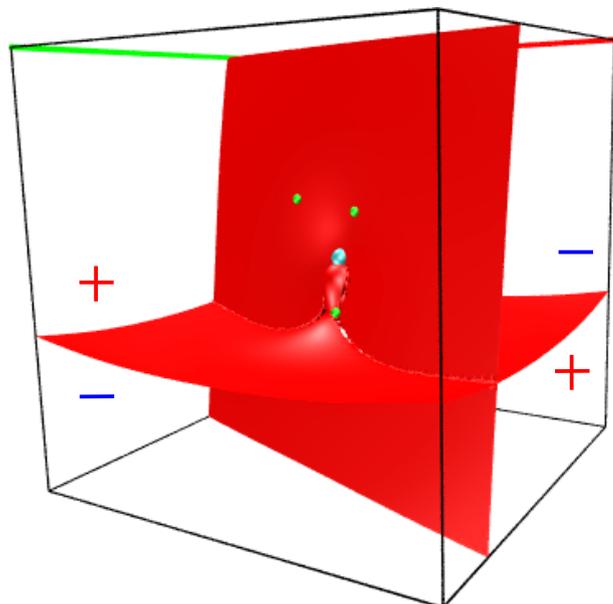
Pfaffians describe nodes more efficiently

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

HF (94.0(2)%)

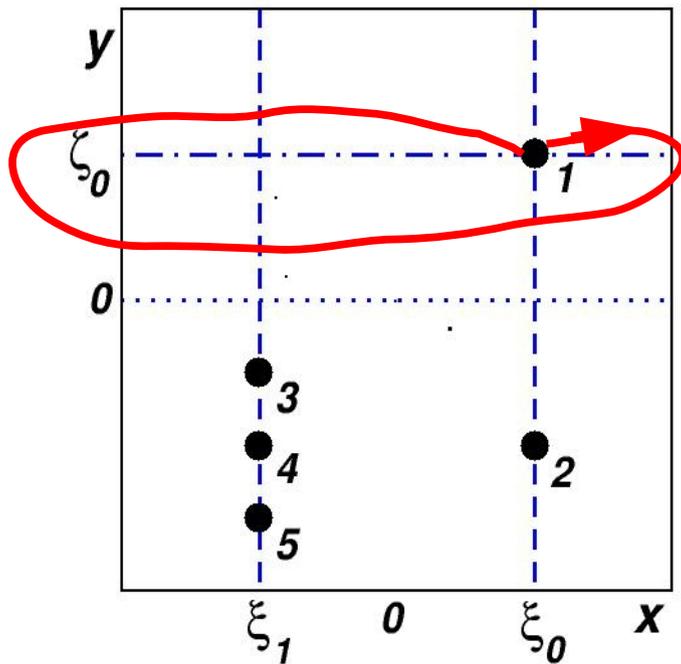
MPF (97.4(1)%)

CI (99.8(3)%)

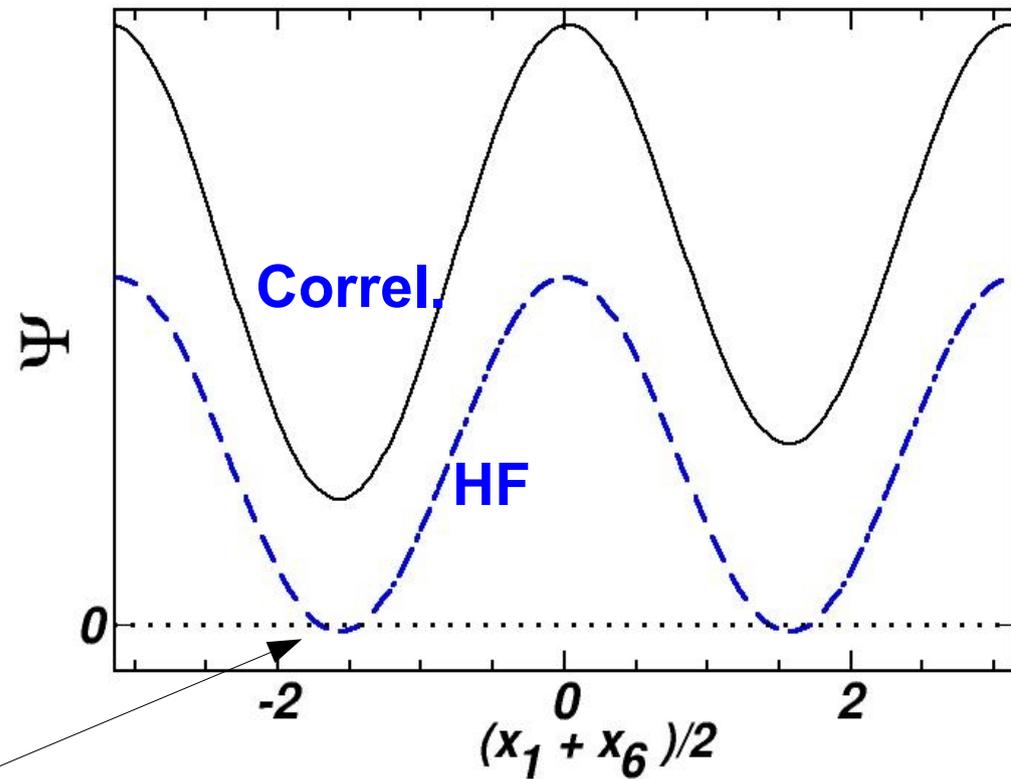


Correlated nodes in homogeneous electron gas: singlet pair of e- winds around the box without crossing the node

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



Wavefunction along the winding path



HF crosses the node, BCS/pfaffian does not (supercond.)

Ultracold atoms in a special state: **unitary gas**

Effective, short-range attractive interaction

Scattering length: a

$$1/a < 0$$

BCS, weakly paired superconductor

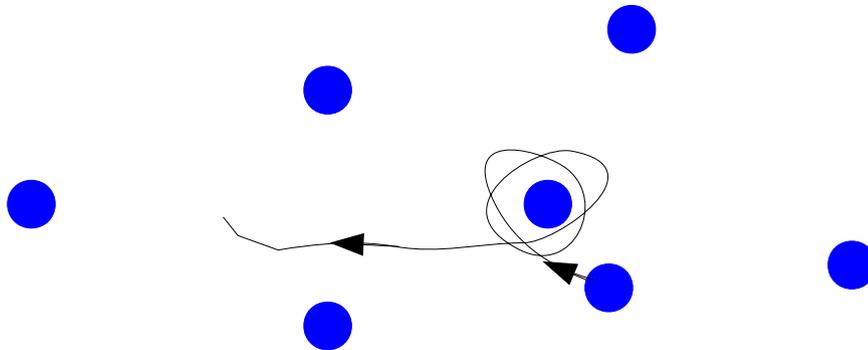
$$1/a > 0$$

BEC of covalently bonded molecules

$$1/a = 0$$

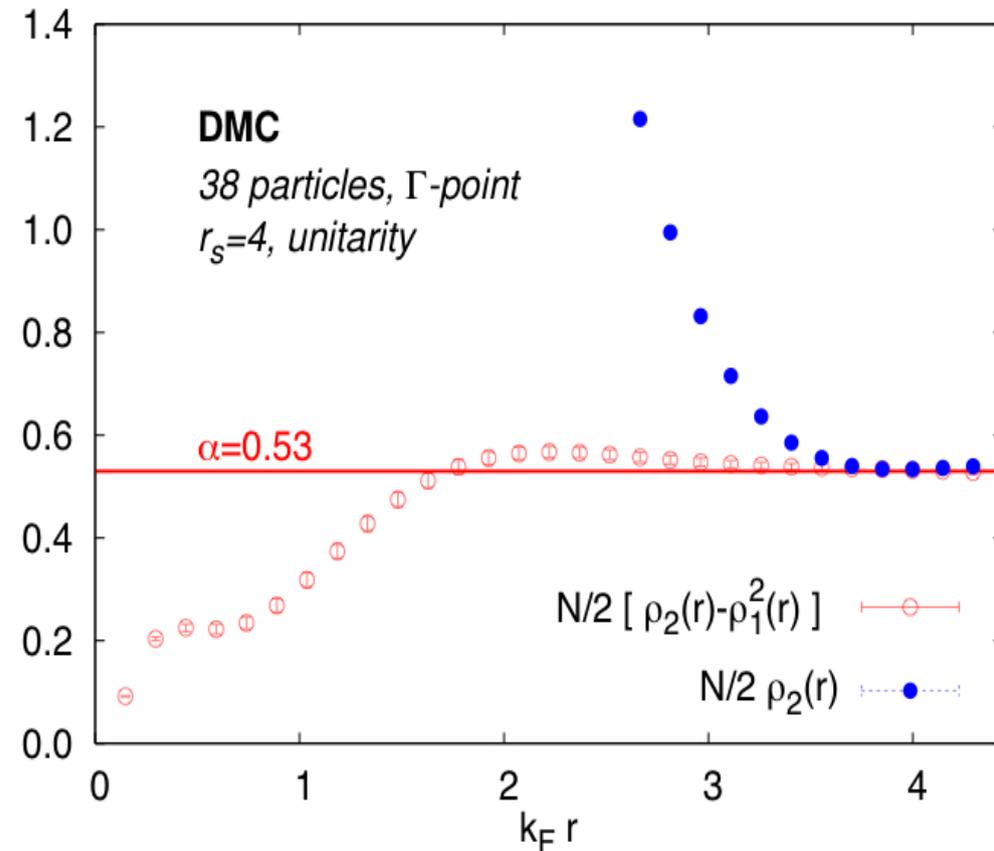
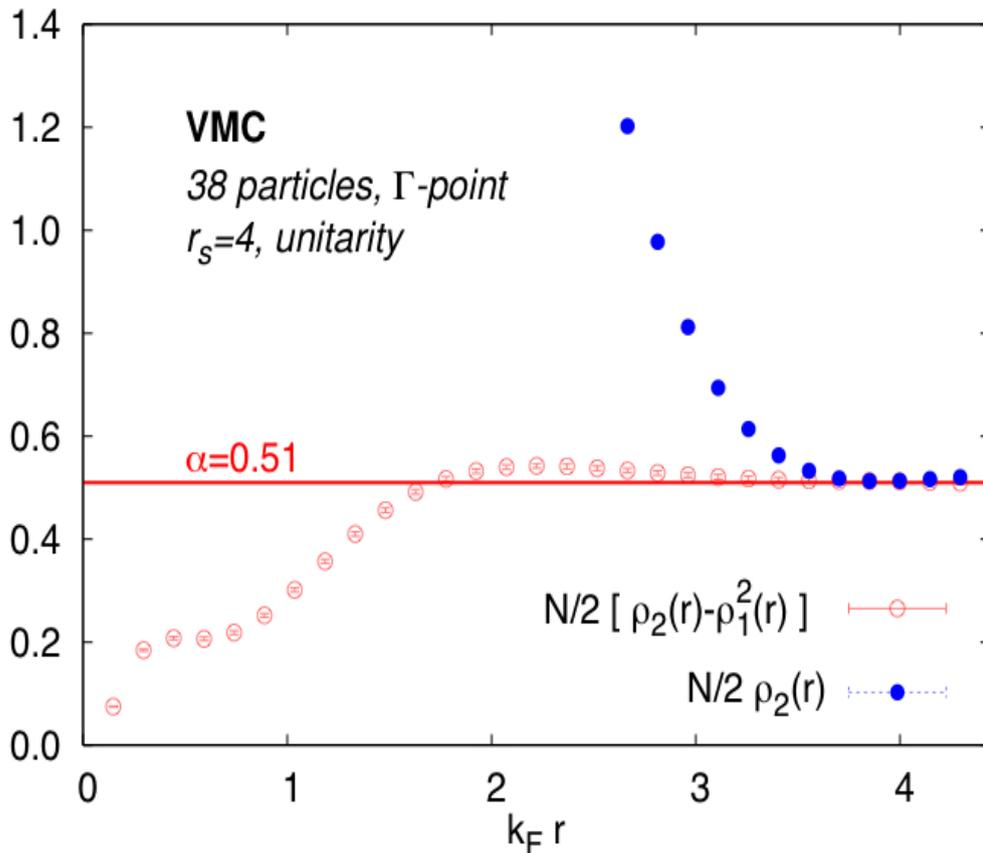
unitary limit \rightarrow the only scale is the density, like a mathematical model (Bertsch limit)

Obtained by tuning the interaction so that a pair is on the verge of forming a bound state (ie, $E=0$) in the lowest attractive channel



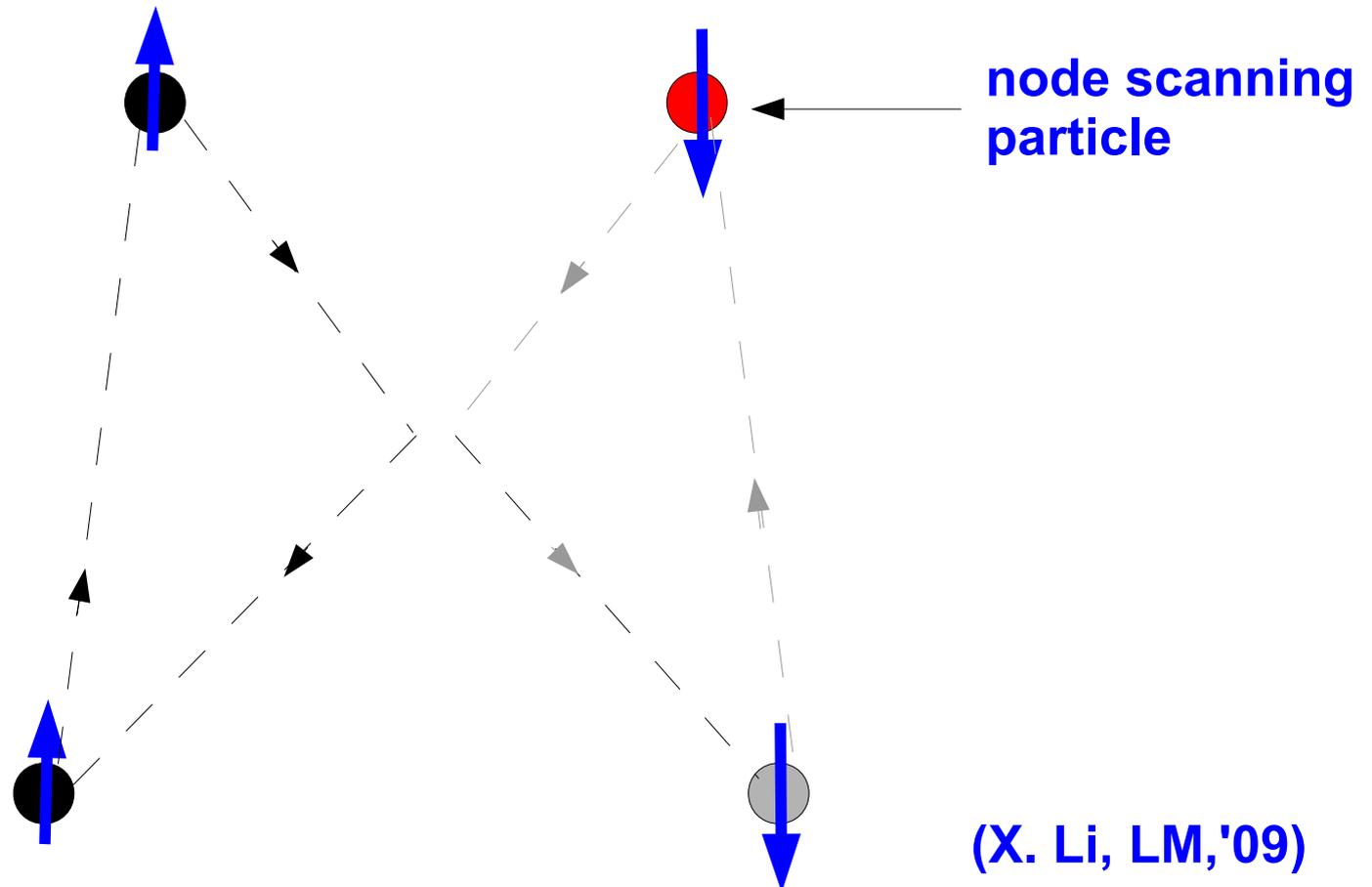
Unitary limit: seemingly a weakly interacting system
Opposite is true: strongly interacting regime, large amount of condensate (BEC \leftrightarrow unitary \leftrightarrow BCS)

Find the amount of the condensate directly: projected two-body density matrix at long-range (using BCS wavefunction)



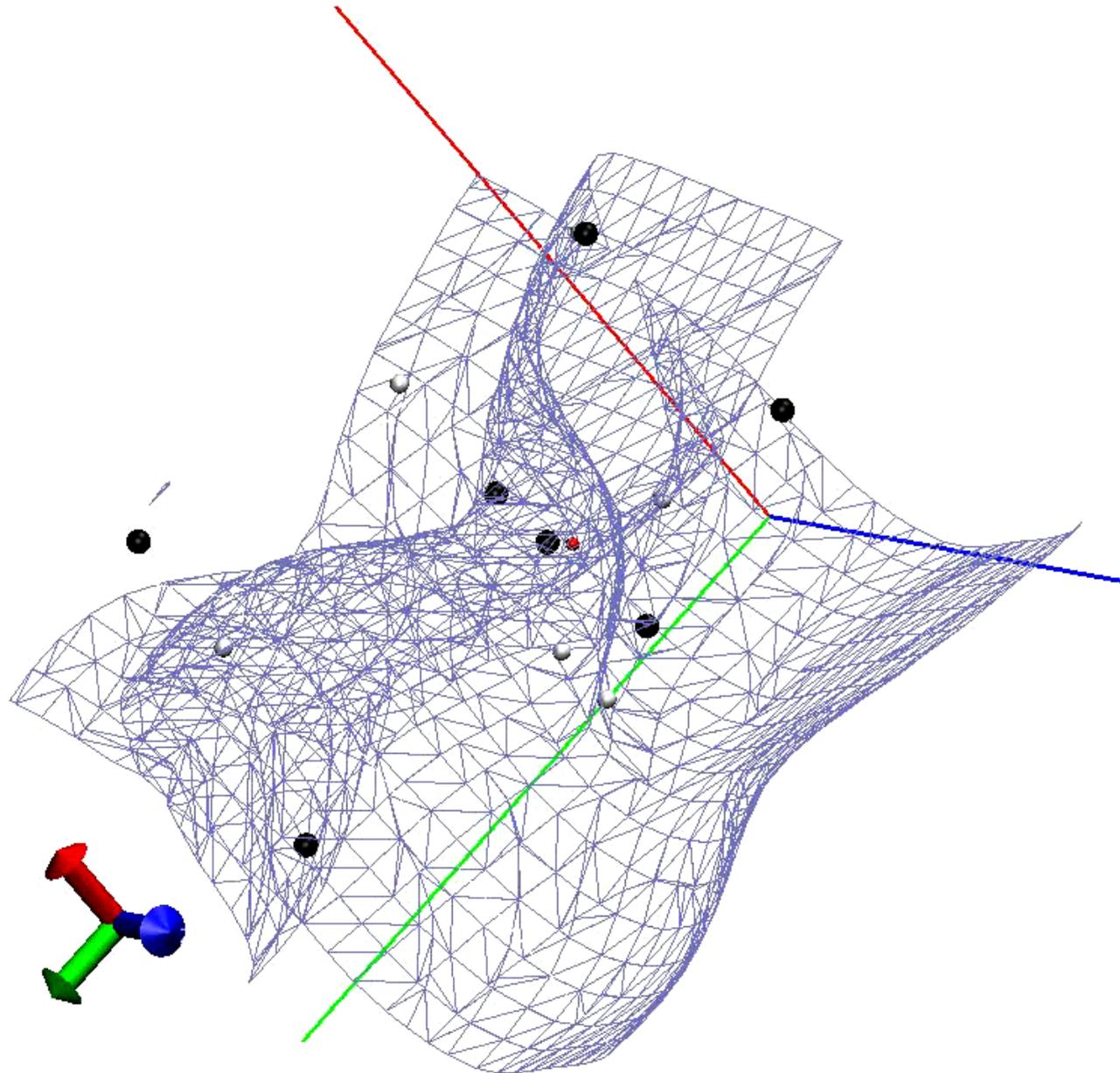
The four particle exchange: illustration of pair exchange without node crossing

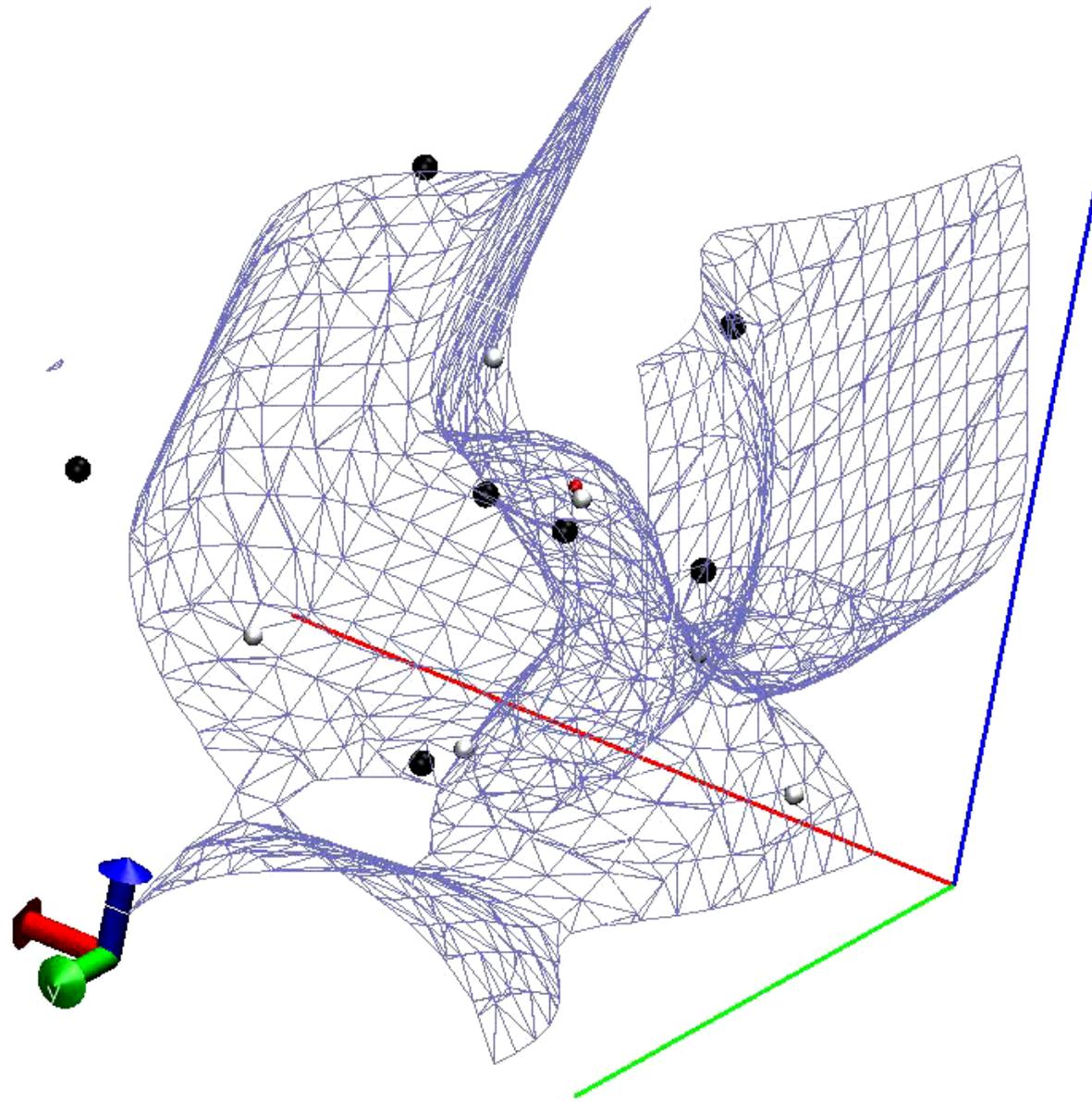
- A) Exchange in each spin channel separately has to cross the node
- B) Concerted both spin channels exchange can avoid the node



(X. Li, LM,'09)

I.





Another type of wavefunction with improved nodes: backflow coordinates

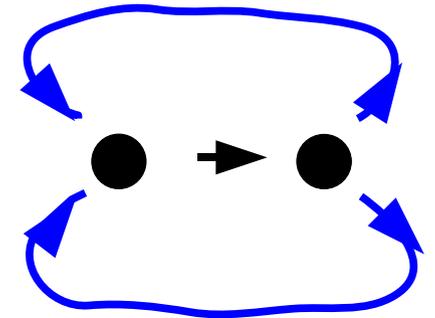
Improve the Slater-Jastrow wf. $\exp(-\tau H)\psi_T \approx \psi_T - \tau H\psi_T$

$$He^{U_{corr}} \det[.] = e^{U_{corr}} (T + V_{el}) \det[.] + \det[.] (T + V_{ee}) e^{U_{corr}} - \nabla e^{U_{corr}} \cdot \nabla \det[.]$$

“spurious” term

$|\nabla \det[.]| \gg |\nabla e^{U_{corr}}|$ -> strongly inhomogeneous -> excitations
(CI, pfaffians) cancel out the spurious terms

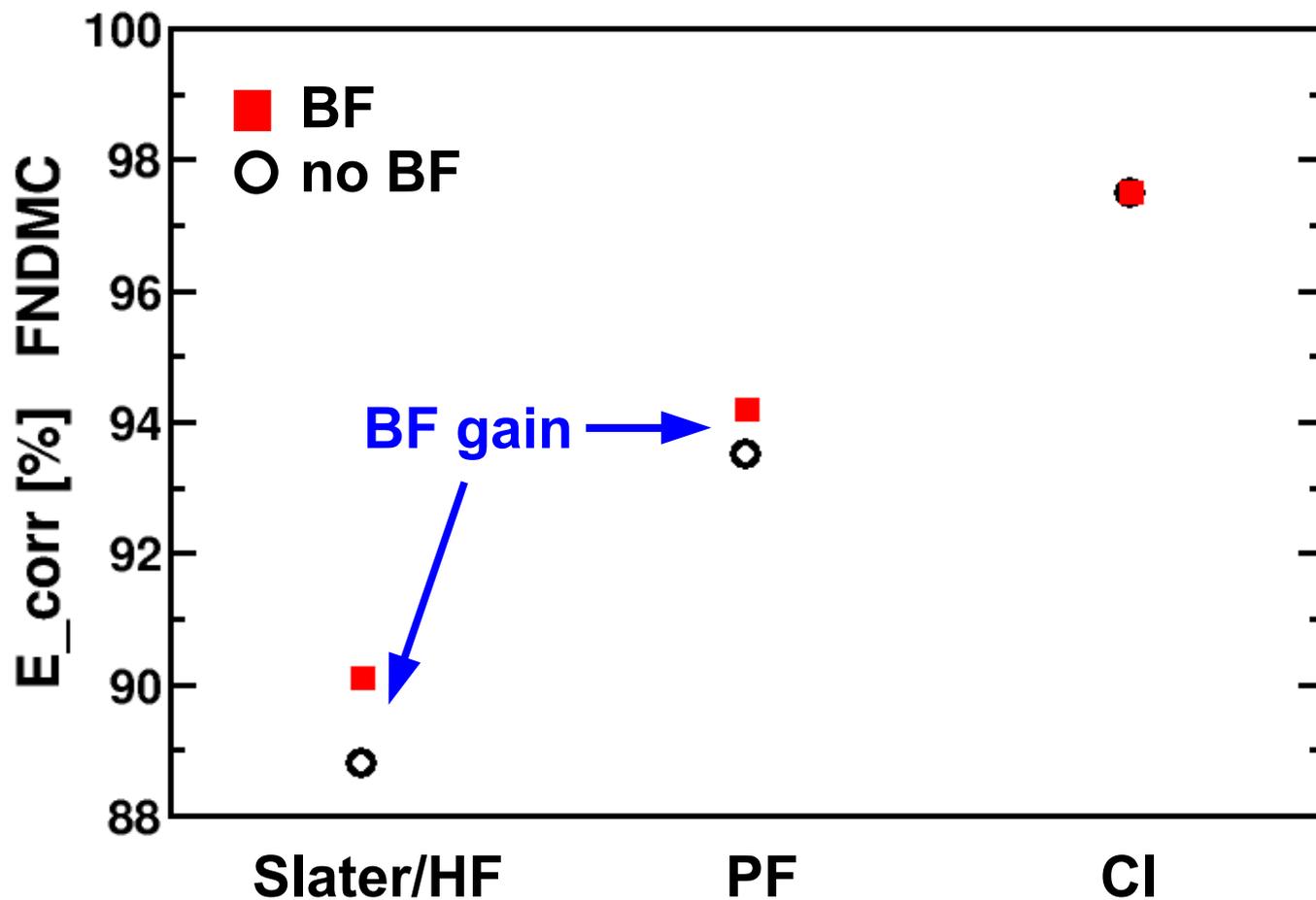
$|\nabla \det[.]| \ll |\nabla e^{U_{corr}}|$ -> backflow terms are effective
(homogeneous systems)



$$\vec{x}_i = \vec{r}_i + \sum_{i < j} \gamma_{ij}(r_{ij}) \vec{r}_{ij}$$

backflow described by “dressed” coordinates
→ combine with pfaffian wavefunctions

FNDMC correlation energies of C₂ molecule for various wavefunctions with and without the backflow



Gains from backflow are rather small ...

Backflow for homogeneous periodic electron gas (Coulomb e-e + neutralizing background)

characterized by a single parameter: r_s → inverse density

r_s	HF	DMC/HF nodes	DMC/BF nodes
1	0.56925	0.53087(4)	0.52990(4)
5	-0.056297	-0.07862(1)	-0.07886(1)
20	-0.022051	-0.031948(2)	-0.032007(2)

About 1% gain but significant since it cuts the fixed-node error by a factor of 2 or so. Works better for homogeneous systems, as expected. Still, not enough understanding!

Signatures of nodes on expectation values, energy in particular, are weak, not informative enough!

Total energy (and other expectations) provide only weak signal of nodes impact on energy → “low energy physics”

- Coulomb: $\sim 2 E_{\text{tot}}$
- exchange: $\sim 10\%$ of E_{tot}
- correlation: $\sim 3\%$ of E_{tot}

Fixed-node bias beyond HF nodes: $\sim 0.2\%$ of E_{tot}

Consider the simplest non-interacting atomic $^3S(1s2s)$, $^3P(1s2p)$ states:

- degenerate in energy, but the nodal shapes are different
- for $^1S(1s^22s^2)$ and $^1S(1s^22p^2)$, the same as above and, in addition, the symmetry is the same, but the nodes differ.

We would like to distinguish and to measure this!

- suggestion that nodes can be fractal at quantum critical point (Kruger & Zaanen, '08) – we need to measure node smoothness, etc

Looking for other (new) measures of nodal properties and characterization

Consider the stationary Schrodinger equation:

$$-(1/2)\nabla^2\psi + V(R)\psi = E\psi, \quad R(r_1, r_2, \dots, r_N)$$

The many-body eigenstate determines the nodal domains

$$N^+ = [R; \psi(R) > 0], \quad N^- = [R; \psi(R) < 0]$$

and the corresponding node ∂N

Integrate Schr. eq. **over** N^+ **domain only** and use Stokes-Green

$$-(1/2)\int_{\partial N} \nabla_R \psi \cdot d\mathbf{S}_n + \int_{N^+} V(R)\psi dR = E \int_{N^+} \psi dR$$

and similarly for the other domain, put together

$$\int_{\partial N} |\nabla_R \psi| dS + \int V(R)|\psi| dR = E \int |\psi| dR$$

The total energy components and other properties of nodal domain averages

“Kinetic” and “potential” components are “one-sided expectations” or, as I propose, **nodal domain averages (nda)**

$$E_{kin}^{nda} = \int_{\partial N} |\nabla_R \psi| dR \ / \ \int |\psi| dR$$

$$E_{pot}^{nda} = \int V(R) |\psi| dR \ / \ \int |\psi| dR$$

Note: E_{kin}^{nda} depends solely on nodal $|\nabla_R \psi|$ and on nodal surface area (captures behavior of quantum amplitudes, not expectations)

Other features:

- although this gives the total energy, no variational properties (!)
- the surface integral (potentially) difficult to evaluate
- still, let us explore this ...

Let us study some solvable cases and compare with usual expressions

Total energy components: conventional vs. nodal domain average (nda) formulation → can distinguish between two different types of nodes

The simplest atomic cases states with $V(r) = -Z/r$ explicitly solvable (energies are in units of Z^2 , dot "." means the same as above)

	E_{tot}	E_{kin}	E_{pot}	E_{kin}^{nda}	E_{pot}^{nda}
${}^3S(1s2s)$	- 5/8	5/8	- 5/4	10/221	- 1185/1768
${}^3P(1s2p)$.	.	.	1/20	- 27/40
A= ${}^1S(1s^22s^2)$	- 5/4	5/4	- 5/2	20/221	- 1185/884
B= ${}^1S(1s^22p^2)$.	.	.	1/10	- 27/20
mix A+cB	.	.	.	dep. on c	dep. on c

btw, mix with $c \sim 0.3$ is the correct eigenstate for pert. weak e-e interaction

Another insight: different states, even different exchange statistics, but equivalent nodes

Three states with $2p^2$ occupation: 3P , 1S , 1D all have the same n da energy components ...

	E_{tot}	E_{kin}	E_{pot}	E_{kin}^{nda}	E_{pot}^{nda}
$^3P, ^1S, ^1D (2p^2)$	-1/4	1/4	-1/2	1/12	-1/3

... why ? Consider the 5D nodes projected into 3D:

3P : electron “sees” a **plane** defined by ang. mom. axis and the second el.

1D : electron “sees” a **plane** which contains ang. mom. axis and is orthogonal to such plane defined by the second electron

1S : electron “sees” a **plane** which is orthogonal to the position vector of the second electron

In all three cases the node is a 5D single-sheet hyperbolic surface in 6D

Quasiclassical limit: nda become usual kinetic and potential energies

Let us consider a special class of atomic excited states: a given subshell $l = n - 1$ with arbitrary occupation, symmetries and statistics

$^{2S+1}X[\phi_l^k]$ state, k is the occupation, one can find

$$E_{kin}^{nda}(k, l) = k Z^2 \frac{l}{2(l+1)^2(l+2)} \quad E_{pot}^{nda}(k, l) = -k Z^2 \frac{1}{(l+1)(l+2)}$$

Since it does not matter what is the symmetry, etc, the noninteracting nodes are all just equivalent hypersurfaces (why ? ... ask)

Also:

$$\lim_{l \rightarrow \infty} E_{kin}^{nda} = E_{kin} \quad \lim_{l \rightarrow \infty} E_{pot}^{nda} = E_{pot}$$

In quasi-classical limit averages over ψ^2 or $|\psi|$ become identical

Nodal domain averages: the key points

- energy defined as new nodal domain averages: “kinetic” surface integral and nodal averaged potential contributions
- reveals nodal differences between some classes of degenerate states, can characterize new mixed eigenstates
- enables to find out that the nodes of many states are equivalent (even for different symmetries and exchange statistics)
- quasi-classical limit agrees with conventional definitions, difference between the values: measure of quantumness

Summary

- **QMC: practical for hundreds of explicitly correlated electrons but also provides new unique insights into many-body effects**
- **explicit proof of two nodal cells for $d > 1$ and arbitrary size with rather general conditions -> fundamental topological property of fermionic ground states: global “P-wave” like**
- **nodal counts are related to further fundamental ideas in spectral theory -> quantum geometry of many-body effects**

Open source code: **QWalk (“Quantum Walk”)** -> www.qwalk.org

Working hypothesis

Geometry is not the only thing, but it is the most important thing

Connolly

Challenges in QMC

Spectra:

- state by state calculations (band edges, band structure scan)
- subtle features (satellites, etc, difficult, costly)
- multi-state calculations (eg, projecting out not a dominant single state but a mixture, evaluate matrix elements, etc, exponentially scaling but for small number of states doable)

Ionic forces:

- noise is a problem (possible routes tried)
 - finite differences with correlated sampling
 - Hellman-Feynman
 - AIMD/DFT with QMC correction by evolving the wave function along the ionic path (surprisingly efficient, factor of 2-3 on the top of AIMD! Grossman & Mitas PRL '05)

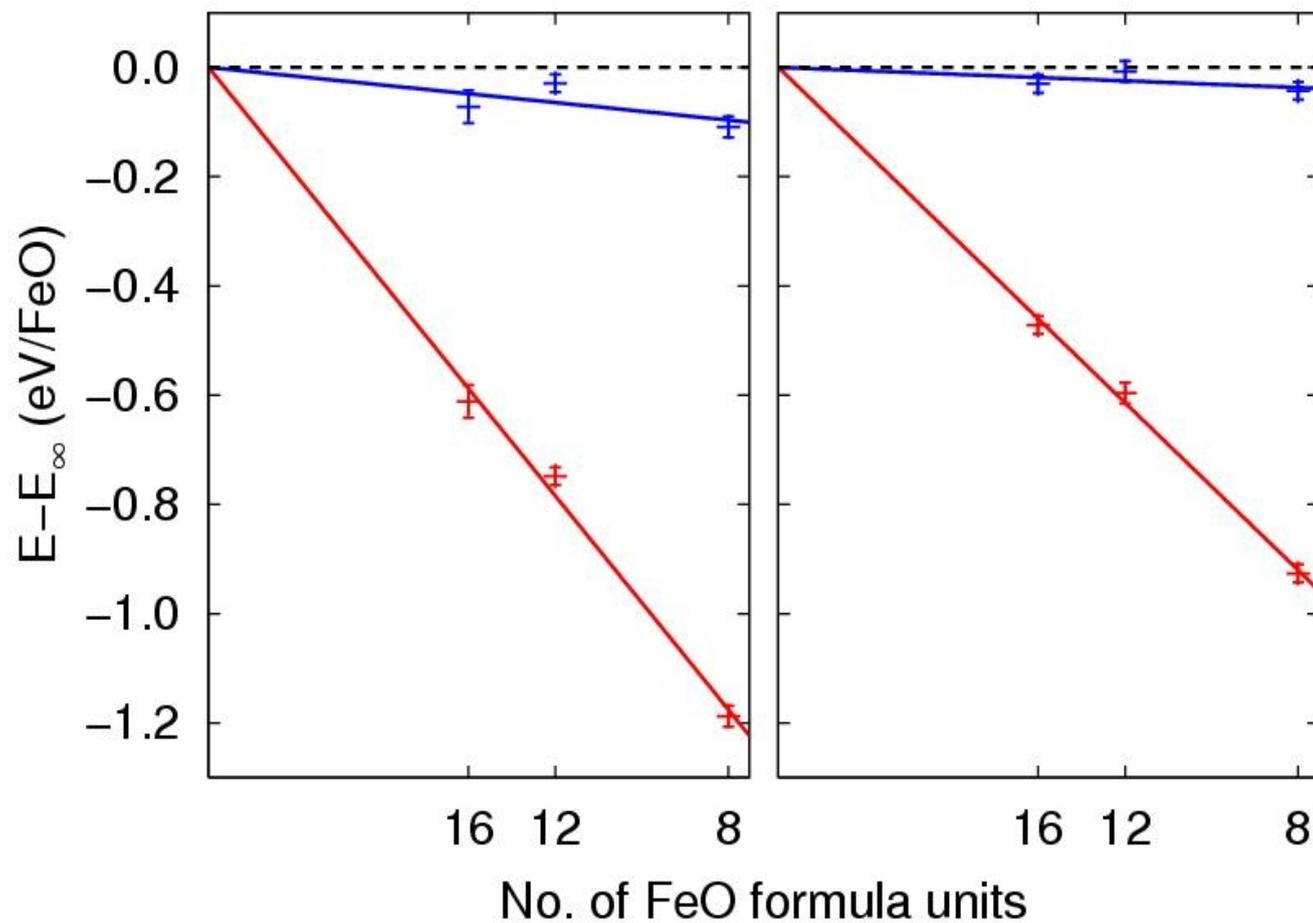
Spins: as a quantum dynamical variables, spin-orbit interactions

Open Source QMC code QWalk (“Quantum Walk”)

www.qwalk.org

- **molecules and solids** (3D periodicity), 1D rings, other systems (effective interactions, model systems, etc), tested on TMOs
- **variety of basis** (gaussian, Slater, PW, numerical, etc) or combination
- **several types of correlated wavefunctions** (CI, pfaffians)
- **variety of methods** (variational, fixed-node DMC, reptation, upper bound for nonlocal operators, optimizations, etc)
- **object-oriented code, C++, 50,000+ lines: GPL open source, community** (L. Wagner, M. Bajdich, J. Koloenc, others)
- **interfaces and converters from GAMESS, CRYSTAL, Gaussian, SIESTA, (Qespresso in progress)**

FeO solid: finite size scaling in QMC (Ewald vs $S(k)$ correction)



Approaches to many-body quantum problems

Many-body effects first, explicitly solve (a.a. NP-hard ?)

Dimensional reduction, expectations: machine

QMC methods

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N), \dots$$

$$\rho(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{r}'_1, \dots, \mathbf{r}'_N)$$

Hamiltonian, Lagrangian, etc

**Physical effects
Expectation values
Predictions**

Traditional reductionism

Dimensional reduction ("integrate-out" N-2 e-)

$$\rho(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$$

$$\rho(\mathbf{r}), \text{ etc}$$

Many-body effects, "implicitly", "inverse prob." (a.a. ill-conditioned ?)

Off-diag DM

$$\rho_2(r_1, r_2; r_1', r_2') = \alpha(N/2) \phi(r_1' - r_2') \phi(r_1 - r_2) + O(1)$$

$$\rho_{1P} = \int \rho_1(r_1 + r, r_1) dr_1$$

$$\rho_{2P}(r) = (2/N) \int \int \rho_2(r_1 + r, r_2 + r, r_1, r_2) dr_1 dr_2$$

$$[\psi(r_1) \psi(r_2)]_{ave} = \sqrt{\alpha N/2} \phi(r_1 - r_2)$$

Band structure of MnO by HF and DFT:

UHF

B3LYP

PW91

