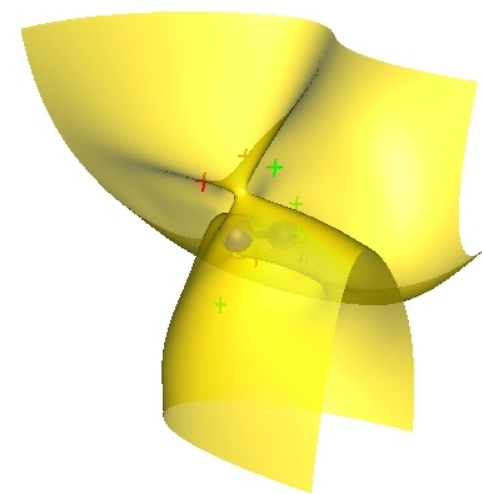
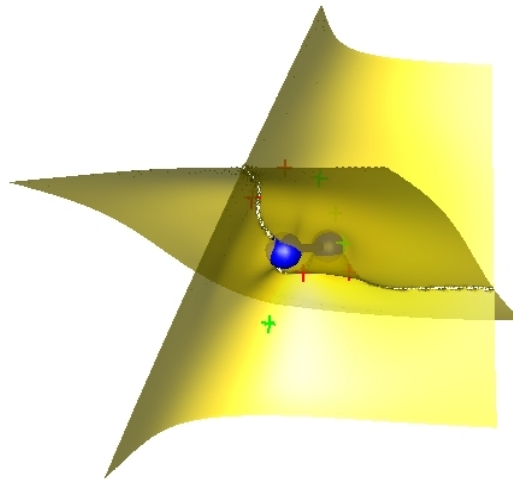
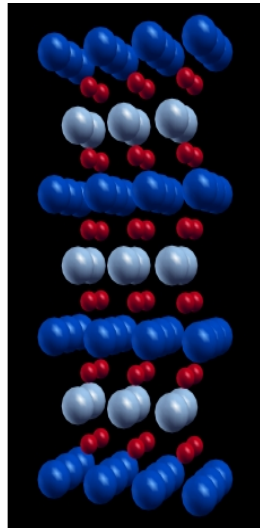
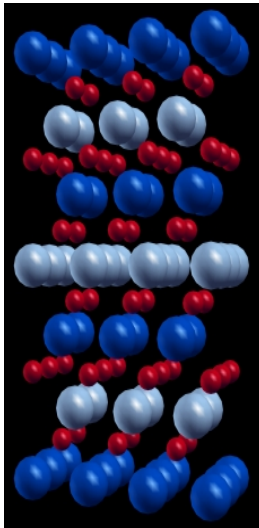


# Electronic structure quantum Monte Carlo: pfaffians and many-body nodes of ground and excited states



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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:

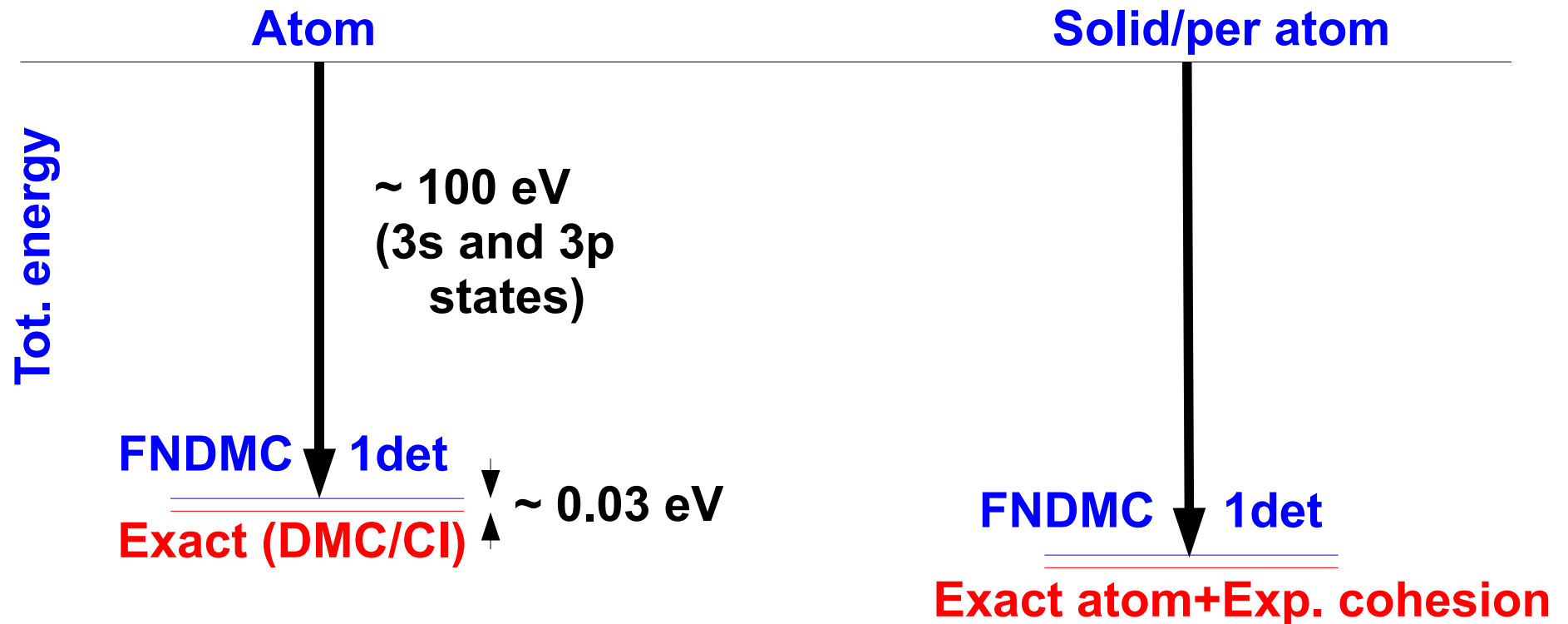
$$\psi_{Trial} = \det^{\uparrow}[\phi_{\alpha}] \det^{\downarrow}[\phi_{\beta}] \exp\left[\sum_{i,j,I} U_{corr}(r_{ij}, r_{iI}, r_{jI})\right]$$

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

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

- Solids:**
- supercells
  - finite size corrections

“Easy” example: solid Si (up to 214 atoms), upper bounds on tot. energy within  $\sim 0.001$  a.u. ( $=0.03$  eV)  
 Both stochastic **and** systematic errors are **small**



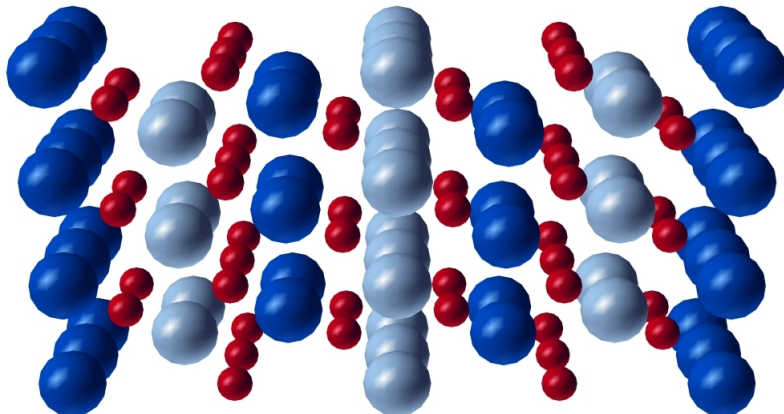
**Cohesion:**

- rigorous lower bound(!) → 6.58(1) eV
- FNDMC (error canc.) → 4.61(1) eV
- experiment → 4.62(8) eV

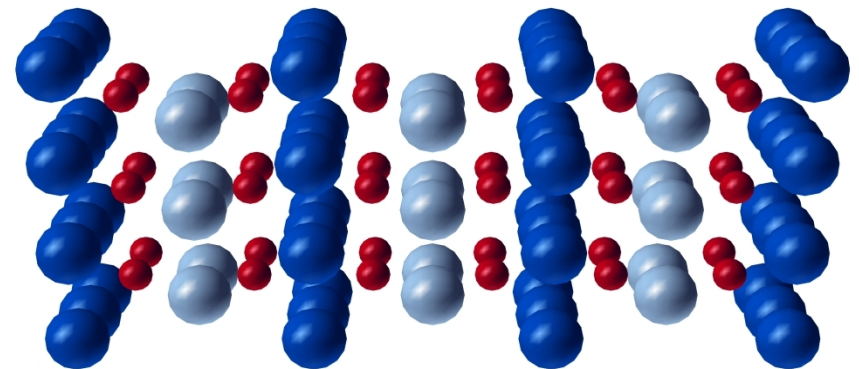
# FeO solid at high pressures

- **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.)

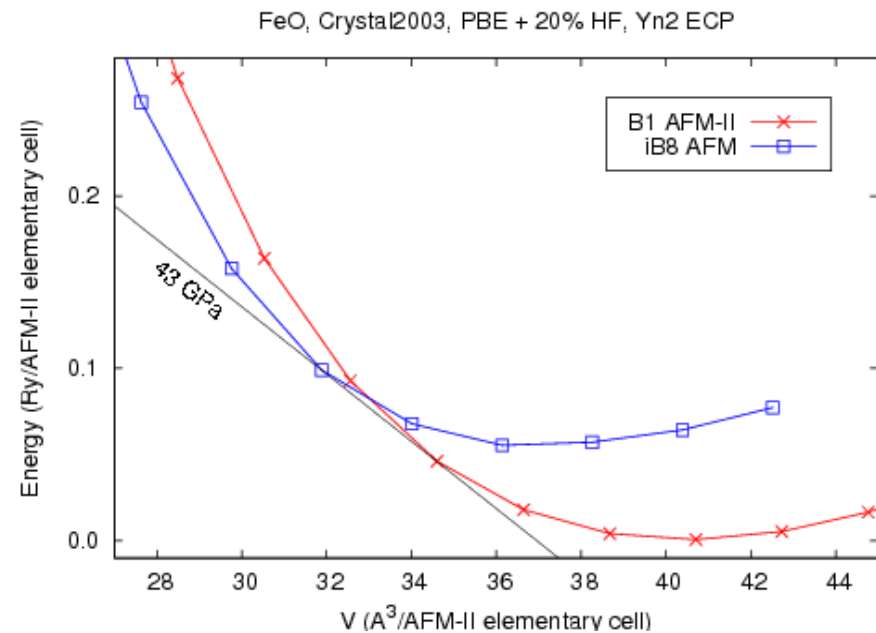
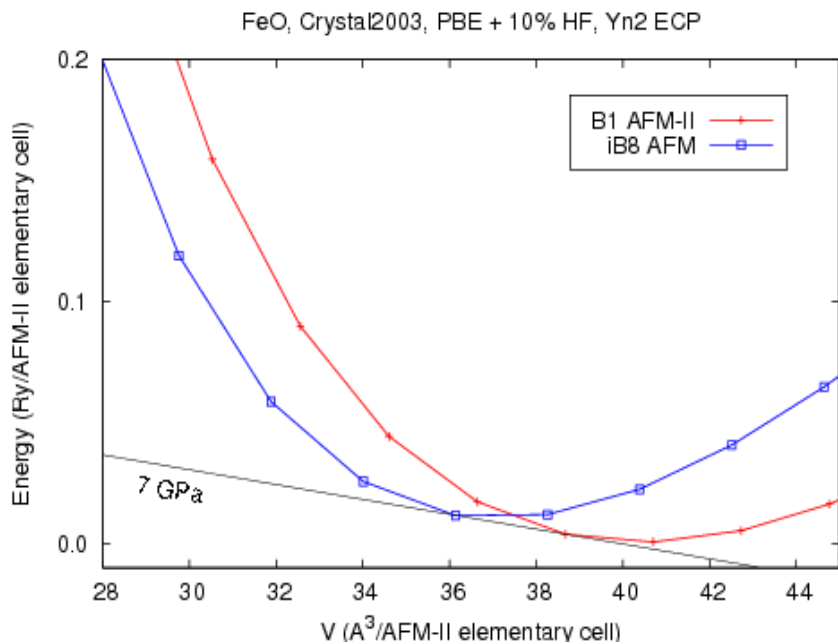


iB8/AFII



# 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



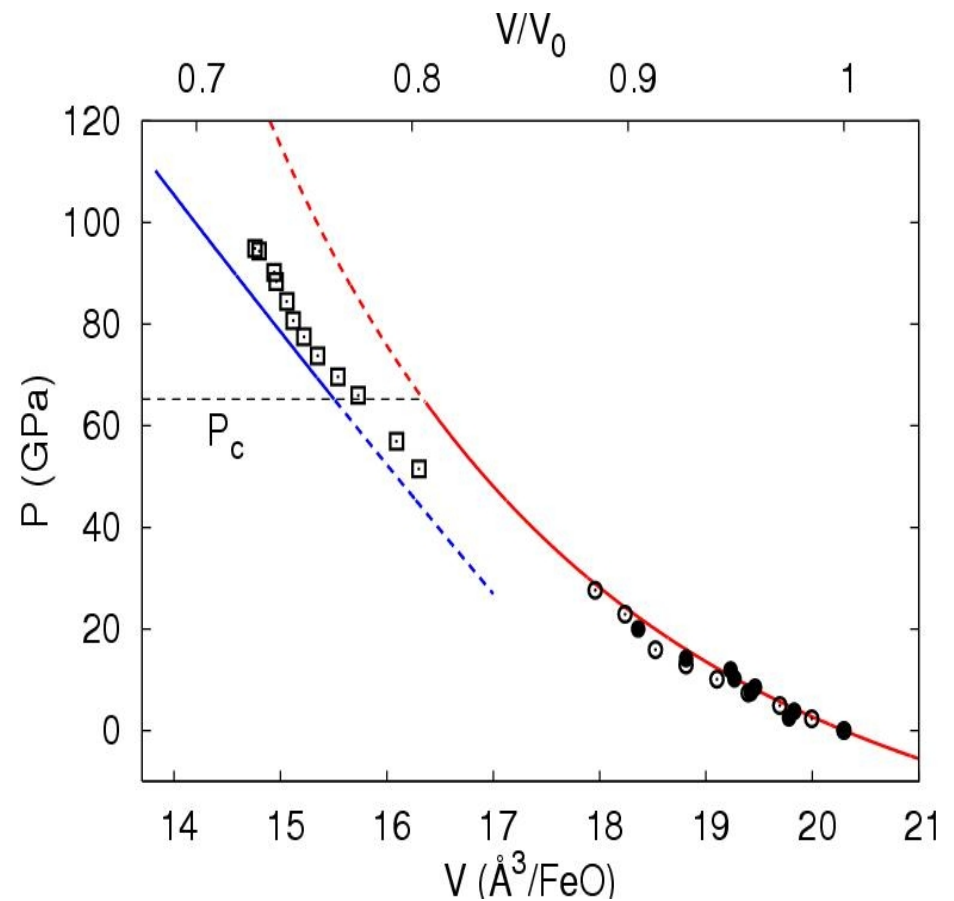
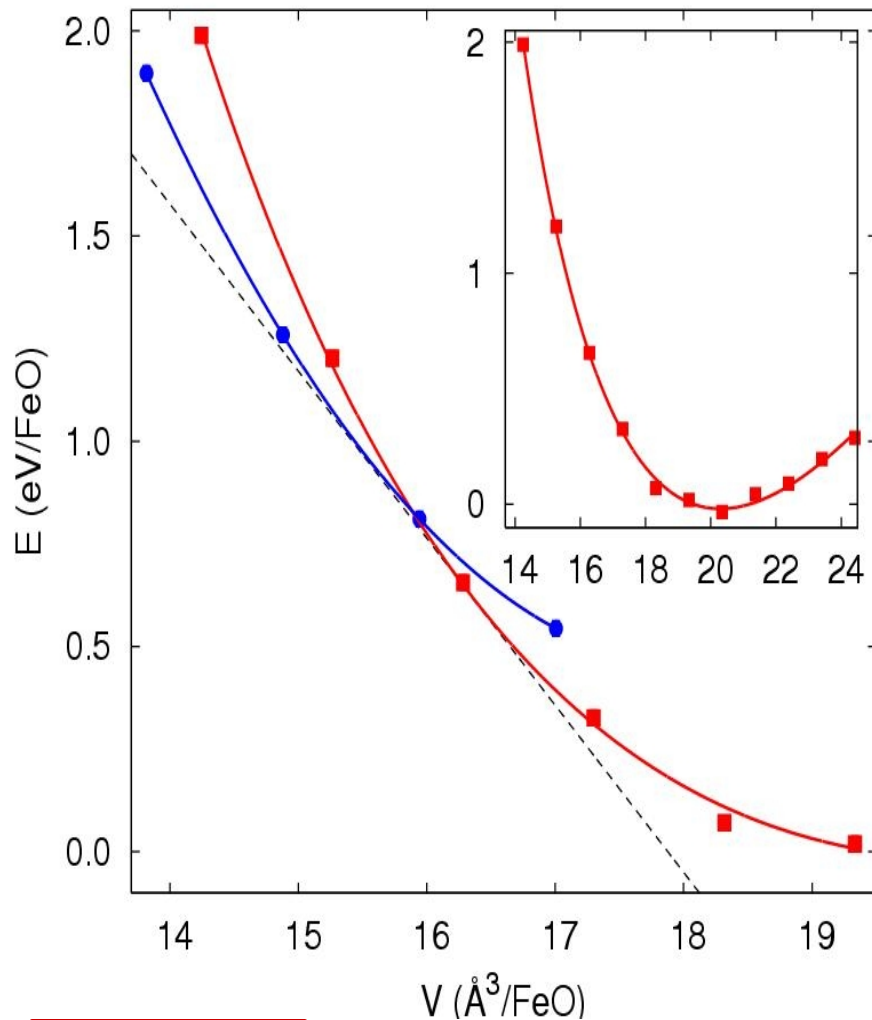
# Comparisons of the FeO solid equilibrium parameters

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

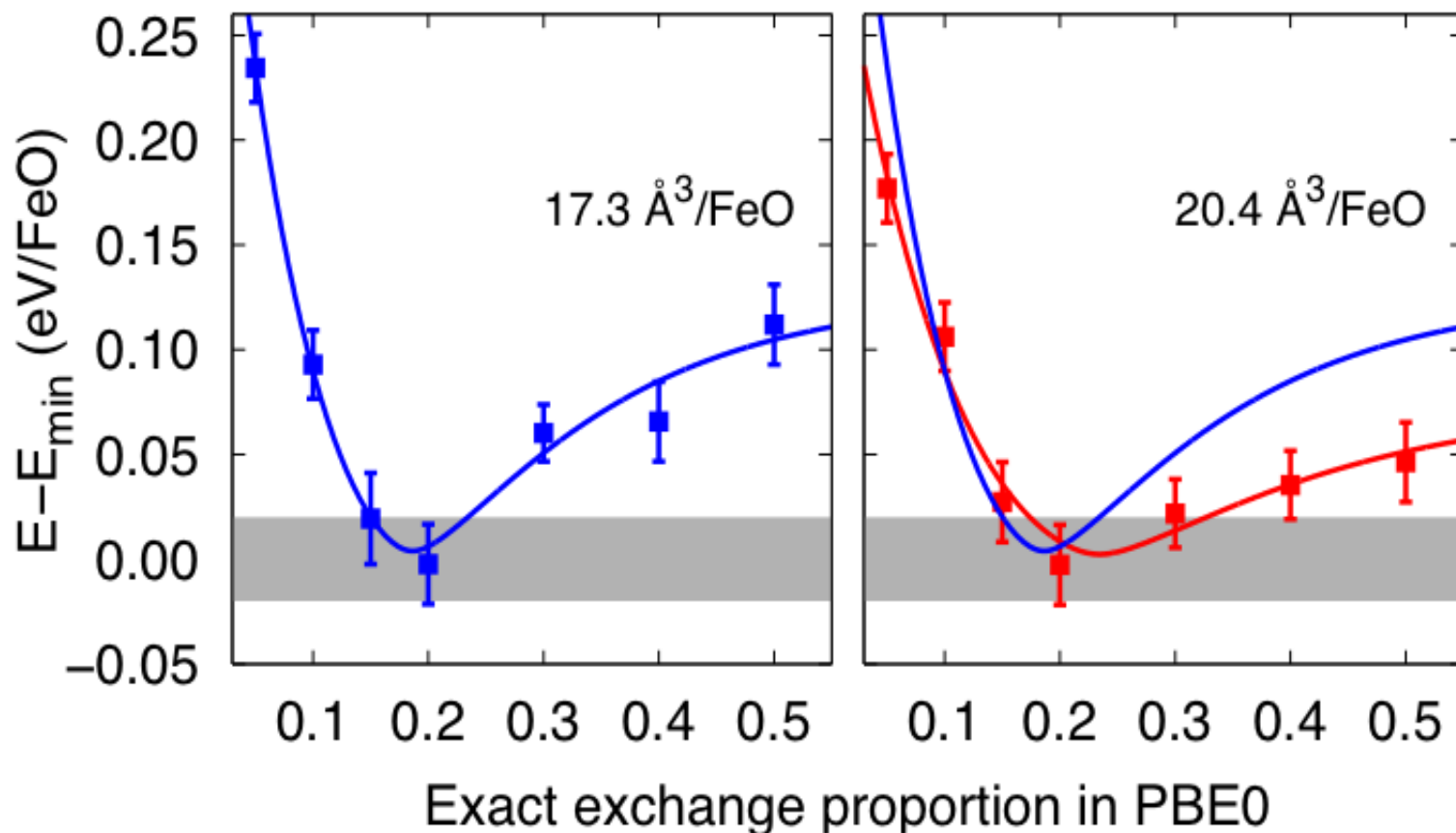


# FeO solid at high pressures

QMC shows transition at  $\sim 65$  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”

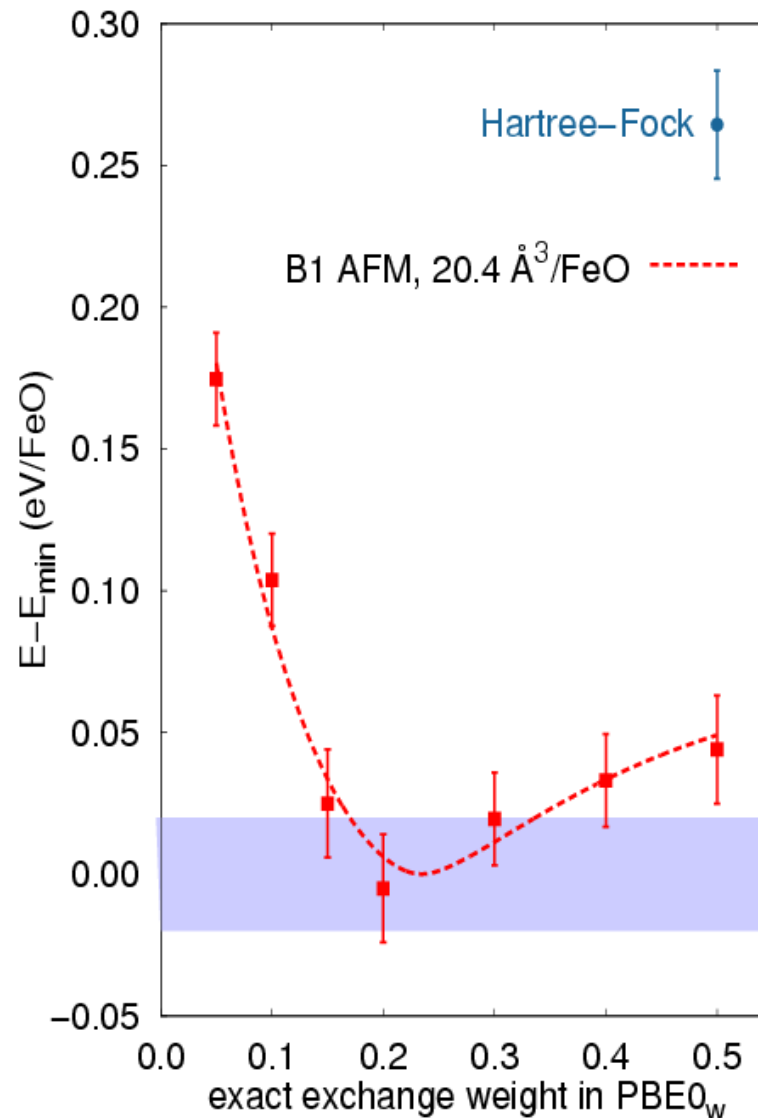
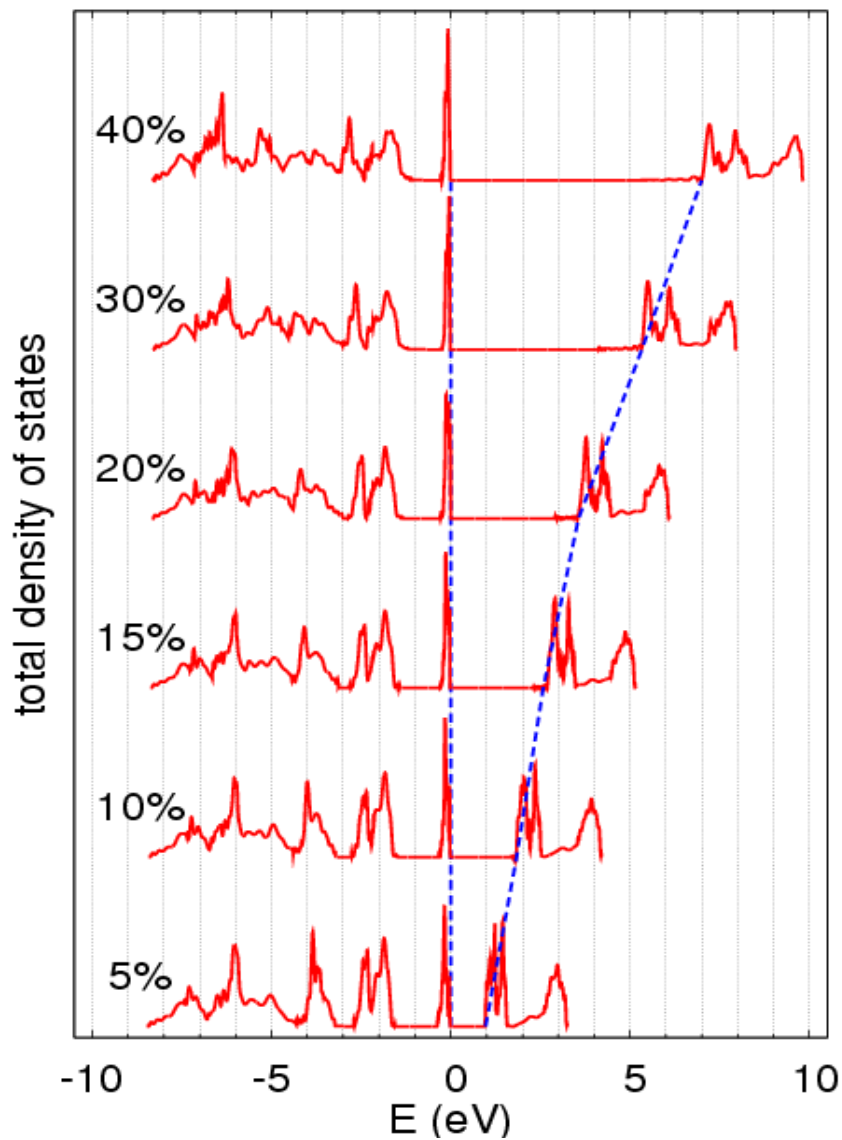
**Note: variational FNDMC optimization of the DFT functional!**

# 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:

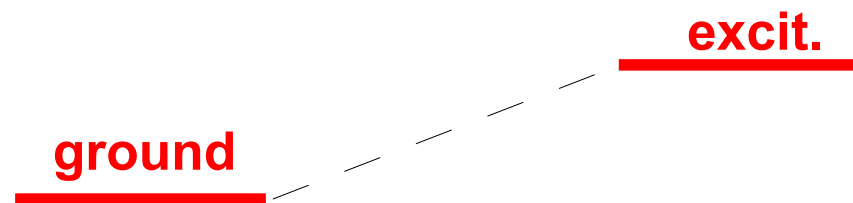
$$\psi_I = \det[1s, 2s, 3s]$$

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

non-interacting

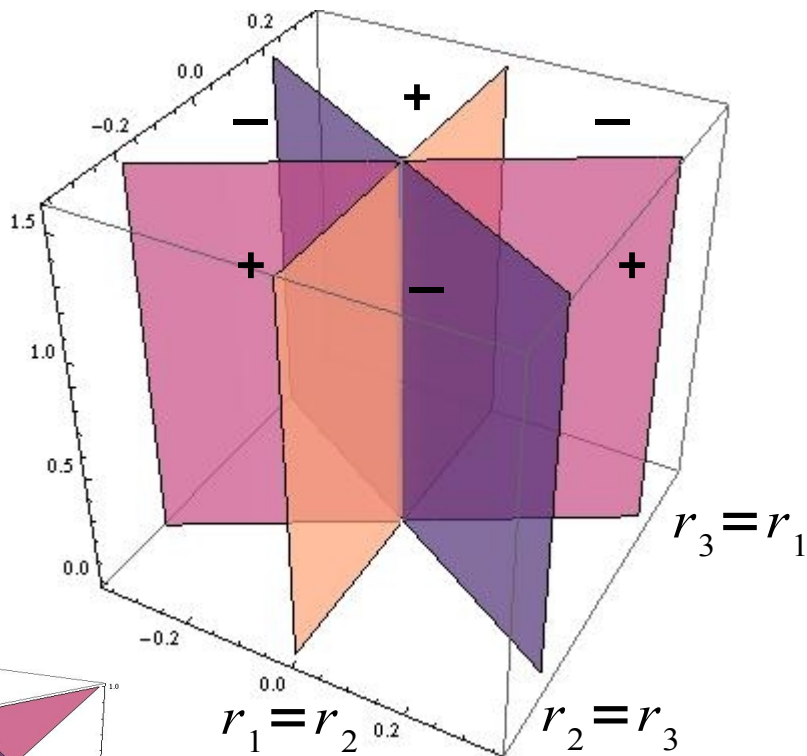


Interaction -> states split (already in HF)



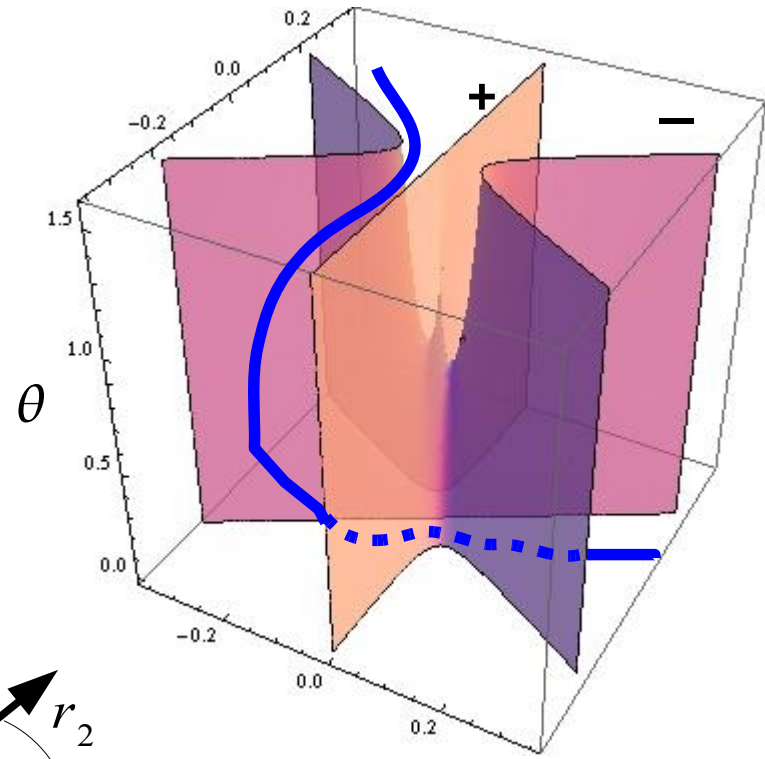
$^4S(1s2s3s)$  HF node:  $(r_1 - r_2)(r_2 - r_3)(r_3 - r_1) = 0 \rightarrow 6$  domains (quasi 1D!)

# 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)
- $\psi_{HF}$  is a special case of  $\psi_{PF}$

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

**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

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

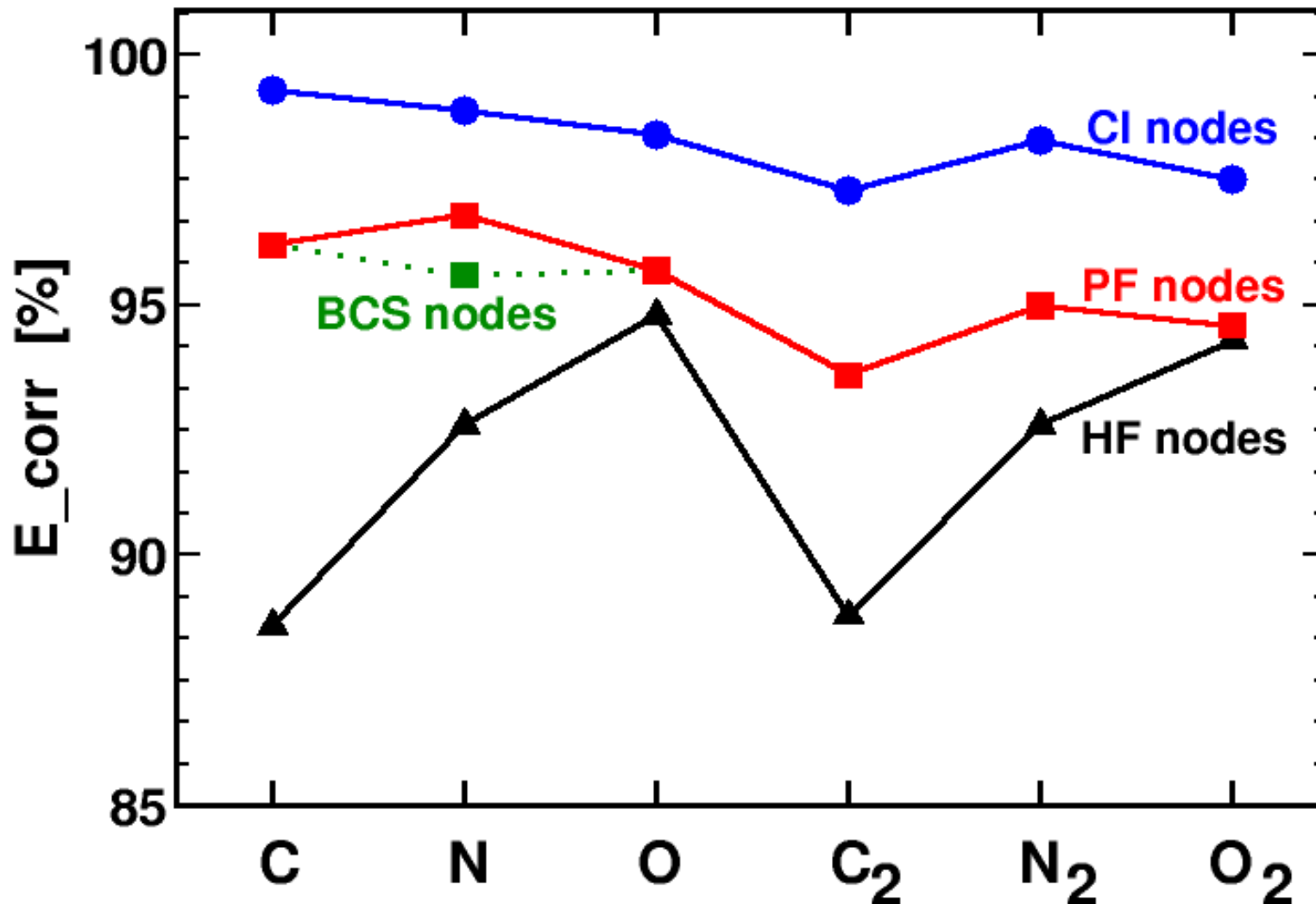
- unpaired

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

**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
<b>DMC/MPF</b>	<b>3</b>	<b>98.9</b>	<b>5</b>	<b>98.4</b>	<b>11</b>	<b>97.2</b>
<b>DMC/CI</b>	<b>98</b>	<b>99.3</b>	<b>85</b>	<b>98.9</b>	<b>136</b>	<b>98.4</b>

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

**Pfaffians describe nodes more efficiently**

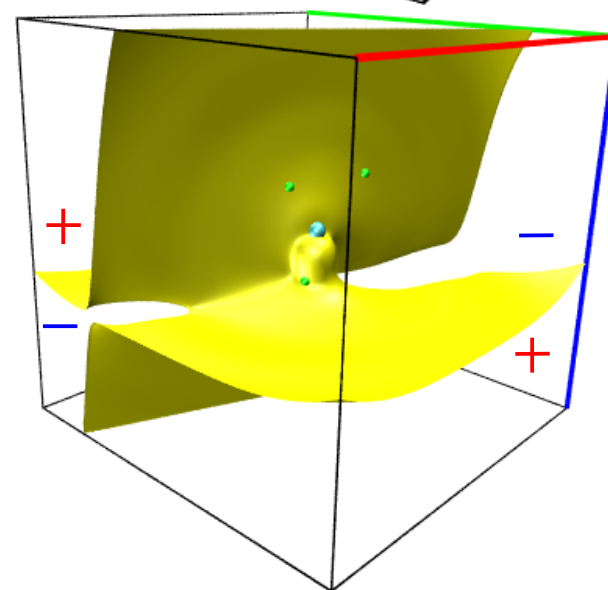
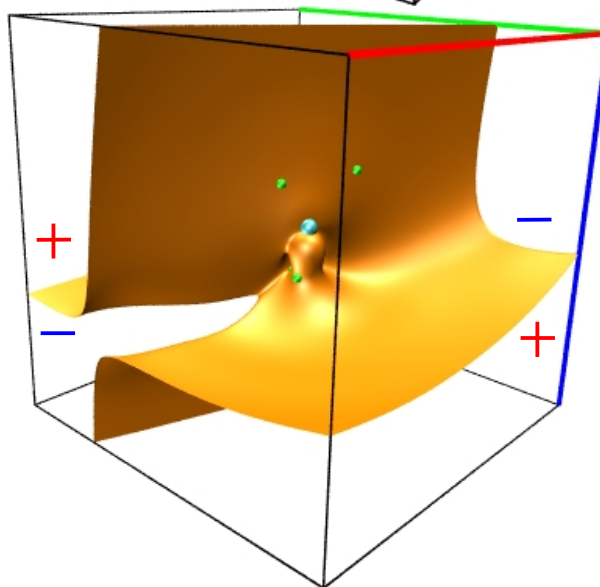
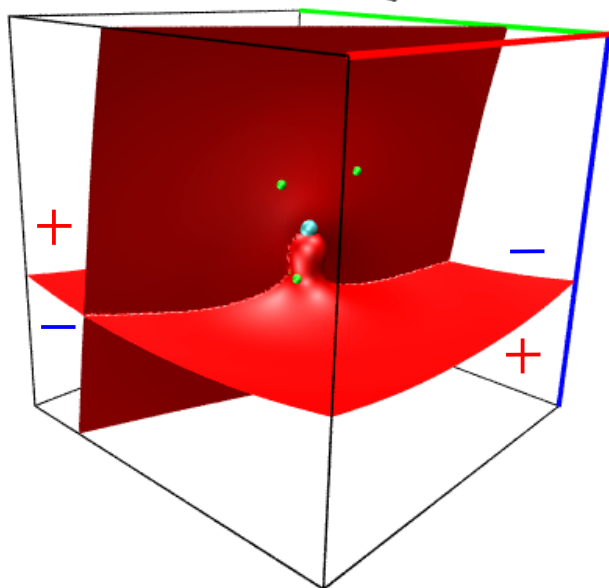
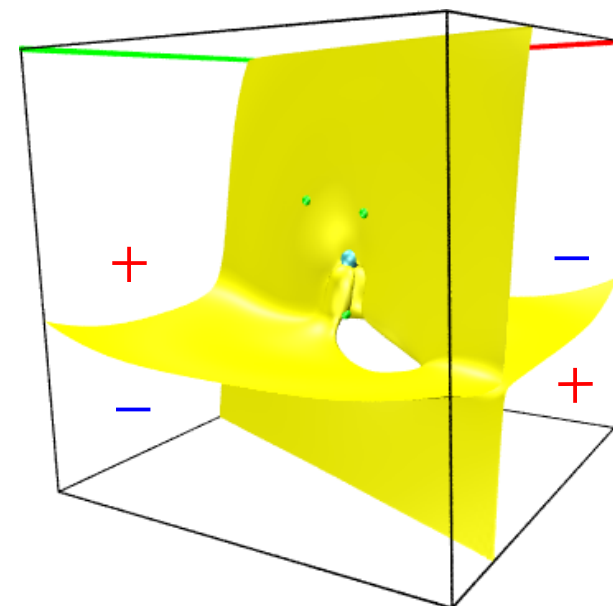
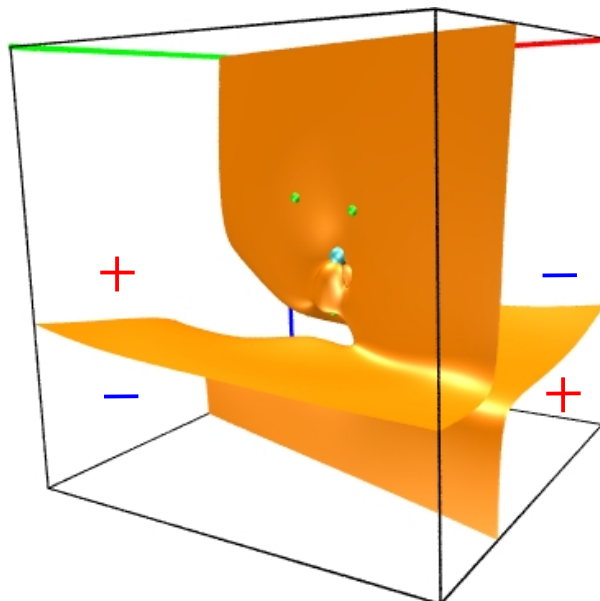
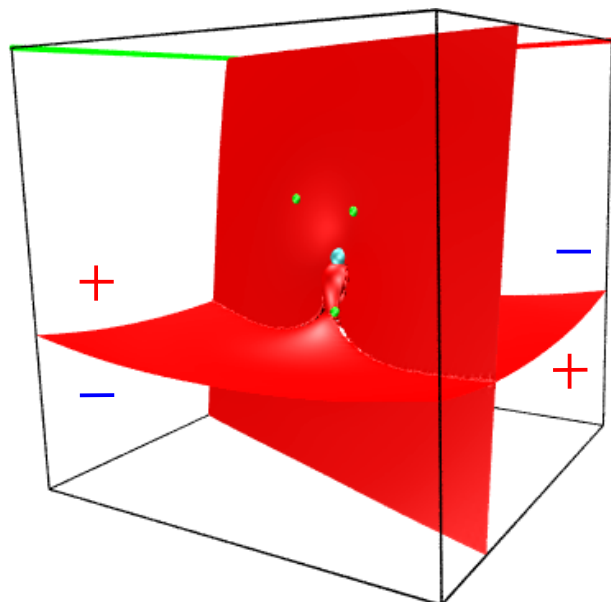


**Nodes of different wfs (%E\_corr in DMC):  
oxygen atom wf scanned by 2e- singlet  
(projection into 3D -> node subset)**

**HF** (94.0(2)%)

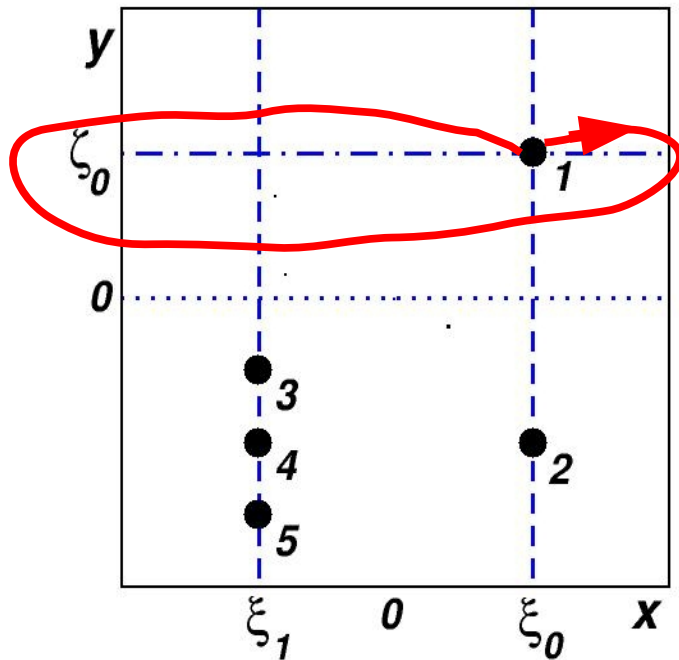
**MPF** (97.4(1)%)

**CI** (99.8(3)%)

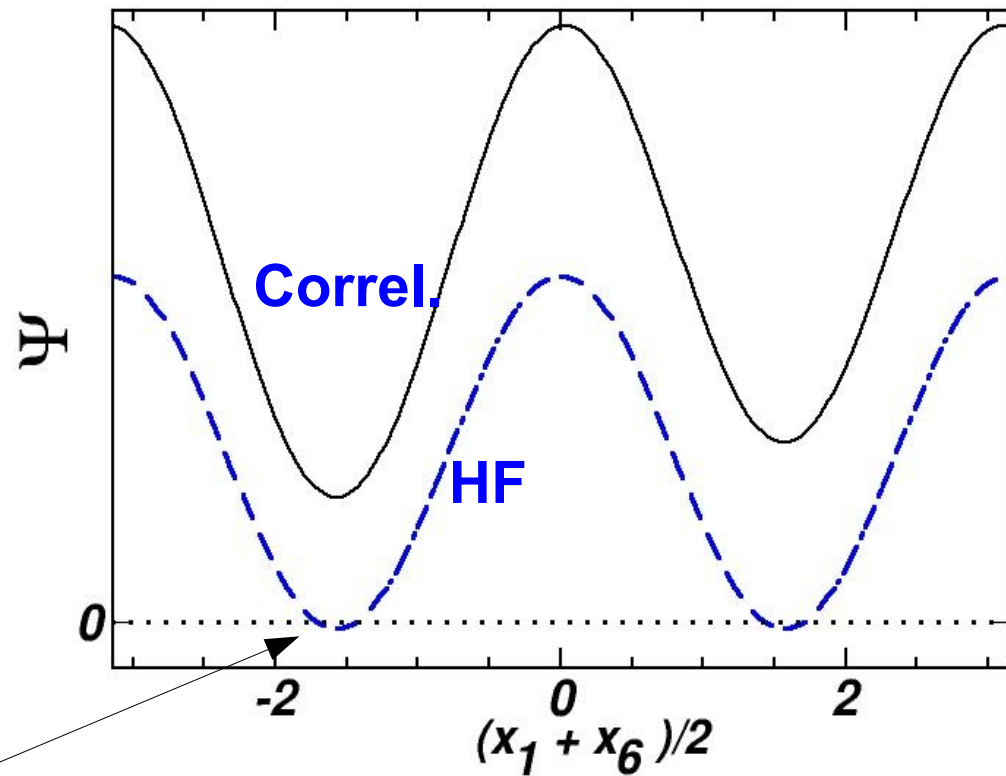


# Correlated nodes in homogeneous electron gas: singlet pair of e- winds around the box without crossing the node

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



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**

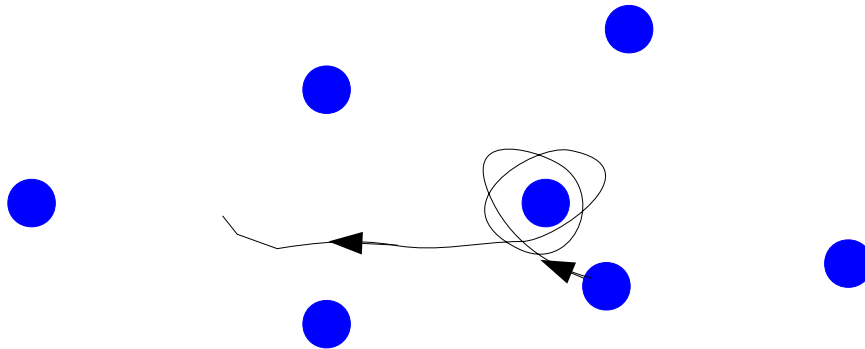
$$1/a > 0$$

**BEC of covalently bonded molecules**

$$1/a = 0$$

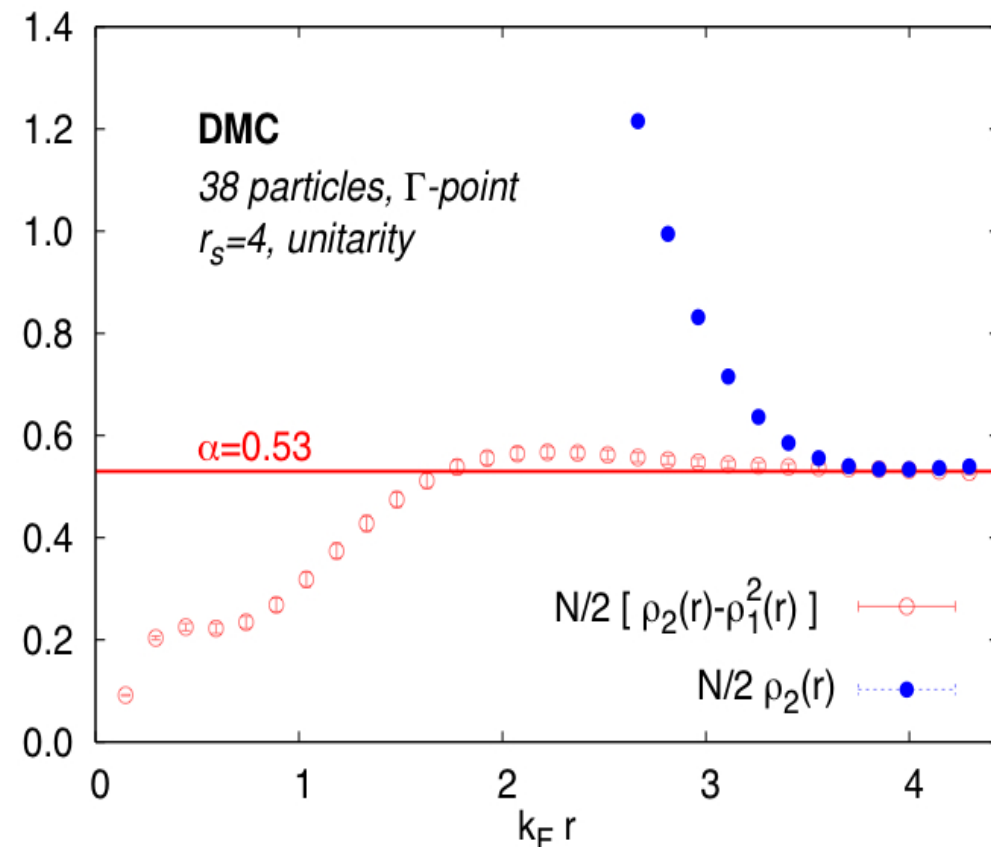
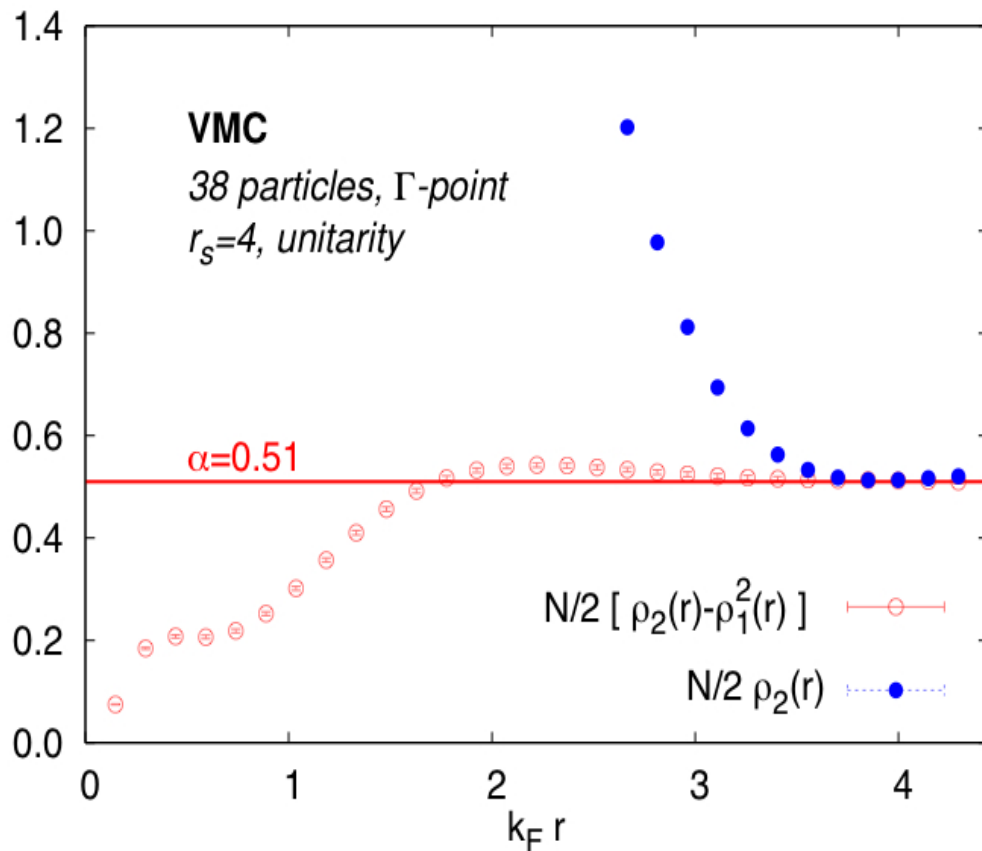
**unitary limit  $\rightarrow$  the only scale is the density, like a mathematical model (Bertsch limit)**

**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**



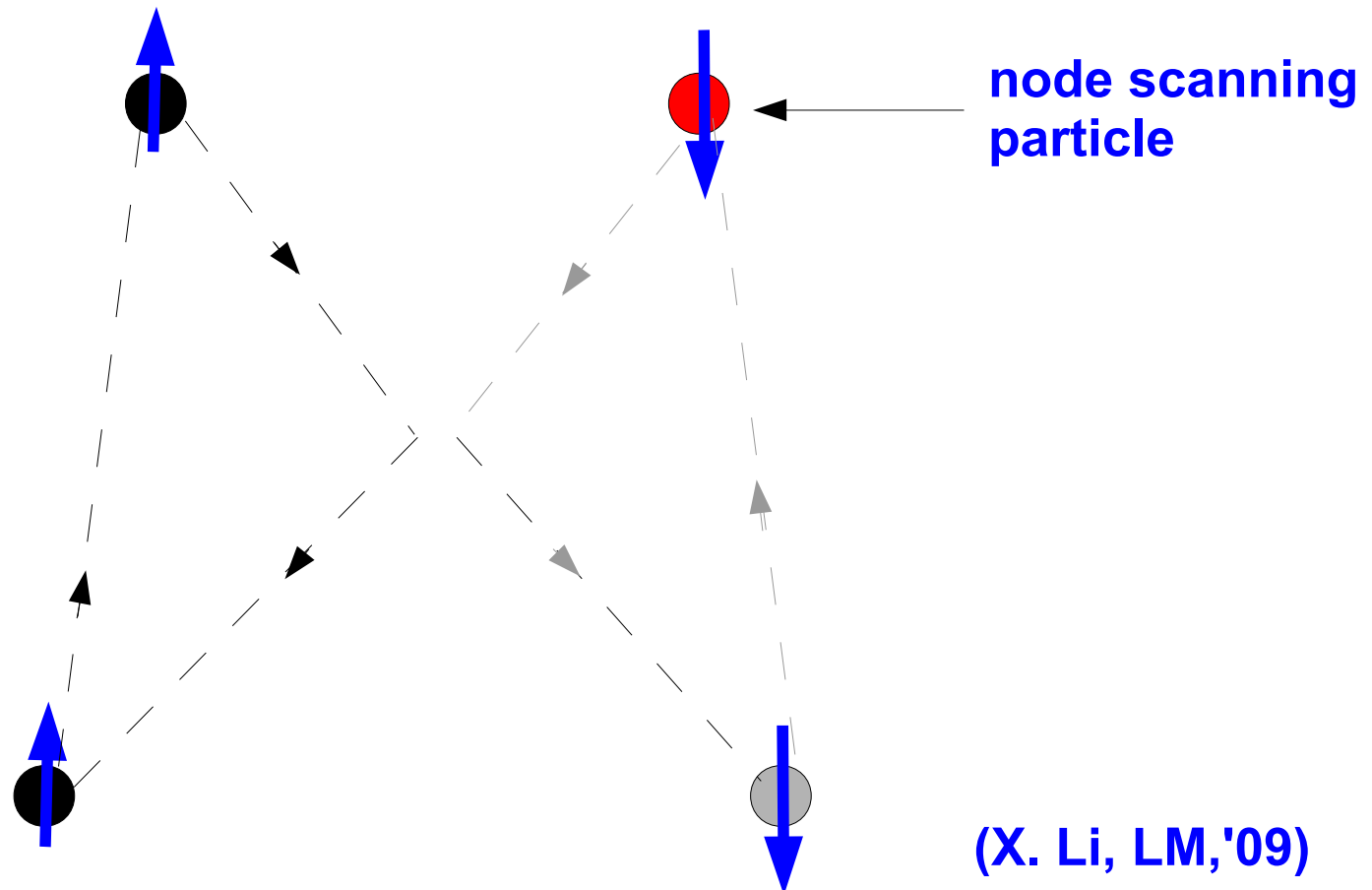
**Unitary limit: seemingly a weakly interacting system**  
**Opposite is true: strongly interacting regime, large amount of condensate (BEC  $\leftrightarrow$  unitary  $\leftrightarrow$  BCS)**

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

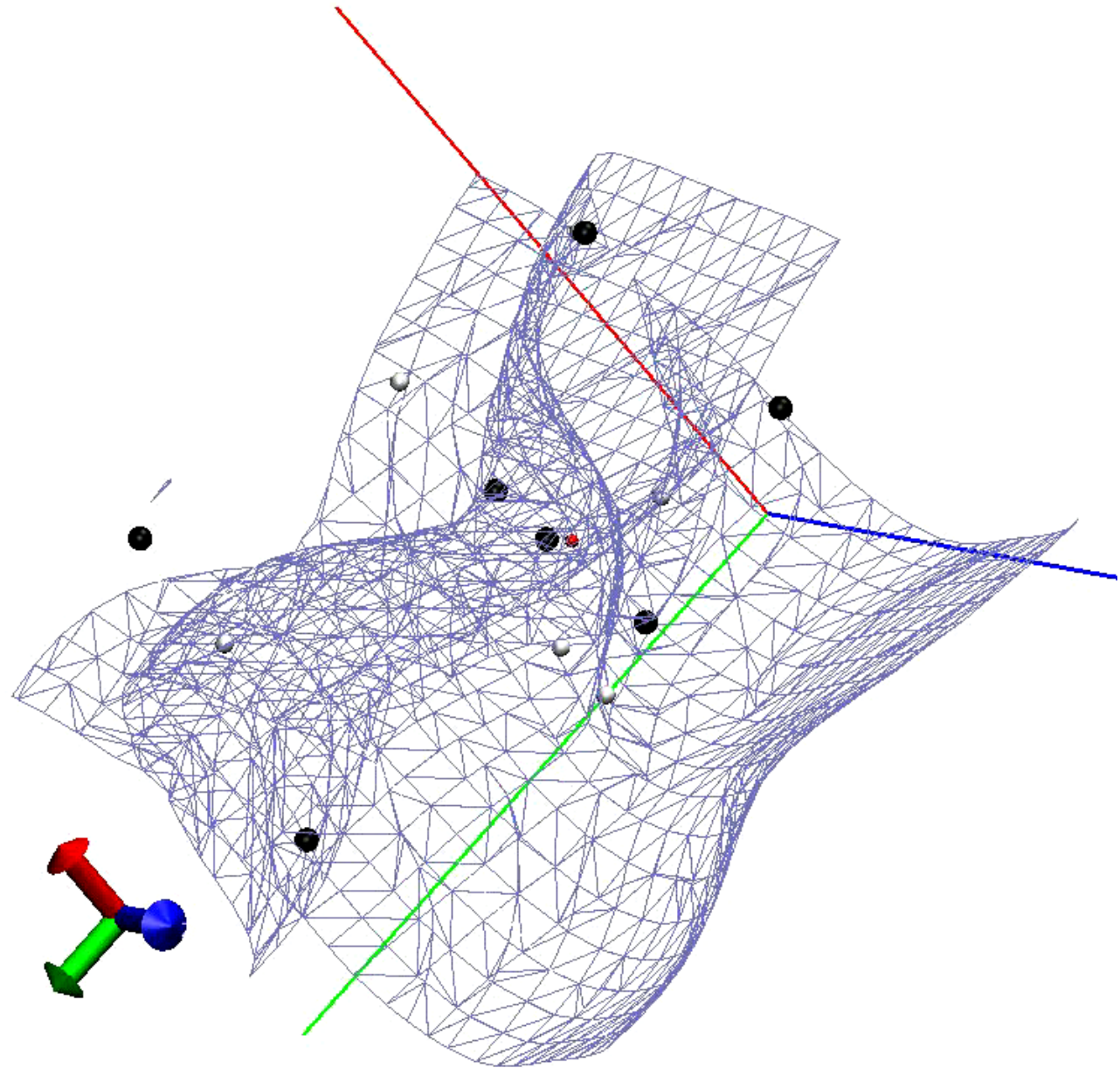


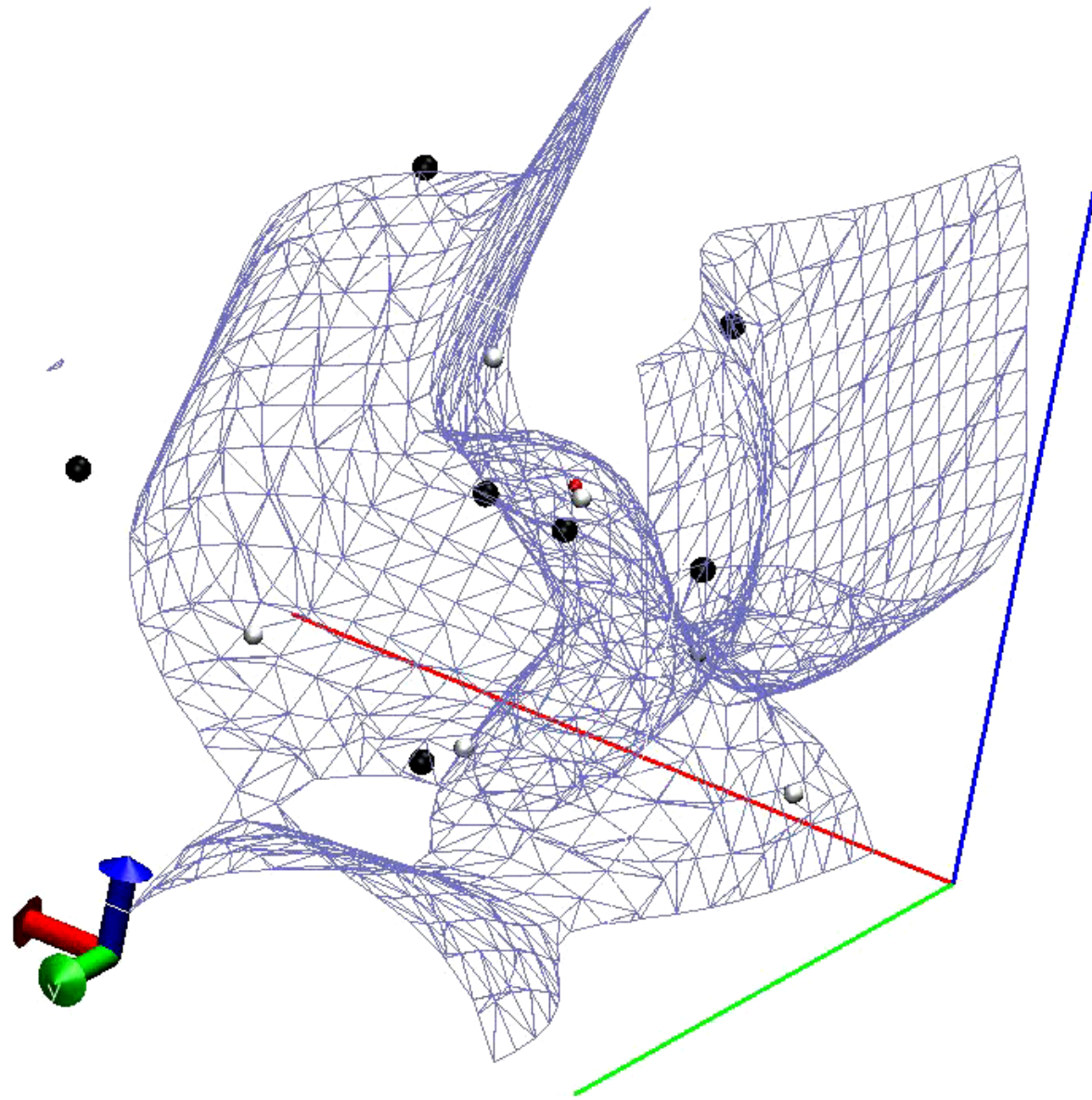
# The four particle exchange: illustration of pair exchange without node crossing

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



I.





# Another type of wavefunction with improved nodes: backflow coordinates

Improve the Slater-Jastrow wf.

$$\exp(-\tau H) \psi_T \approx \psi_T - \tau H \psi_T$$

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

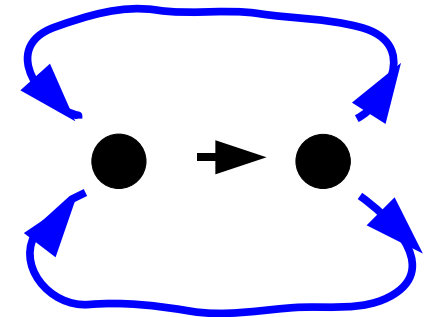
**“spurious” term**

$$|\nabla \det[.]| \gg |\nabla e^{U_{corr}}|$$

-> strongly inhomogeneous -> excitations  
(CI, pfaffians) cancel out the spurious terms

$$|\nabla \det[.]| \ll |\nabla e^{U_{corr}}|$$

-> backflow terms are effective  
(homogeneous systems)

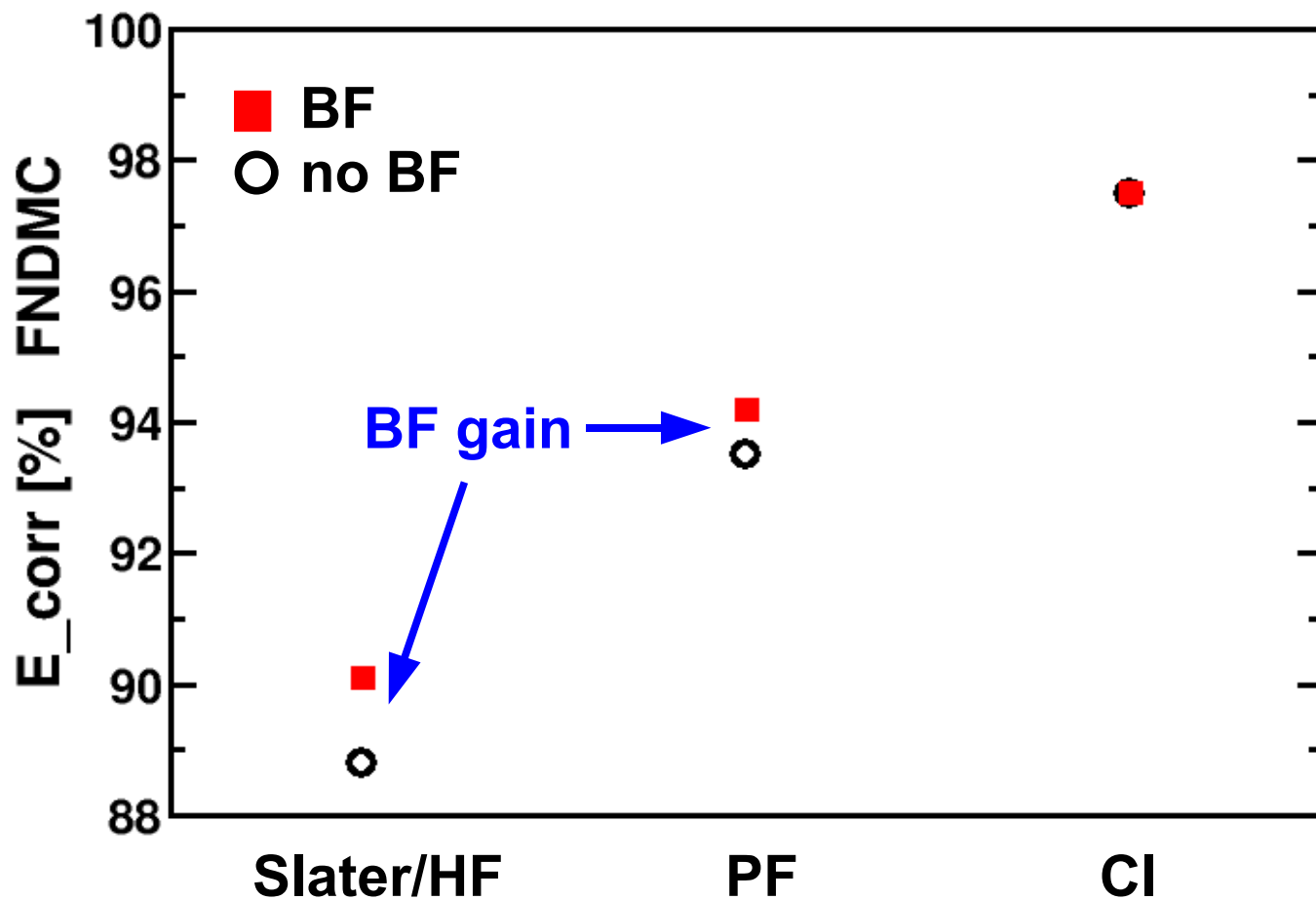


$$\vec{x}_i = \vec{r}_i + \sum_{i < j} \gamma_{ij}(r_{ij}) \vec{r}_{ij}$$

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



# FNDMC correlation energies of C<sub>2</sub> 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  $E_{\text{tot}}$
- correlation:  $\sim 3\%$  of  $E_{\text{tot}}$

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

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  $\partial N$

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  $\psi^2$  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](http://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)

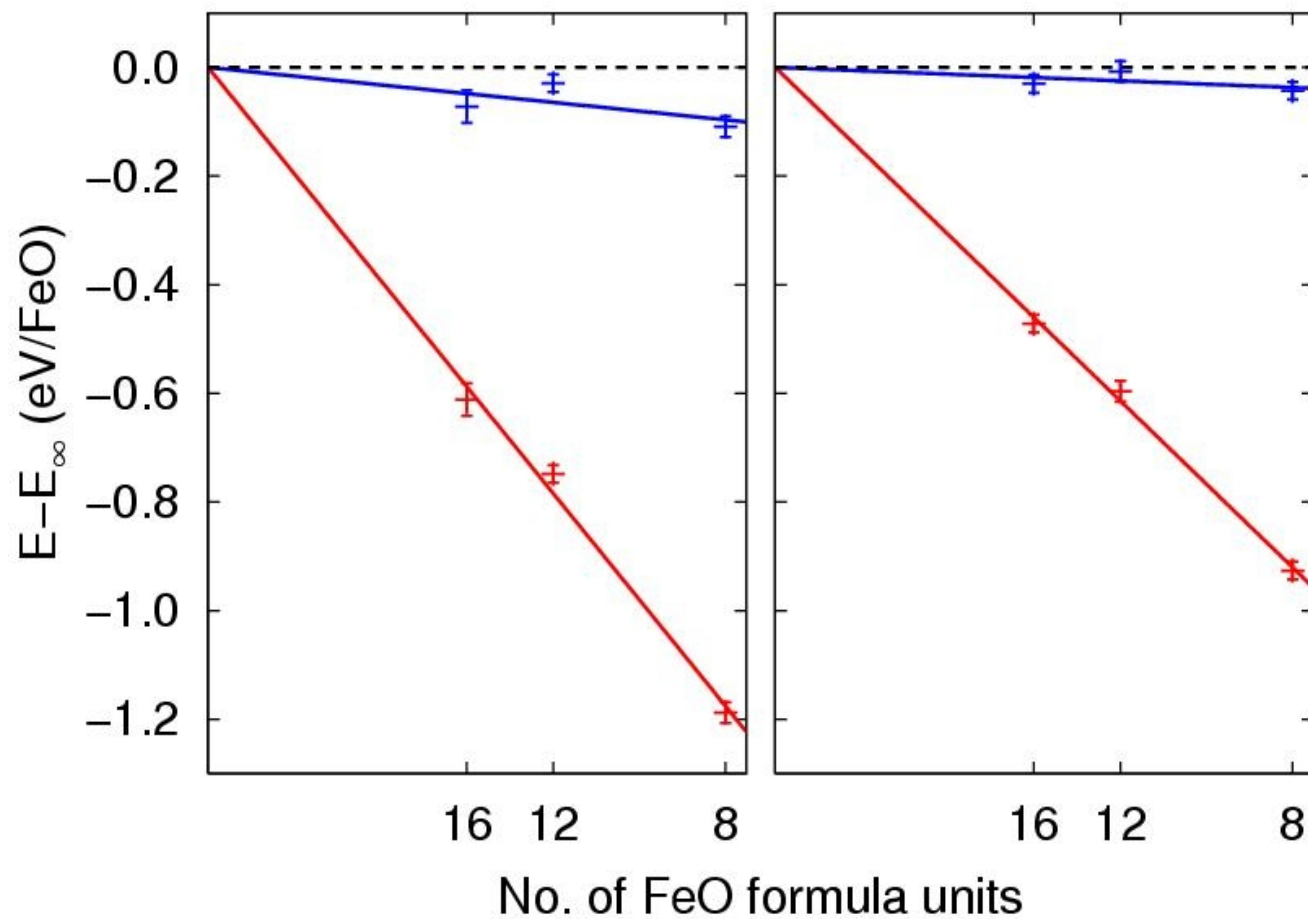
**Spins:** as a quantum dynamical variables, spin-orbit interactions

# Open Source QMC code QWalk (“Quantum Walk”)

[www.qwalk.org](http://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

