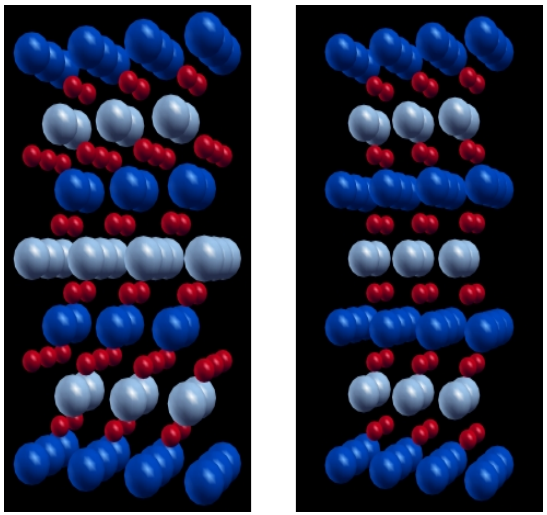
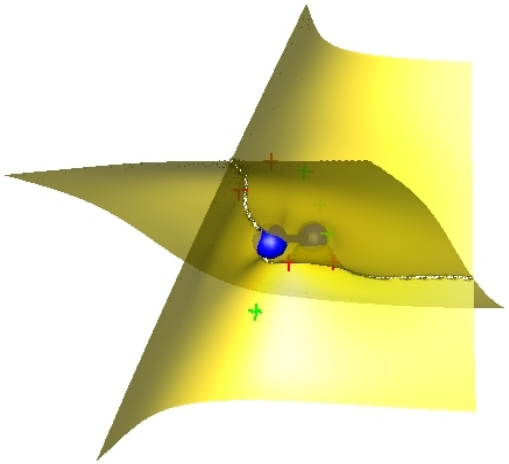
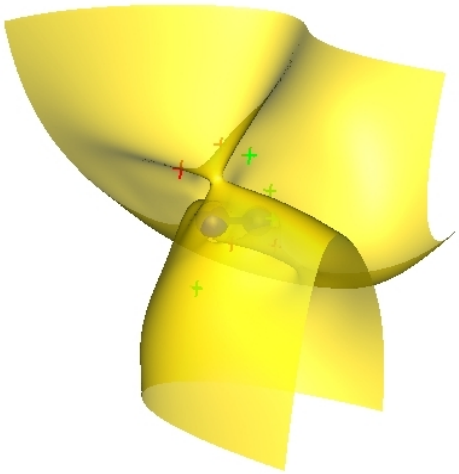
Quantum Monte Carlo: introduction







J. Kolorenc, M. Bajdich, S. Hu, S. Guo, M. Zhu, X. Li, K. Rasch, M. Kostolny, L. Horvathova, R. Derian, I. Stich,

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Method, in a nutshell

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Project out the ground state → imaginary time Schrodinger eq. (Fermi 1933)

$$\psi(\boldsymbol{R},t)=\exp(-tH)\psi_T(\boldsymbol{R}) \quad \rightarrow \quad \psi(\boldsymbol{R},t\rightarrow\infty) \propto \phi_0(\boldsymbol{R})$$

projector in parameter t

trial wave function

ground state of given symm.

H → interacting quantum particles, eg, electrons + ions

$\boldsymbol{R}=(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ → 3N-dim. continuous space

Projection/evolution equation → Euclidian/imaginary time Sch. eq.

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

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

Green's function $G(\boldsymbol{R},\boldsymbol{R}',\tau)=\langle \boldsymbol{R}|\exp(-\tau H)|\boldsymbol{R}'\rangle$ **→ transition probability**

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Stochastic method for solving the evolution

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

Map it onto an equivalent stochastic process:

Value of the wavefunction ↔ density of sampling points in 3N-space

$$\psi(\boldsymbol{R}, t) \;=\; dens\left[\sum_i^{walkers} \delta(\boldsymbol{R} - \boldsymbol{R}_i(t))\right] + \epsilon_{statistical}$$

sampling points → "walkers" → eigenstates of position operator

Solution: take short-time approx. to $G(\boldsymbol{R}, \boldsymbol{R}', \tau)$ and iterate

Essentially: Feynman path integrals in Euclidean time

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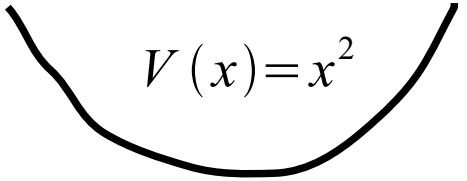
Toy model: 1D harmonic oscillator

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



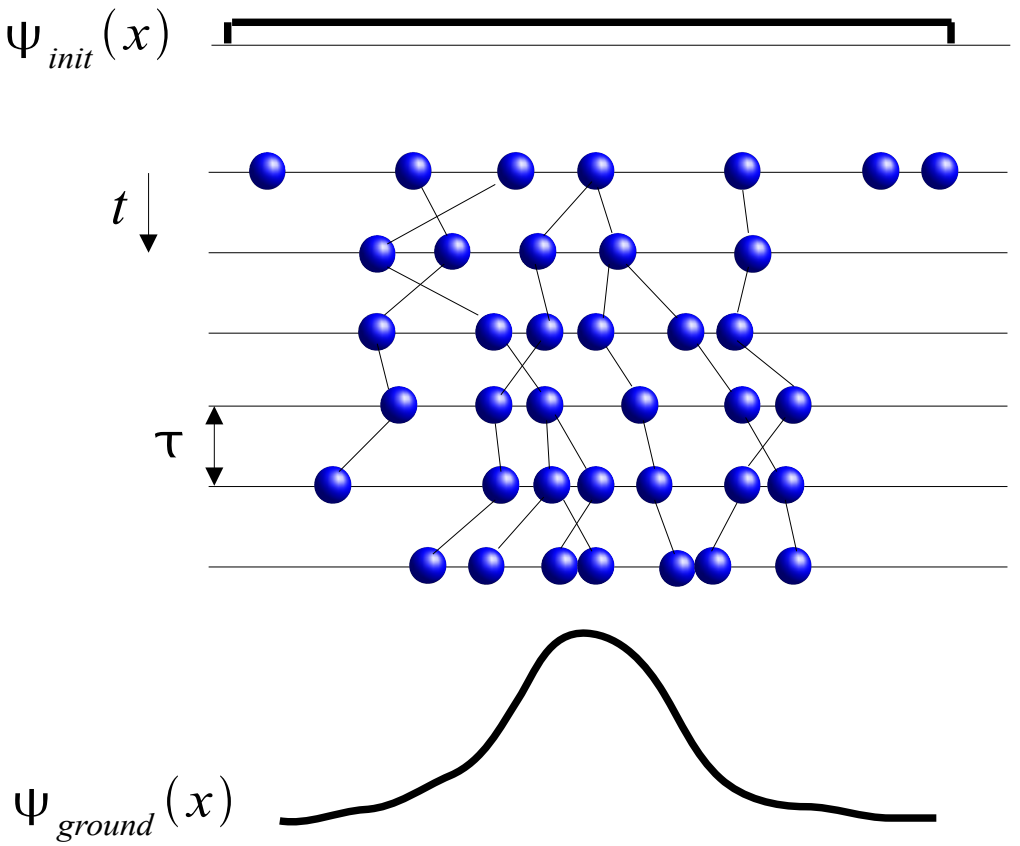
Propagator

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

$$\downarrow$$

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

diffusion **weight**



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Sign problem: fermionic wave functions are both + and -

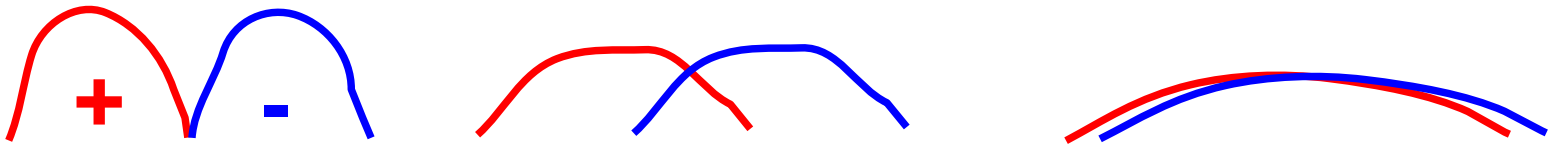
Naïve approach: decompose to + and -

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

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

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

However, + and - components are independent (linearity of Sch. eq.) → both components converge to the lowest energy solution → bosonic !



$$lim_{t\to\infty}\,\Psi^+(\boldsymbol{R},t) - lim_{t\to\infty}\,\Psi^-(\boldsymbol{R},t) \;\propto\; \exp\left[-(E_{Fermionic} - E_{Bosonic})\,t\right]$$

Fermionic "signal" decays exponentially quickly into a bosonic "noise"

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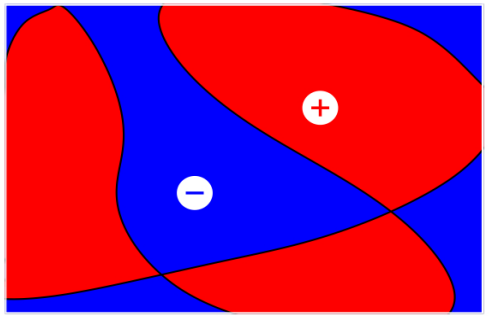
Solution: impose a constraint → fixed-node approximation diffusion Monte Carlo (FNDMC)

Fixed-node (FN) approximation:

$$sign[\phi(\boldsymbol{R},t)] \stackrel{!}{=} sign[\psi_T(\boldsymbol{R})]$$



Then the product is nonnegative: $\psi_T(\boldsymbol{R})\phi(\boldsymbol{R},t)=f(\boldsymbol{R},t)>0$

Modify the Schr. eq. accordingly: $f(\boldsymbol{R},t+\tau)=\int G^*(\boldsymbol{R},\boldsymbol{R}',\tau)f(\boldsymbol{R}',t)d\boldsymbol{R}'$

The projection $f(\boldsymbol{R},t\to\infty) \propto \psi_T(\boldsymbol{R})\phi_{ground}(\boldsymbol{R})$ **now depends on**

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

Clearly, the node divides the configuration space into + and – domains.

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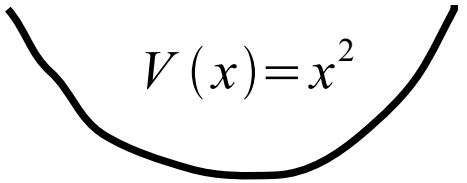
Fermion node toy model: excited state of harmonic oscillator

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



Propagator

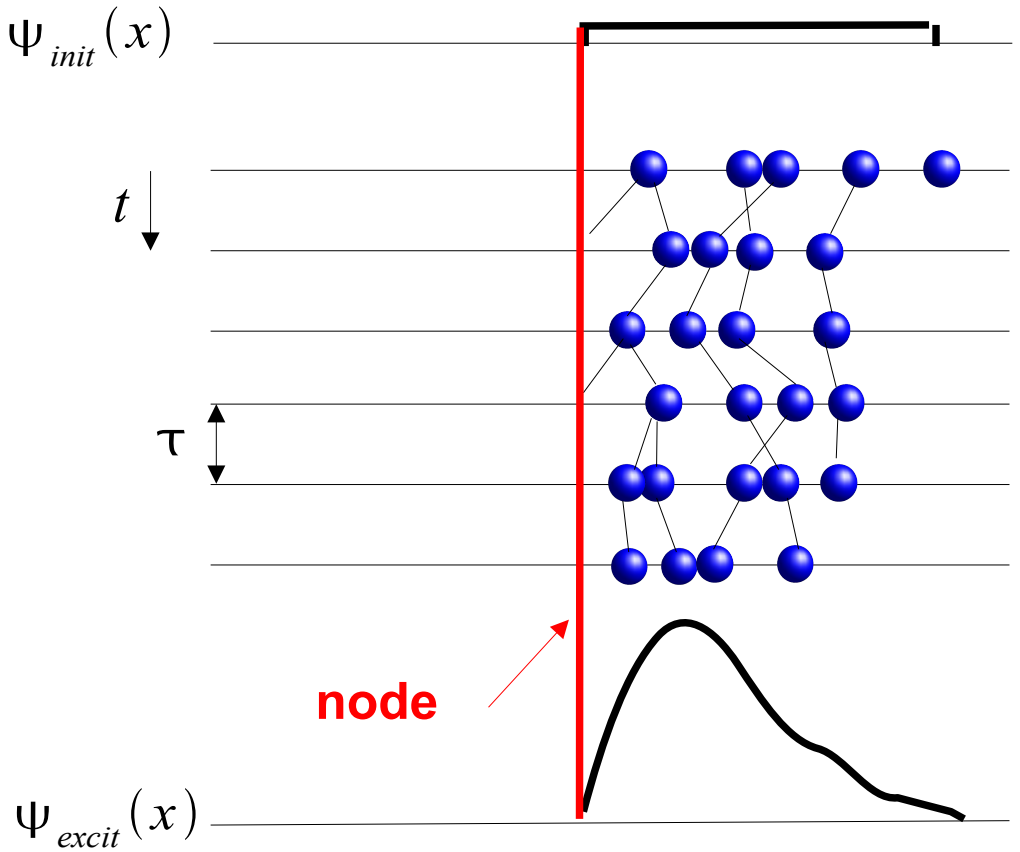
$$G(x, x', \tau)$$

$$\downarrow$$

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

diffusion **renorm**

+ node (boundary cond.)



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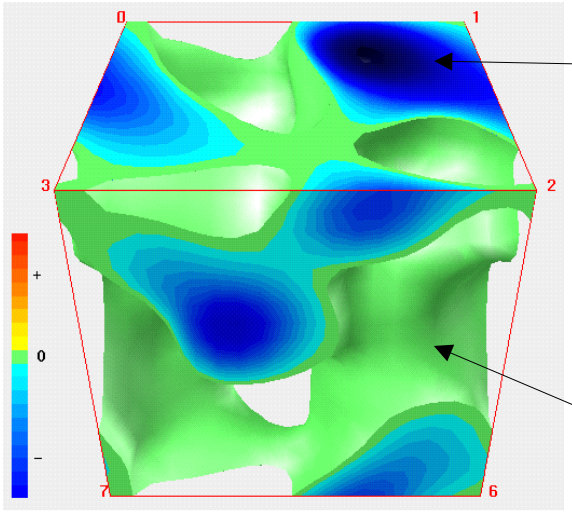
Fixed-node approximation and fermion nodes

- antisymmetry (nonlocal) replaced by a boundary (local) → boundaries are easy to enforce

- exact node implies recovering exact energy (in polynomial time)



wave function value

3D subset of 59-dim. node

- exact nodes generally unknown, however, approximate nodes suprisingly accurate (and systematically improvable)

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QMC calculations: basic steps

Hamiltonian: - often valence e- only, using pseudopots/ECPs
- explicit e-e interactions, full many-many body

Trial wave functions:

- correct symmetries
- sampling efficiency
- capture the physics

Commonly used correlated Slater-Jastrow type:

$$\psi_{Trial} = det^{\uparrow}[\{\phi_{\alpha}\}]\, det^{\downarrow}[\{\phi_{\beta}\}] \exp[U_{corr}]$$

or

$$\psi_{Trial} = \sum_k c_k\, det_k^{\uparrow}[\{\phi_{\alpha}\}]\, det_k^{\downarrow}[\{\phi_{\beta}\}] \exp[U_{corr}]$$

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QMC calculations: basic steps II

Orbitals $\{\phi_\alpha\},\{\phi_\beta\}$ **from :** - Hartree-Fock, post-HF
- Density Functional Theory, hybrid DFT
- possibly CI (natural orbitals), etc

→ **QMC interfaced with other codes**

Explicit correlations: $U_{corr} = \sum_{i,j} f_{e-e}(r_{ij}) + \sum_{i,I} f_{e-ion}(r_{iI}) + \ldots$

- optimized variationally

$$E_{VMC} = \frac{\int \psi_T^2 [H\psi_T/\psi_T] d\boldsymbol{R}}{\int \psi^2 d\boldsymbol{R}} = \frac{1}{M}\sum_{sample}^{M} \frac{H\psi_T(\boldsymbol{R}_{sample})}{\psi_T(\boldsymbol{R}_{sample})} + \epsilon_{stat}(1/\sqrt{(M)})$$

where the samples are distributed as $\psi_T^2(\boldsymbol{R})$

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QMC calculations: basic steps III

Quantities which do not commute with Hamiltonian are more complicated → DMC produces only mixed estimators

$$\langle A \rangle_{DMC} = \langle \psi_T | A | \psi_{DMC} \rangle$$

Correction:

$$\langle A \rangle \approx 2\langle \psi_T | A | \psi_{DMC} \rangle - \langle \psi_T | A | \psi_T \rangle$$

Methods such as reptation MC sample the square of the wave function but significantly more expensive

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QMC calculations of solids

Solids: periodic supercells

- Coulomb potential energy → Ewald sums

- kinetic energy: sampling of k-points of the supercell Brillouin zone → twist averages

- twist average states are not necessarily periodic with the supercell, neither necessarily real (fixed-node can be generalized to fixed-phase, more on the fixed-phase later)

- thermodynamic limit: finite size corrections (for metals this could be a challenge, eg, for a complicated Fermi surface)

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How does it work ?

Let us look at a few applications

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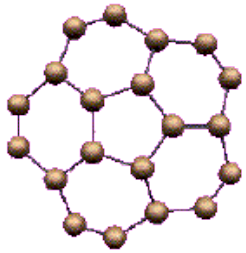
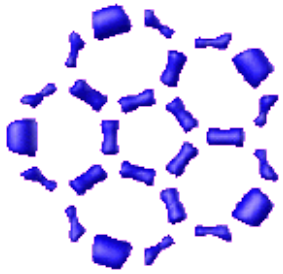
Some history: what is the lowest energy isomer of of C_{20} ???

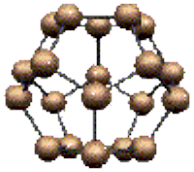
ring

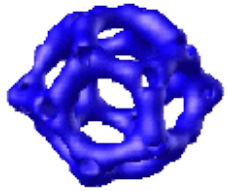
bowl





cage





J.C. Grossman, LM, K. Raghavachari, PRL 75, 3870 (1995)

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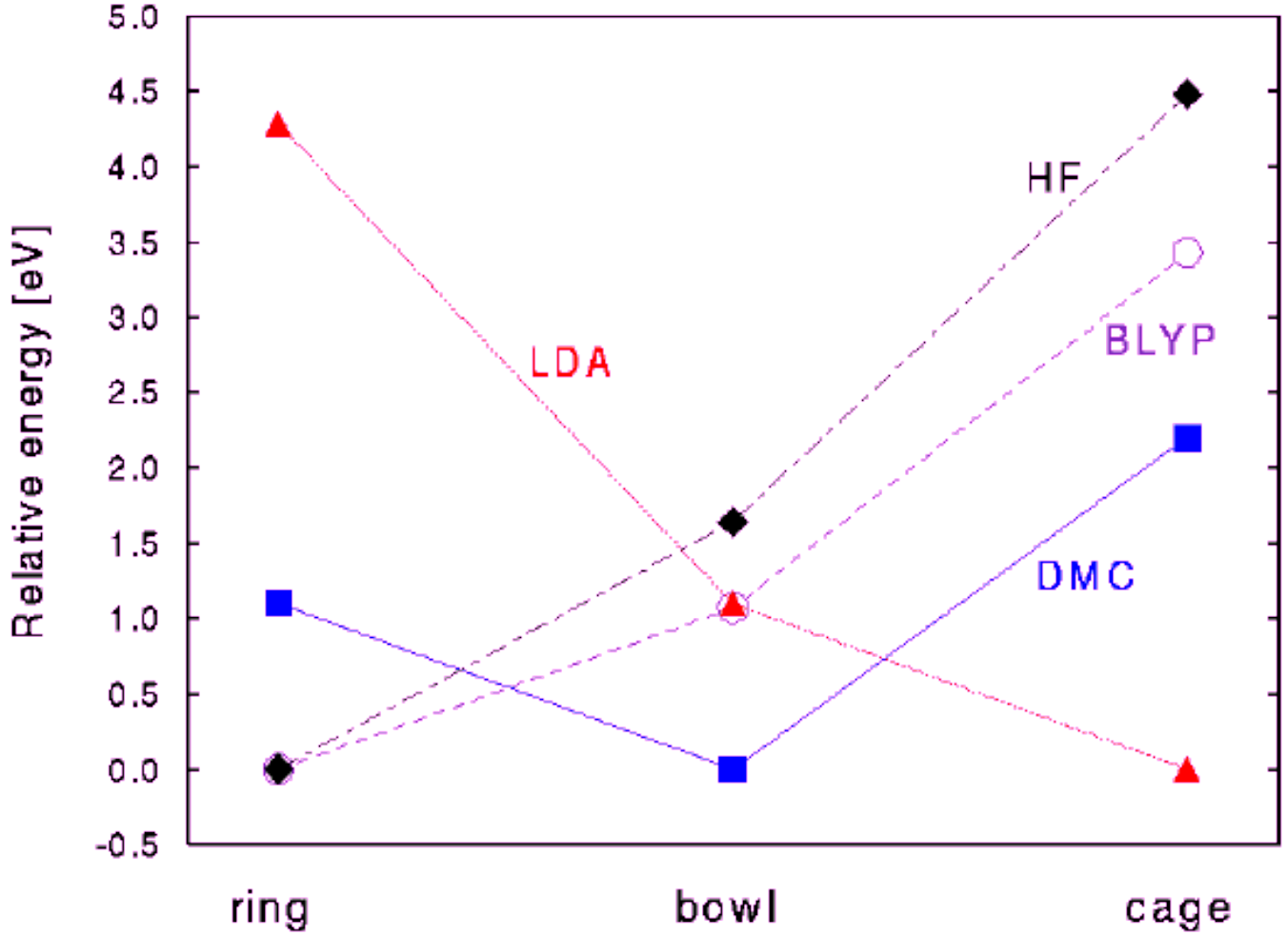
QMC was the first method to predict this (later confirmed by independent methods)



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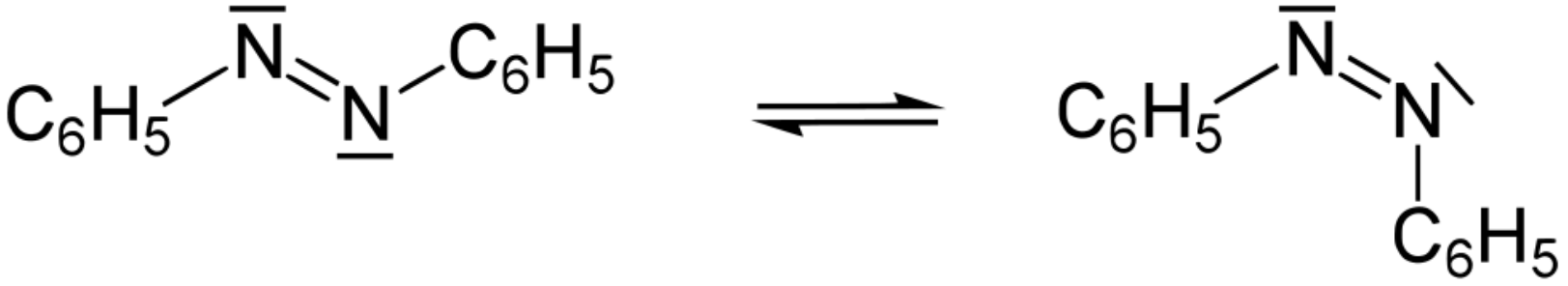
Azobenzene: optically active molecule with photoisomerization



(E) (Z)

M. Kostolny, R. Derian, I. Stich, L.M. 2010

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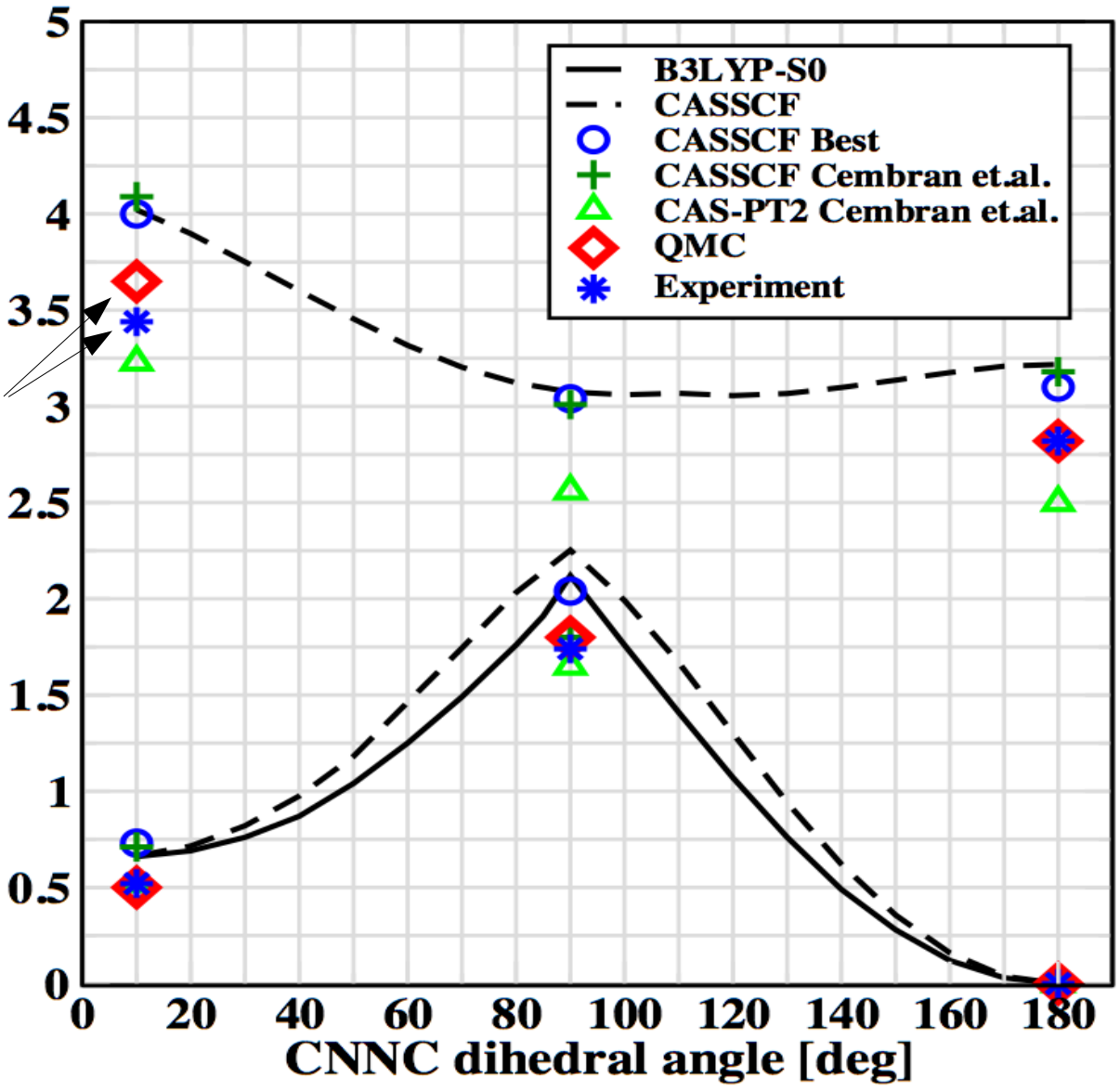
Ground and excited states of azobenzene: ~ 0.04 eV accuracy with FNDMC/multi-det.

Experiment not ok (?)



M. Kostolny, R. Derian, I. Stich, L.M. JCP '10

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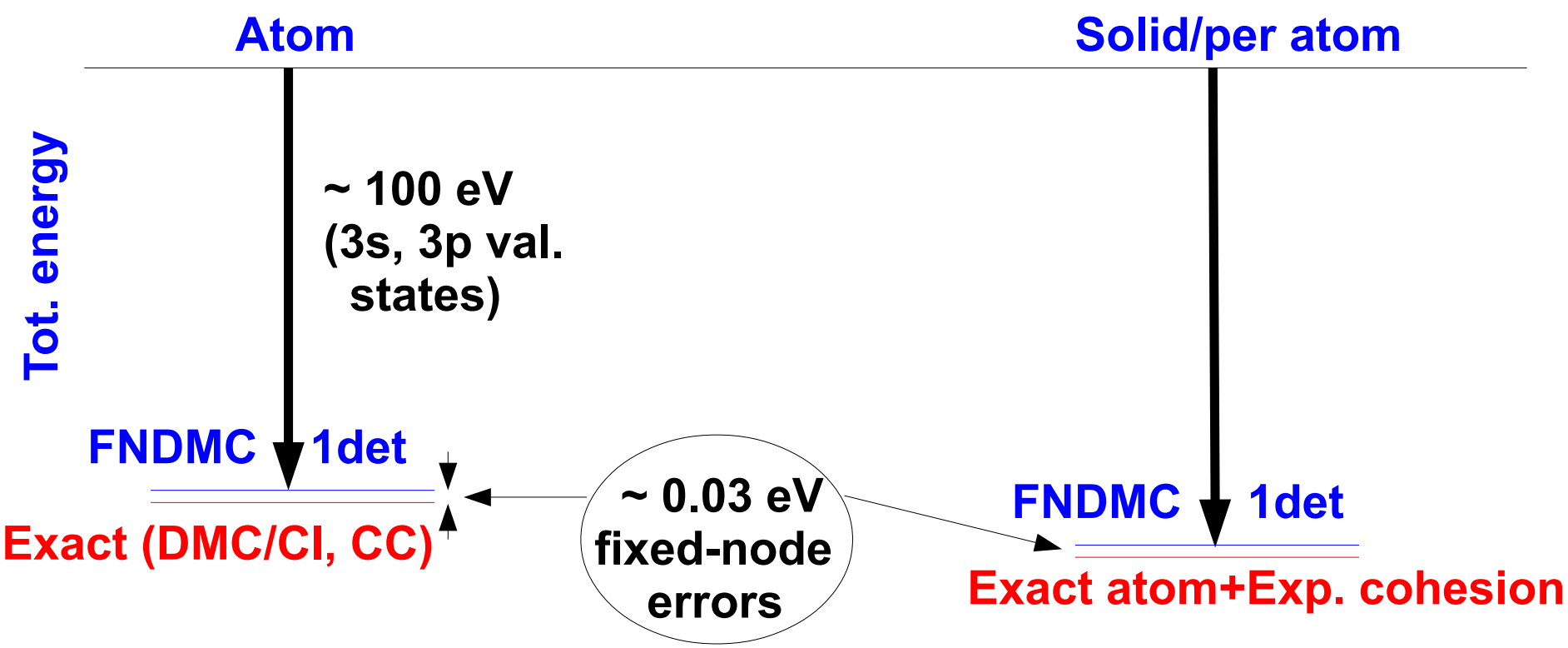
In some cases, exceptional accuracy: solid Si (s-cell up to 214 atoms) FNDMC/single-det/PBE nodes ~ 98 % of correlation!



Cohesion: - FNDMC (error canc.) → 4.59(2) eV
- experiment → 4.62(8) eV

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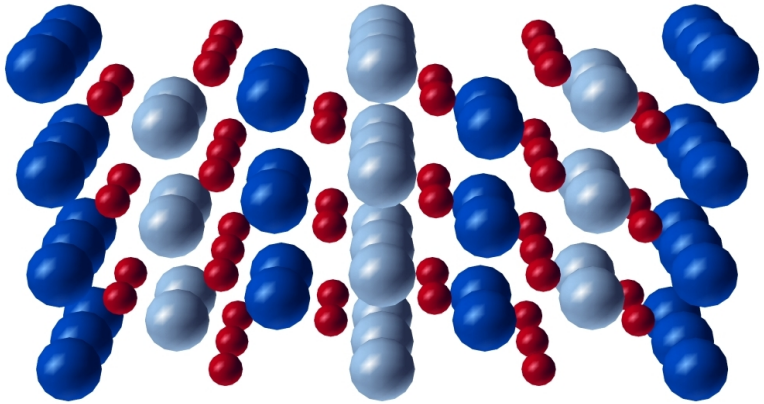
More recent challenge: FeO solid at high pressures

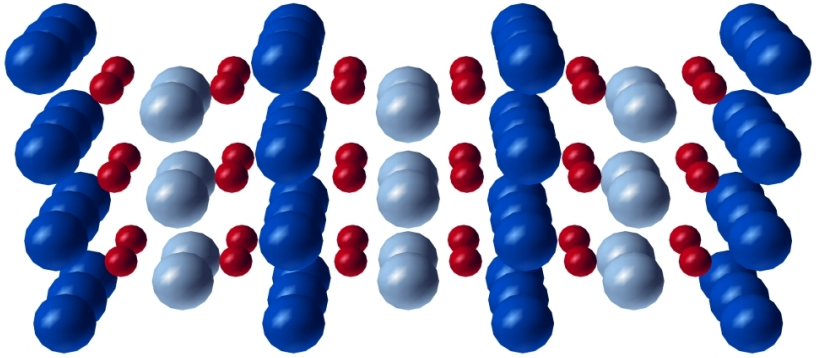
- large e-e correlations, difficult: competition of Coulomb, exchange, correlation and crystal-field effects; open d-shell; important high-pressure physics (Earth interior, for example)

- mainstream Density Functional Theories (DFT) predict:
  - metal instead of a large-gap insulator
  - wrong equilibrium atomic structure

B1 (NaCl) AFII (true equil.)



iB8 (NiAs) AF (high press.)



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Plain vanilla fixed-node DMC for the FeO solid

- Ne-core, scalar relativistic pseudopotentials on Fe

- 8 supercells (176 valence e-) of FeO in DMC, larger supercells in VMC

- total energy about 4000 eV, trying for accuracy 0.1 eV

- Slater-Jastrow wf $\Psi_{Trial} = det^{\uparrow}[\phi_{\alpha}]\, det^{\downarrow}[\phi_{\beta}] \exp[U_{corr}]$

- one-particle orbitals from hybrid DFT (more on that later)

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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 [A]	4.28	4.32(1)	4.31- 4.33
K_0 [GPa]	191	170(10)	140 - 180
Gap [eV]	~ 0 (metal)	2.8(4)	~ 2.4

J. Kolorenc & LM, Phys. Rev. Lett. '08

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Gap and excitations in QMC

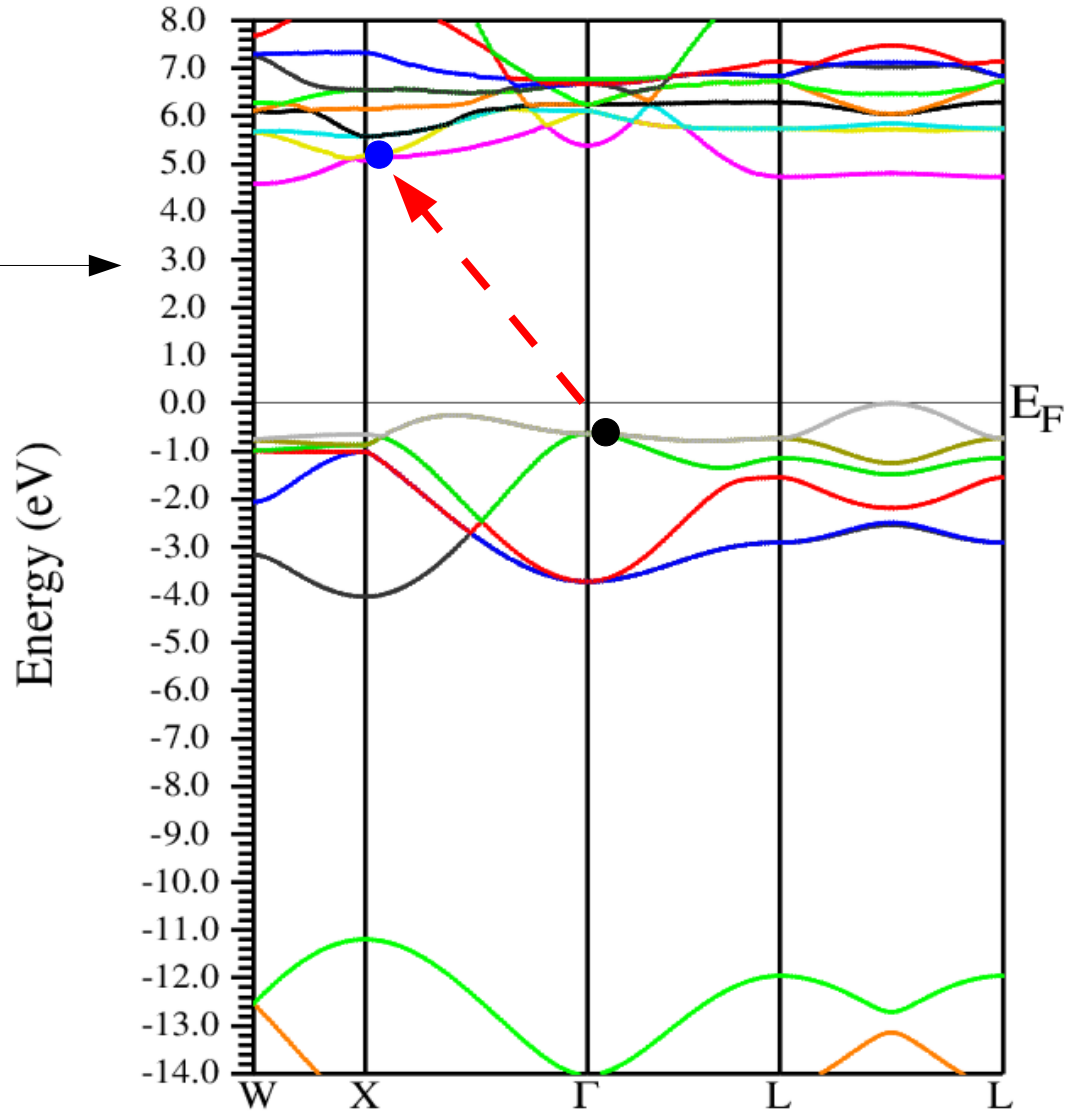
Assume an insulator:

1) Excite a valence state into a conduction state

E_gap ~ E_excit – E_ground

- carry out several of these → "band structure scan"

2) Add an electron (technically more complicated, but doable)



Excitations ? They are not the ground states ...

Still, excitations can be calculated (after all, even the fermionic ground state is an excited state!)

Basic possibilities:

1) Excitation is of a different symmetry → so, the ground state of the given symmetry

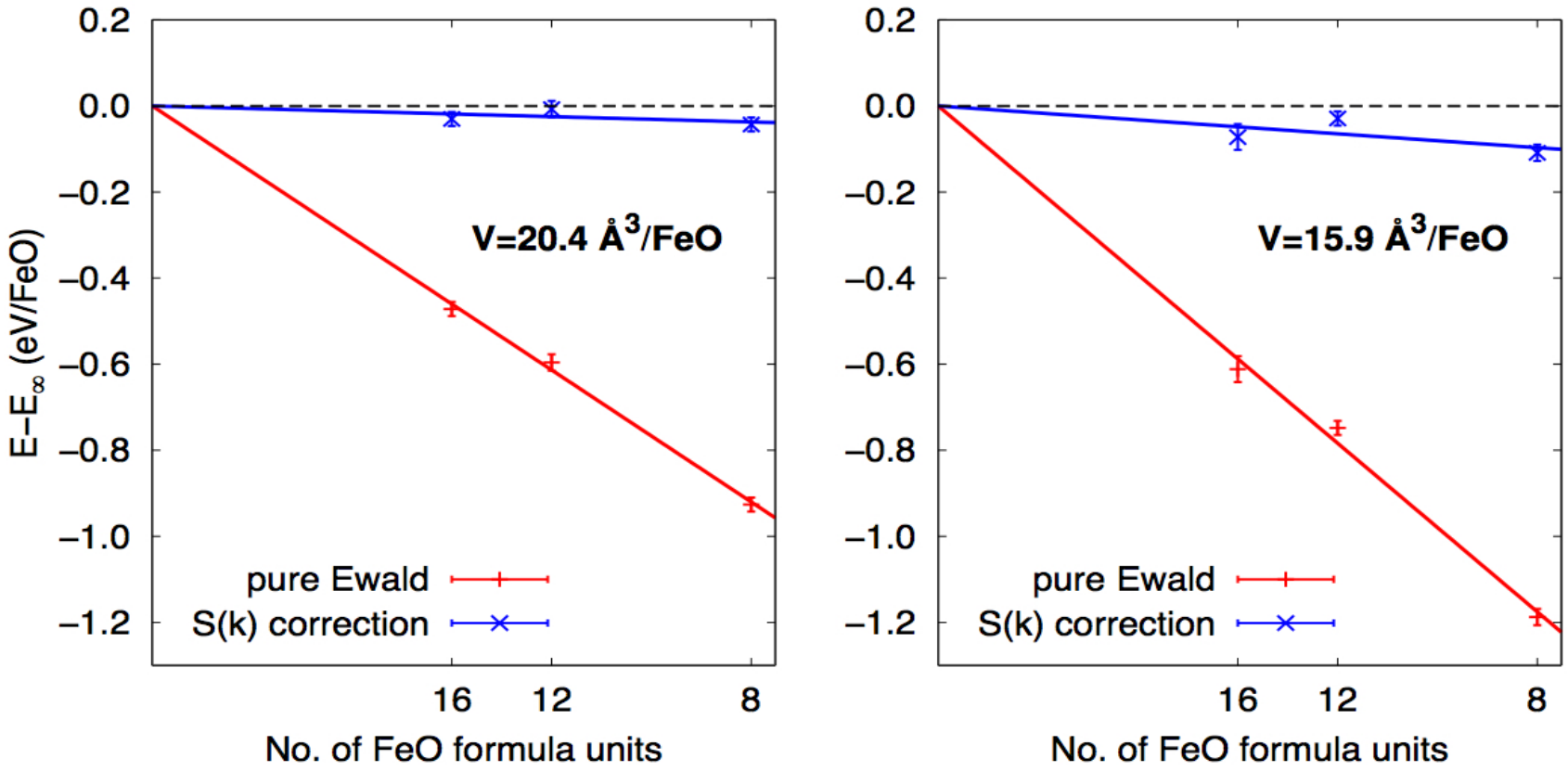
2) Excitation is of the same symmetry → suprisingly, it often works similarly as the ground state calculation.
(How come ? The reason is that the overlap with the ground state is typically much, much smaller than the fixed-node error.)

3) The reasoning in 2) does not apply (it can happen). Then explicitly orthogonalize (that is more complicated but not impossible).

Finite size corrections → works reasonably well for insulators

Extrapolation to the thermodynamic limit at two different volumes: ~ 1/N

S(k) includes corrections both for potential and kinetic energies



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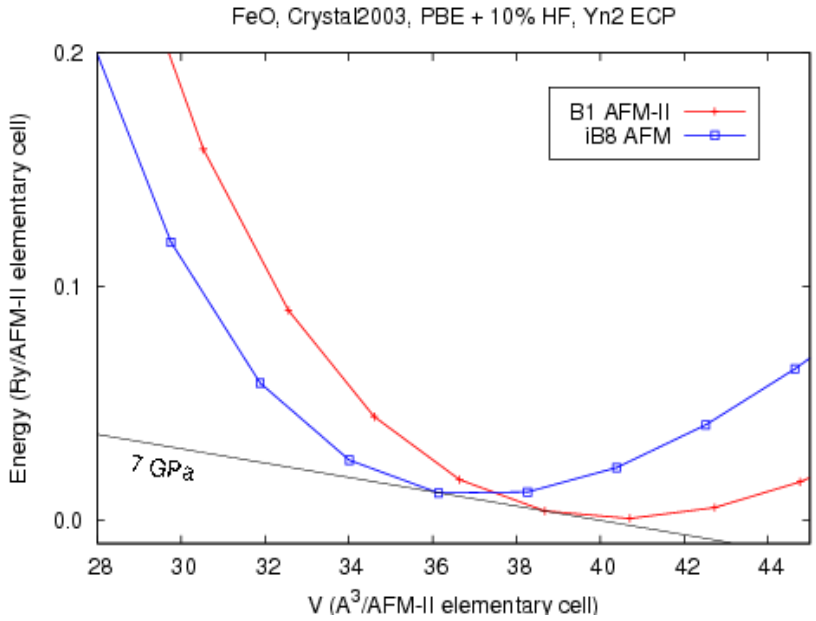
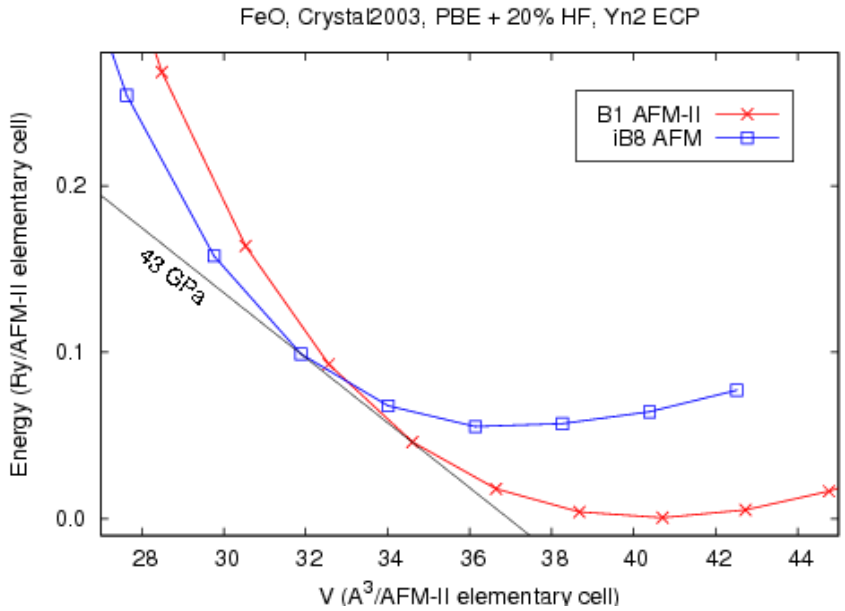
FeO solid at high pressures in DFT: hybrids with weighted exact exchange (or DFT+U)

In order to reconcile DFT with experiment one needs to employ mixing of the exact exchange: transition pressure proportional to mixing …
or to the Hubbard U (eg, Fang,Terakura, Sawada, Miyazaki, Solovyev, '98)

Complicated to justify the "correct" weight or U, non-variational, ...





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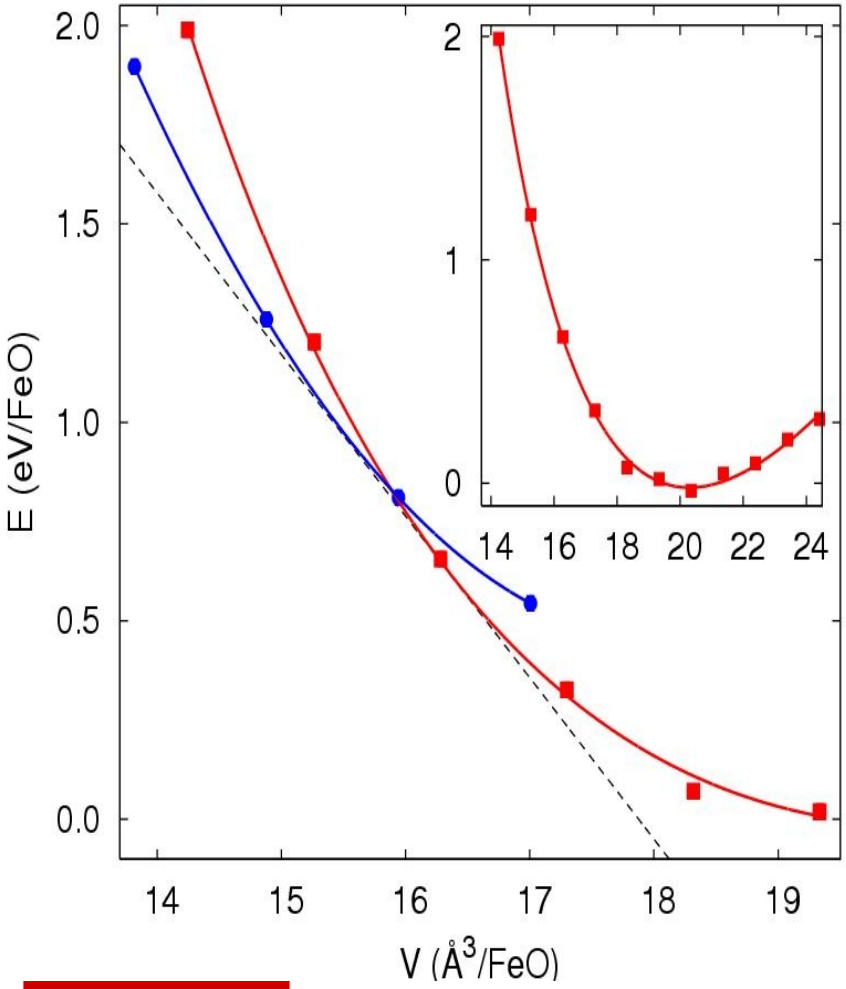
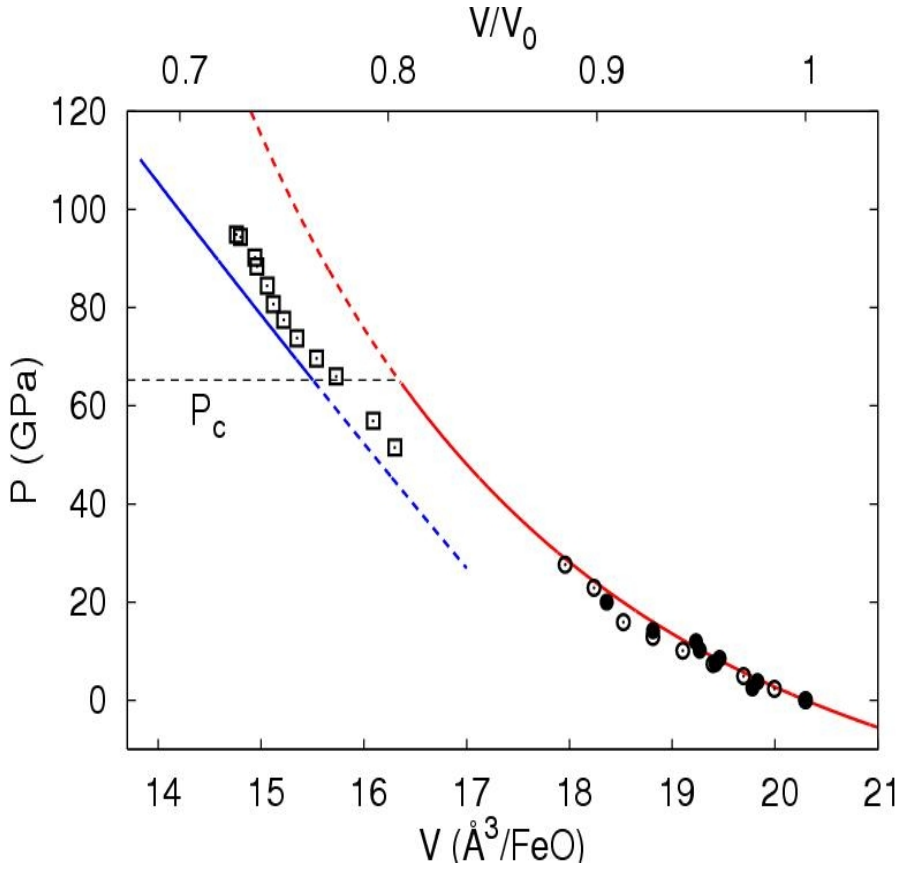
Equation of state of FeO solid at high pressures: QMC shows transition at ~ 65 GPa (Exper. 70-100)





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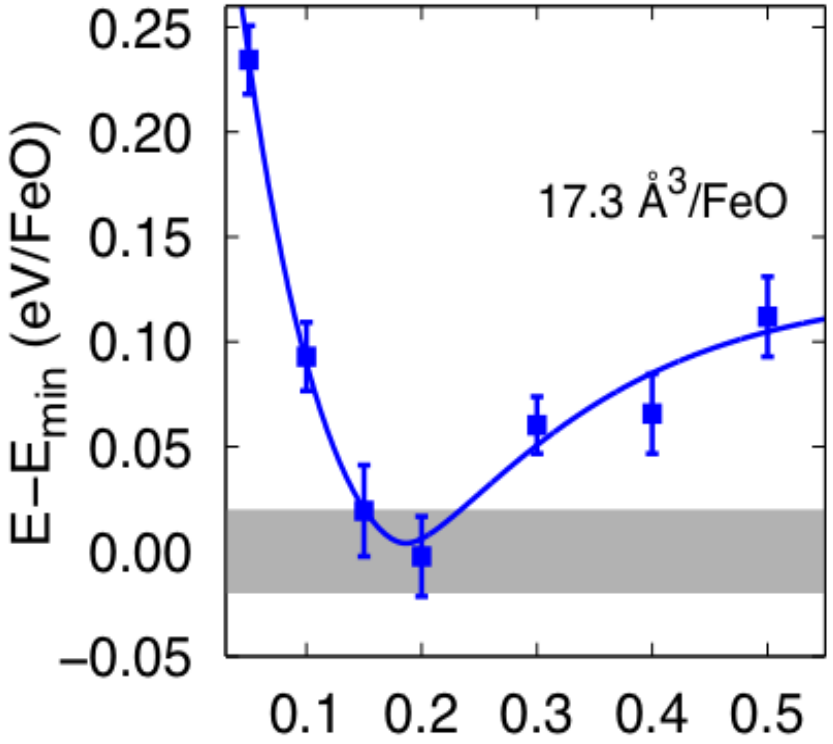
J. Kolorenc & LM, PRL '08

Orbitals: hybrid functional with varying weight of exact/Fock exchange

Weight optimized by FNDMC: clear minimum!

$$\psi_{Trial} = det^{\uparrow}[\{\phi_{\alpha}^{PBE0_w}\}]\, det^{\downarrow}[\{\phi_{\beta}^{PBE0_w}\}] \exp[U_{corr}]$$



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

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

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

- **variationally optimized fixed-node DMC energy**

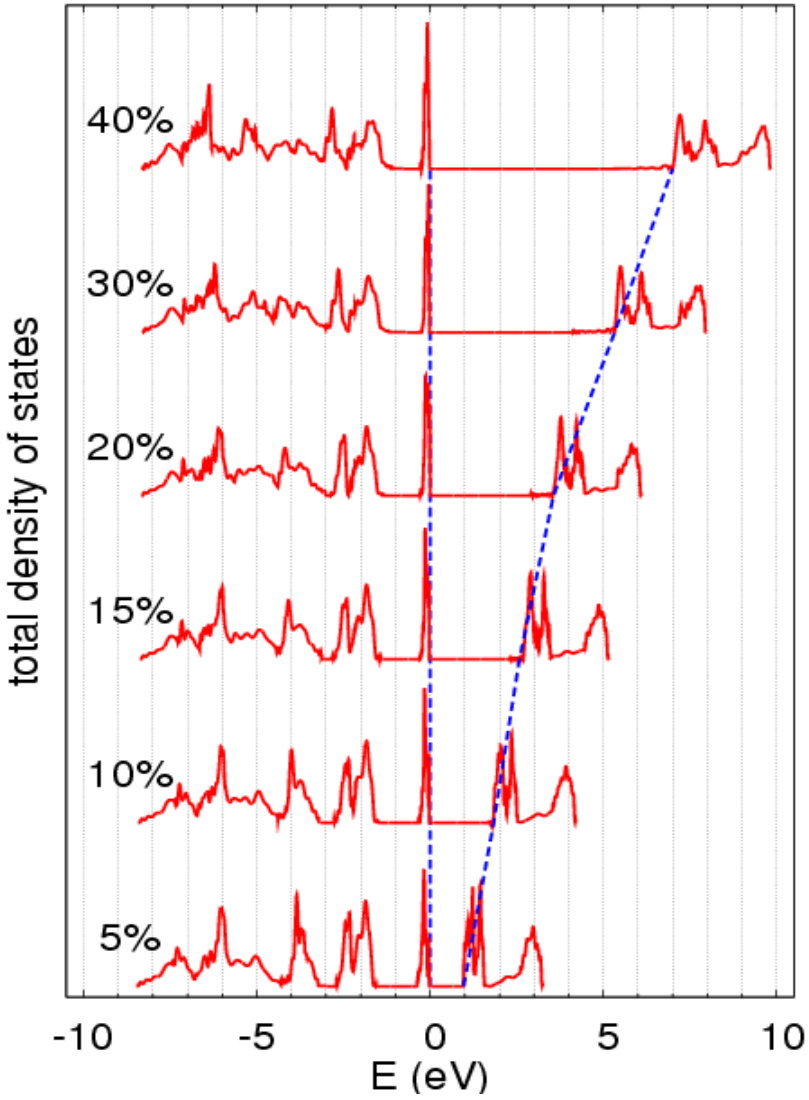
- **orbitals beyond Hartree-Fock → correlated (the most appropriate orbitals need not to necessarily minimize the HF energy)**

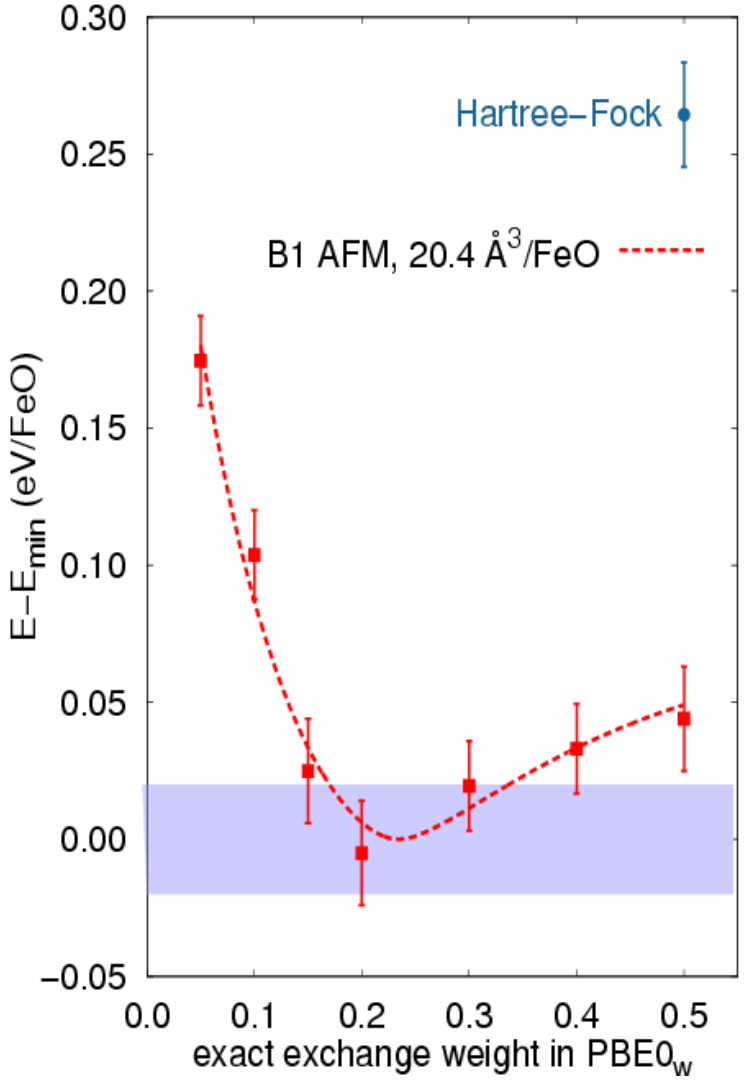
- **points out towards a more general idea/tool: variational space includes not only the wave function but also optimal effective Hamiltonian (possibly more efficient and faster generation of accurate nodes)**

FNDMC used as a variational theory →

J. Kolorenc, S. Hu, LM PRB 82 115108 ('10)

Enables to look ("back") at the optimal one-particle picture within the effective Hamiltonian, density of states, gap, etc





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Beyond Slater-Jastrow wave functions:

BCS and pfaffians

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Why beyond Slater-Jastrow ?

Slater-Jastrow:

$$\psi_{Trial} = det^{\uparrow}[\phi_{\alpha}] \cdot det^{\downarrow}[\phi_{\beta}] \exp[U_{corr}]$$

$$\downarrow$$

$$node = (node^{\uparrow}) \cdot (node^{\downarrow})$$

Strictly speaking, nodes have such product form only in non-interacting systems → the nodal domains count is higher than it should be → sometimes this still an excellent approximation while in other cases it does matter

Possibilities to take unlike spin correlations into account:

1) linear combination of determinants (CI)

2) more general antisymmetric forms

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Possible antisymmetric forms (polynomial complexity)

Slater determinant: $\psi_{HF}(1,2,\ldots,N) = A\prod_i \phi_i(j) = det[\phi_i(j)]$

single-particle orbitals

BCS wave function (spin singlet, fixed-number of pairs, in first quantization):

$$\psi_{BCS} = det[\phi^{\uparrow\downarrow}(i,j)] \qquad i,j = 1,\ldots,N$$

pair orbital

Pfaffian: (any spin state, antisymmetrized pairs of any spin)

$$\psi_{PF} = A[\phi(1,2)\phi(3,4)\ldots] = pf[\phi(i,j)] \qquad i,j = 1,\ldots,2N$$

pair spinorbital

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Pfaffian: signed sum of all distinct pair partitions of permutations (Pfaff, Cayley ~ 1850) → polynomial complexity

$$pf\,[a_{ij}] = \sum_P (-1)^P a_{i_1 j_1} \ldots a_{i_{2N} j_{2N}} \quad , \qquad i_k < j_k \, , \qquad k = 1, \ldots , 2N$$

- **determinant is a special case of pfaffian (pfaffian is more general)**
- **pfaffian algebra similar to determinants (minors, etc) → fast evaluation, O(N^3)**
- Ψ_{HF} , Ψ_{BCS} **special cases 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**

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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 (geminals) 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

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

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

(M. Bajdich et al, PRL '06; PRB '08)

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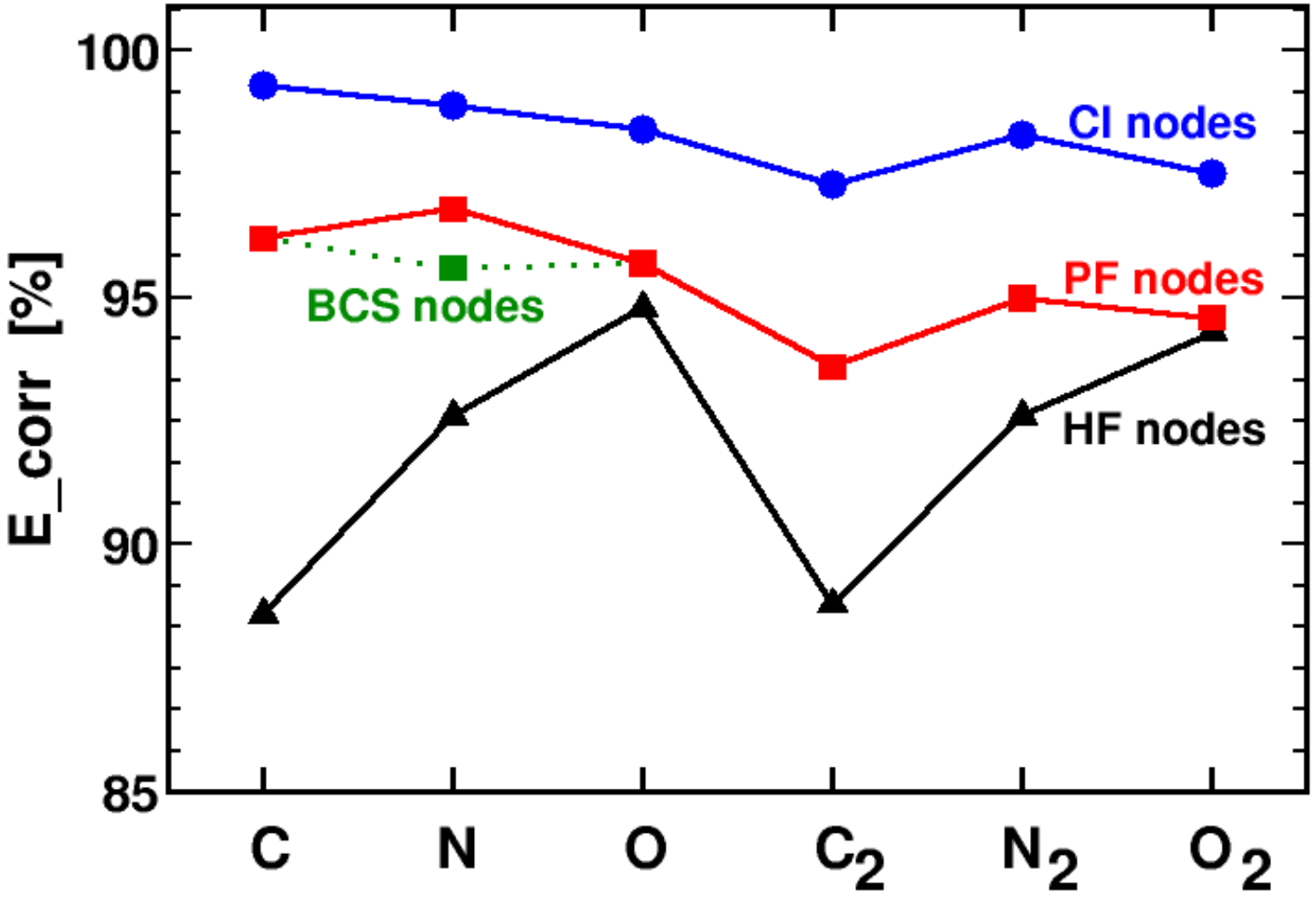
DMC correlation energies of atoms, dimers
Pfaffians: more accurate and systematic than HF while scalable (unlike CI)



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Expansions in many pfaffians for first row atoms: FNDMC ~ 98 % of correlation with a few pfaffians

Table of correlation energies [%] recovered: MPF vs CI nodes

n = # of pfs/dets

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

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

Pfaffians describe nodes more efficiently

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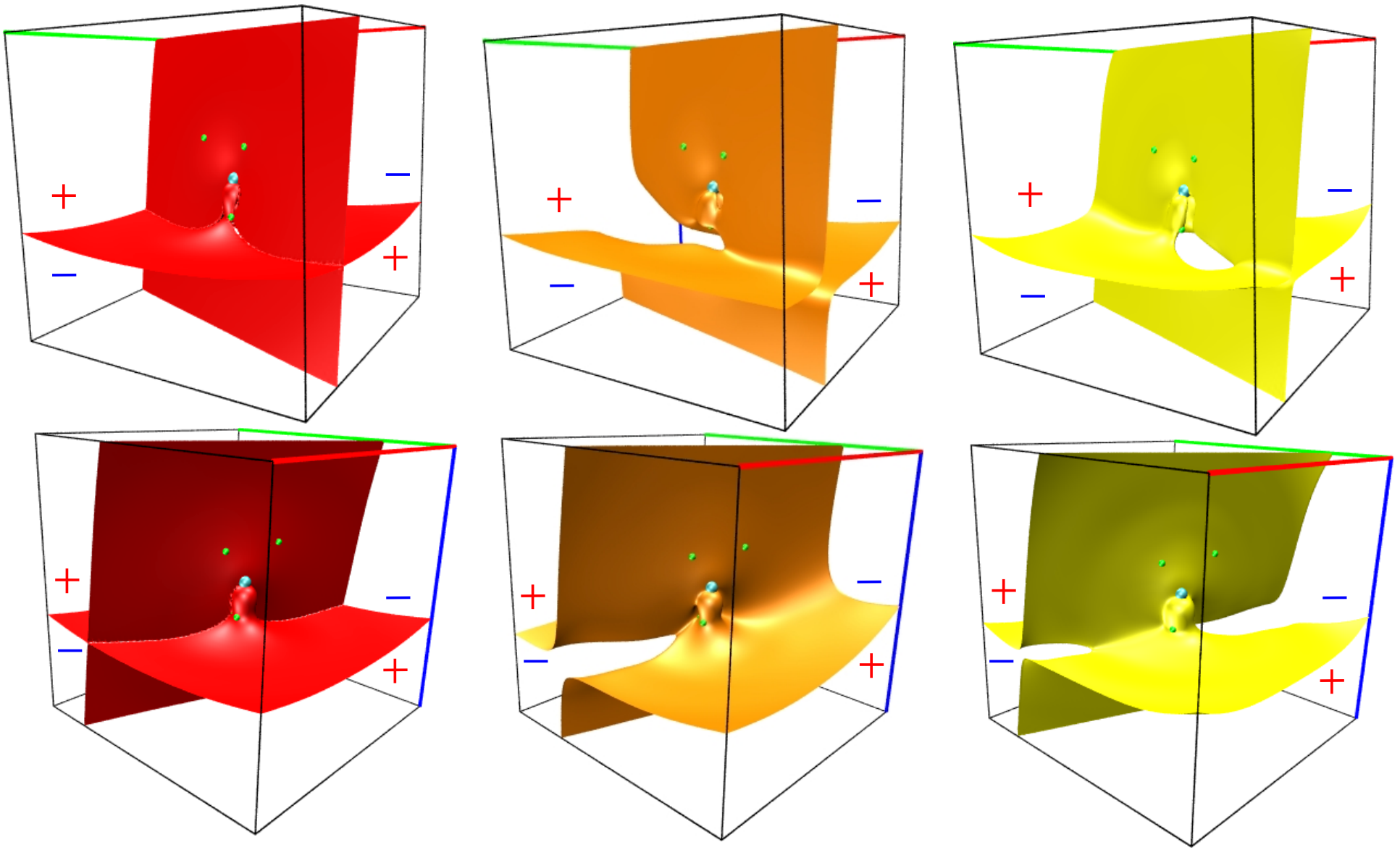
Nodes of different wfs (%E_corr in DMC): atom wf scanned by 2e- singlet (3D node subset) → correlation leads to different topologies

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



Something different from electron-ion Hamiltonians:

Unitary ultracold atoms

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Ultracold fermions system and interactions

- periodic boundary conditions

- interaction tuned to unitarity $V(r_{ij}) = -2\frac{(2/R_{eff})^2}{\cosh^2(2r_{ij}/R_{eff})}$

- extrapolated to R_eff $\rightarrow$ 0

- trial function $\psi_T = \psi_{BCS} = det[\phi^{\uparrow\downarrow}]$

- pairing orbital built from superposition of gaussians+neighb. cells

$$\phi^{\uparrow\downarrow}(r_{ij}) = \sum_{a,b,c}\sum_k c_k^{abc}\exp[-\alpha_k^{abc}(\boldsymbol{r}_{ij} - a\,\boldsymbol{L}_x - b\,\boldsymbol{L}_y - c\,\boldsymbol{L}_z)^2]$$

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Ultracold fermions in a special state: unitary gas (total energy first calculated by QMC)

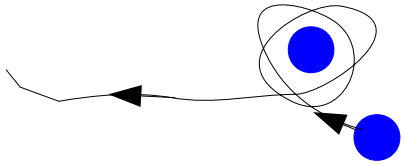
Effective, short-range attractive interaction **Scattering length: a**

1/a < 0 **BCS, weakly paired superconductor**

1/a > 0 **BEC of covalently bonded molecules**

1/a → 0 **unitary limit →** $r_{int} \ll r_s \ll a$,

Interaction is tuned, so that a pair is on the verge of forming a bound state, (ie, E=0)



Total energy: $E_{tot}^{unitary} = \xi E_{tot}^{free}$, $\xi \leftarrow$ *Bertsch parameter*

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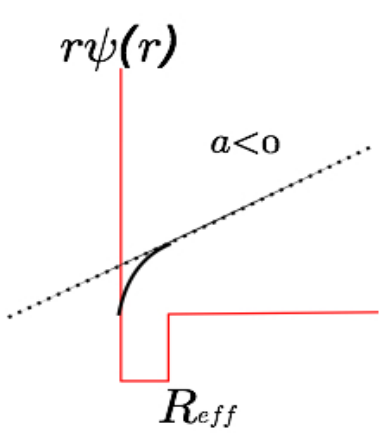
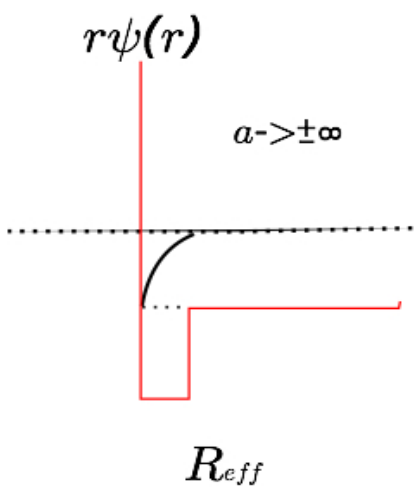
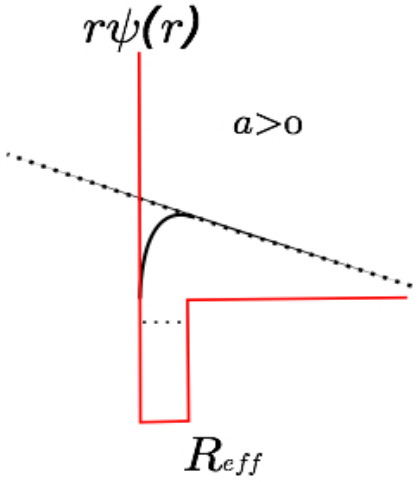
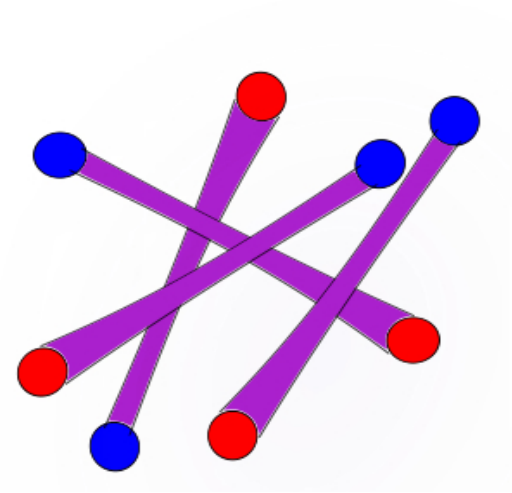
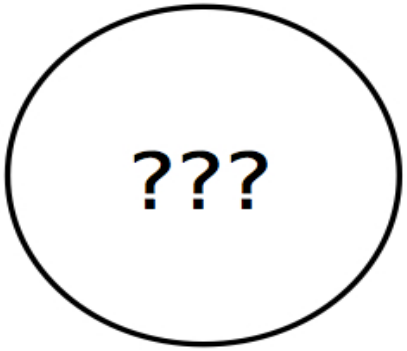
BCS → unitary → BEC crossover

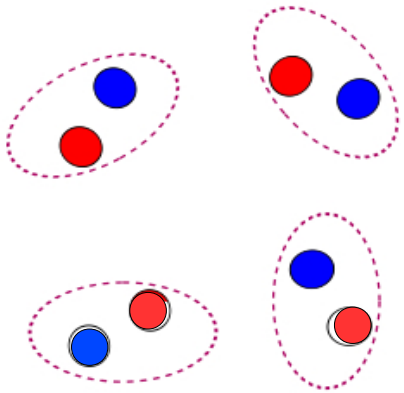












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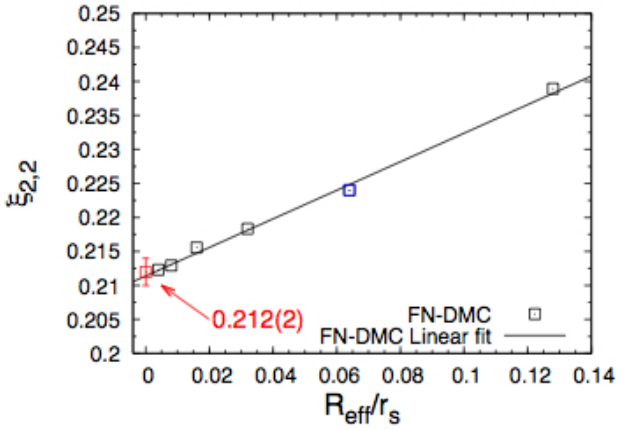
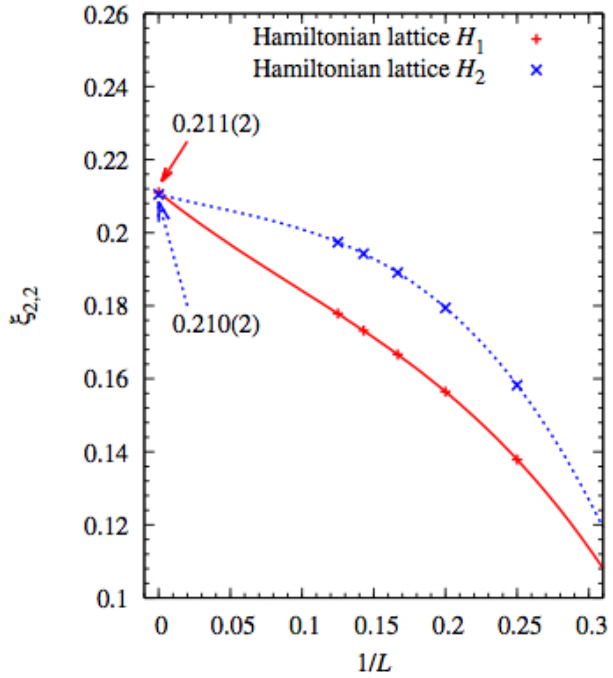
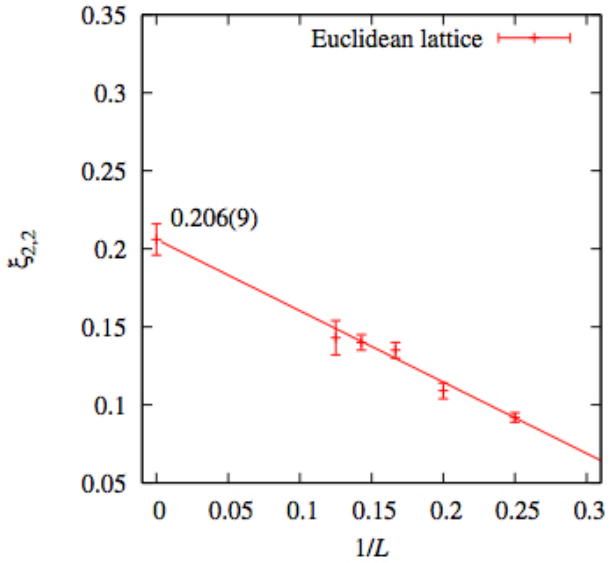
Benchmarking on a small system: 4 unitary fermions
QMC vs two independent lattice many-body methods







	QMC	Direct diag.	Euclid. Lattice MC
ξ	0.212(2)	0.211(2)	0.206(9)

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Bertsch parameter for (infinite) unitary fermions: improving wave functions

$$\xi_{FNDMC} / HF\ nodes = 0.50(1)$$
$$\xi_{FNDMC} / BCS\ nodes = 0.44(1) \qquad J.\ Carlson\ et\ al\ ,\ '03$$
$$\xi_{exact} / BCS\ nodes \leq 0.393(2) \qquad X.\ Li\ ,\ L.M.\ ,\ PRB\ 2011$$

Energy gain from the BCS nodes dramatic: > 20% of the total energy !

(in electronic structure problems it is only ~ 0.03% of the total energy)

Recently, even slightly better energies were obtained, J. Carlson, S. Zhang, S. Gandolfi and coworkers 2011

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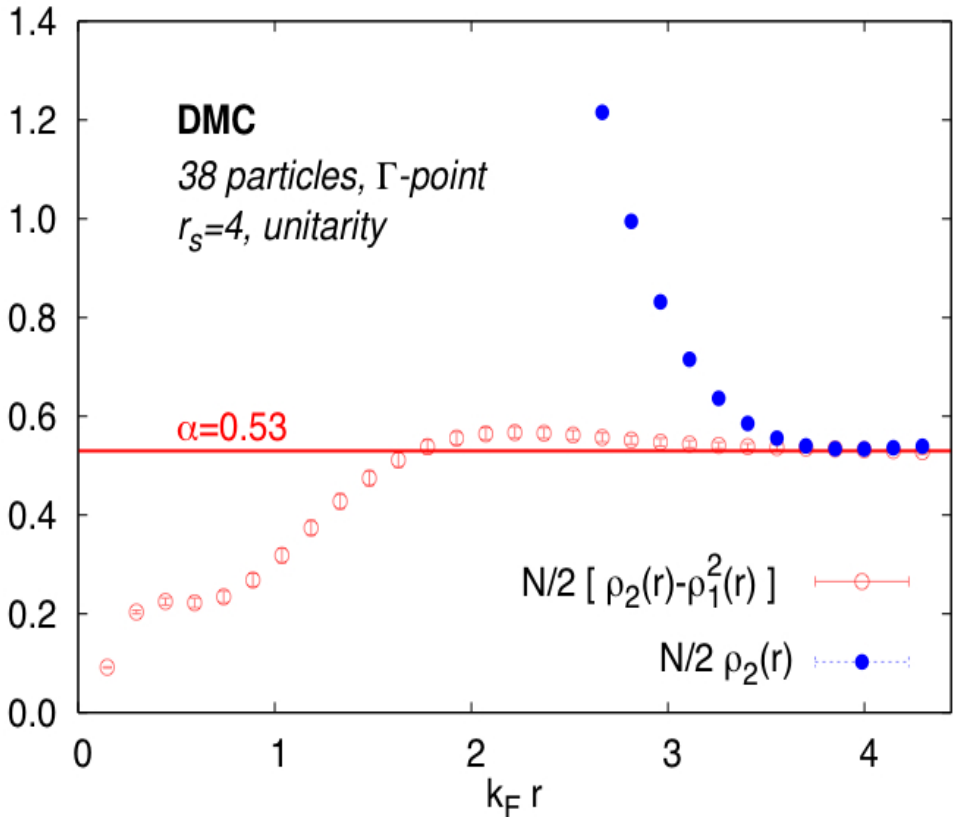
Unitary limit: very robust condensate ~ 53% of particles

Find the amount of the condensate directly: averaged two-body density matrix at long-range and read off the value



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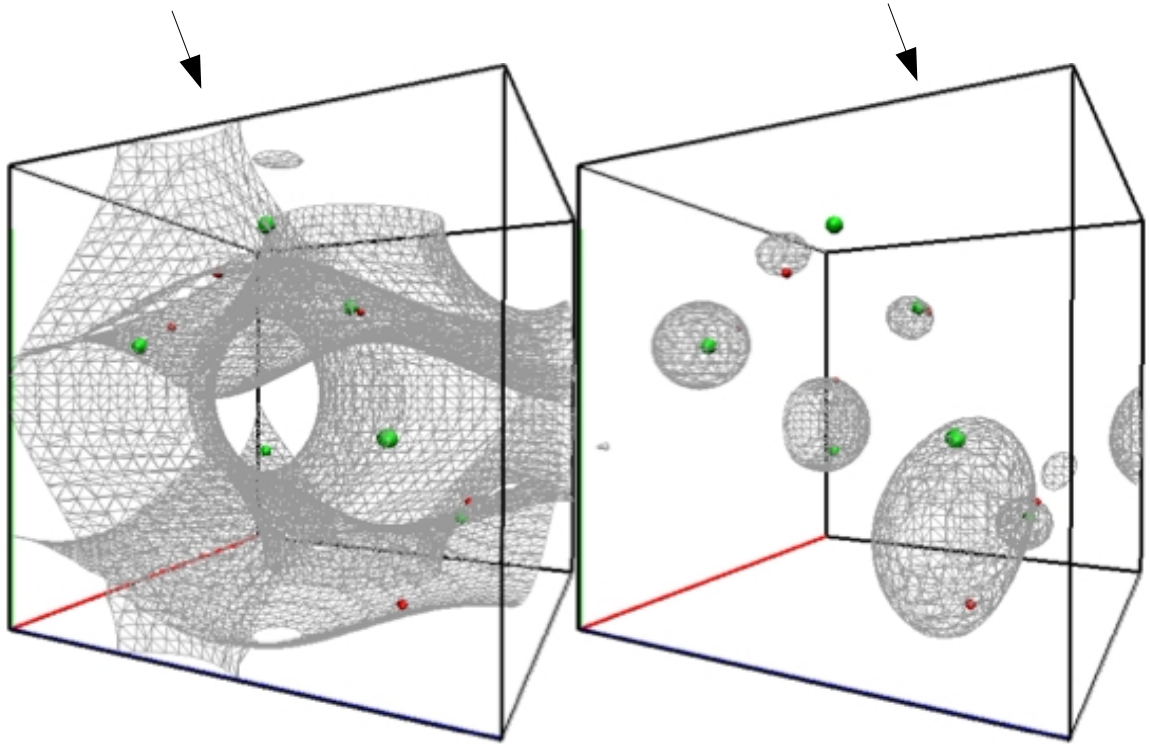
Dramatic change also in the nodes

3D scan with the spin-up and -down particle pair

HF/free particle nodes

BCS/unitary nodes



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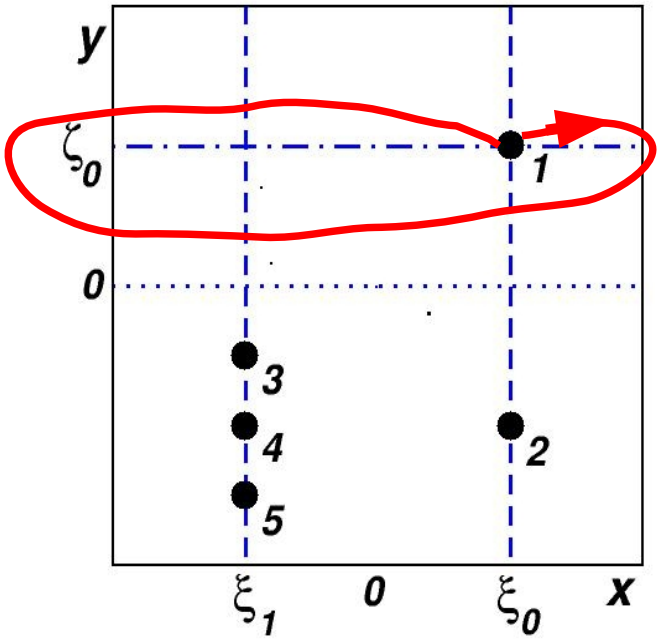
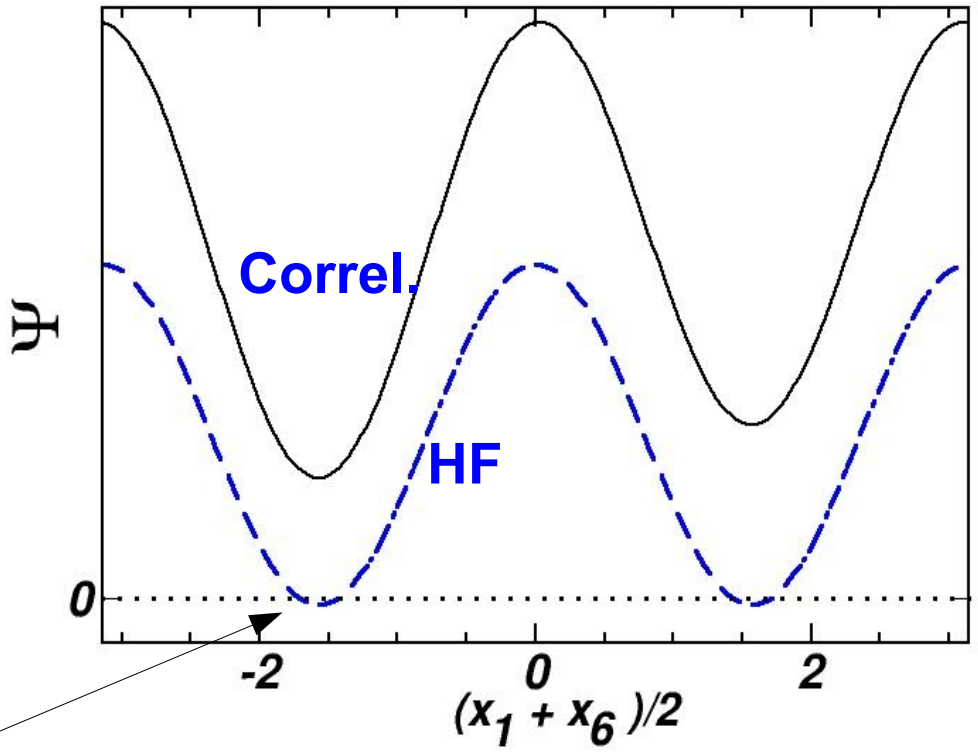
Correlated nodes in a fermion gas: singlet pair of e- winds around the box without crossing the node

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



Wavefunction along the winding path



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

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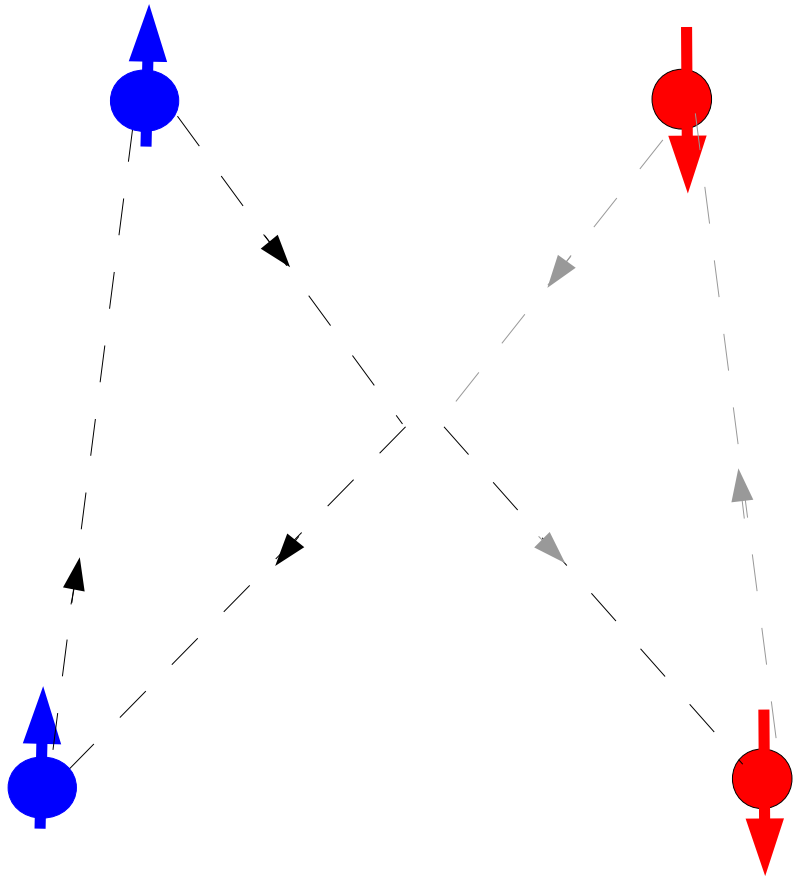
Four particle exchange: pair two-particle simultaneous exchanges without node crossing

Exchange in each spin channel separately has to cross the node, concerted both spin channels exchange can avoid the node



(X. Li, LM,'09)

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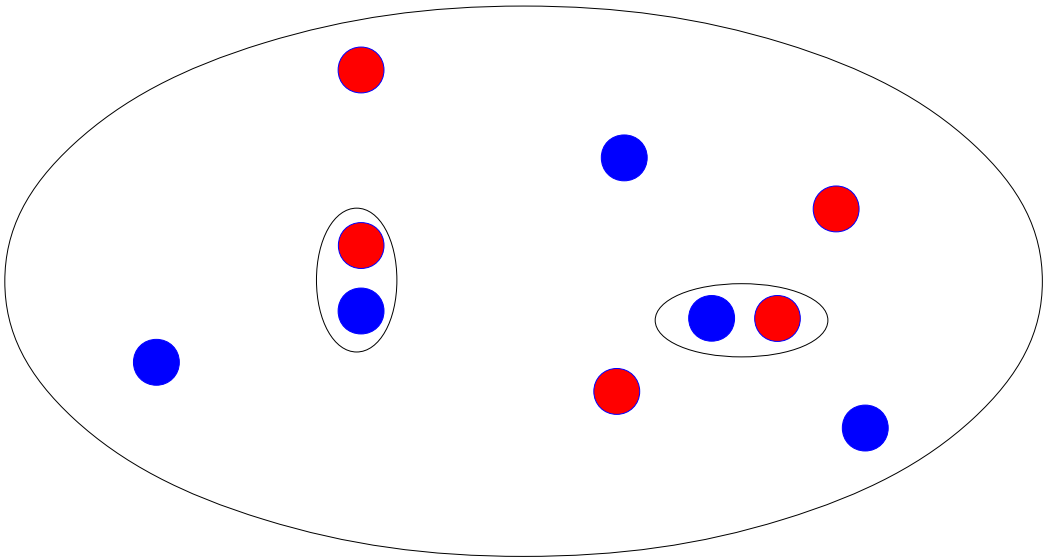
Ultracold unitary fermions: half of the particles in tight but "dynamical" pairs, another half essentially free



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A few summaries and comments

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A few key points about QMC

Practical:

- systems with hundreds of electrons are feasible
- agreement with experiment within few % (problem cornered)
- sometimes “plain vanilla” single-determinant nodes very accurate

Fundamental:

- 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

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QMC and its role in electronic structure of materials (and computational science)

+) history of important benchmarks (eg, correlation energy of homog. el. gas); universally applicable → ultracold atomic condensates with short range attractive interaction, models, etc

- /+) so far computationally 100-1000 times slower than mainstream → helped by easier parallelization and favorable scaling in # of e-

-) hidden cost on human time (need to have not only the code but further infrastructure to make construction of many-body physics efficient → almost nobody works in such detail)

+++) QMC produces not only numbers but also understanding (unitary fermions insights, some more on friday talk)

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Challenges in QMC

Spectra:
- state by state calculations (band edges, band structure scan)
- subtle features (satelites, etc, difficult, costly)
- multi-state calculations (eg, so far exponential scaling)

Weakly bonded systems: difficult, energy resolution is a problem

Ionic forces: - noise is a problem → possible but costly options:
- finite differences with correlated sampling
- Hellman-Feynman, all options costly
  (but AIMD/DFT with QMC correction with evolving wave function along the ionic path is surprisingly efficient, factor of 2-3 on the top of AIMD! Grossman & Mitas PRL '05)

Spins: beyond collinear spin states, spin-orbit interactions
(symposium talk)

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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. Kolorenc, L.M. others)

- interfaces and converters from GAMESS, CRYSTAL, Gaussian, SIESTA, (Qespresso in progress)

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Review papers:

RMP, 73, 33 ('01)

Acta Physica Slovaca 59, 81 ('09)

Rep. Prog. Phys. 74, 026502 ('11)

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