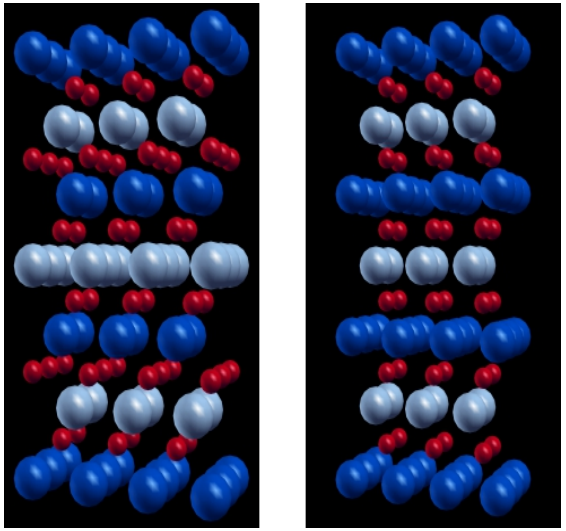
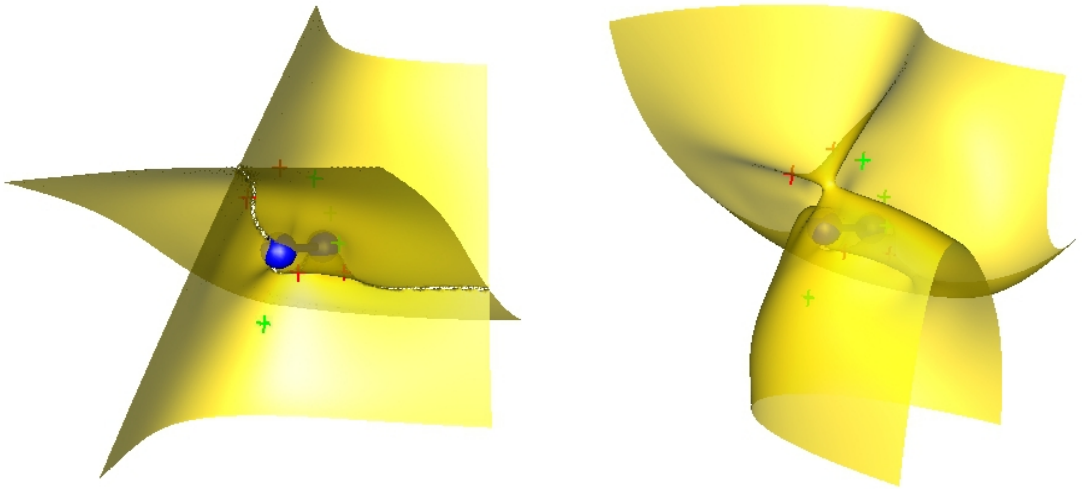
Quantum Monte Carlo: introduction





J. Kolorenc, M. Bajdich, S. Hu, S. Guo, M. Zhu, M. Dubecky, C. Melton, M.C. Bennett, A. Kulahlioglu, A. Ambrosetti, F. Pederiva,

Lubos Mitas

North Carolina State University

XSEDE, INCITE
NSF, DOE

NC STATE UNIVERSITY

Lubos_Mitas@ncsu.edu

Properties of matter: molecules, liquids, solids, ultracold condensates, etc...

→ stationary Schrödinger equation

Hamiltonian of interacting electrons and nuclei

$$H = -\frac{1}{2}\sum_i^N \nabla_i^2 - \sum_{i,I}\frac{Z_I}{r_{iI}} + \sum_{i<j}\frac{1}{r_{ij}} + E_{nucl-nucl}$$

Stationary Schrödinger equation

$$H\,\psi_k(\boldsymbol{R}) = E_k\,\psi_k(\boldsymbol{R}) \qquad \boldsymbol{R} = (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$$

Solution, ie, spectrum $\{E_k, \psi_k\}$ contains all what we need for

- stability/cohesion, eqs. of state, phase diagrams, magnetic order, ...
- excitations: optical properties, transport, responses to ext. fields, ...
→ key inputs for other methods (T>0, atomistic, etc)

$\{E_k, \psi_k\}$ have to be astonishingly accurate → precise treatment of many-body effects, ie, correlations, is crucial for any predictions

Lubos_Mitas@ncsu.edu

accuracy: physics of interest at 6th ... 12th digit of total energies

- binding, cohesion, optical excit.: → 1 eV
- magnetism/spins: T_Neel ~ 1000 – 100K → 0.1 – 0.01 eV
- superconductivity: T_c ~ 100 – 10K → 0.01 – 0.001 eV
- heavy fermions: T ~ 1K → 0.0001 eV

Lubos_Mitas@ncsu.edu

Method, in a nutshell

Lubos_Mitas@ncsu.edu

Project out the ground state → imaginary time Schrodinger eq. (Schrodinger 1930, 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**

Lubos_Mitas@ncsu.edu

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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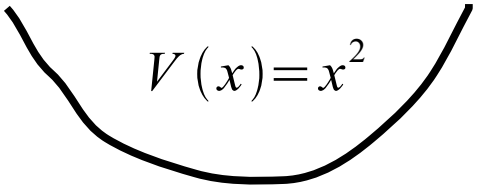
Toy model: 1D harmonic oscillator

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



Propagator

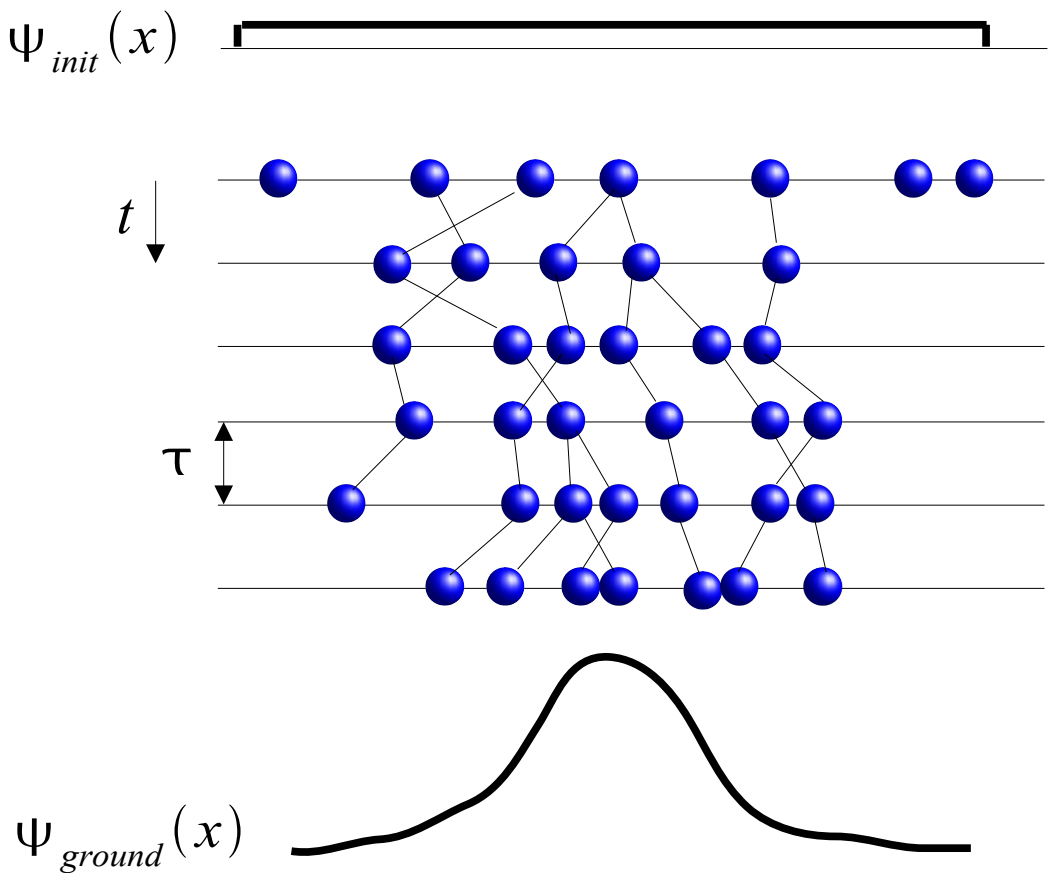
$$G(x, x', \tau)$$

$$\downarrow$$

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

diffusion

weight



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Sign problem: fermionic wave functions are both + and -

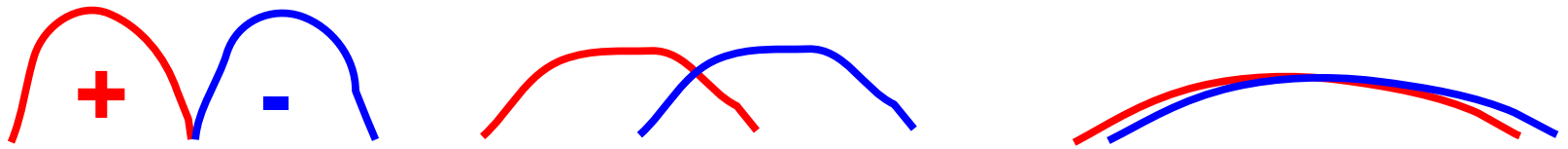
Naïve approach: decompose to + and -

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

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

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

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



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

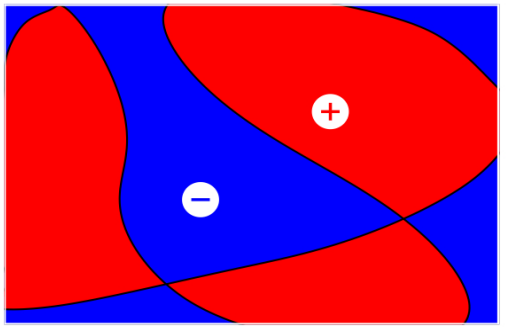
Fermionic "signal" decays exponentially quickly into a bosonic "noise"

Lubos_Mitas@ncsu.edu

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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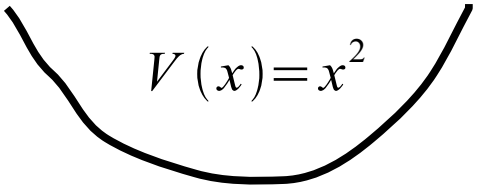
Fermion node toy model: excited state of harmonic oscillator

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



Propagator

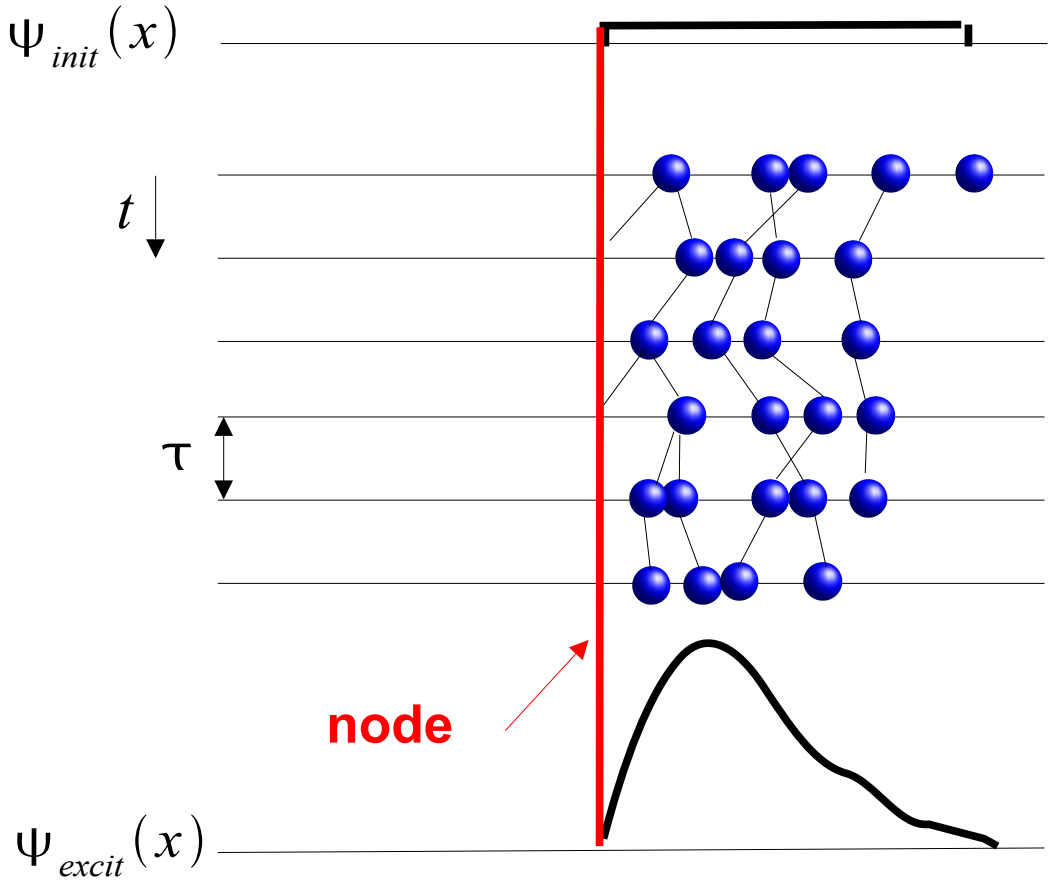
$$G(x, x', \tau)$$

$$\downarrow$$

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

diffusion **renorm**

+ node (boundary cond.)



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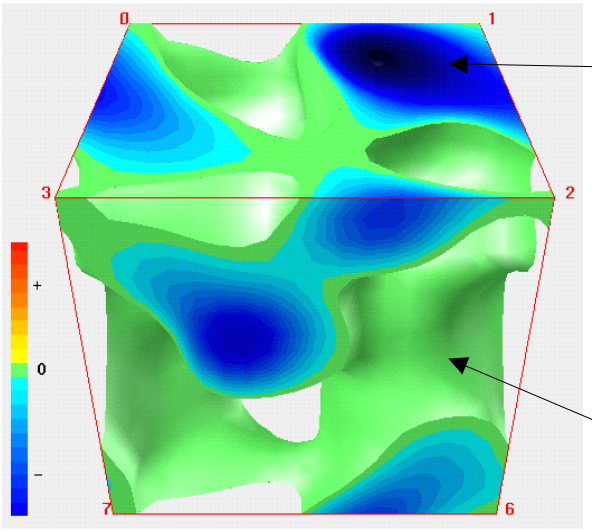
Fixed-node approximation and fermion nodes

- 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)

Lubos_Mitas@ncsu.edu

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

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

Lubos_Mitas@ncsu.edu

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 $\psi_T^2(\boldsymbol{R})$

Lubos_Mitas@ncsu.edu

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

Lubos_Mitas@ncsu.edu

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)

Lubos_Mitas@ncsu.edu

How does it work ?

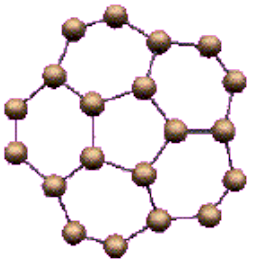
Let us look at a few applications

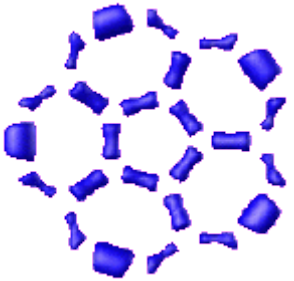
Lubos_Mitas@ncsu.edu

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

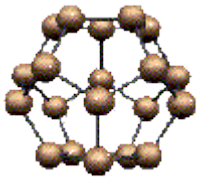
ring

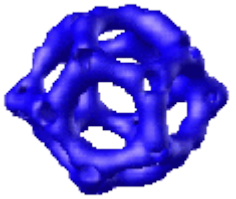
bowl





cage





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

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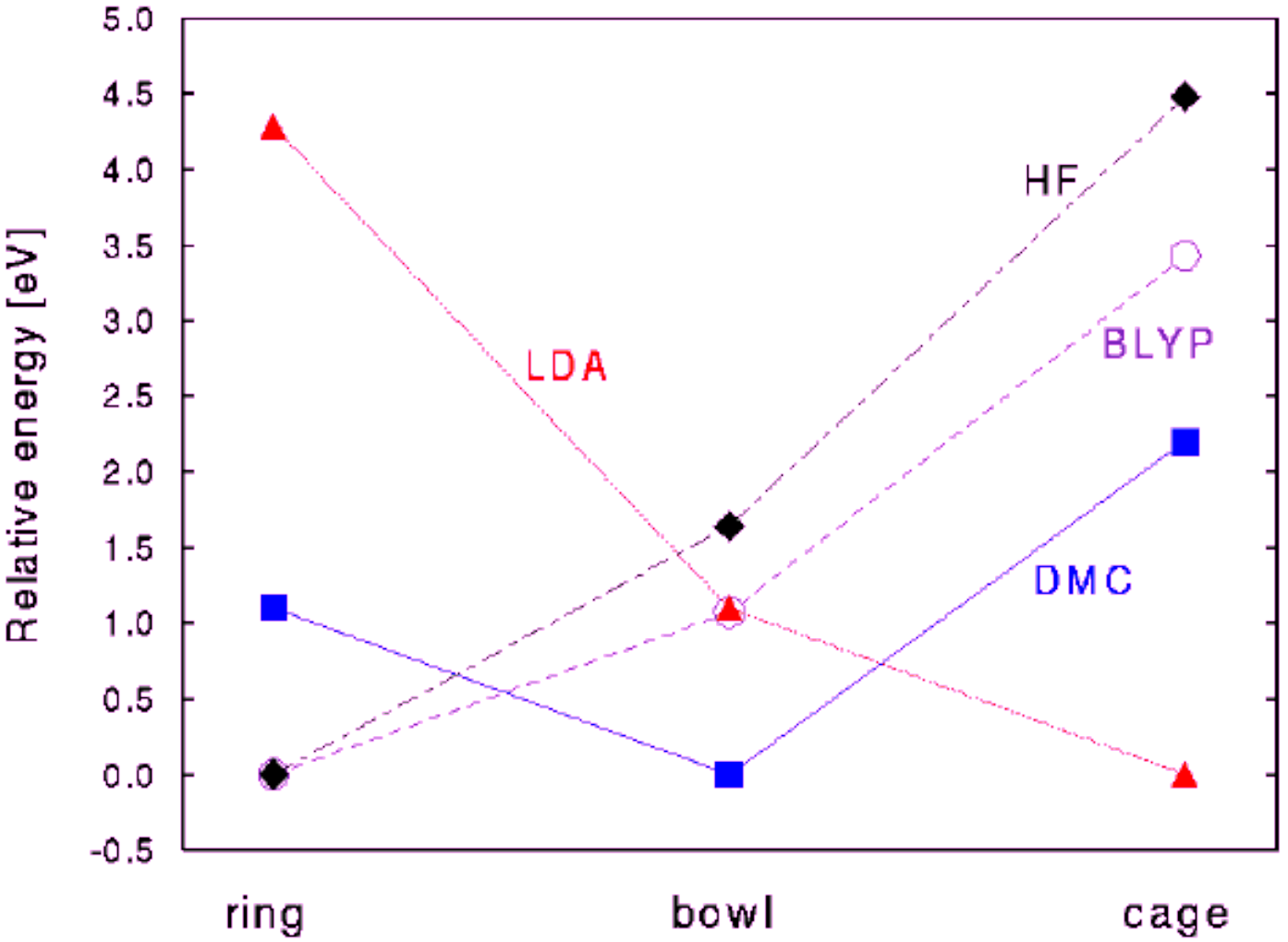
QMC was the first method to predict this (later confirmed by independent methods)



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

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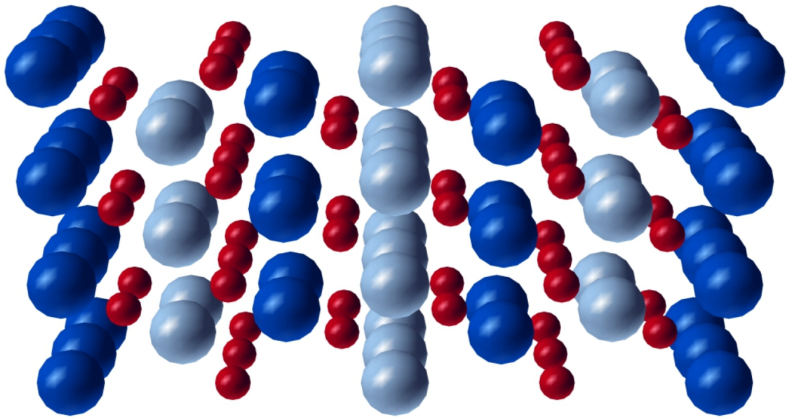
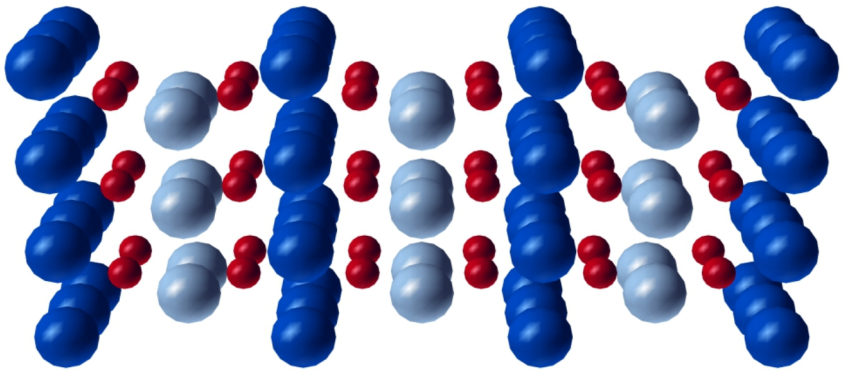
More recent challenge: FeO solid at high pressures

- 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 antiferromagnetic 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)

Lubos_Mitas@ncsu.edu

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

Lubos_Mitas@ncsu.edu

Gap and excitations in QMC

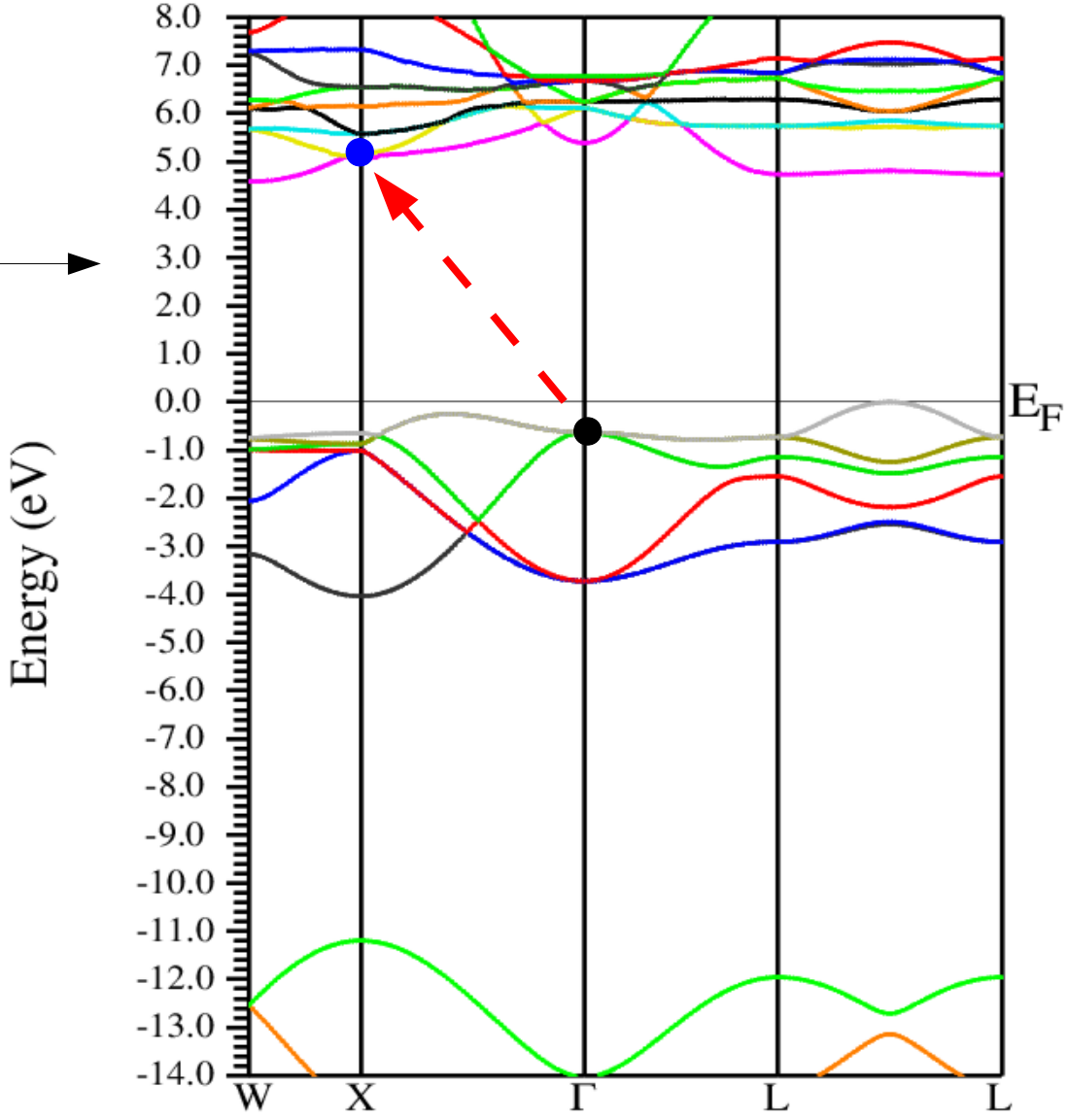
Assume an insulator:

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)



Beyond Slater-Jastrow wave functions:

BCS and pfaffians

Lubos_Mitas@ncsu.edu

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

Lubos_Mitas@ncsu.edu

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

Lubos_Mitas@ncsu.edu

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**

Lubos_Mitas@ncsu.edu

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

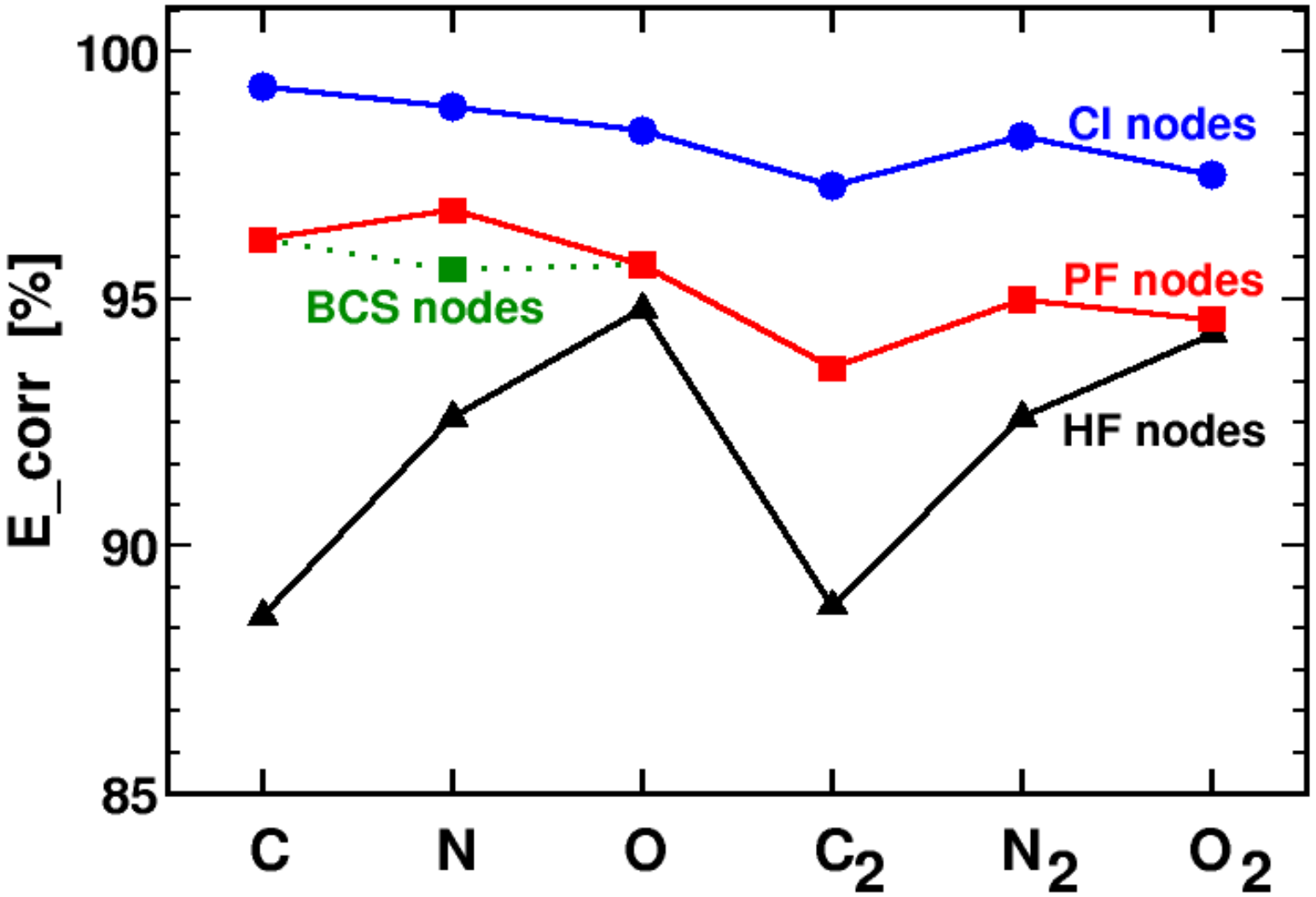
$$\psi(i) = \sum_\alpha c_\alpha h_\alpha(i)$$

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

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

Lubos_Mitas@ncsu.edu

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

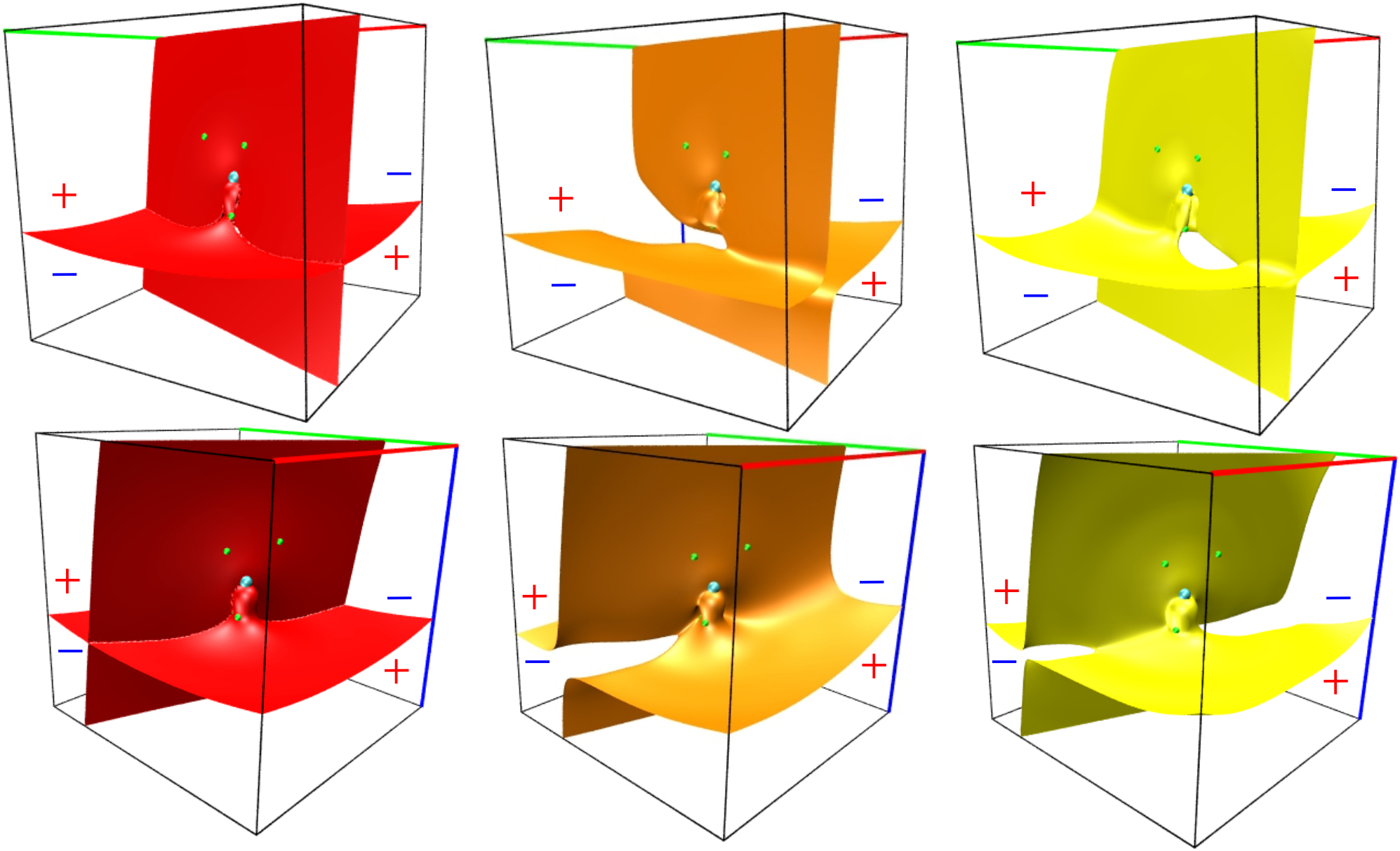
- further generalizations: pairing with backflow coordinates, independent pairs, etc (M. Bajdich et al, PRL 96, 130201 (2006))

Pfaffians describe nodes more efficiently

Lubos_Mitas@ncsu.edu

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)%)



Spin-orbit: how to treat spins as quantum variables

Lubos_Mitas@ncsu.edu

conventional QMC: spin is fixed - but in reality spins vary

Spinless Hamiltonians commute with both individual and total spins → the trial function spin(s) are fixed (spatial problem only)

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

up down ← separate spin channels

Hamiltonians with spin-orbit (SO) terms make the spins to vary, eg, one-particle state is a spinor

$$\phi_n(r_i, s_i) = \alpha \phi^{\uparrow}(r_i) \chi^{\uparrow}(s_i) + \beta \phi^{\downarrow}(r_i) \chi^{\downarrow}(s_i)$$

The simplest antisymm. trial wave function: determinant of spinors

$$\psi_{Trial} = det[\phi_n(r_i, s_i)] \exp(U_{corr})$$

Lubos_Mitas@ncsu.edu

key complications for the projector (DMC) methods

- discrete nature of spin (jumps in the sampling path ?)

$$\chi^{\uparrow}(1/2)=\chi^{\downarrow}(-1/2)=1 \qquad \chi^{\uparrow}(-1/2)=\chi^{\downarrow}(1/2)=0$$

- inherent complexity of the wave functions

- nonlocality of the SO terms

but also “technicalities”, such as

- find accurate spinors

- multi-reference problems, almost by definition

Lubos_Mitas@ncsu.edu

our approach: keep the spinors fixed, smooth out the spin configurations

---

we eliminate discontinuities in spin configurations by using overcomplete but compact representation: one possible choice

$$\chi^{\uparrow}(s)=\exp(+is), \qquad \chi^{\downarrow}(s)=\exp(-is)$$

- smooth projection $\exp(-\tau H)\psi_T$

similarities to Ambrosetti, Gandolfi, Pederiva: "rotating the spinors", but it is actually very different: spinors are fixed, not rotating

advantageous for SO, will see soon

Lubos_Mitas@ncsu.edu

complexity of the wave function, and SOREPs: fixed-phase

$$\psi = \rho(\boldsymbol{R}, \boldsymbol{S}) \exp[i\phi(\boldsymbol{R}, \boldsymbol{S})]$$

so that the Schrodinger equation breaks into Re and Im

$$-\partial_t \rho = [T + V + W^{\Re} + (1/2)(\nabla\phi)^2]\rho$$

$$-\partial_t \phi = [T\phi - \nabla \ln\rho \cdot \nabla\phi + W^{\Im}]$$

the first equation gives the energy eigenvalue and we invoke the fixed-phase (FP) approximation (Ortiz, Martin, Ceperley '92)

$$\phi \approx \phi_T$$

FP seems looks like a step into an unknown territory, but it is not: fixed-node is a limit of the fixed-phase (not too difficult to show)

$$(\nabla\phi)^2 \quad \rightarrow \quad C_\infty \delta[\boldsymbol{R} - \boldsymbol{R}_{node}]$$

Lubos_Mitas@ncsu.edu

sampling of the spin configurations

effective free-particle Hamiltonian (kinetic term) for spins

$$H \to H + H_{spin}, \qquad H_{spin}(s_i) = -\frac{1}{2\mu_s}\left[\frac{\partial^2}{\partial s_i^2} - 1\right]$$

note that H_spin annihilates arbitrary spinor (and arbitrary products)

$$H_{spin}(s_i)[\alpha\phi^{\uparrow}(r_i)\chi^{\uparrow}(s_i) + \beta\phi^{\downarrow}(r_i)\chi^{\downarrow}(s_i)] = 0$$

therefore, to the leading order, no contribution to the energy

nonlocal SOREP term → locality approximation (LM et al '91)

$$W^{\Re} \approx W_T^{\Re} = \Re[\psi_T^{-1} W \psi_T]$$

Lubos_Mitas@ncsu.edu

fixed-phase spin-orbit DMC → FPSODMC

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tests on small systems against independent (nominally exact)

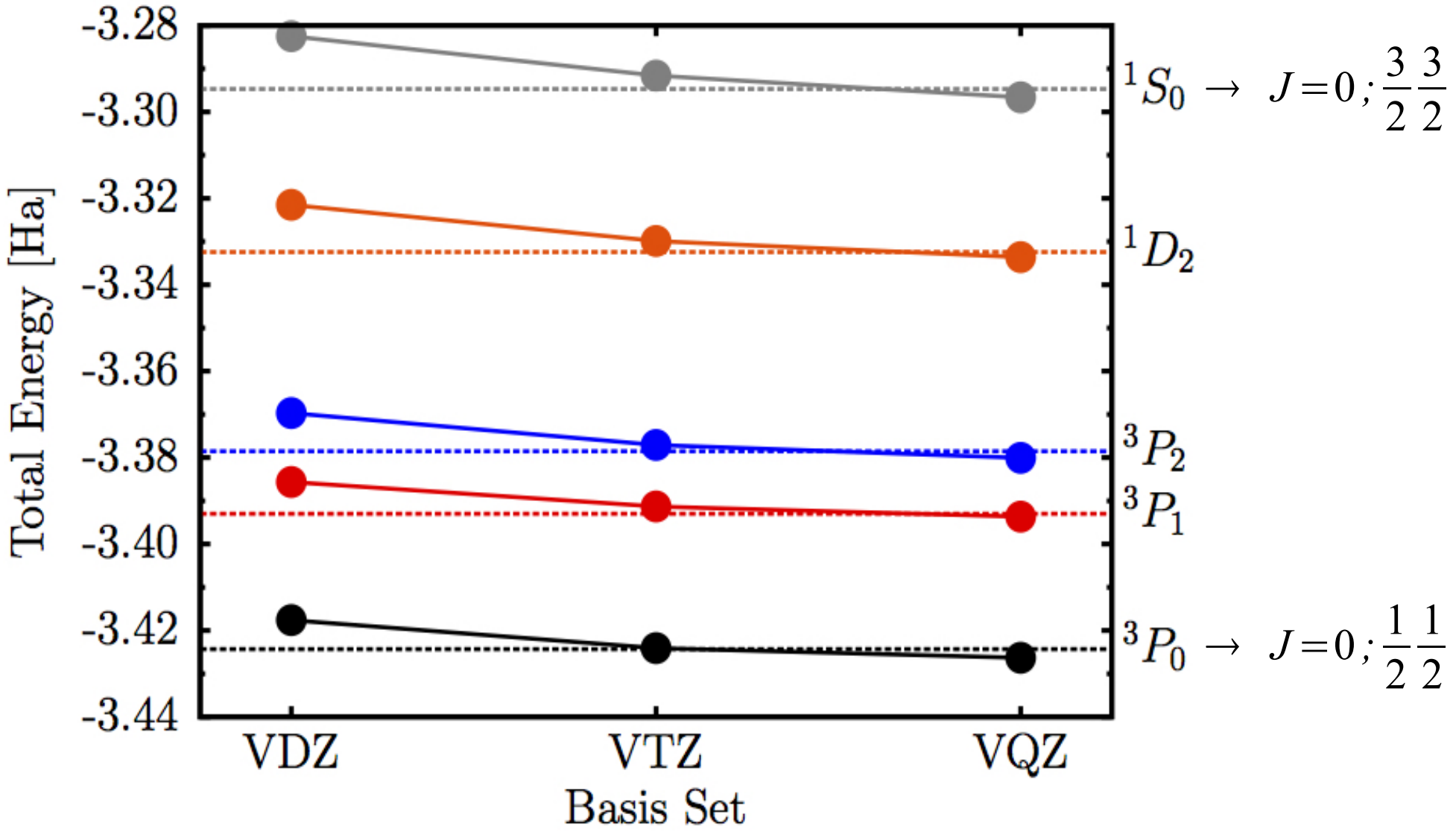
vs large-scale CI in explicit two-component/spinor formalism

C. Melton, M. Zhu, S. Guo, A. Ambrosetti, F. Pederiva, L.M.,
Phys. Rev. A 93, 042502 (2016)

Lubos_Mitas@ncsu.edu

total energies Pb atom with valence $6s^2 6p^2$

FPSODMC(….) vs CI with ccpVxZ basis(—●—)



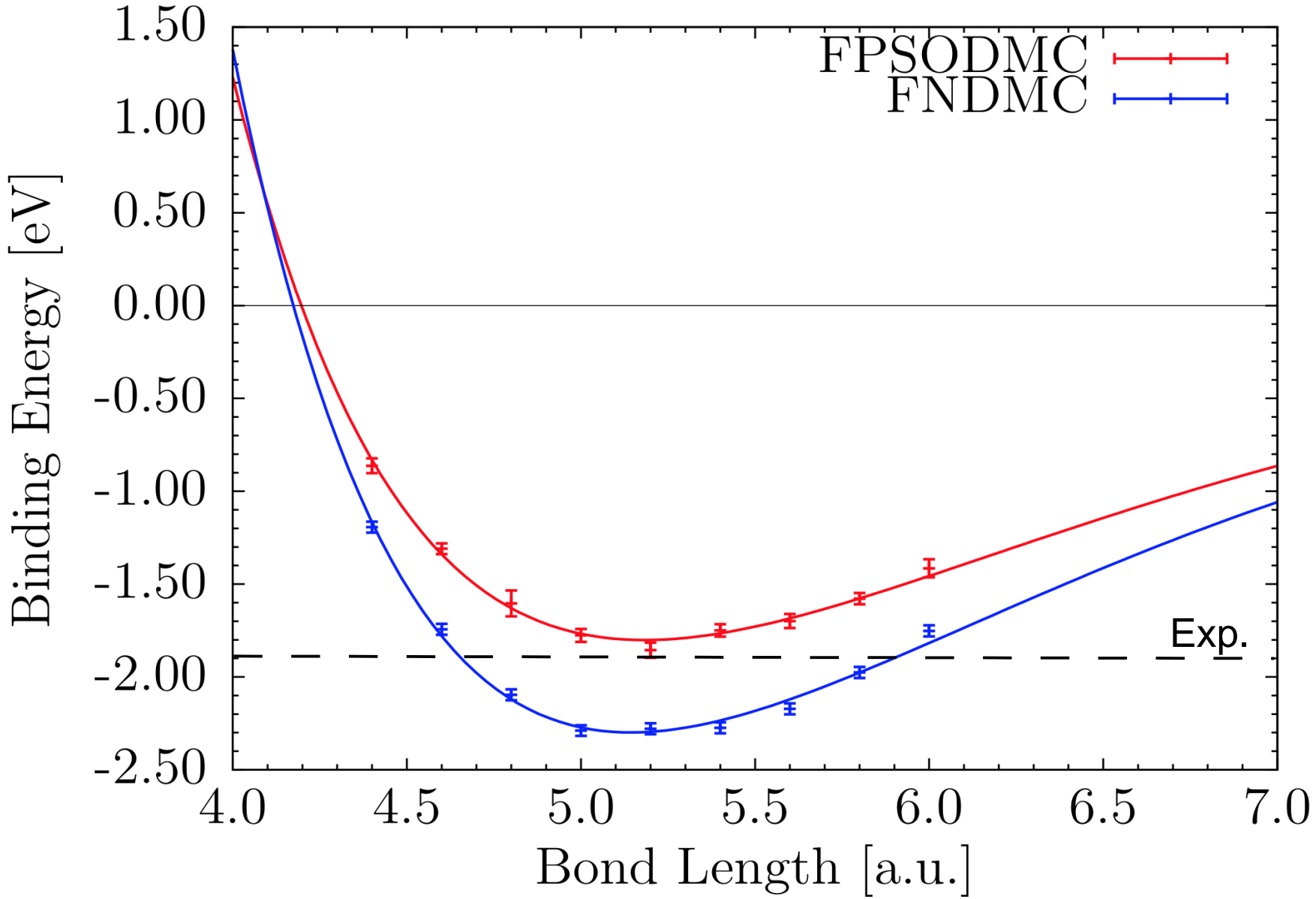
W atom is isovalent with Cr and Mo, but different ground state: $5d^4 6s^2\ {}^5D_0$, instead of $5d^5 6s^1\ {}^7S_3$

Config.	State	COSCI	DMC/COSCI	CISD	DMC/rCISD	Exp
$5d^4 6s^2$	${}^5D_1$	0.10	0.13(1)	0.10	0.15(1)	0.21
$5d^5 6s^1$	${}^7S_3$	- 0.85	- 0.19(1)	0.12	0.19(1)	0.37
$5d^4 6s^2$	${}^5D_2$	0.24	0.30(1)	0.13	0.30(1)	0.41
$5d^4 6s^2$	${}^5D_3$	0.42	0.49(1)	0.29	0.51(1)	0.60
$5d^4 6s^2$	${}^5D_4$	0.60	0.69(1)	0.45	0.69(1)	0.77

both SO and correlation needed to flip the states !

Lubos_Mitas@ncsu.edu

Sn_2 dimer should be simple, it is in the fourth row … but SO correction is ~ 0.5 eV ! (small core SOREP, 44 val. e-)

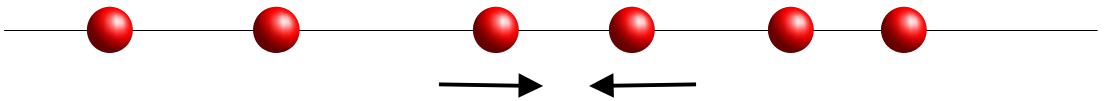


QMC is perhaps more than an accurate method only …

Lubos_Mitas@ncsu.edu

Topology of fermion antisymmetry: what do we know ?

1D: the ground state node of N fermions on a line is known exactly,



since each time two fermions cross each other they hit the node and the system passes from one domain to another → N! domains

3D: a few special cases of 2e-, 3e- atoms nodes known exactly, eg,

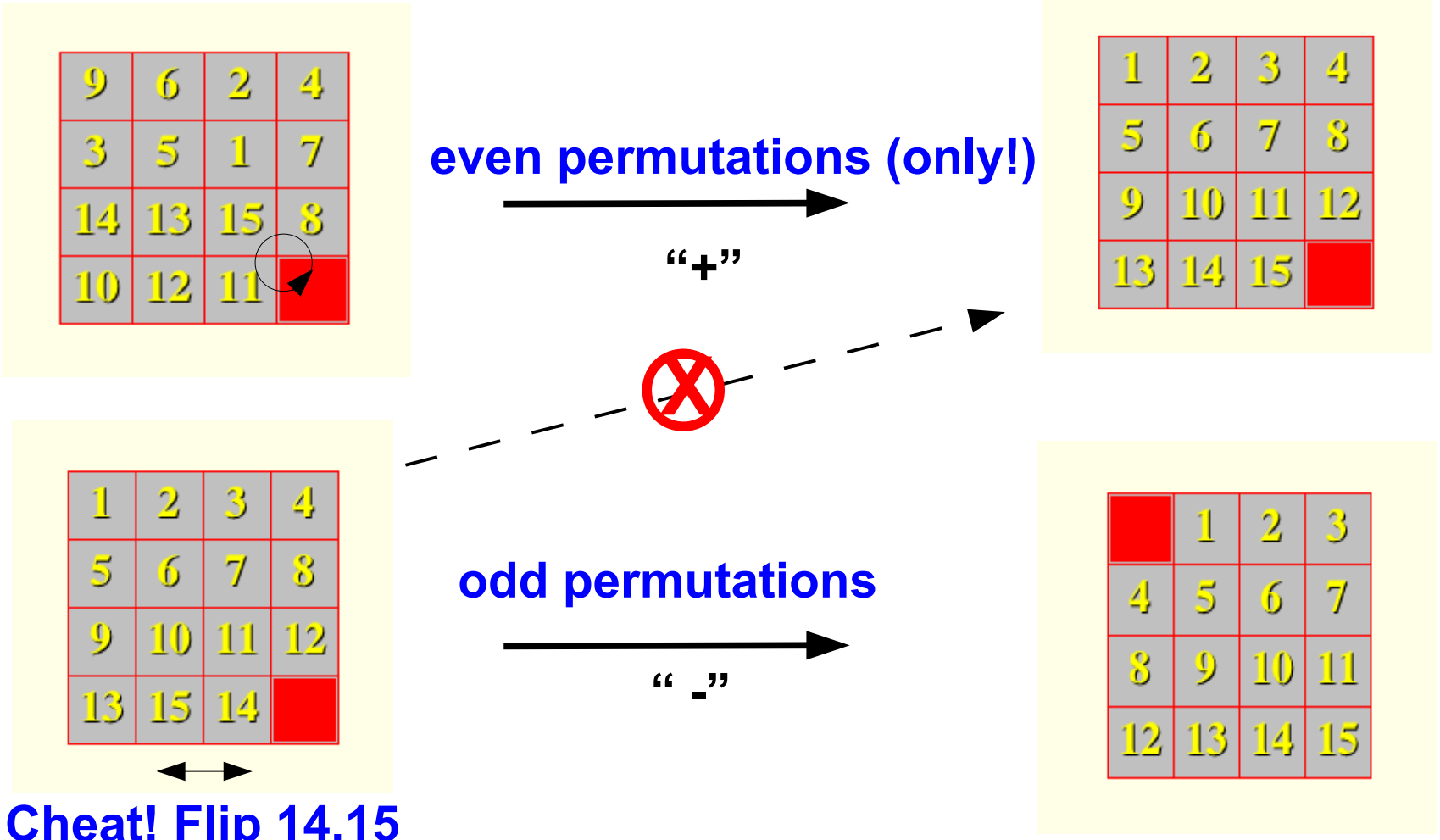
2e- He atom triplet ^{3}S[1s2s] exact node: $|r_1|^2 - |r_2|^2 = 0$

two domains (one +, one -) → $r_1 > r_2$ or $r_2 > r_1$

In fact, in 2D/3D the two nodal domains appear to be generic → fundamental property of ground state fermionic wave functions → global "p-waves"

Lubos_Mitas@ncsu.edu

"Kiddie proof": sliding 15-puzzle: an example of 3-cycle (triple exchange) permutation cluster → 15 fermions in 2D



Cheat! Flip 14,15

Lubos_Mitas@ncsu.edu

instead of conclusions: working hypothesis

Geometry is not everything, but it is the most fundamental thing

Connolly

Lubos_Mitas@ncsu.edu