Electronic structure quantum Monte Carlo methods and variable spins: beyond fixed-phase/node approximations

Cody Melton, M. Chandler Bennett, L. Mitas,
with A. Ambrosetti, F. Pederiva

North Carolina State University
Universities of Trento and Padova

CPSFM | Center for Predictive Simulation of Functional Materials

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NC STATE UNIVERSITY

Lubos_Mitas@ncsu.edu

electronic structure qmc

- ground and excited states, T=0

- energy differences ~ eVs, accuracy target 0.05 eV
  (Hartree-Fock as reference, E_corr = E_exact - E_HF)

interest in:

1) so far spins were just static labels (up, down) but we need spin-orbit, etc, varying spins

2) maybe, unify static and variable spins formulations

3) beyond the fixed-node/phase

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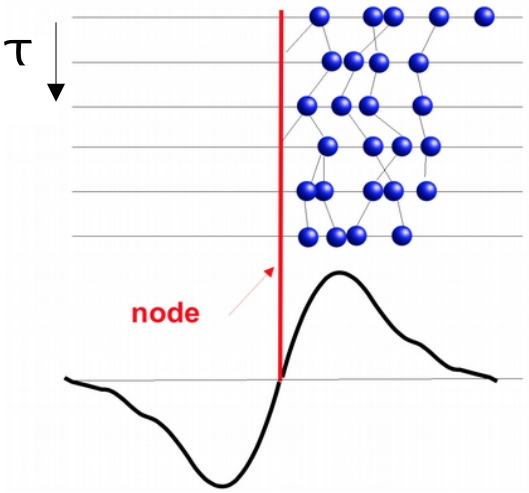
projector QMC and variational fixed-node → "standard model" FNDMC (90-95% of E_corr)

Hamiltonian: interacting electrons in ionic potentials (or ECP)

QMC/DMC: $\psi_0(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) = lim_{\tau\to\infty} \exp(-\tau H)\psi_{T(rial)} \quad \rightarrow \quad H\psi_0 = E_0\psi_0$

$\psi_T\psi_{0,FN} =$



node

$\Gamma(\psi) = \{\boldsymbol{R}; \psi(\boldsymbol{R}) = 0\}$

$dim(\Gamma(\psi)) = 3N - 1$

codimension 1

fixed-node (FN) approx. $\Gamma(\psi_{0,FN}) \overset{!}{=} \Gamma(\psi_T) \quad \rightarrow \quad \psi_T\psi_{0,FN} \geq 0$

trial function Slater-Jastrow: $\psi_T = \sum_k c_k det_k^{\uparrow}[\phi_\alpha] det_k^{\downarrow}[\phi_\beta] \exp[U_{corr}]$

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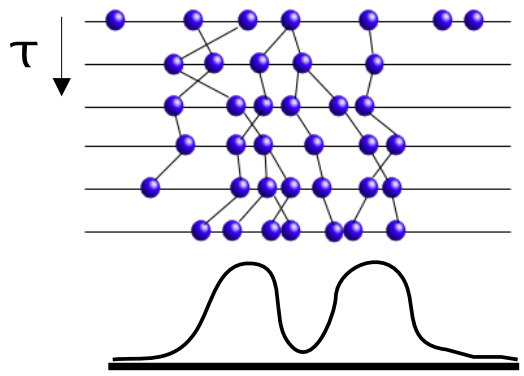
if eigenstate is inherently complex (eg, stationary current): fixed-phase approximation

write $\psi = \rho e^{i\Phi}; \quad \rho \geq 0$

$$\rho_0 = lim_{\tau\to\infty} \exp[-\tau(H + (\nabla\Phi_0)^2/2)]\rho_{T(rial)} \quad \rightarrow \quad (H + (\nabla\Phi_0)^2/2)\rho_0 = E_0\rho_0$$

$\rho_T \rho_{0,FP} =$



$dim(\Gamma(\rho)) = 3N - 2$

codimension 2

fixed-phase (FP) approx. $\Phi_0 \overset{!}{=} \Phi_T \rightarrow V_{eff,T} = (\nabla\Phi_T)^2/2$

$$\psi_T = \sum_k c_k det_k^{\uparrow}[\phi_\alpha] det_k^{\downarrow}[\phi_\beta] \exp[U_{corr}] = \rho_T e^{i\Phi_T}$$

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fixed-phase → special case of fixed-node (sketch)

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let $\psi_T(\boldsymbol{R})$ **be real, fermionic, with nodes at** $\boldsymbol{R}_{node,T} \in \Gamma(\psi_T)$

construct

$$\tilde{\psi} = \psi_T + ia\,\psi_{symm,>0}$$

$$\tilde{\phi} = \arctan\left[(\Re\,\tilde{\psi})/|\tilde{\psi}|^2\right]$$

then the limit of potential from the phase → node

$$lim_{a\to 0}(\nabla\tilde{\phi})^2 \quad \to \quad C_\infty(1/a)\,\delta[\boldsymbol{R}-\boldsymbol{R}_{node,T}]$$

ie, can write also the fixed-node as effective singular potential

$$H \quad \to \quad H + V_\infty(\boldsymbol{R}_{node,T})$$

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from spatial orbitals to spinorbitals

spinless electrons-ions Hamiltonian → spatial-only problem,

spin channels factorized: $\psi_T = \sum_k c_k \, det_k^{\uparrow}[\phi_\alpha(\boldsymbol{r}_i)] \, det_k^{\downarrow}[\phi_\beta(\boldsymbol{r}_j)] \exp[U_{corr}]$

now, include spin-orbit → $\phi_n(r_i, s_i) = \alpha \phi^{\uparrow}(r_i)\chi^{\uparrow}(s_i) + \beta \phi^{\downarrow}(r_i)\chi^{\downarrow}(s_i)$

determinant of spinors $\psi_{Trial} = \psi_{Trial}(\boldsymbol{R}, \boldsymbol{S}) = det[\phi_n(r_i, s_i)] \exp(U_{corr})$

spin functions and "coordinates" : $\chi^{\uparrow}(1/2) = \chi^{\downarrow}(-1/2) = 1 \quad \chi^{\uparrow}(-1/2) = \chi^{\downarrow}(1/2) = 0$

- wf complex, good quantum number J

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projection is more involved and less straightforward

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some ideas:

- **work in 80s on nuclei (Kalos, Carlson, Schmidt, others)**

- **sample the spinors (Pederiva, Gandolfi, Ambrosetti 2000s) with spinor updates ("stochastic rotations of spinors")**

- **smooth out spin configurations + fixed-phase approximation (Melton, Ambrosetti, Pederiva, LM et al, 2016)**

- **...**

we smooth out spin configurations/paths

- continuous (overcomplete) representation, ie, “coordinates”, possible choice:

$$\chi^{\uparrow}(s)=\exp(+is), \qquad \chi^{\downarrow}(s)=\exp(-is); \quad s\in(0,2\pi)$$

different from “rotating spinors”, here: spinors are fixed

why this choice in particular ? (… later)

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how can you do that ?

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atomic spin-orbit acting on a valence electron i can be recast as

$$\boldsymbol{L}_i \cdot \boldsymbol{S}_i \quad \rightarrow \quad \sum_{l,j,m_j} |l,j,m_j> \; v_{lj}(r_i) \; <l,j,m_j|$$

correct action of SO and expectations need matrix elements

$$\langle l,j,m_j \,|\, \chi \rangle \;=\; \langle a\chi^{\uparrow} + b\chi^{\downarrow} \,|\, c\chi^{\uparrow} + d\chi^{\downarrow} \rangle$$

$$I \;\rightarrow\; \sum_{s=1/2,-1/2} \quad \int_0^{2\pi} ds$$

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sample the spin configurations as free d.o.f.
→ fixed-phase spinorbit DMC (FPSODMC)

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effective free-particle Hamiltonian (kinetic term) for spins

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

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

therefore, to the leading order no contribution to the energy (subleading contribution overshadowed by the fixed-phase bias since SO is small)

FPSODMC method: tests on atomic and molecular systems

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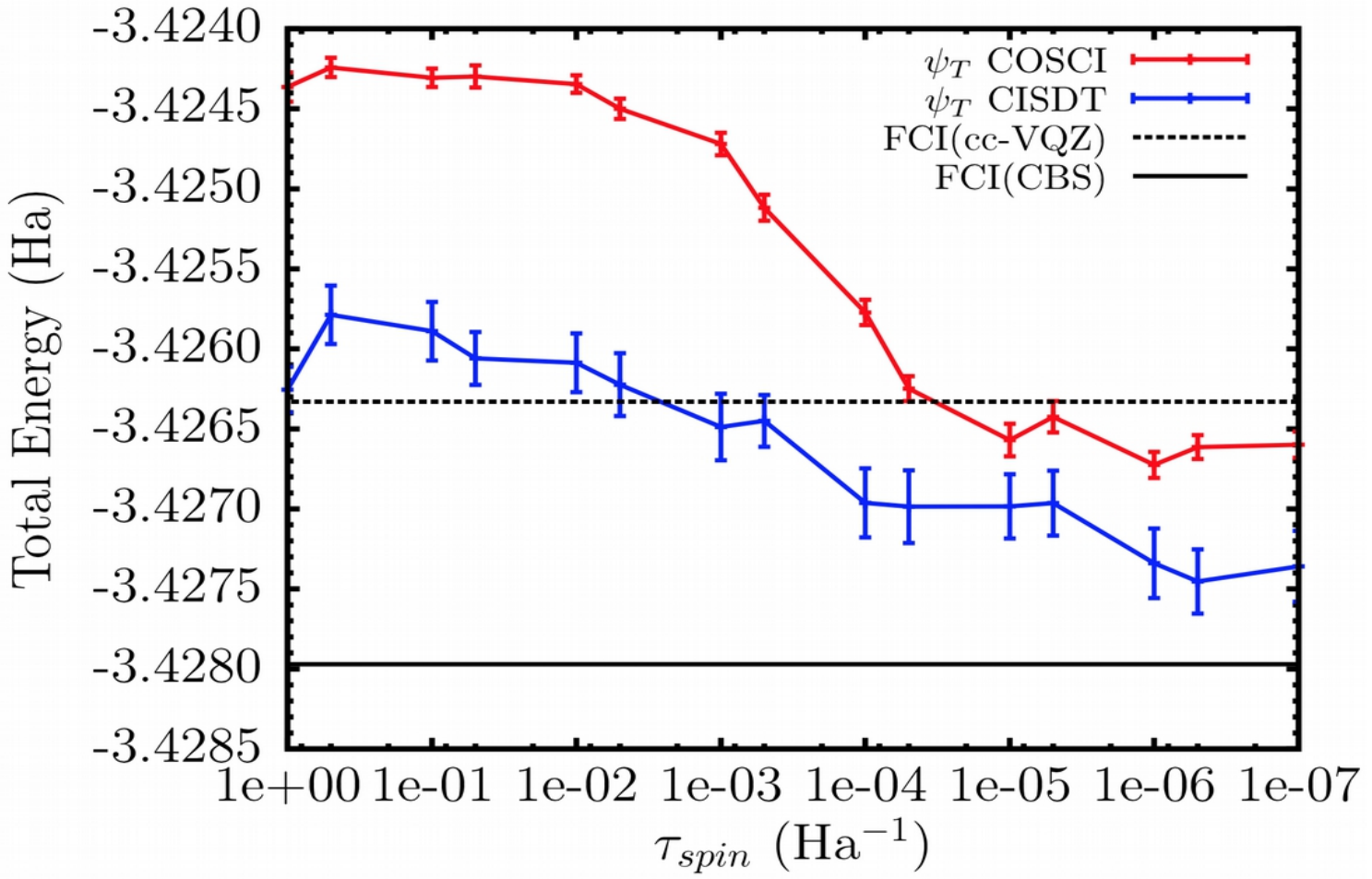
total energies: Pb atom valence only, vary effective mass, proportional to 1/(spin time step)

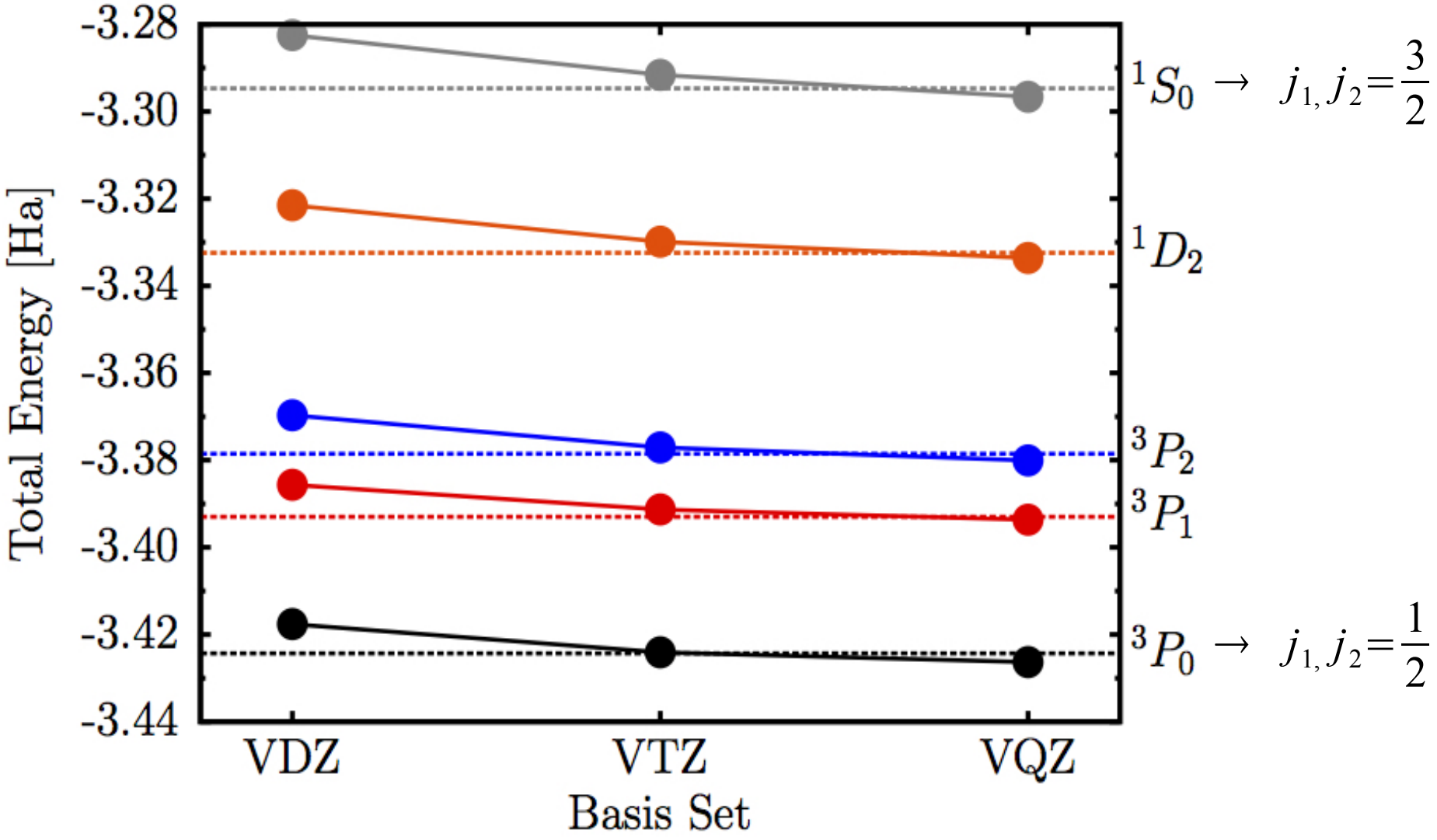


0.1 eV

(small ← spin effective mass → large)

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

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



Cr and Mo atoms electronic ground states → $^7S_3$ (d^5s^1)

W atom is isovalent, what is its ground state ?

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averaged SO (CI, QMC)	$^7S_3$ ($5d^5 6s^1$)
explicit SO two-component, open-shell only CI	$^7S_3$ ($5d^5 6s^1$)
explicit SO two-component, full CI or FPSODMC/rCI	$^5D_0$ ($5d^4 6s^2$)

both SO and correlation needed to flip the state !

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W atom SO splitted *sd*-manifold of excitations: correct ground state in FPSODMC

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

Lubos_Mitas@ncsu.edu

W atom: also correct order of excitations!

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
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$5d^4 6s^2$	$^5D_4$	0.60	0.69(1)	0.45	0.69(1)	0.77

FPSODMC agrees with experiment, higher accuracy needs better ECP

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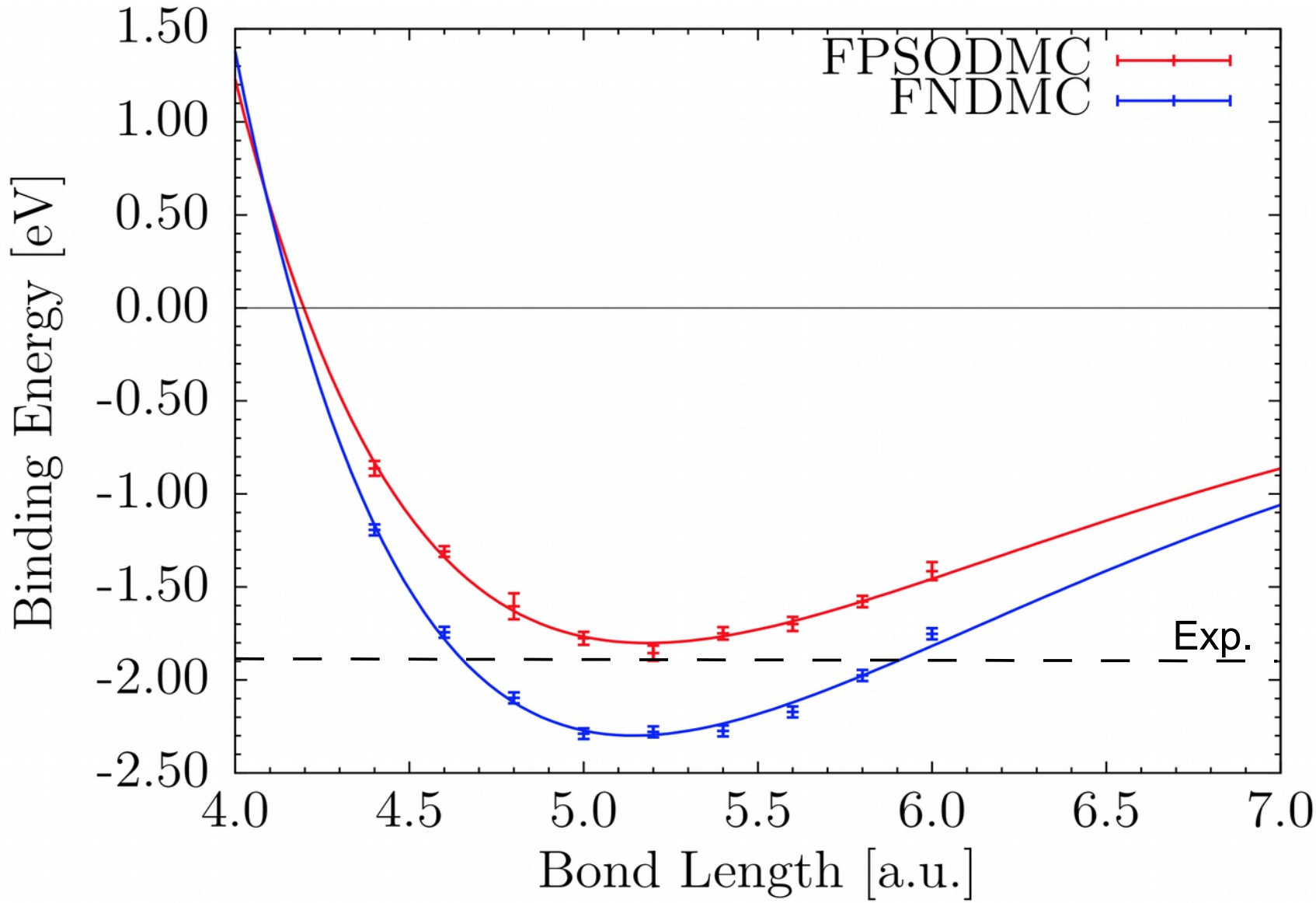
Sn_2 dimer should be simple, it is only the fourth row … but SO correction is ~ 0.5 eV ! (small cores, 44 val. e-)



why this in particular ?

$$\chi^{\uparrow}(s)=\exp(+is), \qquad \chi^{\downarrow}(s)=\exp(-is); \quad s\in(0,2\pi)$$

- similar to spatial coords but much smaller space

- no divergencies, no jumps, importance sampling ok

- simplifies dealing with pseudopotentials (effective cores) and generate similar bias, “close” to fixed-node regime

but more

- enables to smoothly “complexify” also real eigenstates

- and still more ...

Lubos_Mitas@ncsu.edu

interestingly, from such spinor wf, one can recover the spin-labeled fixed-node trial form ...

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in spinors $\chi_\alpha(\boldsymbol{r},s)=\phi_\alpha(\boldsymbol{r})e^{is}, \;\; \chi_\beta(\boldsymbol{r},s)=\phi_\beta(\boldsymbol{r})e^{-is}$

adjust to two values: $\{up\}=\{s_i\}\rightarrow s, \quad \{down\}=\{s_j\}\rightarrow s', \quad s\neq s'$

$$\det\begin{bmatrix} \varphi_1(1)e^{is} & \varphi_1(2)e^{is'} & \varphi_1(3)e^{is} & \varphi_1(4)e^{is'} & \dots \\ \varphi_1(1)e^{-is} & \varphi_1(2)e^{-is'} & \varphi_1(3)e^{-is} & \varphi_1(4)e^{-is'} & \dots \\ \varphi_2(1)e^{is} & \varphi_2(2)e^{is'} & \varphi_2(3)e^{is} & \varphi_2(4)e^{is'} & \dots \\ \varphi_2(1)e^{-is} & \varphi_2(2)e^{-is'} & \varphi_2(3)e^{-is} & \varphi_2(4)e^{-is'} & \dots \\ & & \dots & & \end{bmatrix}$$

$$[\sin(s'-s)]^{N/2}\det\begin{bmatrix} \varphi_1(1) & \varphi_1(3) & 0 & 0 & \dots \\ \varphi_2(1) & \varphi_2(3) & 0 & 0 & \dots \\ 0 & 0 & \varphi_1(2) & \varphi_1(4) & \dots \\ 0 & 0 & \varphi_2(2) & \varphi_2(4) & \dots \\ & & \dots & & \end{bmatrix}$$

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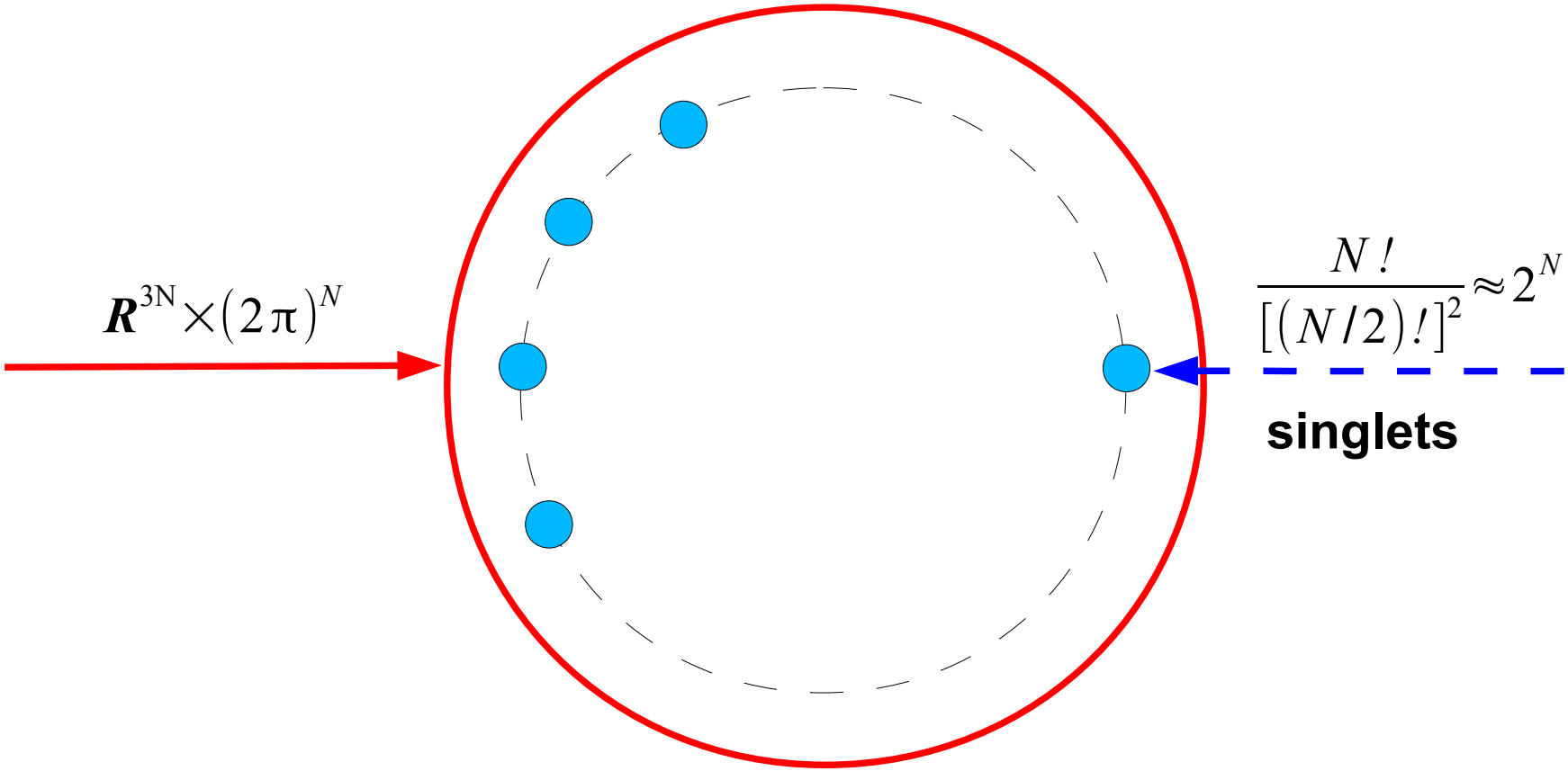
full sampling of all possible spin states and configurations: cartoon



N-electron continuous spin-position space

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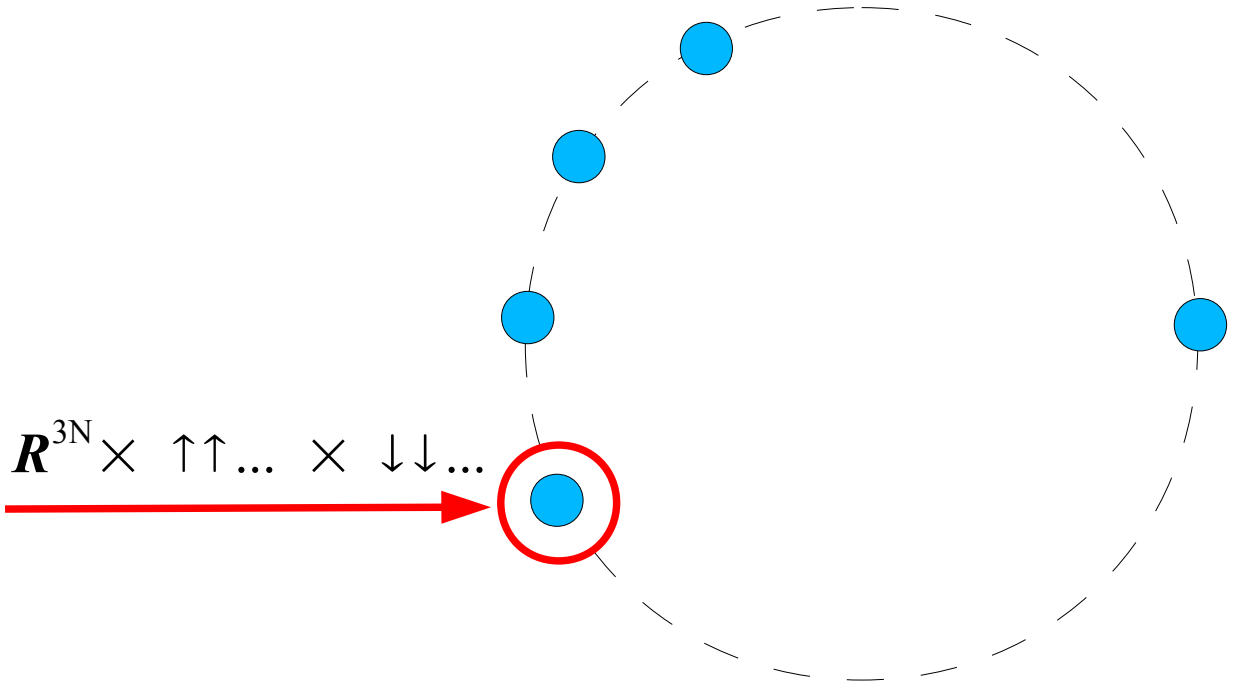
restricting spins into particular “up” and “down” subspace



one (N/2)*(N/2) choice → fixed-node

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fixed-node trial wf form but with a complex twist

spins factorize out of the determinant and we get up.down product:

$$\psi_T = det[\chi_j(r_k, s_k)] \quad \rightarrow \quad \psi_T = fac(s, s')\, det^{\uparrow}[\phi_i(r_k)]\, det^{\downarrow}[\phi_j(r_{k'})]$$

- the most interesting regime: $\{up\} = \{s_i\} \approx s \qquad \{down\} = \{s_j\} \approx s',$

- basically, the fixed-node limit but complexified, ie, it has properties of the fixed-phase, as can be achieved by:

  - the choice of spin variables (one assigns a set of particles as spin-up or -down, ie, particular subset of permutations)

  - explore how close/far to fixed-node by τ_{spin}/τ_{space}

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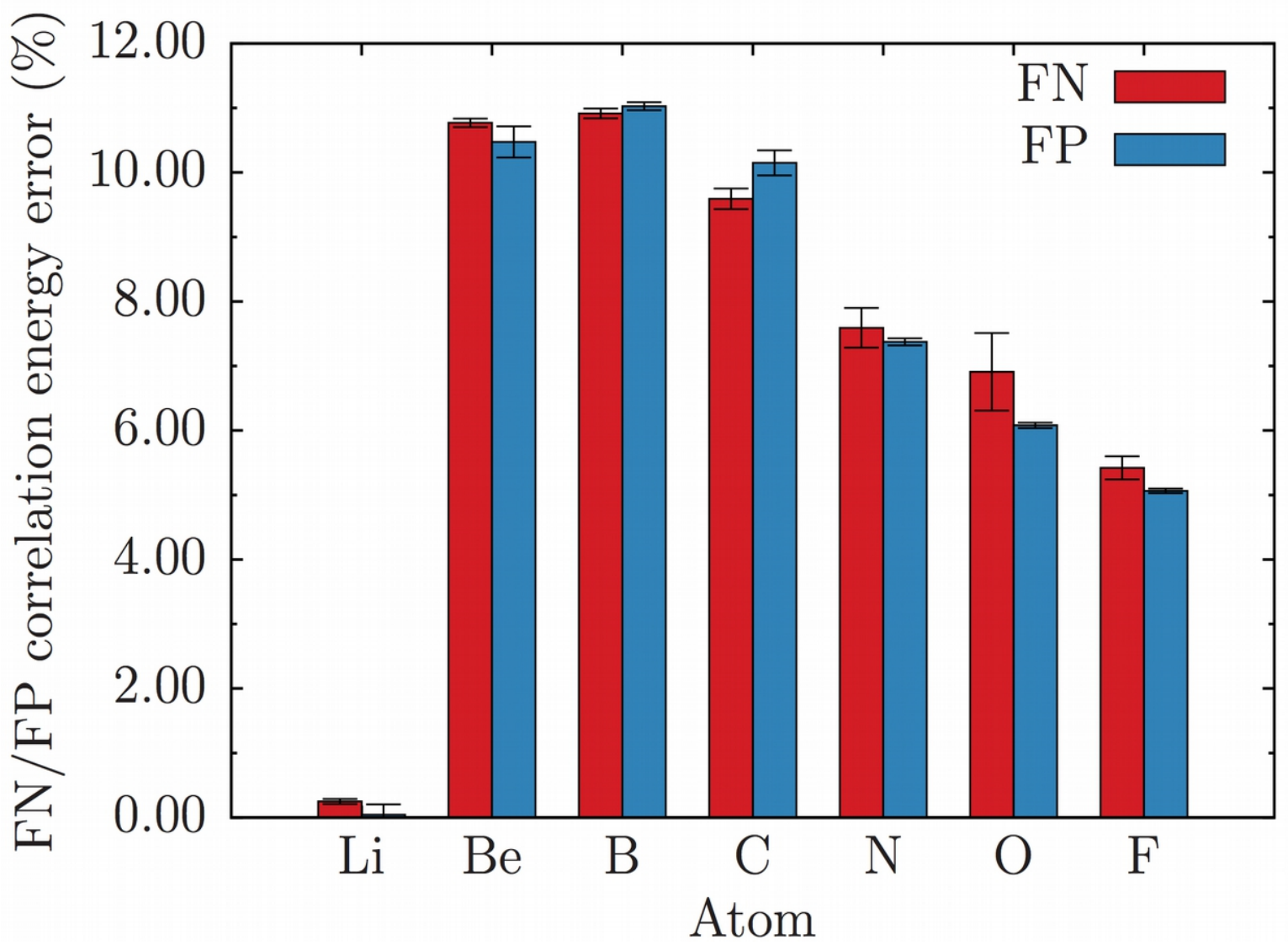
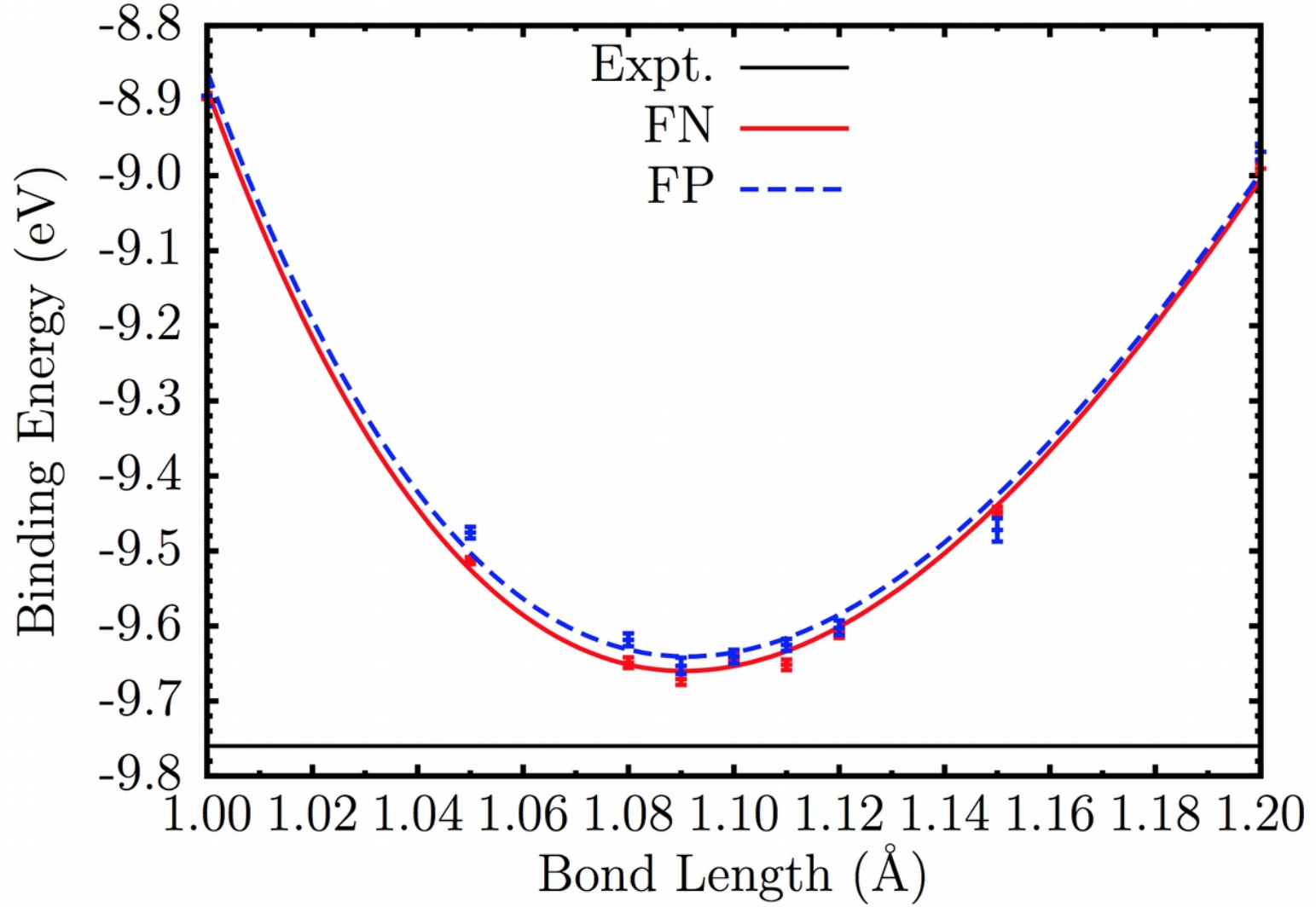
fixed-node vs fixed-phase biases in atoms:
FN real w.f. vs FP at the FN limit
essentially the same



similar for molecules now including nonlocal ECPs
FN vs FP at the FN limit: binding curves of N_2



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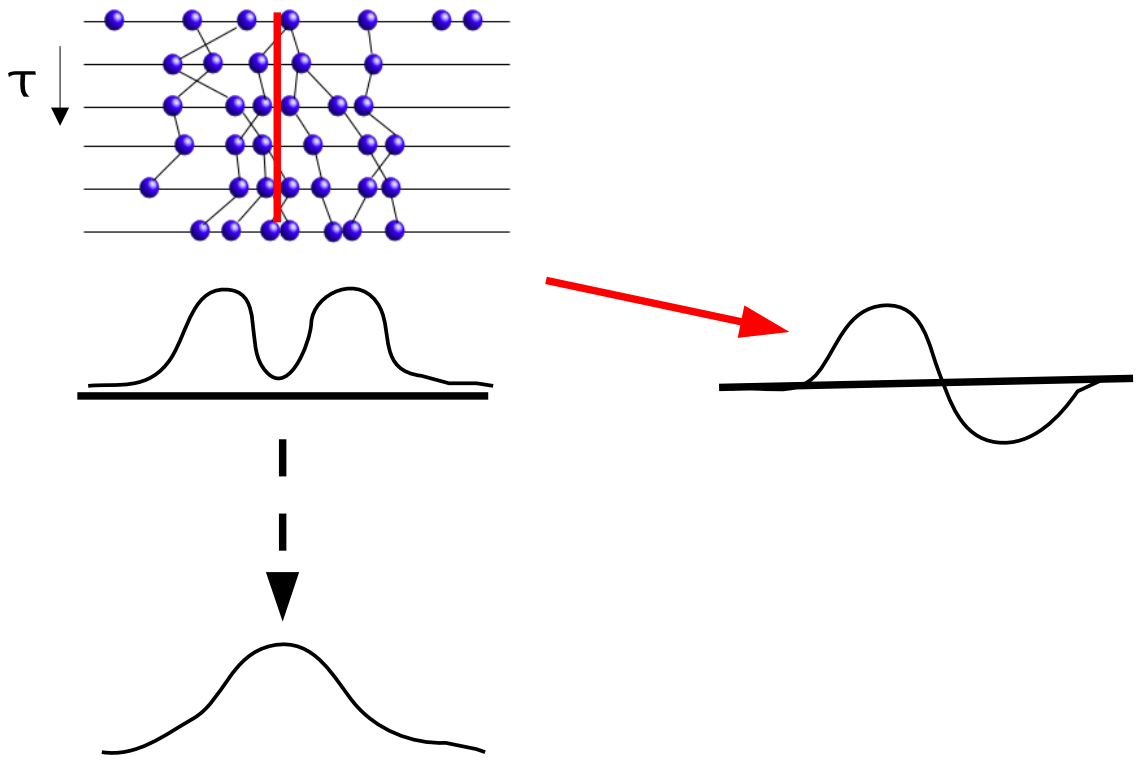
released-node



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released-node:
importance sampling with symmetric guiding function while projecting out the fermionic component

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antisymm. $\psi_T \xrightarrow{\text{FNDMC}} \psi_T \psi_{FN}$

$$E_{FN} = \frac{\int \psi_{FN} \psi_T [(H \psi_T)/\psi_T]}{\int \psi_{FN} \psi_T}$$

symm. $\psi_G \xrightarrow{\text{RNDMC}} \psi_G \psi_{RN} = \underline{symm + antisymm}$

$$E_{RN} = \frac{\int \psi_{RN} \psi_G (\psi_T/\psi_G)[(H \psi_T)/\psi_T]}{\int \psi_{RN} \psi_G (\psi_T/\psi_G)}$$

Lubos_Mitas@ncsu.edu

choice of guiding function

$\psi_G = \rho_T$

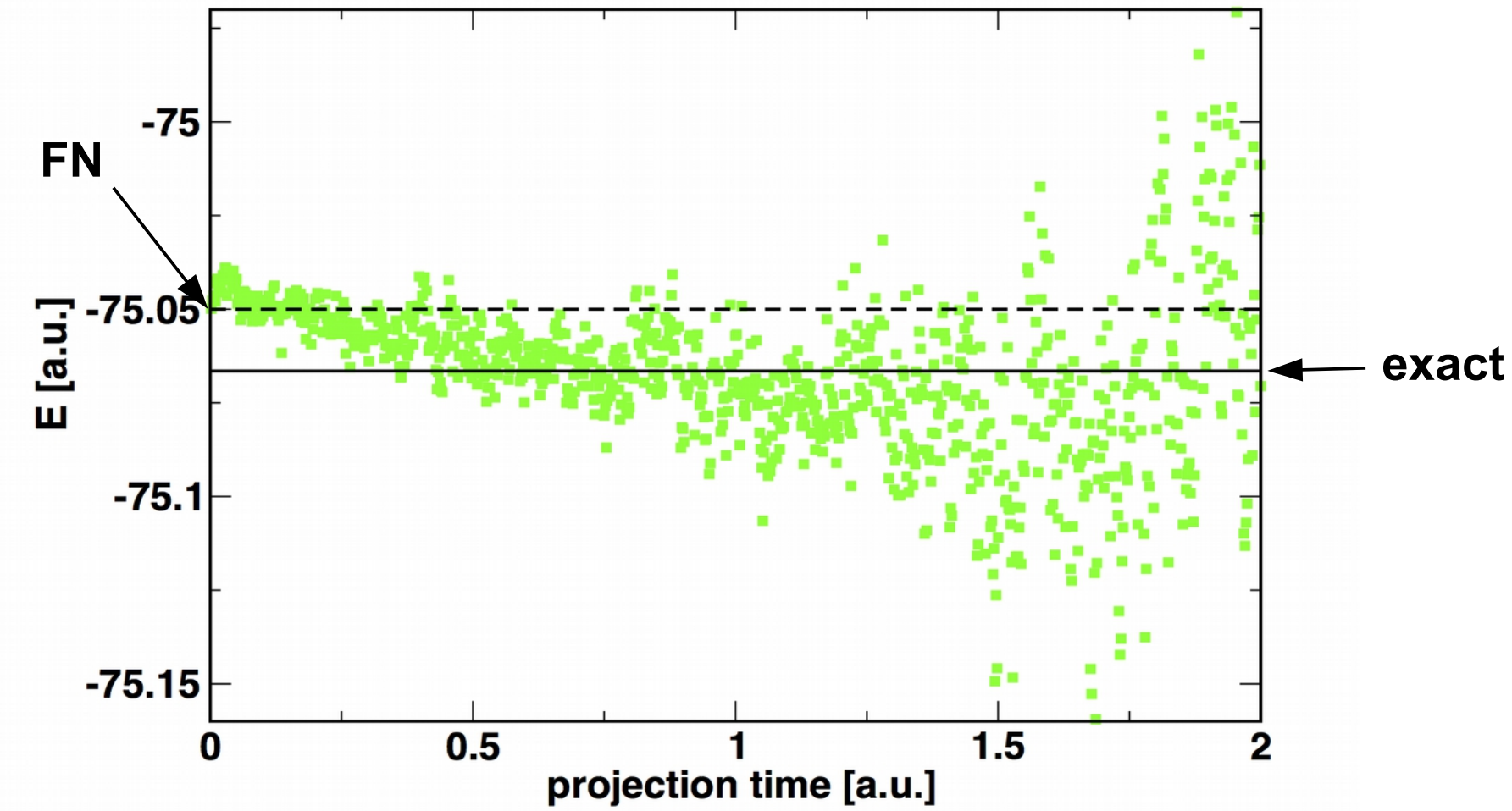
$$\psi_T = \rho_T(\boldsymbol{R}, S)\exp[i\phi_T(\boldsymbol{R}, S)]$$

why ?

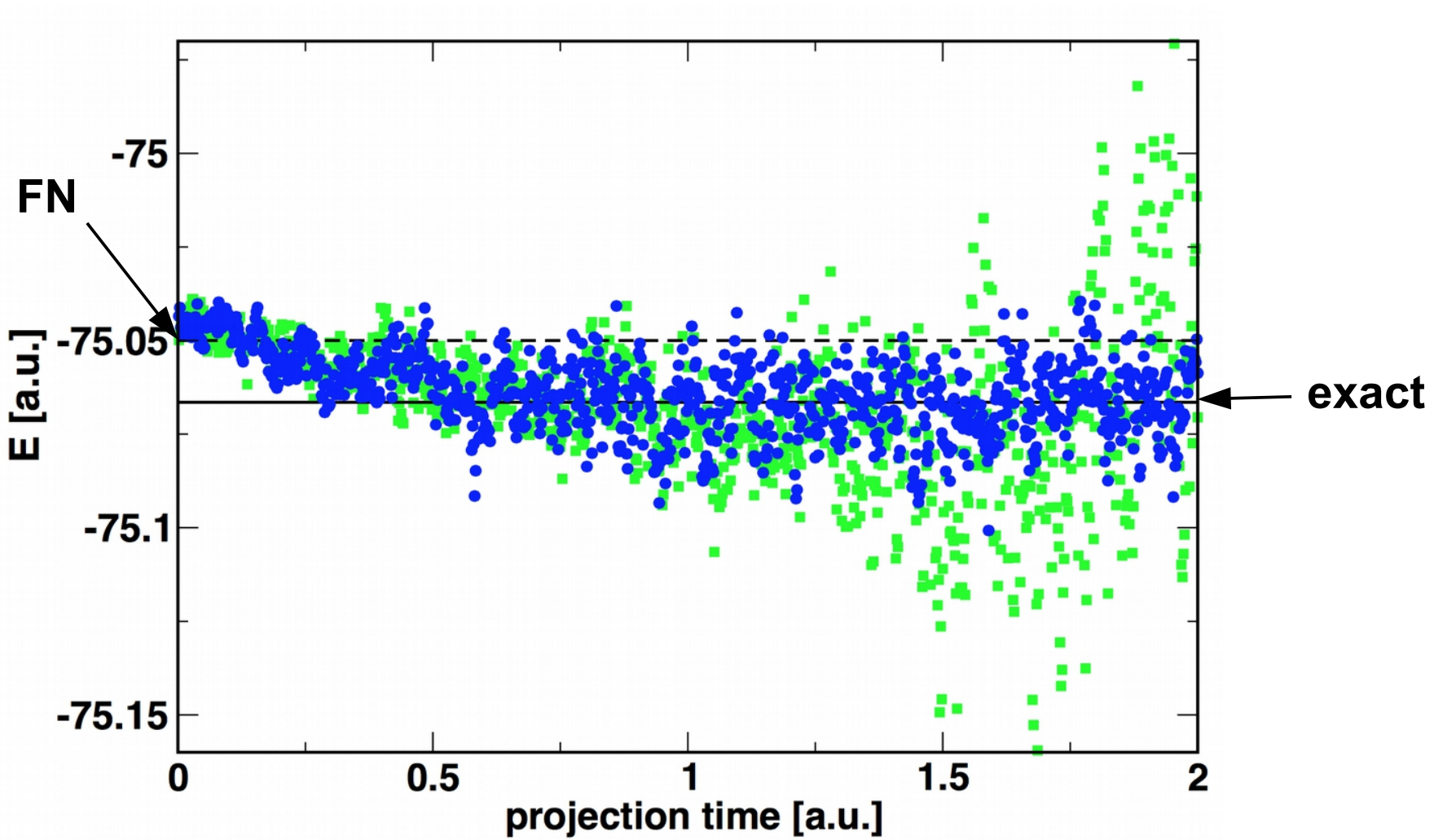
- **amplitude is symmetric by definition**
- **its node is codimension 2, ie, generically ergodic sampling**
- **it is "close" to ψ_T $\rightarrow$ that implies close to optimal importance sampling**
  $\rightarrow$ local energy fluctuations almost the same

Lubos_Mitas@ncsu.edu

few electron system (all-el O atom): released-node and the well-known exponential noise



better tuned algorithm:
released-node eliminates the bias fully



summary

- unifying formalism FPSODMC, FN and FP, static/variable spins,

  sampling + nodes → sampling + effective potential

- wave functions with phase/spins are more general, more smooth, ergodic sampling (zeros codim 2)

- new options for attacking fixed-node/phase bias

- more variational freedom (?)

PRA 2016, JCP 2016, PRE 2017 + more coming

Lubos_Mitas@ncsu.edu