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

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SIGN 2017, INT, U. Washington, Seattle
projector QMC, Slater-Jastrow trial functions (single, multi-ref) and the fixed-node approximation → “standard model” FNDMC

Hamiltonian with (valence) electrons and ions

QMC/DMC: $\phi_0 = \lim_{\tau \to \infty} \exp(-\tau H) \psi_{T(rial)} \rightarrow H \phi_0 = E_0 \phi_0$

- trial function $\psi_T = \sum_k c_k \det^\uparrow_k [\phi_\alpha] \det^\downarrow_k [\phi_\beta] \exp[U_{corr}]$

sampled in coord. space with fixed-node approx.
EoS FeO solid at high pressures: FNDMC transition at $\sim 65$ GPa (exper. 70-100); also agreement for cohesion, gaps, bulk moduli, etc $\rightarrow \sim 95(2)\%$ of $E_{corr}$
but so far static spins only, while we need spins to vary

spinless electrons-ions Hamiltonian → spatial-only problem,

spin channels factorized: \[ \psi_T = \sum_k c_k \det_k^\uparrow [\phi_\alpha(r_i)] \det_k^\downarrow [\phi_\beta(r_j)] \exp[U_{\text{corr}}] \]

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 \[ \psi_{\text{Trial}} = \psi_{\text{Trial}}(R, S) = \det[\phi_n(r_i, s_i)] \exp(U_{\text{corr}}) \]
spin “coordinates” : \[ \chi^\uparrow(1/2) = \chi^\downarrow(-1/2) = 1 \quad \chi^\uparrow(-1/2) = \chi^\downarrow(1/2) = 0 \]
what is the problem then? variationally ok

just sampling of a larger space

\[ \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \rightarrow \sum_{\sigma_1} \cdots \sum_{\sigma_N} \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \]

e.g., A. Ambrosetti, F. Pederiva, LM ,..., Phys. Rev. B 85, 045115 ('12)

(also already in 1985 by J. Carlson and M. Kalos for nuclei ...)

<table>
<thead>
<tr>
<th></th>
<th>VMC [eV]</th>
<th>Exper. [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tl</strong></td>
<td>J=3/2/g.s. J=1/2</td>
<td>0.85(5)</td>
</tr>
<tr>
<td><strong>Pb</strong></td>
<td>J=1 /g.s. J=0</td>
<td>0.88(7)</td>
</tr>
<tr>
<td><strong>Pb</strong></td>
<td>J=2 /g.s. J=0</td>
<td>1.23(6)</td>
</tr>
<tr>
<td><strong>Bi</strong></td>
<td>J=3/2 /g.s. J=3/2</td>
<td>1.31(8)</td>
</tr>
</tbody>
</table>
however, projection QMC (DMC etc) is less straightforward

discrete moves between \(2^N\) points:
- moves of fixed length (no time step)
- no smooth importance guiding
- increased local energy fluctuations

\(\Rightarrow\) inefficient with \(N\)

more issues:
- inherently complex wave functions
- nonlocal SO pseudopots (PP) for heavy elements

suggested ideas:

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

- smooth out spin configurations + fixed-phase approximation (Melton, Ambrosetti, Pederiva, LM et al, 2016)
step one: smooth out spin configurations/paths

we make spin configurations non-discrete by using continuous (overcomplete) and compact representation, possible choice:

\[ \chi^\uparrow(s) = \exp(+is), \quad \chi^\downarrow(s) = \exp(-is); \quad s \in (0, 2\pi) \]

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

since the spinors are fixed one can use projection onto trial function to eliminate nonlocality of PP and SO terms

\[ W_{SORPP} = \sum_i \left[ W_{ARPP}^{(i)} + \sum_i W_{SO}^{(i)} \right] \quad W_{SO}^{(i)} = \sum_{j,l} v_{jl}(r_i) P_{jl}^{(i)} l_i \cdot s_i P_{jl}^{(i)} \]

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

\[ W^\Re \approx W_T^\Re = \Re \left[ \psi_T^{-1} W \psi_T \right] \]
step two: complex wave function $\rightarrow$ fixed-phase (FP)

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

the Schrodinger equation breaks into Re and Im

$$
-\partial_r \rho = [T + V + W^R + (1/2)(\nabla \phi)^2] \rho
$$

$$
-\partial_r \phi = [T \phi - (\nabla \ln \rho) \cdot \nabla \phi + W^\Im]
$$

the first equation gives the energy eigenvalue and we invoke the fixed-phase (FP) approximation (Ortiz et al '92)

$$
\phi \approx \phi_T \rightarrow V_{\text{eff}} = (1/2) (\nabla \phi_T)^2
$$

FP seems like a step into an unknown territory, but it is not: fixed-node is a limit/special case of the fixed-phase for real wfs

$$
(\nabla \phi_T)^2 \rightarrow C_\infty \delta[R - R_{\text{node}, T}]
$$
fixed-phase → special case of fixed-node, sketch of a demonstration

let $\psi_T(R)$ be real, fermionic, with nodes at subset $R_{node,T}$

construct

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

$\tilde{\phi} = \arctan \left( \frac{\Re \tilde{\psi}}{|\tilde{\psi}|^2} \right)$

then the limit of potential from the phase $\rightarrow$ node

$\lim_{a \to 0} (\nabla \tilde{\phi})^2 \rightarrow C_\infty \delta [R - R_{node,T}]$
step three: sampling of the spin configurations
→ fixed-phase spinorbit DMC (FPSODMC)

effective free-particle Hamiltonian (kinetic term) for spins

\[ H \rightarrow H + H_{\text{spin}}, \quad H_{\text{spin}}(s_i) = - \frac{1}{2\mu_s} \left[ \frac{\partial^2}{\partial s_i^2} + 1 \right] \]

\( H_{\text{spin}} \) annihilates arbitrary spinor \( H_{\text{spin}}(s_i) [\alpha \phi^\dagger(r_i) \chi^\dagger(s_i) + \beta \phi^\dagger(r_i) \chi^\dagger(s_i)] = 0 \)

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

- effective spin mass → time step on the spin subspace
  (overall, basically two time steps, spatial and spin)

FPSODMC method: tests on atomic and molecular systems
total energies: Pb atom with valence $6s^26p^2$

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

$1^1S_0 \rightarrow J=0; \frac{3}{2} \frac{3}{2}$

$1^1D_2$

$3^3P_2$

$3^3P_1$

$3^3P_0 \rightarrow J=0; \frac{1}{2} \frac{1}{2}$
Cr and Mo atoms ground states → $^7S_3$ ($d^5s^1$)

W atom is isovalent, what is its ground state?

- averaged SO, any method (DFT, CI, QMC) → $^7S_3$ ($5d^56s^1$)
- explicit SO two-component, open-shell only CI → $^7S_3$ ($5d^56s^1$)
- explicit SO two-component, full CI or FPSODMC/rCl → $^5D_0$ ($5d^46s^2$)

Both SO and correlation needed to flip the state!
### W atom SO splitted sd-manifold of excitations

<table>
<thead>
<tr>
<th>Config.</th>
<th>State</th>
<th>COSCI</th>
<th>DMC/COSCI</th>
<th>CISD</th>
<th>DMC/rCISD</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5d^46s^2$</td>
<td>$^5D_1$</td>
<td>0.10</td>
<td>0.13(1)</td>
<td>0.10</td>
<td>0.15(1)</td>
<td>0.21</td>
</tr>
<tr>
<td>$5d^56s^1$</td>
<td>$^7S_3$</td>
<td>-0.85</td>
<td>-0.19(1)</td>
<td>0.12</td>
<td>0.19(1)</td>
<td>0.37</td>
</tr>
<tr>
<td>$5d^46s^2$</td>
<td>$^5D_2$</td>
<td>0.24</td>
<td>0.30(1)</td>
<td>0.13</td>
<td>0.30(1)</td>
<td>0.41</td>
</tr>
<tr>
<td>$5d^46s^2$</td>
<td>$^5D_3$</td>
<td>0.42</td>
<td>0.49(1)</td>
<td>0.29</td>
<td>0.51(1)</td>
<td>0.60</td>
</tr>
<tr>
<td>$5d^46s^2$</td>
<td>$^5D_4$</td>
<td>0.60</td>
<td>0.69(1)</td>
<td>0.45</td>
<td>0.69(1)</td>
<td>0.77</td>
</tr>
</tbody>
</table>

FPSODMC agrees with experiment “ok”, but better RPPs needed!
**FPSODMC applied to the PbH molecule (the averaged SO treatment off by 1 eV!)**

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_{\text{bind}}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>spin-average CCSD(T)</td>
<td>2.66</td>
</tr>
<tr>
<td>spin-average FNDMC</td>
<td>2.58(1)</td>
</tr>
<tr>
<td>MRCIS/SO+pert. spin-average CCSD(T)</td>
<td>1.61-1.71</td>
</tr>
<tr>
<td><strong>FPSODMC</strong></td>
<td><strong>1.63(1)</strong></td>
</tr>
<tr>
<td>Exper.</td>
<td>~ 1.69(5)</td>
</tr>
</tbody>
</table>

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Sn\textsubscript{2} dimer should be simple, it is the fourth row ... but SO correction is \(~ 0.5 \text{ eV} \)! (small core SORPP, 44 val. e-)

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![Graph showing binding energy vs bond length for different methods: FPSODMC and FNDMC. The experimental values are also plotted.]
interestingly, one can go “back” to fixed-node, ie, recover the spin-labeled fixed-node trial form ...

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

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

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

$$
[sin(s' - s)]^{N/2} \text{det} \begin{vmatrix}
\varphi_1(1) & \varphi_1(3) & 0 & 0 \\
\varphi_2(1) & \varphi_2(3) & 0 & 0 \\
0 & 0 & \varphi_1(2) & \varphi_1(4) \\
0 & 0 & \varphi_2(2) & \varphi_2(4) \\
\vdots & \vdots & \vdots & \vdots
\end{vmatrix}
$$
fixed-node trial form but with a complex twist

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

\[ \psi_T = \text{det}[\chi_j] \rightarrow \psi_T = \text{const} \times [\sin((s-s')^N/2)] \text{det}^\uparrow[\phi_i] \text{det}^\downarrow[\phi_j] \]

- the most interesting regime: \( \{\text{up}\} = \{s_i\} \approx s \quad \{\text{down}\} = \{s_j\} \approx s' \),

- basically the fixed-node limit but complexified, i.e., has properties of the fixed-phase

- this can be achieved by the choice of spin variables and by adjusting the time step for spin variables
two limits: slow spins → fixed-node
fast spins → full fixed-phase

- group the spins to two distinct values → up, down and run FP
  C atom, all e-

~ 5% $E_{\text{corr}}$

indep. calculated FN value ($\sim 95\%$ of $E_{\text{corr}}$)

0 ← spin time step → large
fixed-node vs fixed-phases biases from:
independent FN real wf vs FP at the FN limit
fixed-phase: some considerations

- has a form of effective (many-body) potential/field

\[ V_{ph} = \frac{1}{2} (\nabla \phi)^2 \]

\[ - \partial_t \rho = \left[ T + V + V_{ph} \right] \rho \]

- \( \rho(R) \geq 0 \), its zeros are codimension 2 (unlike FN codimension 1)

- ergodicity generically ok (no artificial nodal domains → important for calculations of other properties than energy)

- smaller fluctuations and easier sampling (no recrossing)
fixed-phase amplitude zeros: codimension 2

- 2 harmonic electrons, $^3P(sp)$ state $\rightarrow \psi_{exact} = g(r_1, r_2, r_{12}) \det[1, Y_{11}]$

  \begin{align*}
  \text{fixed-node: } V_{FN} &= V_\infty \delta(x_1 - x_2) \\
  \partial \Gamma &= \{(x_1 = x_2) \otimes R^4\} \rightarrow d = 5 \text{ line} \\
  \Pi_0 &= \{(x_{12}^2 + y_{12}^2 = 0) \otimes R^4\} \rightarrow d = 4 \text{ point}
  \end{align*}

- three periodic electrons $\psi_T = \det[1, e^{ix}, e^{iy}]$

  \begin{align*}
  \text{fixed-node: } \psi_T &= \Re \{\det[1, e^{ix}, e^{iy}]\} \\
  \text{fixed-phase: } \rho_T &= |\psi_T|
  \end{align*}

  2 nodal domains one domain
coming back to spatial-only nodes: some properties

- roots of 1D polynomial/function “anchor” its behavior
- nodes are roots of multivariate polynomial/function
  \[ \psi(r_1, r_2, ..., r_N) = \psi(R) = 0 \]
- in addition, nodes of eigenst. of Schrodinger equation are special:
  - nodal domain averages \( \rightarrow \text{nda} \)
  - nodal surface averages \( \rightarrow \text{nsa} \)
nda: nodal domain averages  
(not usual expectations, direct imprint from amplitudes)

write the total energy as “kinetic” and “potential” components that are “one-sided expectations”, or, nodal domain averages (nda):

\[
E = E_{\text{kin}}^{\text{nda}} + E_{\text{pot}}^{\text{nda}}
\]

\[
E_{\text{kin}}^{\text{nda}} = \int_{\partial \Gamma} |\nabla_R \psi| \, d \tilde{R} / \int |\psi| \, d R \quad E_{\text{pot}}^{\text{nda}} = \int V(R)|\psi| \, d R / \int |\psi| \, d R
\]

\[
E_{\text{kin}}^{\text{nda}} \text{ determined by } |\nabla_R \psi| \text{ solely on the node } \partial \Gamma = \{ R ; \psi(R) = 0 \}
\]

- nda components enable to distinguish between degenerate states with different nodes (eg, different symmetries)

- enables to show some unexpected equivalences, eg, fermionic and bosonic (excited) nodes equivalent, just “rotated”

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different states, even different statistics, but equivalent nodes

three atomic states, 2p² occupation: \(^3\)P, \(^1\)S, \(^1\)D all have the same nda energy components …

\[
\begin{array}{ccccc}
E_{\text{tot}} & E_{\text{kin}} & E_{\text{pot}} & E^{\text{nda}}_{\text{kin}} & E^{\text{nda}}_{\text{pot}} \\
\end{array}
\]

\(^3\)P, \(^1\)S, \(^1\)D (2p²)  
-1/4  
1/4  
-1/2  
1/12  
-1/3

… why? Consider the 5D node projected into 3D:

\(^3\)P: electron sees a plane defined by ang. mom. axis and the second el.

\(^1\)D: electron sees a plane which contains ang. mom. axis and is orthogonal to such plane defined by the second electron

\(^1\)S: electron sees a plane which is orthogonal to the position vector of the second electron

in all three cases the node is a 5D hyperbolic surface in 6D

arxiv: 1307.5567
nsa: nodal surface averages

Total energy as the following “kinetic” and “potential” components

\[ E = E^{\text{nsa}}_{\text{kin}} + E^{\text{nsa}}_{\text{pot}} \]

\[ E^{\text{nsa}}_{\text{kin}} = \int_{\partial \Gamma} h(R) |\nabla_R \psi|^{-2} \ldots \text{expression is too long} \]

\[ E^{\text{nsa}}_{\text{pot}} = \int_{\partial \Gamma} h(R) V(R) d \tilde{R} / \int_{\partial \Gamma} h(R) d \tilde{R} \]

\( h(R) \) is a weight function, all integrals only over the nodal surface

- choose \( h(R) \) such that the average of potential over the node gives the eigenvalue (note: kinetic part vanishes)

\[ \int_{\partial \Gamma} h(R) [V(R) - E] d \tilde{R} = 0 \]

- node is special: any other level set needs more information
summary

- unifying formalism: FN and FP, static and variable spins
- sampling advantages of codimension 2 (for excitations, especially)
- wave functions with phase/spins are more general, possible additional variational freedom
- nodal surfaces are unique → properties can possibly reveal how to construct them more efficiently

PRA 2016, JCP 2016, 1605.03813, 1703.03481 + to be submitted soon
total energies Bi atom with valence $6s^26p^3$
FPSODMC/COS(\_\_\_), FPSODMC/restr.CI(\_\_\_) vs CI(\_\_\_)
similar for molecules now including nonlocal ECPs and differences dimer – atoms, example of N₂

small difference but within the scale of FN biases
Bi atom excitations/splittings compared with experiment

Bi atom SO splittings [eV] (w.r.t. to the g.s. |J=3/2>)

<table>
<thead>
<tr>
<th></th>
<th>J; j1,j2,j3&gt;</th>
<th>DF</th>
<th>CI</th>
<th>FPSODMC</th>
<th>Exper.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3/2;&gt;</td>
<td>4.42</td>
<td>4.00</td>
<td>4.01(1)</td>
<td>4.04</td>
</tr>
<tr>
<td></td>
<td>1/2;&gt;</td>
<td>3.11</td>
<td>2.69</td>
<td>2.63(1)</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>5/2;&gt;</td>
<td>2.13</td>
<td>1.89</td>
<td>1.84(1)</td>
<td>1.91</td>
</tr>
<tr>
<td></td>
<td>3/2;&gt;</td>
<td>1.54</td>
<td>1.44</td>
<td>1.31(1)</td>
<td>1.42</td>
</tr>
</tbody>
</table>
key points about FPSODMC method

- fixed-phase: no sign, basis or ergodicity problem → $\rho(R)$ is nonzero except for isolated points (ie, codimension 2)

- zero variance property → energy fluctuations decrease with $\psi_T$ error squared (as for the fixed-node)

$$\psi_T \leftrightarrow V_{eff} \text{ one-to-one mapping for any state}$$

- treatment of SO terms natural to its nonlocality → localization

- reuse of much existing QMC methodology/codes from static spins

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Green's function for spinor sampling

example of Rashba SO in 2D*: $V_{\text{Rashba}} = \lambda \sum_j \left[ p_j^y \sigma_j^x - p_j^x \sigma_j^y \right]$ 

$$G_{j}^{\text{spin}} = \begin{pmatrix} 
\cos(\gamma \delta r_j) & \sin(\gamma \delta r_j) \frac{-i \delta y_j + \delta x_j}{\delta r_j} \\
-\sin(\gamma \delta r_j) \frac{i \delta y_j + \delta x_j}{\delta r_j} & \cos(\gamma \delta r_j) 
\end{pmatrix}$$

where $\gamma \propto \lambda$ and $\delta r_j, \delta x_j, \delta y_j$ are spatial displacements

- similar to Hubbard-Stratonovitch approaches

*A. Ambrosetti, F. Pederiva, E. Lipparini, S. Gandolfi, PRB 80, 125306 ('09)
2D fermion gas with Stoner and Rashba interactions: spin-polarization vs. interaction strength

FIG. 3: Polarization of Fermi gas along the $z$ direction as a function of the two-body interaction scattering length $a$. Results are given in absence of SO interaction ($\lambda = 0$) and for two different Rashba interaction strengths ($\lambda = 0.15, 0.30$).

FNDMC vs traditional correlated wf methods: nodes converge in basis very rapidly, augTZV or so