Orbital-dependent backflow transformations in quantum Monte Carlo

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Variational and diffusion Monte Carlo

VMC and DMC are stochastic methods to solve the Schrödinger equation.

Aspects in common:

- Sample real-space configurations $\{\mathbf{R}\}$ using guiding wave function $\Psi_T(\mathbf{R})$
- Evaluate $E_L(\mathbf{R}) = \Psi_T^{-1}(\mathbf{R})\hat{H}(\mathbf{R})\Psi_T(\mathbf{R})$ to give variational estimate of ground-state energy E_0

Introduction   **VMC and DMC**
Orbital-dependent backflow   Optimization
Summary   Wave functions

Variational and diffusion Monte Carlo

VMC works like this:

- $\{\mathbf{R}\}$ distributed according to $|\Psi_T(\mathbf{R})|^2$
- $E_{\mathrm{VMC}} = \langle \Psi_T | \hat{H} | \Psi_T \rangle$
- Quality of E_{VMC} depends on quality of Ψ_T

DMC works like this:

- Define $\Phi(\mathbf{R})$ as the exact solution of Schrödinger equation subject to: $\Phi(\mathbf{R}) = 0 \Leftrightarrow \Psi_T(\mathbf{R}) = 0$
- $\{\mathbf{R}\}$ distributed according to $|\Phi(\mathbf{R})\Psi_T(\mathbf{R})|$
- $E_{\mathrm{DMC}} = \langle \Phi | \hat{H} | \Phi \rangle$
- Quality of E_{DMC} depends on quality of **nodes** of Ψ_T

Wave function optimization

Optimization procedure:

- Generate set of VMC configurations $\{\mathbf{R}\}(\boldsymbol{\alpha})$
- Optimize target function with respect to $\boldsymbol{\alpha}$ using fixed configurations

Target function can be:

- Energy, since VMC is variational
- Measure of spread of local energies (e.g., variance), since eigenstates of $\hat{H}$ yield constant local energies

Slater-Jastrow wave function

For electronic systems one typically uses Slater determinants with HF orbitals times a Jastrow correlation factor:

> Slater-Jastrow trial wave function
>
> $$\Psi_{SJ}(\mathbf{R}) = \exp[J(\mathbf{R})] \det[\phi_i(\mathbf{r}_j)]$$

where $J(\mathbf{R})$ consists of e–e, e–n, e–e–n, ... terms which contain optimizable parameters

- J typically recovers $70-90\%$ of correlation energy in VMC
- J does not change DMC result since it does not affect nodes of Ψ_T

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Beyond Slater-Jastrow

One can use:

- Multi-determinant expansions
- Geminal-/Pfaffian-based wave functions
- Multi-Jastrow wave function
- Backflow transformation:

> ### Slater-Jastrow-backflow trial wave function
>
> $$\Psi_{BF}(\mathbf{R}) = \exp[J(\mathbf{R})] \det\{\phi_i[\mathbf{x}_i(\mathbf{R})]\}$$

where $\mathbf{x}_i(\mathbf{R}) = \mathbf{r}_j + \boldsymbol{\xi}_j(\mathbf{R})$, and $\boldsymbol{\xi}$ consists of e–e, e–n, e–e–n,
... terms containing optimizable parameters.

- Can be thought of as a correlated orbital correction method
- In VMC recovers 50% of the correlation energy remaining at SJ
- Same accuracy as system size increases (fixed # parameters)

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Definition of ODBF wave function

Could use different backflow transformations for different orbitals:

> **ODBF trial wave function**
>
> $$\Psi_{\mathrm{ODBF}}(\mathbf{R}) = \exp\left[J(\mathbf{R})\right] \det\left\{\phi_i\left[\mathbf{x}_j^{t_i}(\mathbf{R})\right]\right\}$$

where $\mathbf{x}_j^{t_i}(\mathbf{R}) = \mathbf{r}_j + \boldsymbol{\xi}_j^{t_i}(\mathbf{R})$

- Potentially very good since different orbitals in principle require different corrections
- Questions to answer:
  - Is it worth it? (it'd better be!)
  - Does it break size-extensivity?

54-electron gas

For a paramegnetic HEG consisting of 54 electrons at $r_s = 2$:

Ψ_T	E (a.u.)	V (a.u.)
Ψ_{HF}	0.01876736	
Ψ_{SJ}	-0.01245(1)	0.148(1)
Ψ_{BF}	-0.013801(7)	0.0344(5)
Ψ_{OBDF} (by k^2)	-0.013815(6)	0.0346(6)

Carbon atom

For an all-electron carbon atom (single-determinant):

Ψ_T	E (a.u.)	V (a.u.)	CE (%)
Ψ_{HF}	-37.688619		0.0
Ψ_{SJ}	-37.8086(6)	0.139(1)	76.7(4)
Ψ_{BF}	-37.8286(4)	0.067(2)	89.5(3)
Ψ_{OBDF} (by l)	-37.8301(3)	0.0561(8)	90.5(2)
Ψ_{OBDF} (by n)	-37.8312(3)	0.053(1)	91.2(2)
Ψ_{OBDF} (by n,l)	-37.8330(3)	0.0451(9)	92.3(2)
Exact	-37.8450		100.0

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Neon atom

For an all-electron neon atom (single-determinant):

Ψ_T	E (a.u.)	V (a.u.)	CE (%)
Ψ_{HF}	-128.547098		0.0
Ψ_{SJ}	-128.8975(6)	1.048(9)	89.7(2)
Ψ_{BF}	-128.9224(4)	0.341(2)	96.1(1)
Ψ_{OBDF} (by l)	-128.9263(3)	0.247(4)	97.11(8)
Ψ_{OBDF} (by n)	-128.9269(3)	0.239(3)	97.26(8)
Ψ_{OBDF} (by n,l)	-128.9278(3)	0.221(2)	97.49(8)
Exact	-128.9376		100.0

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The freedom to form linear combinations of orbitals

Replacing the set of orbitals by linear combinations of them leaves the wave function unchanged up to a multiplicative factor:

Determinant property

$$\begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \phi_3(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \phi_3(\mathbf{r}_2) \\ \phi_1(\mathbf{r}_3) & \phi_2(\mathbf{r}_3) & \phi_3(\mathbf{r}_3) \end{vmatrix} \propto \begin{vmatrix} \{\phi_1 + k\phi_2\}(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \phi_3(\mathbf{r}_1) \\ \{\phi_1 + k\phi_2\}(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \phi_3(\mathbf{r}_2) \\ \{\phi_1 + k\phi_2\}(\mathbf{r}_3) & \phi_2(\mathbf{r}_3) & \phi_3(\mathbf{r}_3) \end{vmatrix}$$

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The freedom to form linear combinations of orbitals

However if one applies orbital-dependent backflow to both sides of the previous equation the results differ:

Determinant property

$$
\begin{vmatrix}
\phi_1(\mathbf{x}_1^1) & \phi_2(\mathbf{x}_1^2) & \phi_3(\mathbf{x}_1^3) \\
\phi_1(\mathbf{x}_2^1) & \phi_2(\mathbf{x}_2^2) & \phi_3(\mathbf{x}_2^3) \\
\phi_1(\mathbf{x}_3^1) & \phi_2(\mathbf{x}_3^2) & \phi_3(\mathbf{x}_3^3)
\end{vmatrix}
\not\propto
\begin{vmatrix}
\{\phi_1 + k\phi_2\}(\mathbf{x}_1^1) & \phi_2(\mathbf{x}_1^2) & \phi_3(\mathbf{x}_1^3) \\
\{\phi_1 + k\phi_2\}(\mathbf{x}_2^1) & \phi_2(\mathbf{x}_2^2) & \phi_3(\mathbf{x}_2^3) \\
\{\phi_1 + k\phi_2\}(\mathbf{x}_3^1) & \phi_2(\mathbf{x}_3^2) & \phi_3(\mathbf{x}_3^3)
\end{vmatrix}
$$

This means that we have additional variational freedom which should be exploited.

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Orbital mixing

Orbital mixing destroys properties of original orbitals (eigenvalues, quantum numbers, etc.), so:

- How do we assign different backflow transformations to the new orbitals?
- Can we still use fewer transformations than there are orbitals?
- Can the mixing be sensibly restricted? E.g., can we only mix same-n orbitals and get good results?

I don't know the answers, but I suspect that orbital mixing is more important in the HEG than in the atoms.

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