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Approaching exact solutions of the electronic Schrödinger equation with deep quantum Monte Carlo

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Electronic Schrödinger equation

$$\hat{H}\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = E\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

$$\hat{H} := \sum_i \left(-\frac{1}{2}\nabla^2_{\mathbf{r}_i} - \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right) + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- Fundamental law of chemistry and materials science
- Electron coordinates: $(\mathbf{r}_1, \ldots, \mathbf{r}_N) \equiv \mathbf{r}$
- Hamiltonian operator $\hat{H}$ specified by charges Z_I and coordinates $\mathbf{R}_I$ of M atomic nuclei
- Solution: eigenstates ψ_n and their energies E_n, including the ground state ψ_0, E_0
- Analytically solvable only for $M = N = 1$, but many approximate numerical methods in quantum chemistry

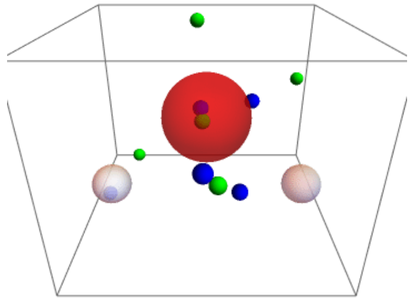
Electronic wave functions and antisymmetry

- Hamiltonian has no spin – electrons have spin coordinates, but those can be considered fixed

$$\psi(\mathbf{r}_1^{\uparrow}, \ldots, \mathbf{r}_{N_{\text{up}}}^{\uparrow}, \mathbf{r}_{N_{\text{up}}+1}^{\downarrow}, \ldots, \mathbf{r}_N^{\downarrow}), \quad s_i = \begin{cases} \uparrow & i \leq N_{\text{up}} \\ \downarrow & i > N_{\text{up}} \end{cases}$$

- Electrons are fermions – wave function must be *antisymmetric* w.r.t. exchange of same-spin electrons ($s_i = s_j$)

$$\psi(\ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots) = -\psi(\ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots)$$



- $\psi(\mathbf{r}) = 0$ defines a $(3N-1)$-dimensional *nodal surface* – *sign problem* in diffusion quantum Monte Carlo
- Expansion in Slater determinants – rapid scaling of computational cost with system size

Variational quantum Monte Carlo

$$E_0 = \min_{\psi} E[\psi] \leq \min_{\boldsymbol{\theta}} E[\psi_{\boldsymbol{\theta}}],$$

$$E[\psi] := \int \mathrm{d}\mathbf{r}\, \psi(\mathbf{r}) \hat{H} \psi(\mathbf{r})$$

- Standard quantum chemistry: $E[\psi]$ can be evaluated analytically
- Quantum Monte Carlo (QMC): quantum *expectation* value expressed as statistical *expected* value of local energy

$$E[\psi] = \mathbb{E}_{\mathbf{r}\sim|\psi|^2}\left[E_{\mathrm{loc}}[\psi](\mathbf{r})\right]$$

$$E_{\mathrm{loc}}[\psi] = \hat{H}\psi/\psi$$

- Traditional ansatz of the Slater–Jastrow–backflow type[1]

$$\psi_{\mathrm{SJBF}}(\mathbf{r}) := \mathrm{e}^{J(\{\mathbf{r}_i^{\uparrow}\},\{\mathbf{r}_i^{\downarrow}\})} \sum_p c_p \det[\varphi_{\mu_p}(\mathbf{r}_i^{\uparrow})] \det[\varphi_{\mu_p}(\mathbf{r}_i^{\downarrow})]$$

$$\mathbf{r}_i \to \mathbf{r}_i + \mathbf{q}_i(\mathbf{r})$$

- Accuracy of variational QMC limited only by the parametric flexibility of the ansatz – use neural networks[2]

[1]Brown et al., *J. Chem. Phys.* **126**, 224110 (2007) [2]Carleo & Troyer, *Science* **355**, 602 (2017)

PauliNet: Deep-learning trial wave function

$$\psi_{\boldsymbol{\theta}}(\mathbf{r}) = \mathrm{e}^{\gamma(\mathbf{r})+J_{\boldsymbol{\theta}}(\mathbf{r})} \sum_p c_p \det[\tilde{\varphi}^{\uparrow}_{\boldsymbol{\theta},\mu_p i}(\mathbf{r})] \det[\tilde{\varphi}^{\downarrow}_{\boldsymbol{\theta},\mu_p i}(\mathbf{r})], \qquad \tilde{\varphi}_{\boldsymbol{\theta},\mu i}(\mathbf{r}) = \varphi_{\mu}(\mathbf{r}_i) f_{\boldsymbol{\theta},\mu i}(\mathbf{r})$$

- Slater–Jastrow–backflow ansatz with Jastrow and backflow represented by neural networks
- Generalized backflow
- Built-in n–e and e–e cusp conditions
- Permutation-equivariant cusp-less graph neural networks to retain antisymmetry and cusp conditions

- $\varphi_{\mu}(\mathbf{r}_i)$: HF orbitals
- $J_{\boldsymbol{\theta}}(\mathbf{r})$: Jastrow-factor NN
- $\mathbf{f}_{\boldsymbol{\theta}}(\mathbf{r})$: backflow NN
- $\gamma(\mathbf{r})$: e–e cusp conditions

Hermann, Schätzle & Noé, *Nat. Chem.* **12**, 891 (2020)

PauliNet: Deep-learning trial wave function

Neural network

- Adapted SchNet architecture[1] as the underlying graph-neural network

$$\mathbf{x}_i^{(0)} := \mathbf{X}_{\boldsymbol{\theta},s_i}$$

$$\mathbf{z}_i^{(n,\pm)} := \sum\nolimits_{j\neq i}^{\pm} \mathbf{w}_{\boldsymbol{\theta}}^{(n,\pm)}\big(\mathbf{e}(|\mathbf{r}_i-\mathbf{r}_j|)\big)\odot\mathbf{h}_{\boldsymbol{\theta}}^{(n)}\big(\mathbf{x}_j^{(n)}\big)$$

$$\mathbf{z}_i^{(n,\mathrm{n})} := \sum\nolimits_{J} \mathbf{w}_{\boldsymbol{\theta}}^{(n,\mathrm{n})}\big(\mathbf{e}(|\mathbf{r}_i-\mathbf{R}_J|)\big)\odot\mathbf{Y}_{\boldsymbol{\theta},J}$$

$$\mathbf{x}_i^{(n+1)} := \mathbf{x}_i^{(n)} + \sum\nolimits_{\pm} \mathbf{g}_{\boldsymbol{\theta}}^{(n,\pm)}\big(\mathbf{z}_i^{(n,\pm)}\big)+\mathbf{g}_{\boldsymbol{\theta}}^{(n,\mathrm{n})}\big(\mathbf{z}_i^{(n,\mathrm{n})}\big)$$

$$J := \eta_{\boldsymbol{\theta}}\Big(\sum\nolimits_i \mathbf{x}_i^{(N)}\Big)$$

$$\mathbf{f}_i := \boldsymbol{\kappa}_{\boldsymbol{\theta}}\big(\mathbf{x}_i^{(N)}\big)$$

Algorithm

- Energy expectation value directly as a loss function
- Hermiticity of Hamiltonian enables efficient evaluation of the loss gradient

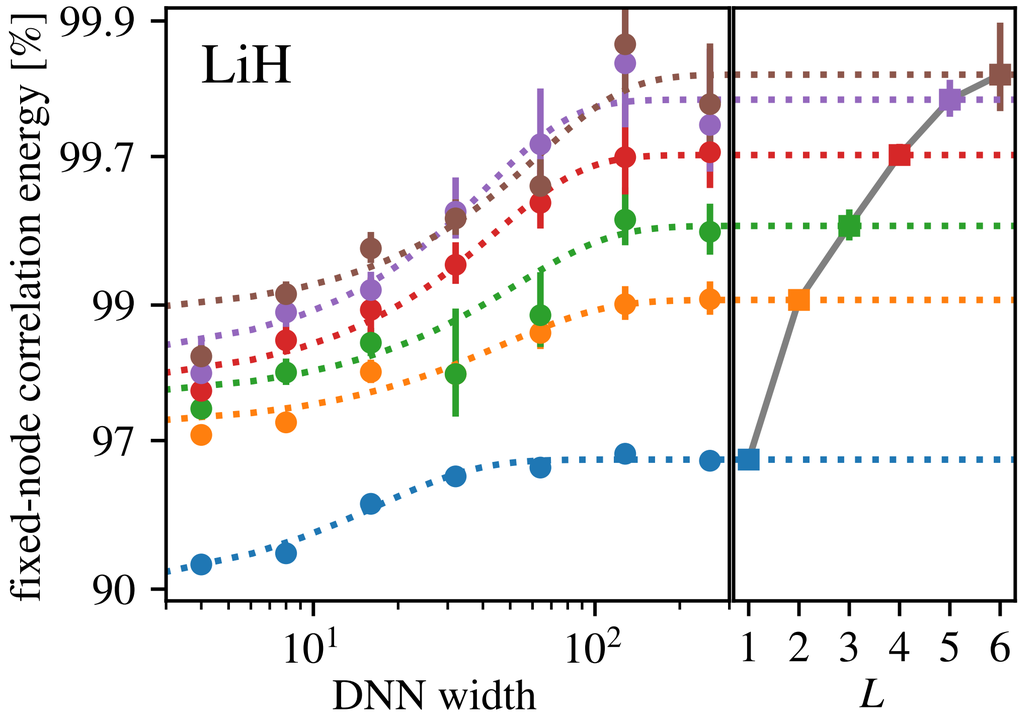
$$\mathscr{L}(\boldsymbol{\theta}) = \mathbb{E}_{\mathbf{r}\sim|\psi'^2|}\big[E_{\mathrm{loc}}[\psi_{\boldsymbol{\theta}}](\mathbf{r})\big] \quad \big(\equiv E[\psi_{\boldsymbol{\theta}}]\big)$$

$$\nabla_{\boldsymbol{\theta}}\mathscr{L}(\boldsymbol{\theta}) = 2\mathbb{E}_{\mathbf{r}\sim|\psi'^2|}\big[\big(E_{\mathrm{loc}}[\psi_{\boldsymbol{\theta}}](\mathbf{r})-E[\psi_{\boldsymbol{\theta}}]\big)\nabla_{\boldsymbol{\theta}}\ln|\psi_{\boldsymbol{\theta}}|\big]$$

- Alternating sampling (Markov-chain Monte Carlo) and optimization (Adam)

[1] Schütt et al., *J. Chem. Phys.* **148**, 241722 (2018)

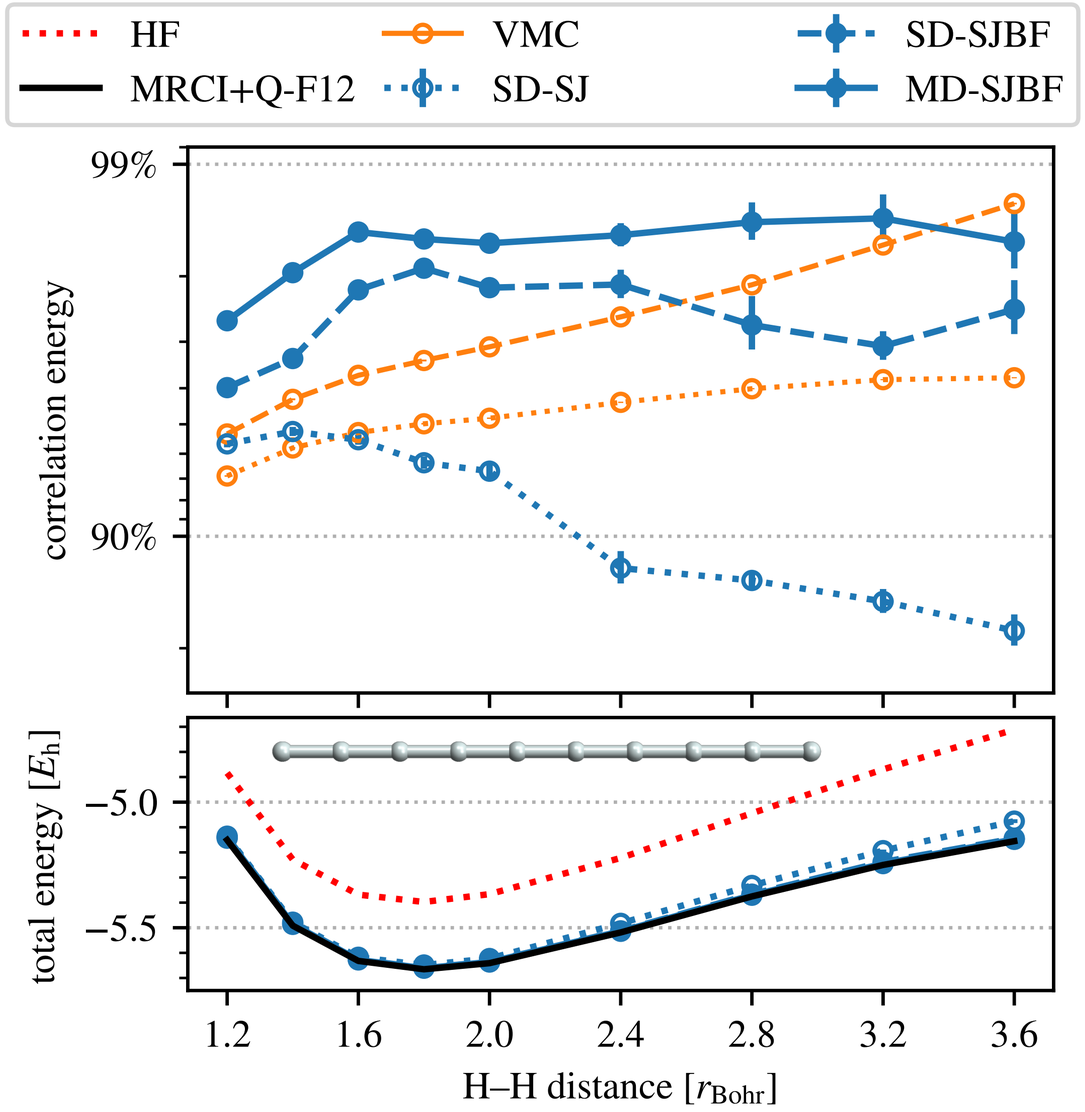
Approaching the exact solution



- Diffusion quantum Monte Carlo provides the exact variational energy for a given nodal surface
- The PauliNet Jastrow factor can be systematically converged to reach the exact fixed-node energy
- Beyond fixed nodes with backflow – how is sign problem manifested in deep variational QMC?

Schätzle, Hermann & Noé, *J. Phys. Chem.* (in print)

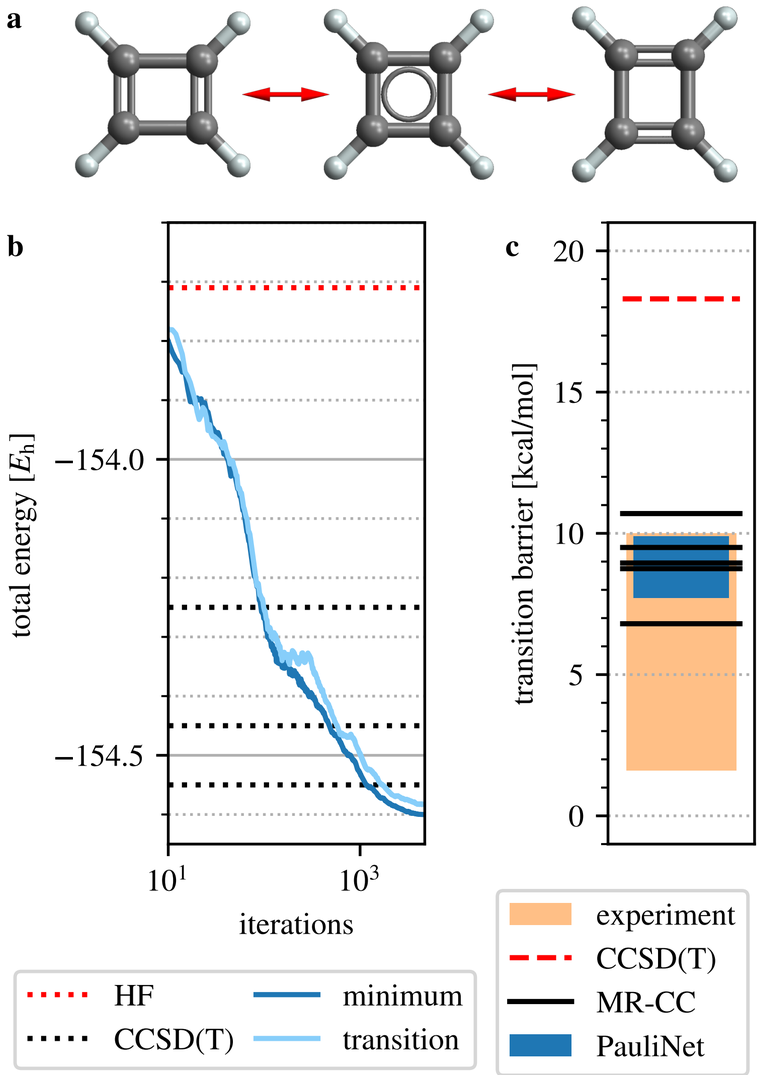
Capturing strong correlation



- Dissociation of linear H_{10} as a test case of *strong correlation*[1] – baseline HF gives unphysical dissociation energy
- PauliNet with 16 determinants captures 98–99% of the correlation energy along the dissociation
- PauliNet surpasses a traditional VMC approach specifically adapted for H_{10}

[1]Motta et al., *Phys. Rev. X* **7**, 031059 (2017)

Targeting state-of-the-art quantum chemistry



- Barrier of the automerization of cyclobutadiene (28 electrons) still not fully resolved[1]
- Strong multireferential character—CCSD(T) overestimates two-fold
- Experiment: 1.6–10 kcal/mol, multireference coupled clusters 7–11 kcal/mol
- PauliNet with 10 determinants: 8–10 kcal/mol
- 3 days on GTX 1080 Ti GPU, comparable to multireference methods, but better scaling

[1]Lyakh et al., *Chem. Rev.* **112**, 182 (2012)

Summary & outlook

- Deep QMC opens a new path to highly accurate electronic structure methods with favorable scaling with system size
- Reuse all standard techniques: diffusion QMC, pseudopotentials
- Improvements in neural network architecture
- Will the performance gain translate straightforwardly to solids?
- How quickly do we lose accuracy as we go to larger systems?

- Code at github.com/deepqmc/deepqmc

```python
from deepqmc import Molecule, train
from deepqmc.wf import PauliNet

mol = Molecule.from_name('LiH')
net = PauliNet.from_hf(mol).cuda()
train(net)
```