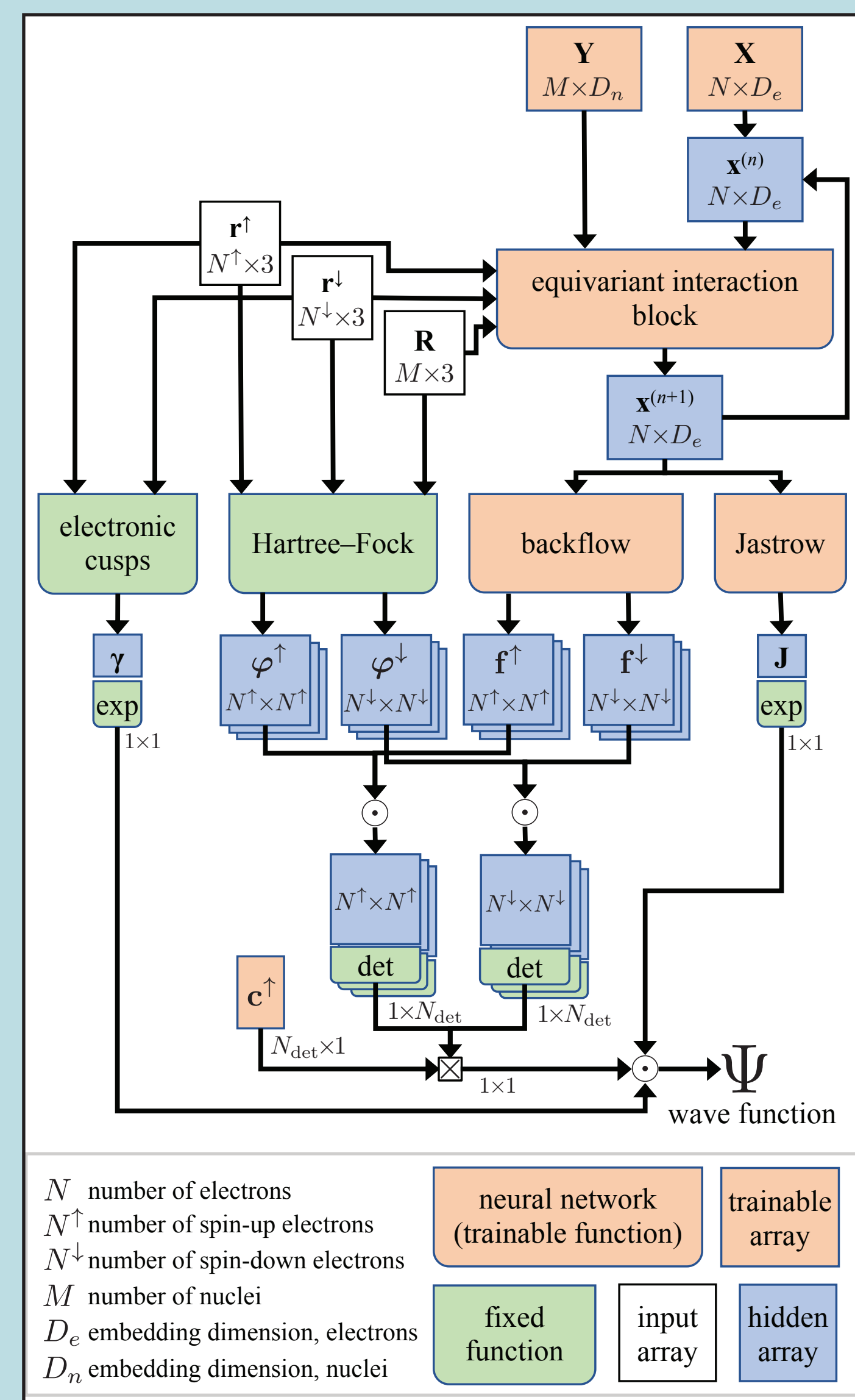


PauliNet trial wavefunction ansatz [1]

– highly expressive Slater-Jastrow-backflow type trial wavefunction

$$\psi_{\theta}(\mathbf{r}) = e^{\gamma(\mathbf{r}) + J_{\theta}(\mathbf{r})} \sum_p c_p \det[\tilde{\varphi}_{\theta, \mu p i}^{\uparrow}(\mathbf{r})] \det[\tilde{\varphi}_{\theta, \mu p i}^{\downarrow}(\mathbf{r})]$$

$$\tilde{\varphi}_{\theta, \mu i}(\mathbf{r}) = \varphi_{\mu}(\mathbf{r}_i) f_{\theta, \mu i}^{\otimes}(\mathbf{r}) + f_{\theta, \mu i}^{\oplus}(\mathbf{r})$$

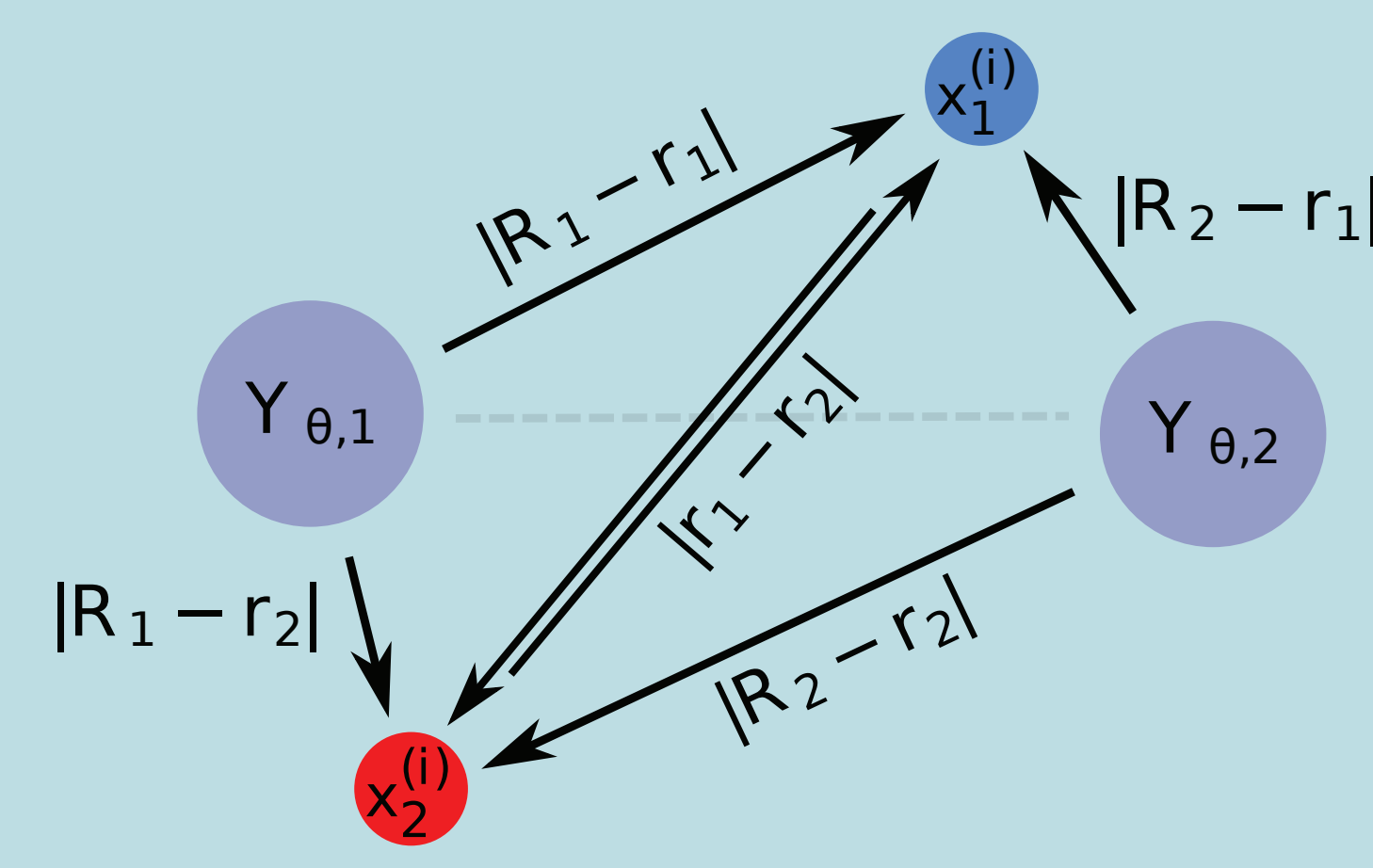


- utilize expressiveness of DNNs
- permutation-invariant **Jastrow factor**
- $J_{\theta}(\mathbf{r}) := \eta_{\theta}(\sum_i \mathbf{x}_i^{(L)}(\mathbf{r}))$
- permutation-equivariant **backflow**
- $\mathbf{f}_{\theta, i}(\mathbf{r}) := \kappa_{\theta}(\mathbf{x}_i^{(L)}(\mathbf{r}))$
- $\eta_{\theta}, \kappa_{\theta}$ – fully-connected DNNs
- $\mathbf{x}_i(\mathbf{r})$ – latent-space many-body representation
- implement physical knowledge
- Slater determinants
- satisfy antisymmetry constraint of fermionic wavefunctions
- cusped conditions
- invoke analytically known asymptotics for short distances
- quantum chemistry baseline
- initialisation from Hartree Fock (HF) or MCSCF calculation

[1] J. Hermann, Z. Schätzle, and F. Noé, Deep-neural-network solution of the electronic Schrödinger equation, Nature Chemistry 12, 891 (2020)
 [2] K. T. Schütt, et al, SchNet – A deep learning architecture for molecules and materials J. Chem. Phys. 148, 241722 (2018)

Graph-convolutional neural network [2]

– generating a permutation-equivariant latent-space many-body representation for the electrons



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

$$\mathbf{x}_i^{(n+1)} := \mathbf{x}_i^{(n)} + \chi_{\theta}^{(n)}(\{\mathbf{x}_j^{(n)}, \{\mathbf{r}_j - \mathbf{r}_i\}\}) + \chi_{\theta}^{\prime(n)}(\{\mathbf{Y}_{\theta, j}, \{\mathbf{R}_j - \mathbf{r}_i\}\})$$

$\mathbf{X}_{\theta, \pm}, \mathbf{Y}_{\theta, I}$ – electronic / nuclear embeddings
 $\chi_{\theta}^{(n)}, \chi_{\theta}^{\prime(n)}$ – continuous-filter convolution

Training procedure - VMC optimization

- sample probability density associated with wavefunction
- minimize energy on minibatches of electron configurations

$$\mathcal{L}(\theta) = \mathbb{E}_{\mathbf{r} \sim \psi_{\theta}^2} \left[\frac{H\psi_{\theta}(\mathbf{r})}{\psi_{\theta}(\mathbf{r})} \right]$$

Quantum chemistry background

The electronic structure problem

– Solve the Schrödinger equation for the electronic degrees of freedom

$$H\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}) \quad \psi_n \in \mathcal{H}^{-}$$

for the clamped-nucleus Coulomb Hamiltonian

$$H = \sum_{i=0}^N \Delta_i - \sum_{i=0}^N \sum_{j=0}^M \frac{1}{|\mathbf{r}_i - \mathbf{R}_j|} + \sum_{i=0}^N \sum_{j=0}^i \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

The fermionic antisymmetry constraint

– Electronic wavefunctions must be antisymmetric under the exchange of two same-spin electrons

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

entailing a nodal surface across which the wavefunction changes sign.

The variational approach of quantum mechanics

– Apply the variational principle

$$E_0 = \min_{\psi} \langle \psi | H | \psi \rangle \leq \min_{\theta} \langle \psi_{\theta} | H | \psi_{\theta} \rangle \quad \psi_{\theta} \in \mathcal{H}^{-}$$

choose trial wavefunction and solve the optimization problem

$$\theta^* = \operatorname{argmin}_{\theta} \langle \psi_{\theta} | H | \psi_{\theta} \rangle$$

Variational quantum Monte Carlo (VMC)

– Approximate the expectation value via Monte Carlo integration

$$\langle \psi_{\theta} | H | \psi_{\theta} \rangle = \int \psi_{\theta}(\mathbf{r}) H \psi_{\theta}(\mathbf{r}) d\mathbf{r}$$

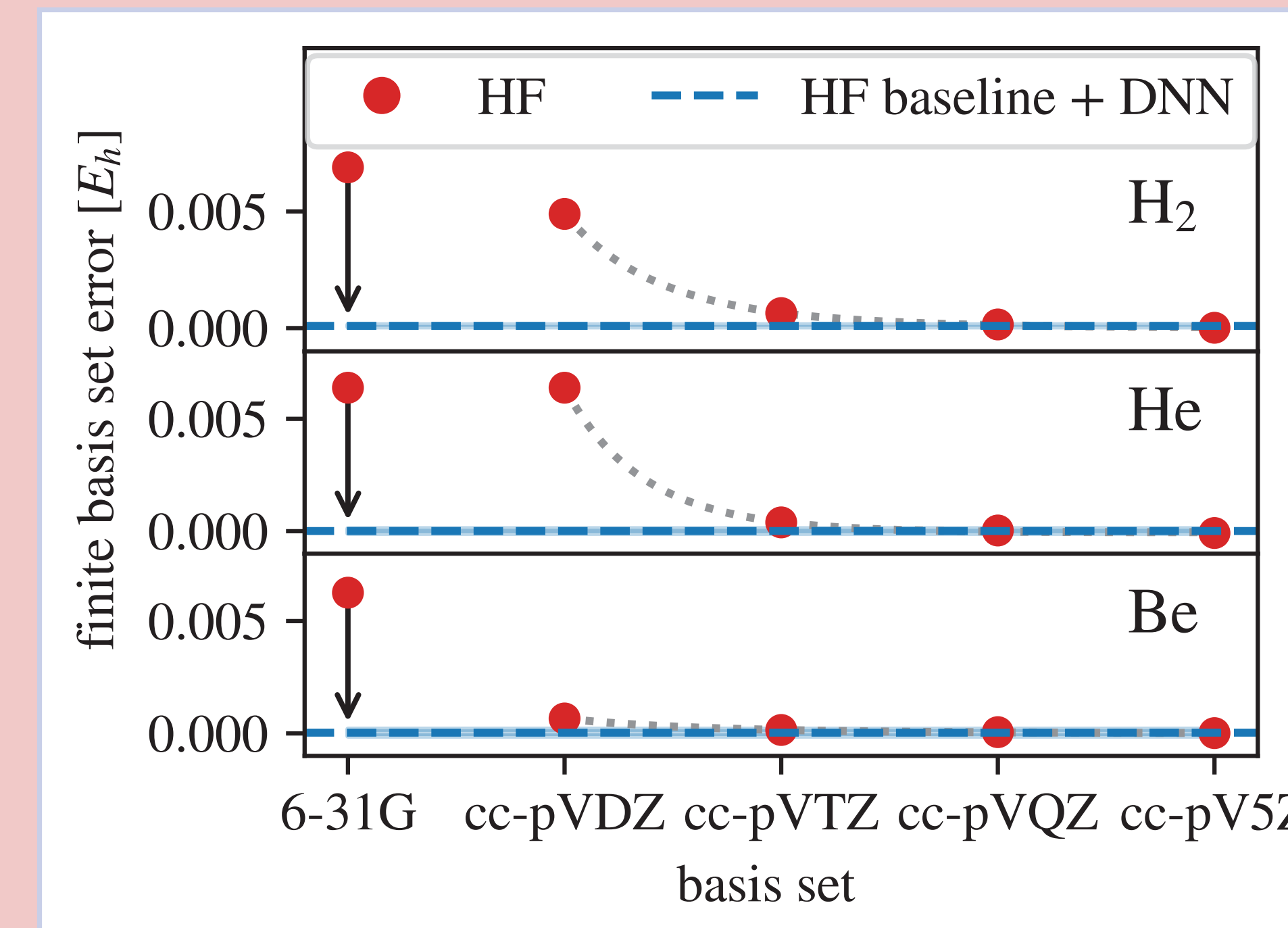
$$= \int \psi_{\theta}(\mathbf{r})^2 \frac{1}{\psi_{\theta}(\mathbf{r})} H \psi_{\theta}(\mathbf{r}) d\mathbf{r} \approx \sum_{\mathbf{r} \sim \psi_{\theta}^2} \frac{H \psi_{\theta}(\mathbf{r})}{\psi_{\theta}(\mathbf{r})}$$

Results – restricted variants of PauliNet for different levels of theory

Deep orbital correction := single-particle version of PauliNet backflow correction

Deep Jastrow := PauliNet without backflow correction

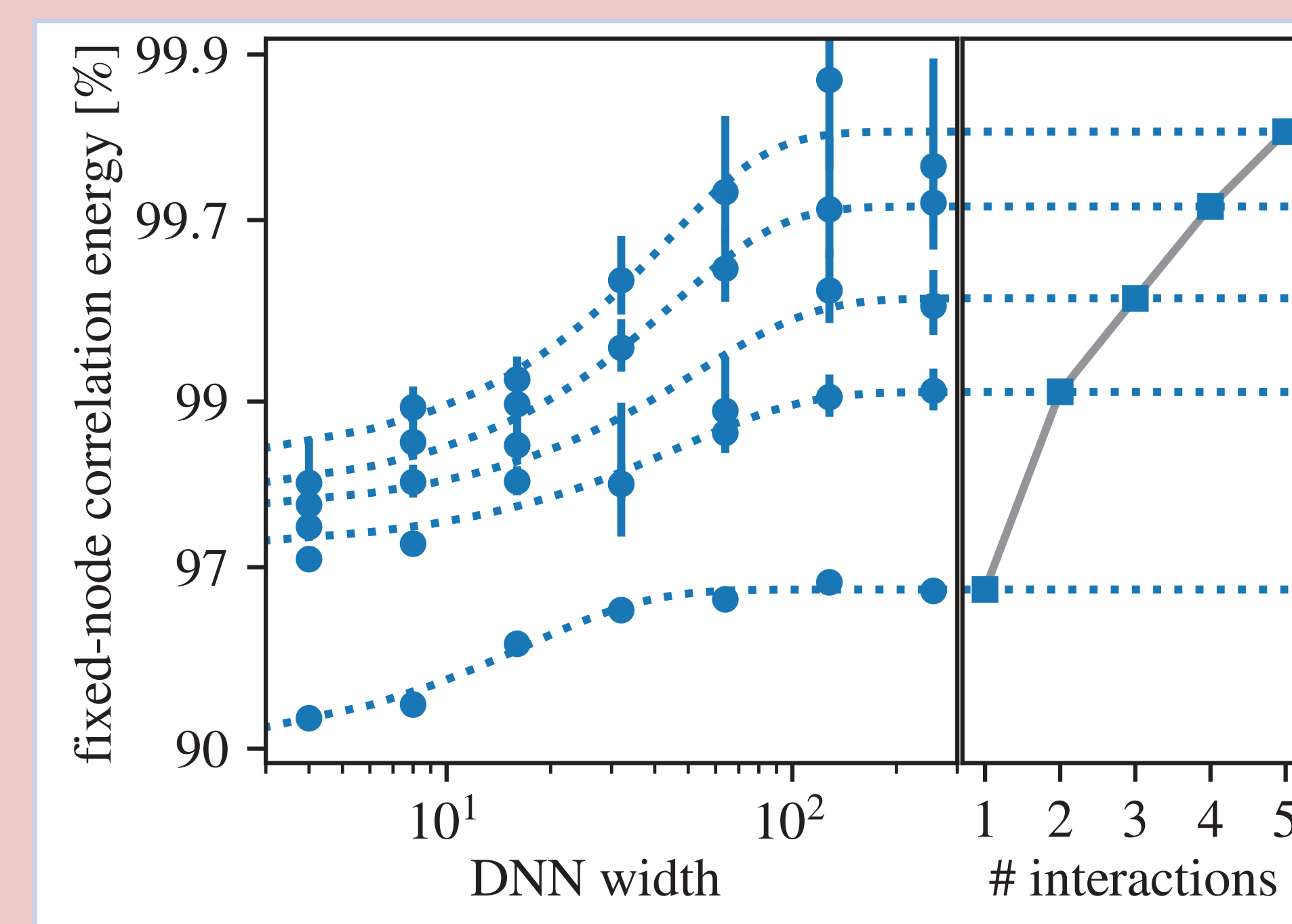
Deep orbital correction – position-space correction of Hartree Fock (HF) orbitals



deep orbital correction reducing the finite-basis-set error of an imprecise HF baseline for H₂, He, and Be below 0.1 mH

“finite-basis-set error”
 Error arising due to the projection on a finite single particle basis set.

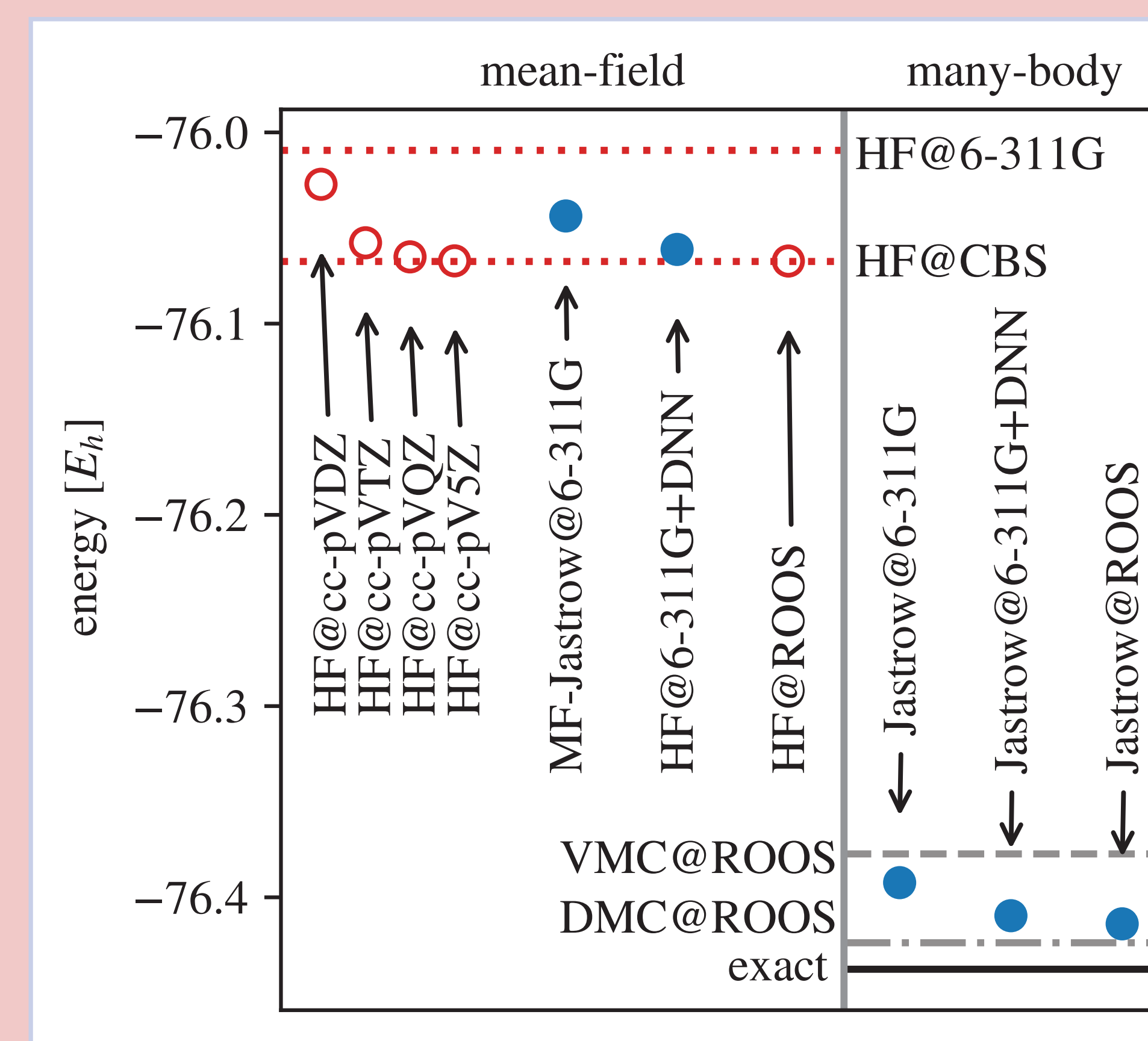
Deep Jastrow – systematic approach to the fixed-node limit



hyperparameter scan for LiH, showing a convergence to the fixed-node limit with increasing network size

“fixed-node correlation energy”
 Energy difference between mean-field energy and exact energy up to the error due to fixing the nodal surface of the trial wavefunction.

Deep Jastrow & orbital correction – application to the water molecule



fixed-node correlation energy for deep Jastrow factor with HF determinant

- in ROOS basis: 97.2(1)%
- with orbital correction: 96.0(2)%

surpassing the accuracy of reference single determinant VMC calculations from even a minimal baseline