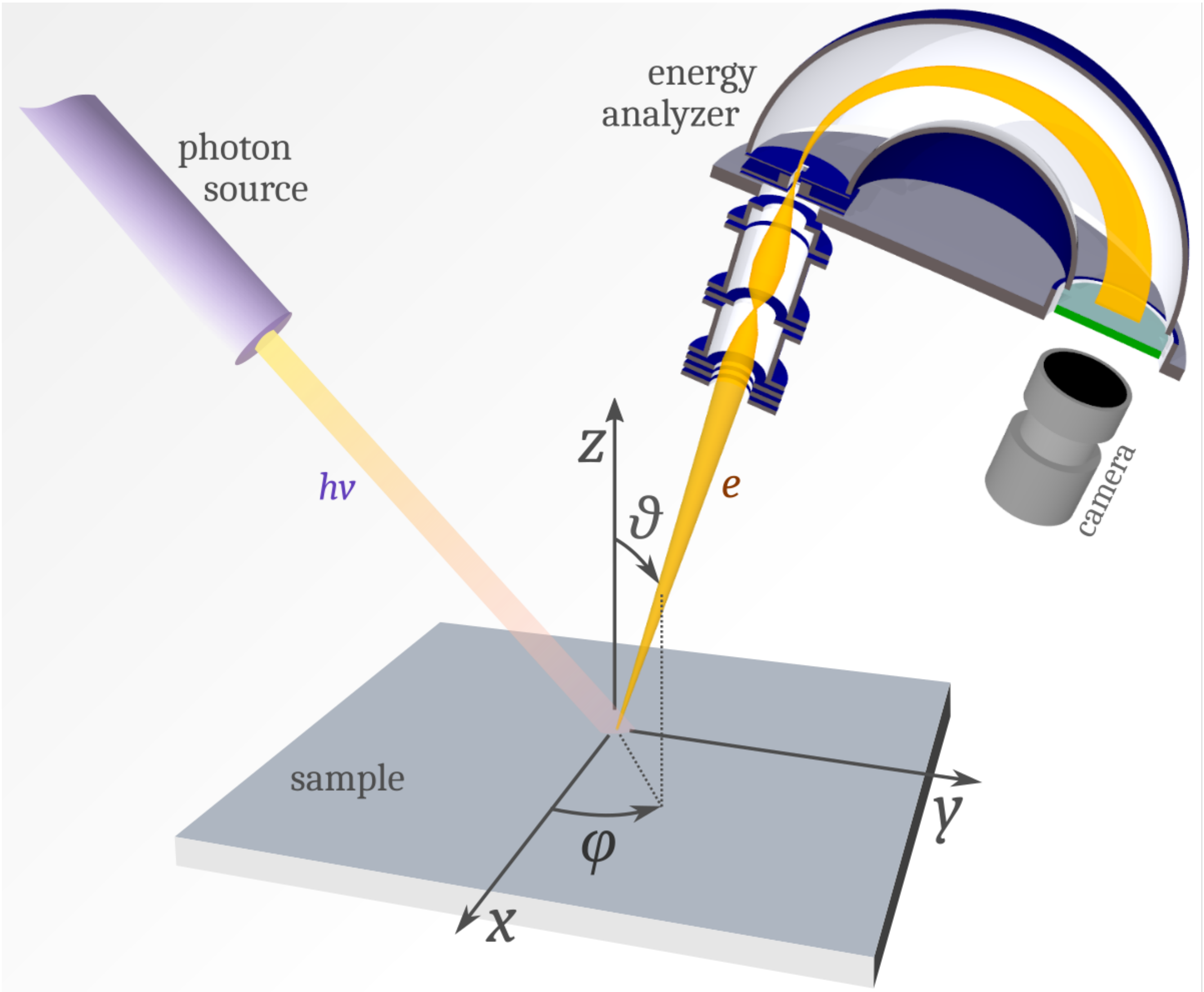
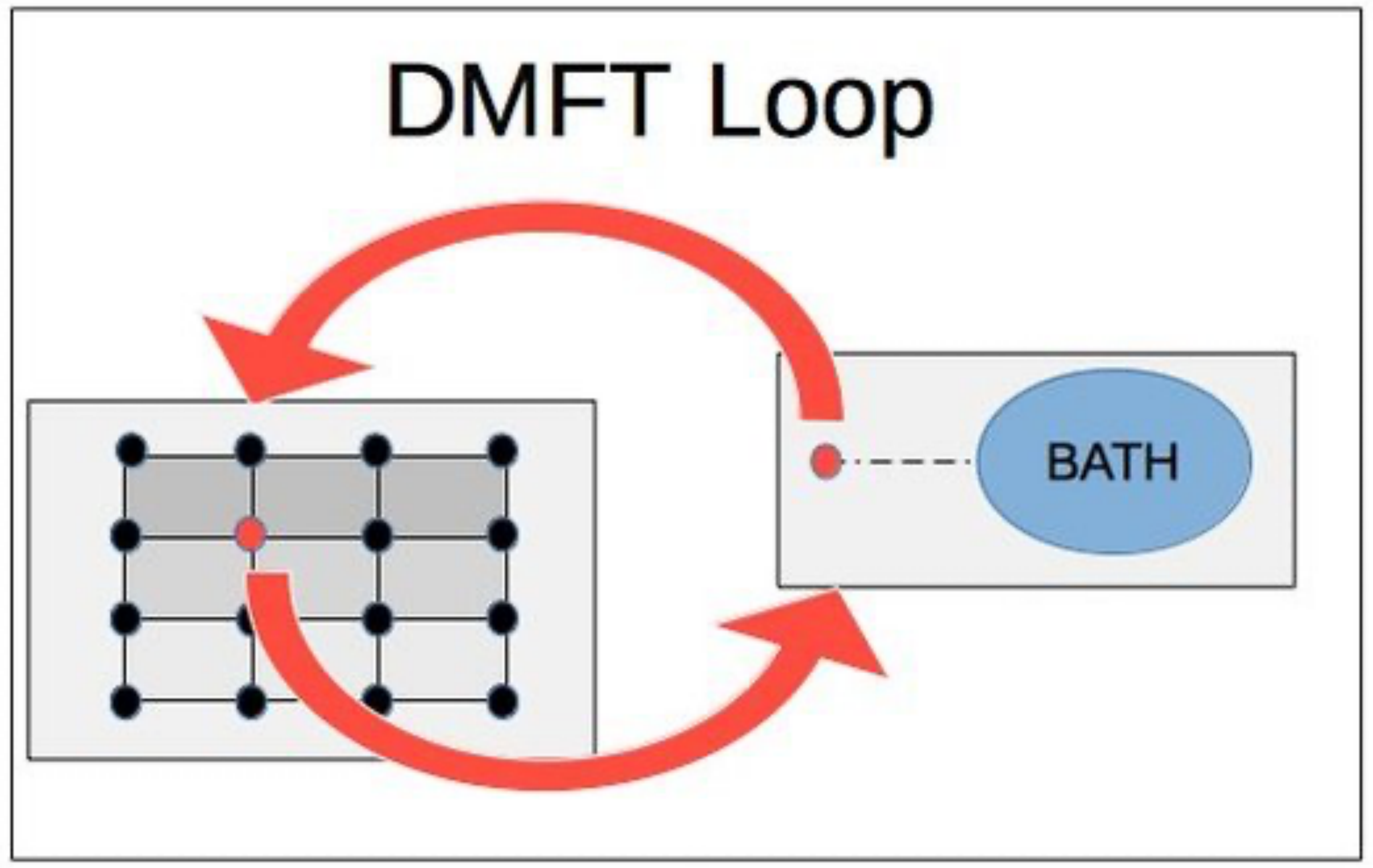
Efficient Molecular Spectroscopy via Hybrid Subspace Methods

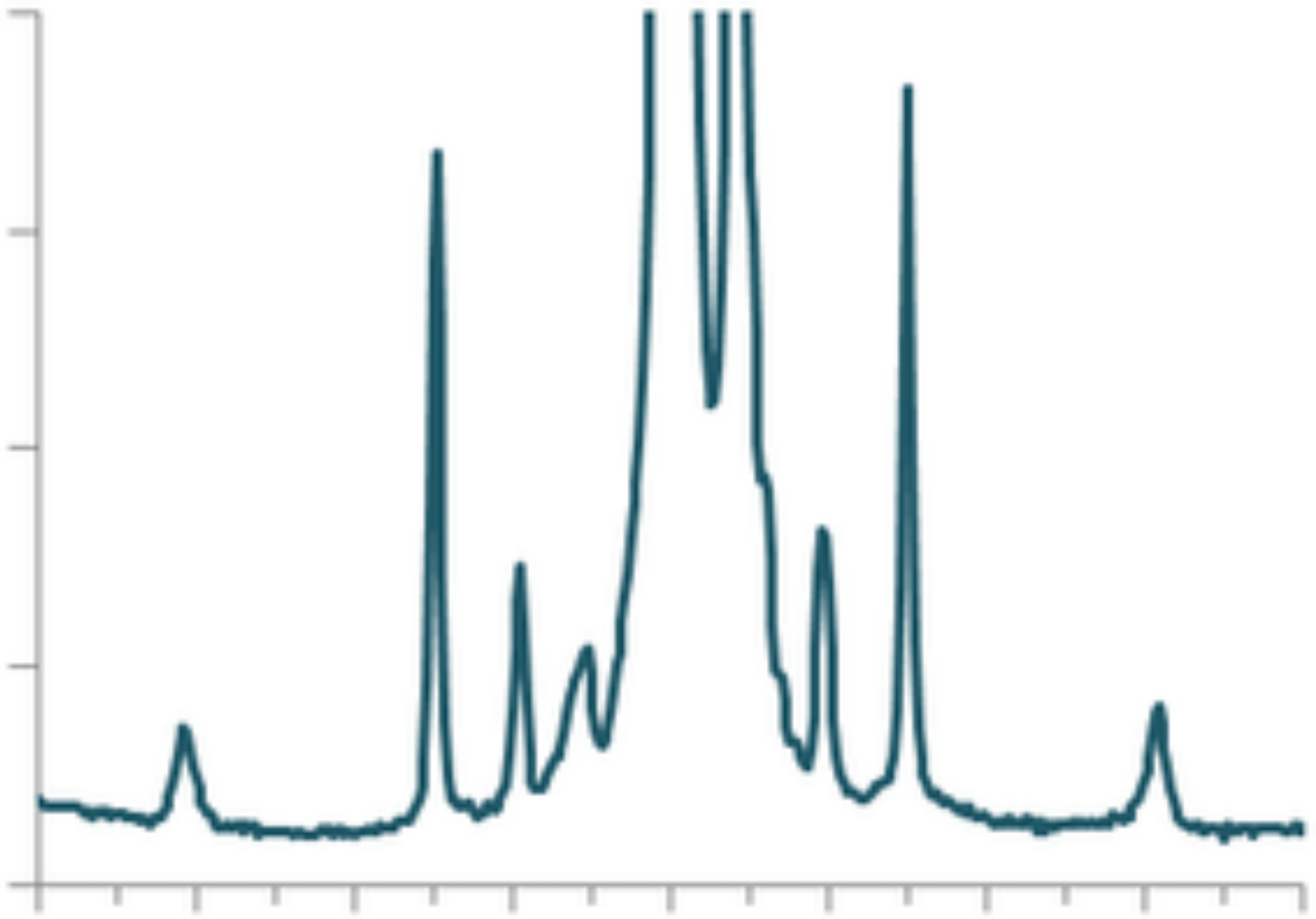
AQAM-2025 - 20/11/2025 - Alessandro Santini

Why do we care about spectral functions

- Spectral functions encode **excitations energies** and **intensities**
- They connect directly to experiments (ARPES, photoemission ..)
- Needed in materials, impurity models (DMFT)







Why do we care about spectral functions

- Spectral functions encode **excitations energies** and **intensities**
- They connect directly to experiments (ARPES, photoemission ..)
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Compute real-time correlations for extract spectra

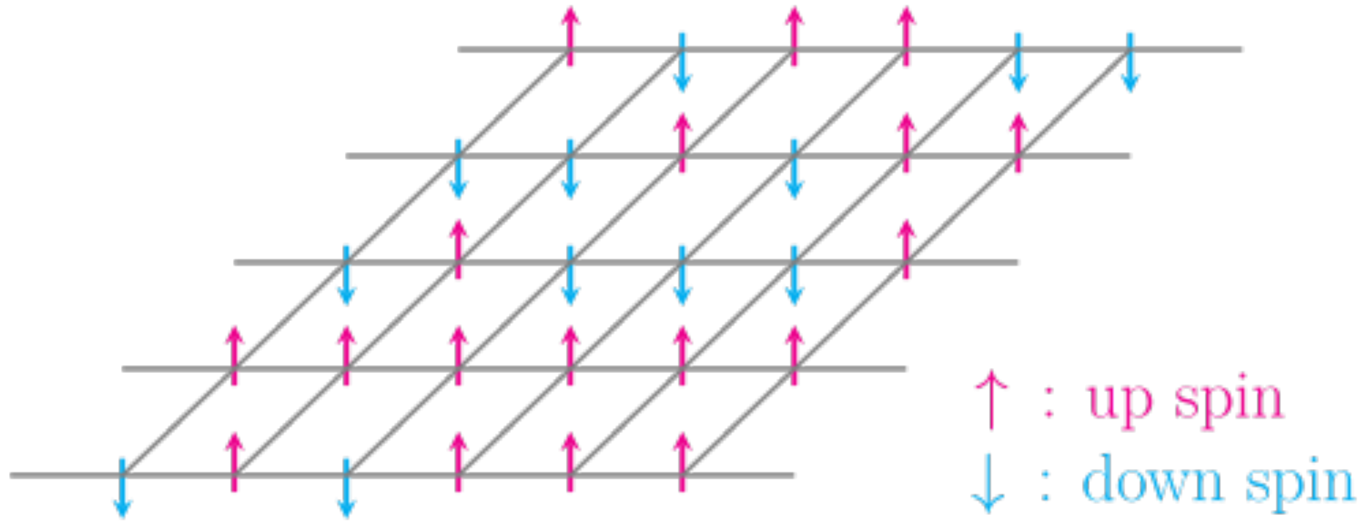
$$G_A(t', t) = \langle \psi_0 | A^\dagger(t') A(t) | \psi_0 \rangle$$

Link theory to experiments

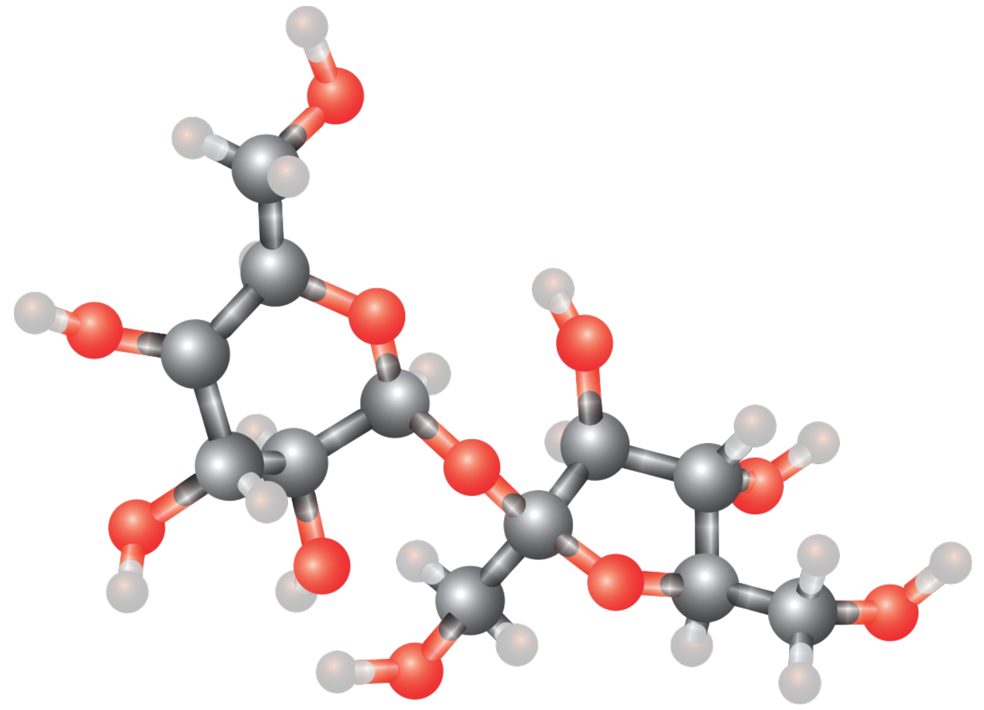
Many-body Quantum Problem

Equilibrium properties	$\hat{H}\,|\psi_0\rangle = E_0\,|\psi_0\rangle$
Dynamical Response	$i\hbar\frac{\mathrm{d}}{dt}\,|\psi(t)\rangle = \hat{H}\,|\psi(t)\rangle$

Lattice Models



Quantum Chemistry



Quantum Technologies

Static Ground State Calculation

$$H|\psi_\theta\rangle = E|\psi_\theta\rangle$$

$$\theta_{\text{tg}} = \arg\min_\theta \left[\langle\psi_\theta|H|\psi_\theta\rangle\right]$$

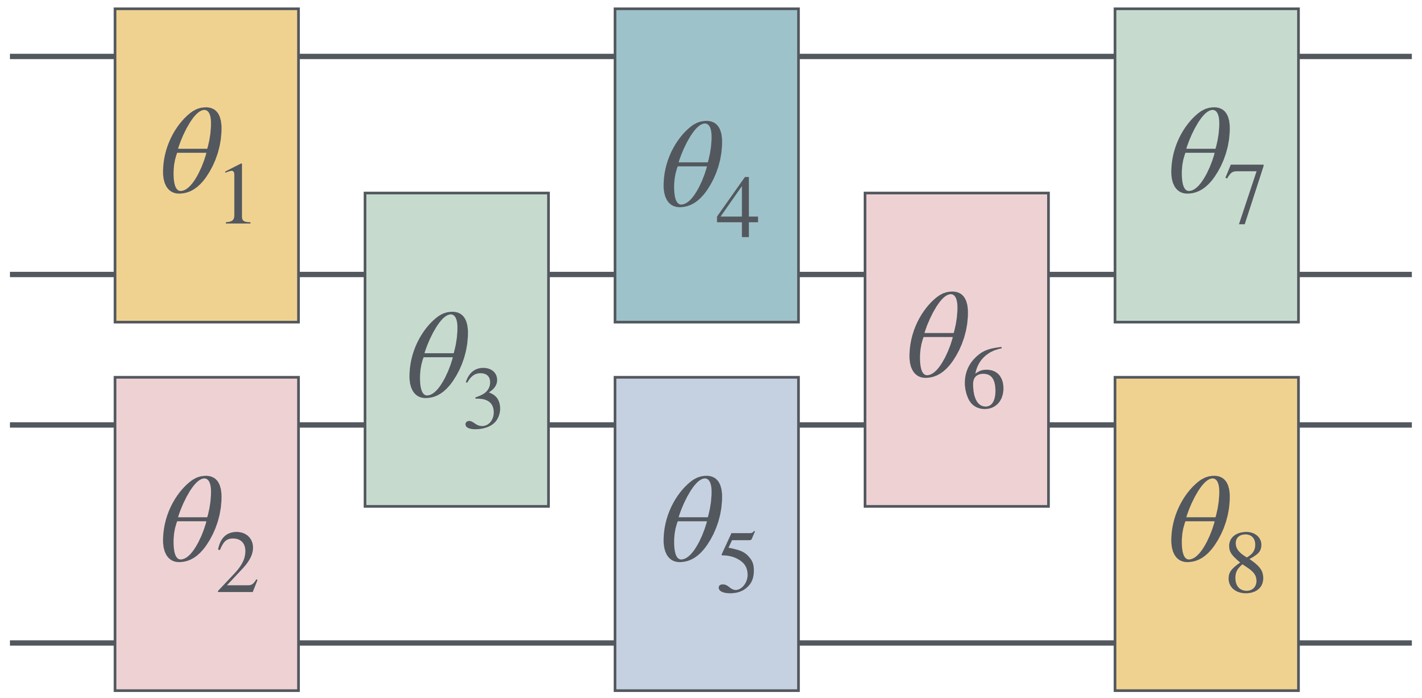
Classical variational methods work well

- DMRG/Tensor networks
- Variational Quantum Montecarlo (VMC)

$$|\psi_\theta\rangle = \sum_x \psi_\theta(x)\,|x\rangle$$

Quantum variational methods struggle

- Optimization cost (number of shots)
- Sampling noise
- Barren Plateaux



Real time dynamics is the hard part

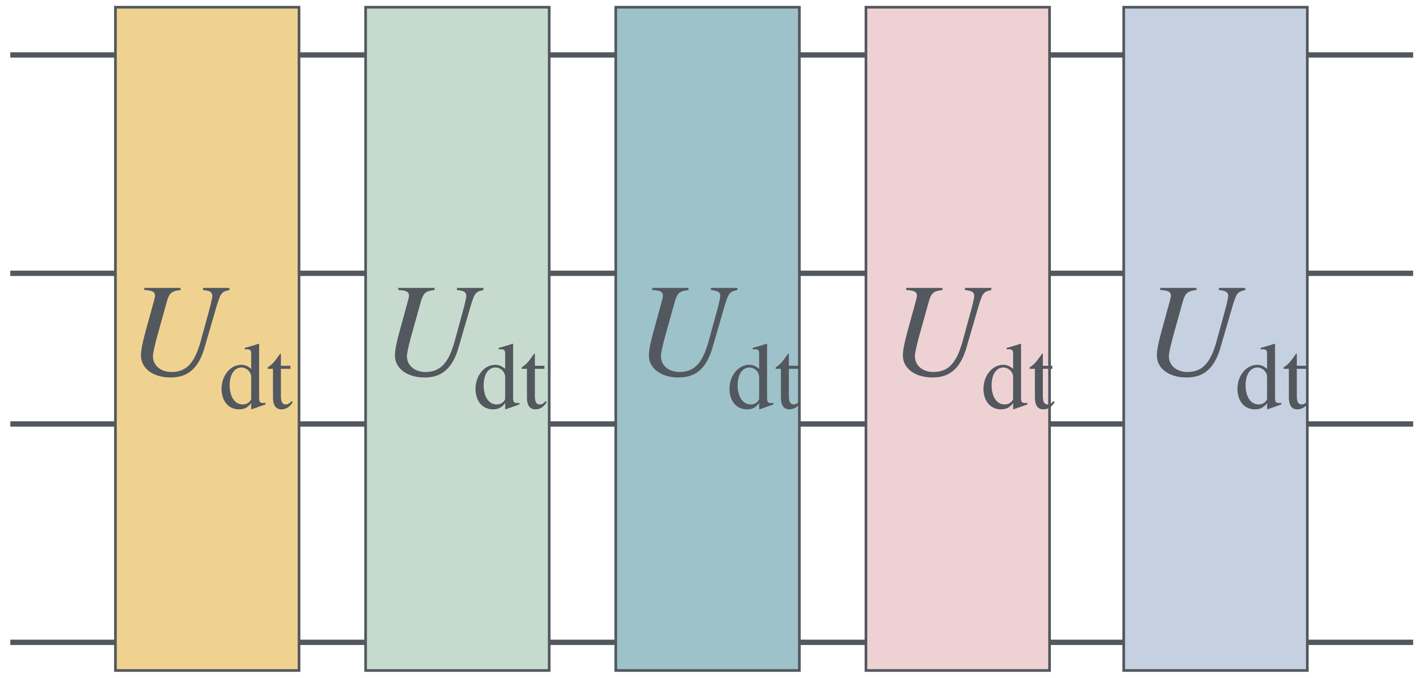
$$|\psi_0\rangle \xrightarrow{e^{-i\hat{H}t}} |\psi_t\rangle$$

Classical variational methods

- Tensor network: bond dimension explodes with entanglement
- t-VMC: Sampling problems large time dynamics
- ED, Clifford simulation, Pauli propagation ….

Quantum Hardware

- Brute force not variational dynamics native on a quantum hardware



Plan of the talk

I. Ground states with Classical simulations

   I. Introduction to Variational Monte Carlo

   II. Recent advances: Reaching chem. Precision with Importance sampling

II. Hybrid subspace algorithm

III. Extension to impurity models

Ground states with Classical simulations

Looking elsewhere: improving variational Monte Carlo gradients by importance sampling
A. Misery, L. Gravina, **AS**, F. Vicentini
arXiv preprint arXiv:2507.05352

Variational Quantum Montecarlo

$$E = \frac{\langle \psi_\theta | H | \psi_\theta \rangle}{\langle \psi_\theta | \psi_\theta \rangle} = \sum_x \underbrace{\frac{|\langle x | \psi_\theta \rangle|^2}{\langle \psi_\theta | \psi_\theta \rangle}}_{p_\theta(x)} \underbrace{\frac{\langle \psi_\theta | H | x \rangle}{\langle \psi_\theta | x \rangle}}_{H_{\mathrm{loc}}(x)}$$

Computational complexity

$$H_{yx} = \sum_y \langle y | H | x \rangle$$

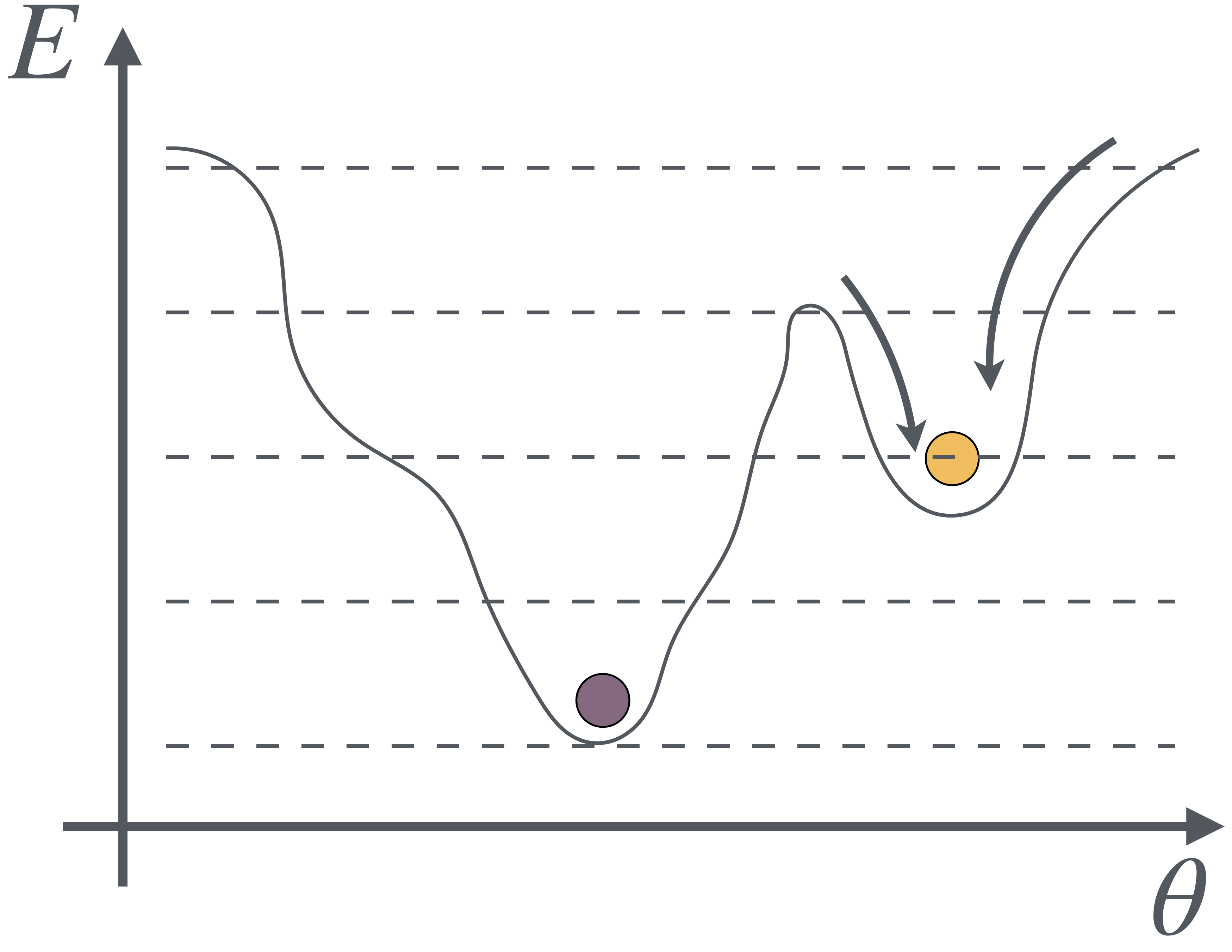
Sparsity of H_{yx}

Variational Quantum Montecarlo

$$E = \frac{\langle \psi_\theta | H | \psi_\theta \rangle}{\langle \psi_\theta | \psi_\theta \rangle} = \sum_x \underbrace{\frac{|\langle x | \psi_\theta \rangle|^2}{\langle \psi_\theta | \psi_\theta \rangle}}_{p_\theta(x)} \underbrace{\frac{\langle \psi_\theta | H | x \rangle}{\langle \psi_\theta | x \rangle}}_{H_{\mathrm{loc}}(x)}$$

$$\partial_{\theta_k} E = \langle \partial_{\theta_k} \log \psi_\theta \, \Delta H_{\mathrm{loc(x)}} \rangle$$

$$\theta_{k+1} = \theta_k - \eta \partial_{\theta_k} E$$



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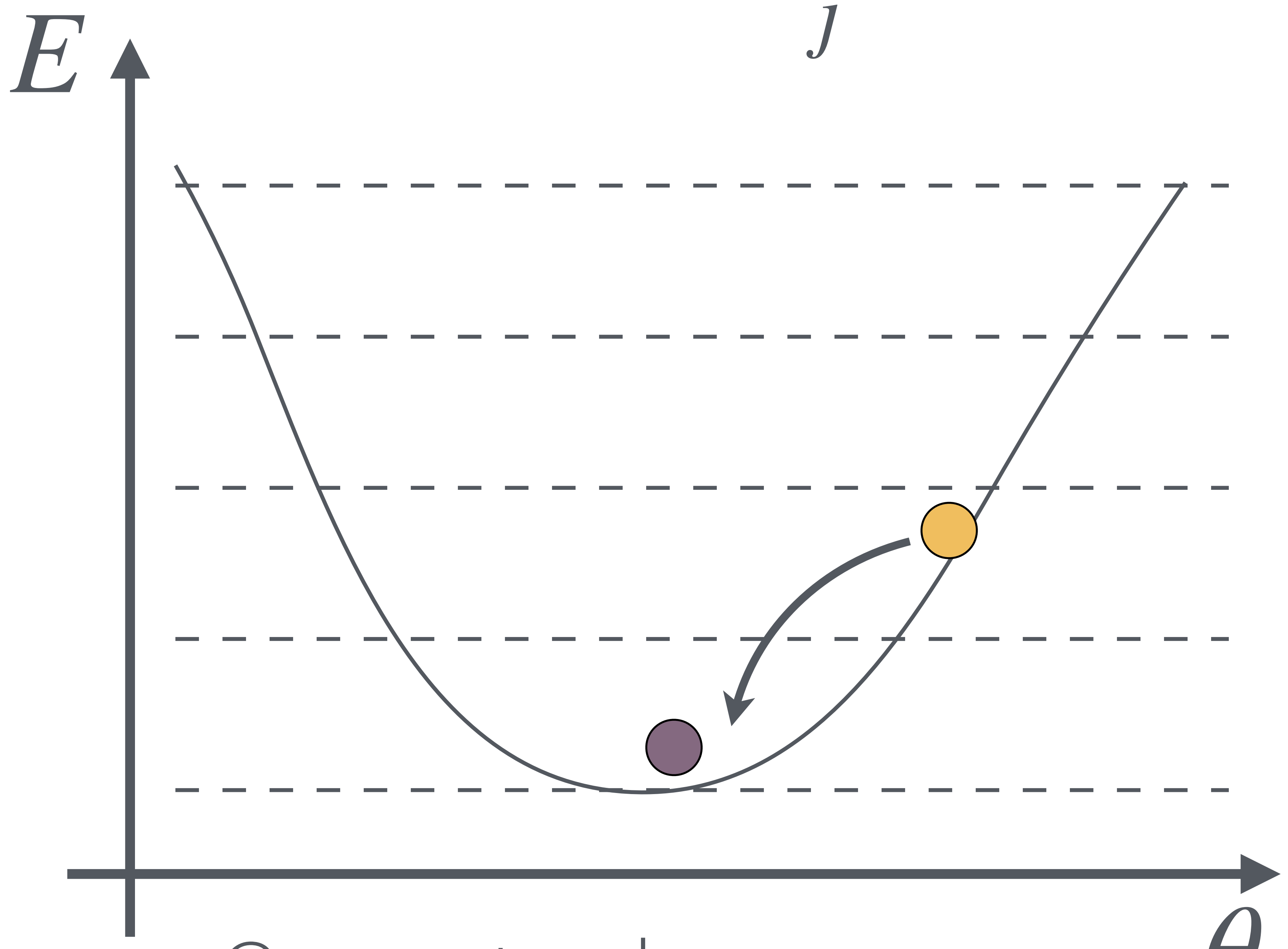
$$\partial_{\psi_\theta} \langle \psi_\theta | H | \psi_\theta \rangle$$

$$\theta_{k+1} = \theta_k - \eta \sum_j S^{-1}_{kj} \partial_{\theta_j} E$$



Guaranteed convergence

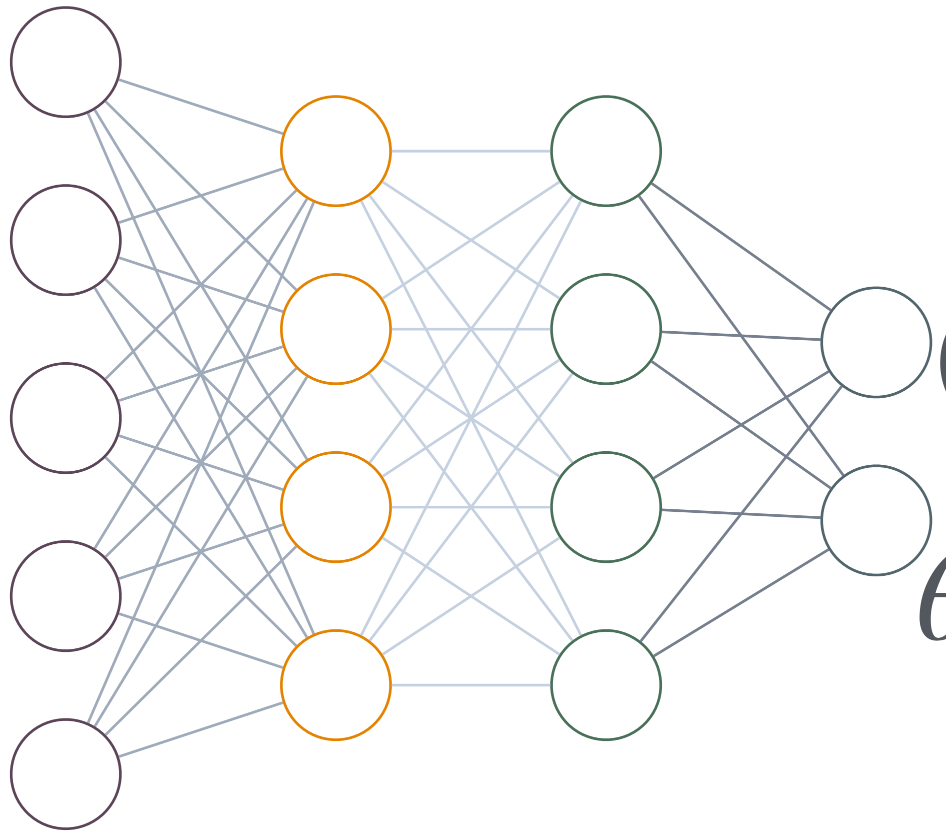
Computational complexity

$$H_{yx} = \sum_y \langle y | H | x \rangle$$

Sparsity of H_{yx}

Neural Network Quantum States (NQS)

$$|\psi_\theta\rangle = \sum_{\mathbf{x}}$$

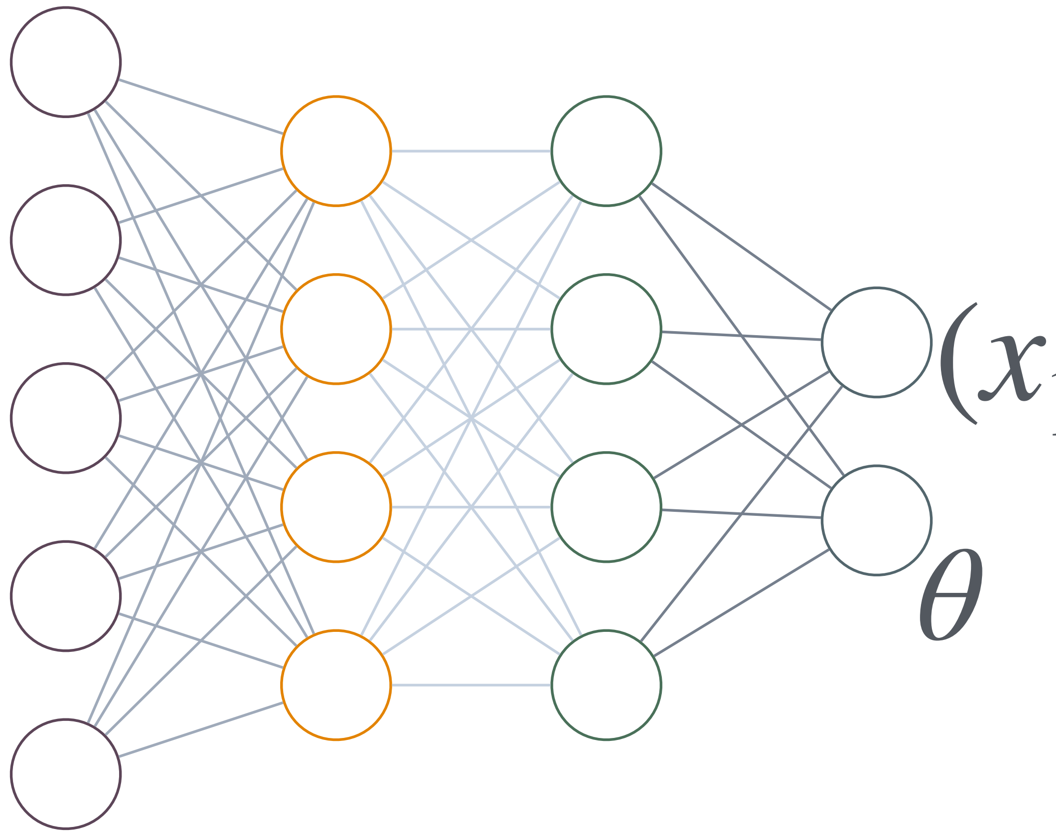


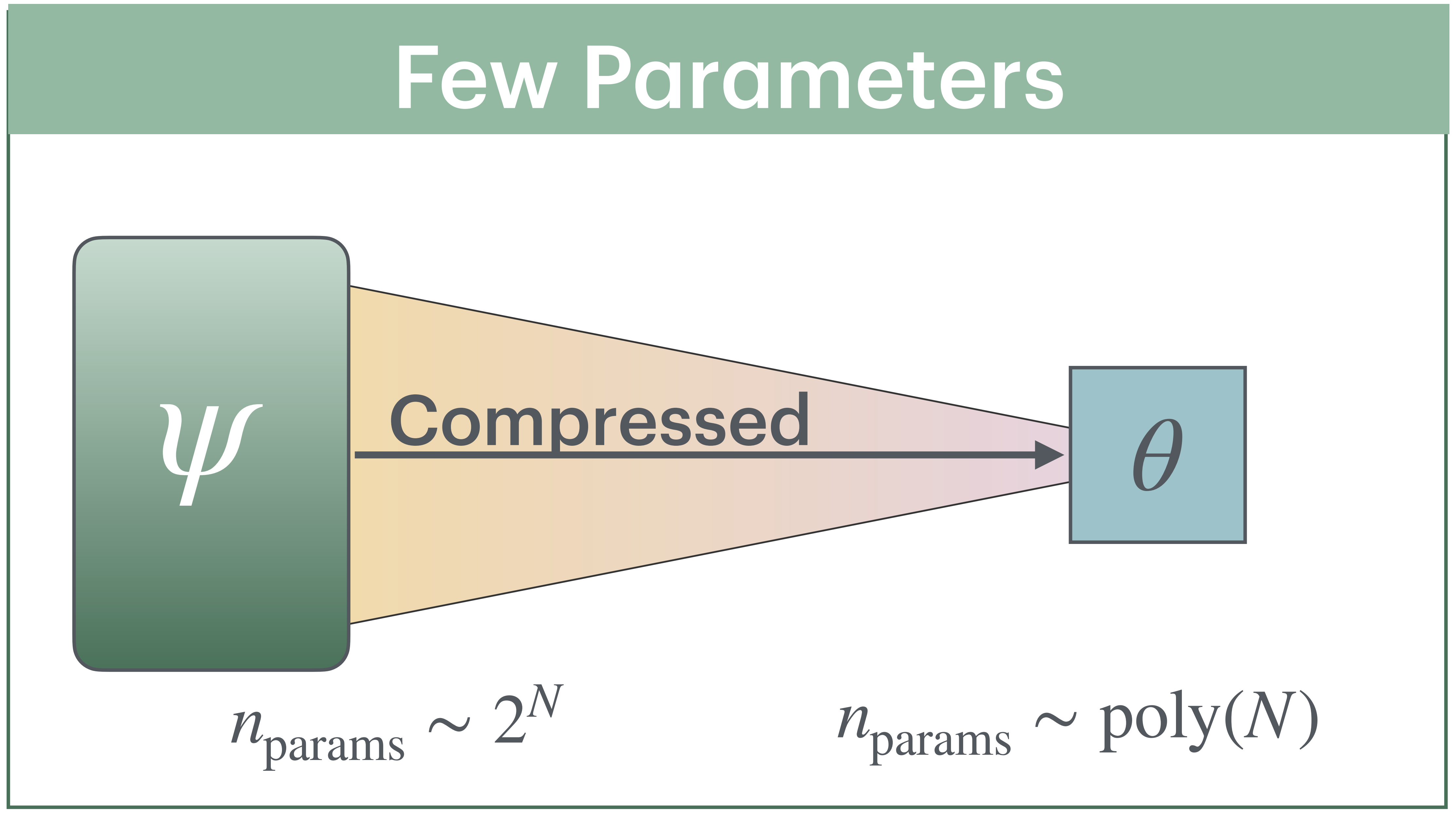
$$(x_1, \ldots, x_N)\,|x_1 \ldots x_N\rangle$$

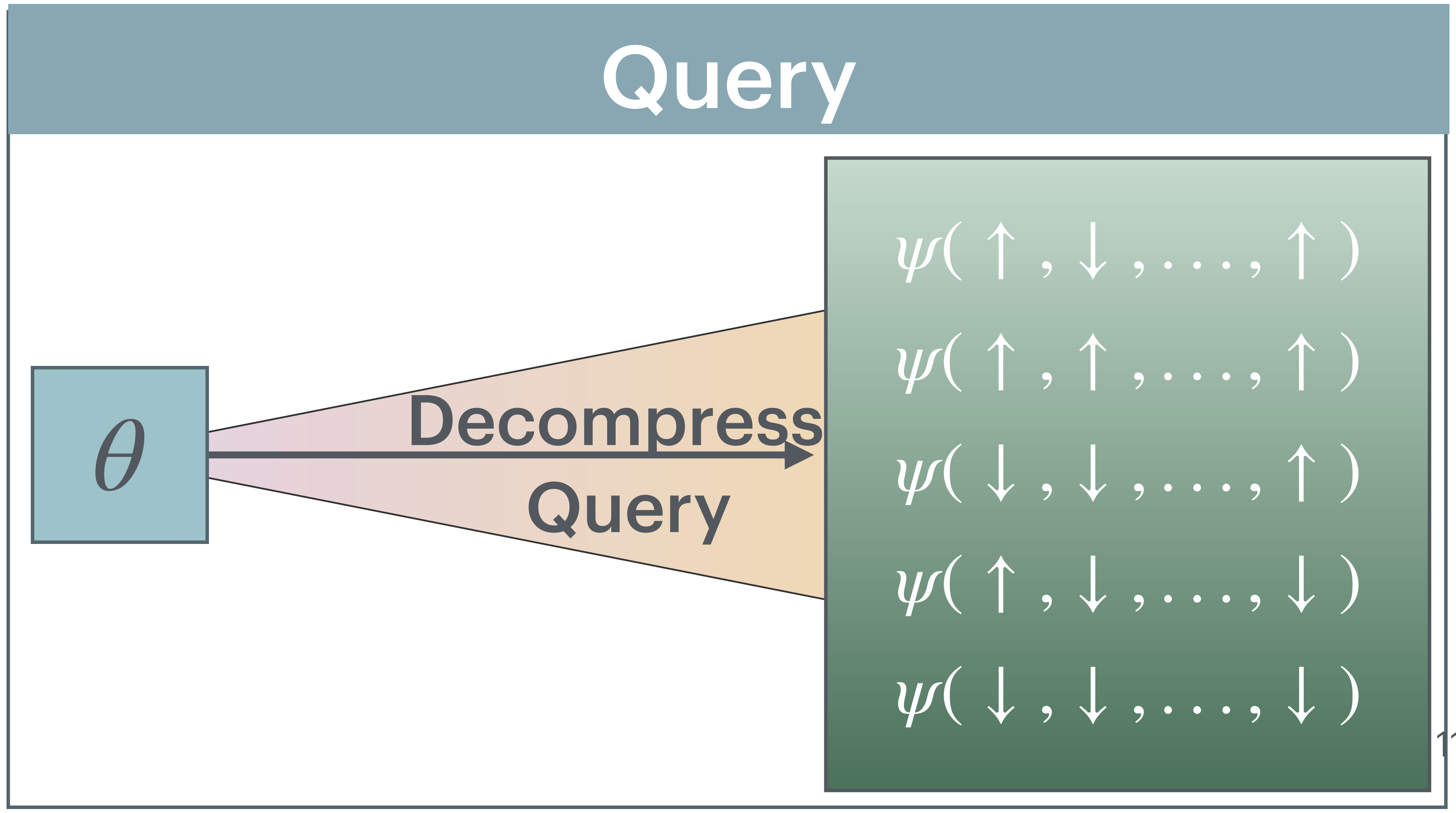
θ

Neural Network Quantum States (NQS)

$$|\psi_\theta\rangle = \sum_{\mathbf{x}} \;(\text{NN})_\theta\,(x_1, \ldots, x_N)\,|x_1 \ldots x_N\rangle$$

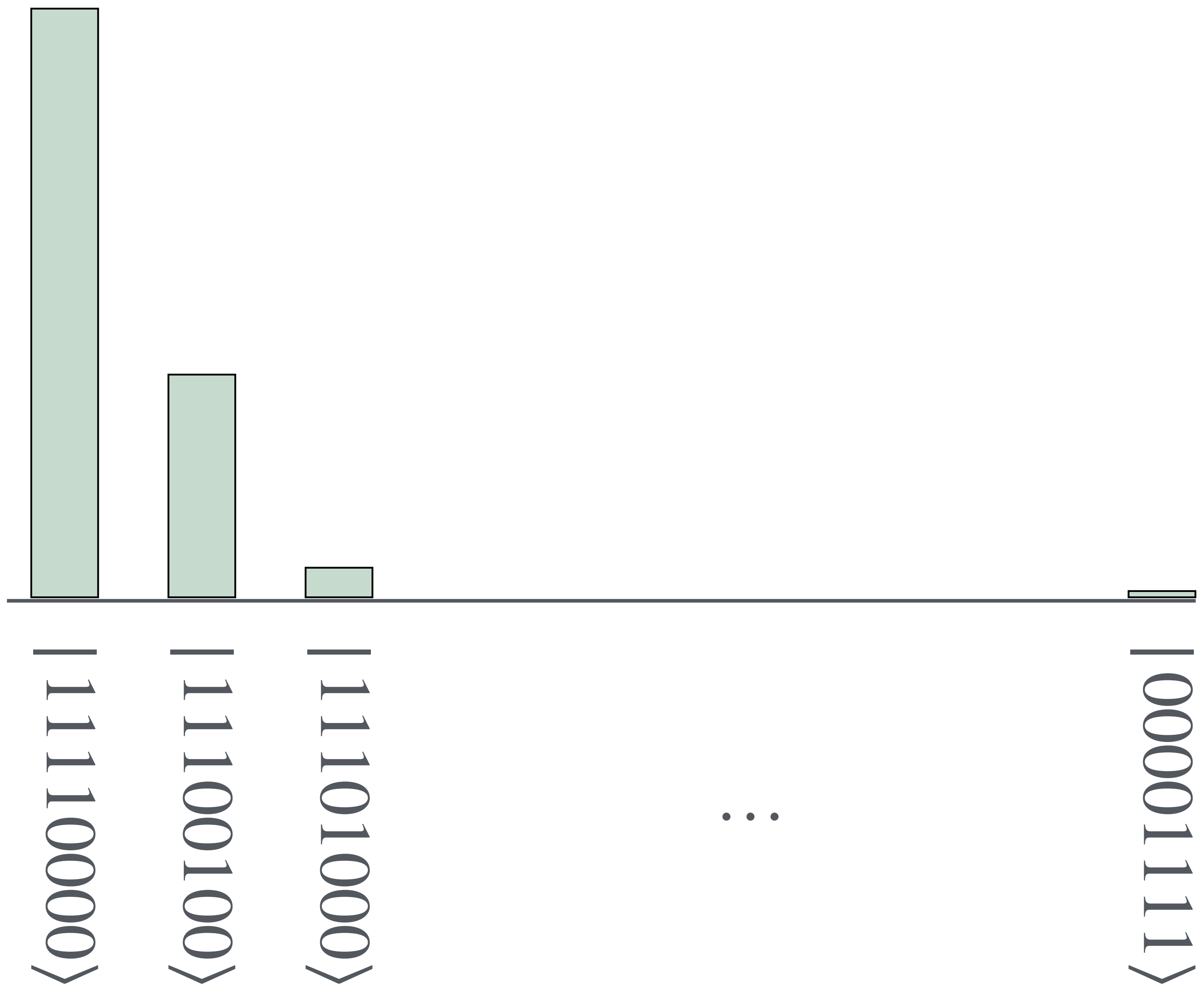




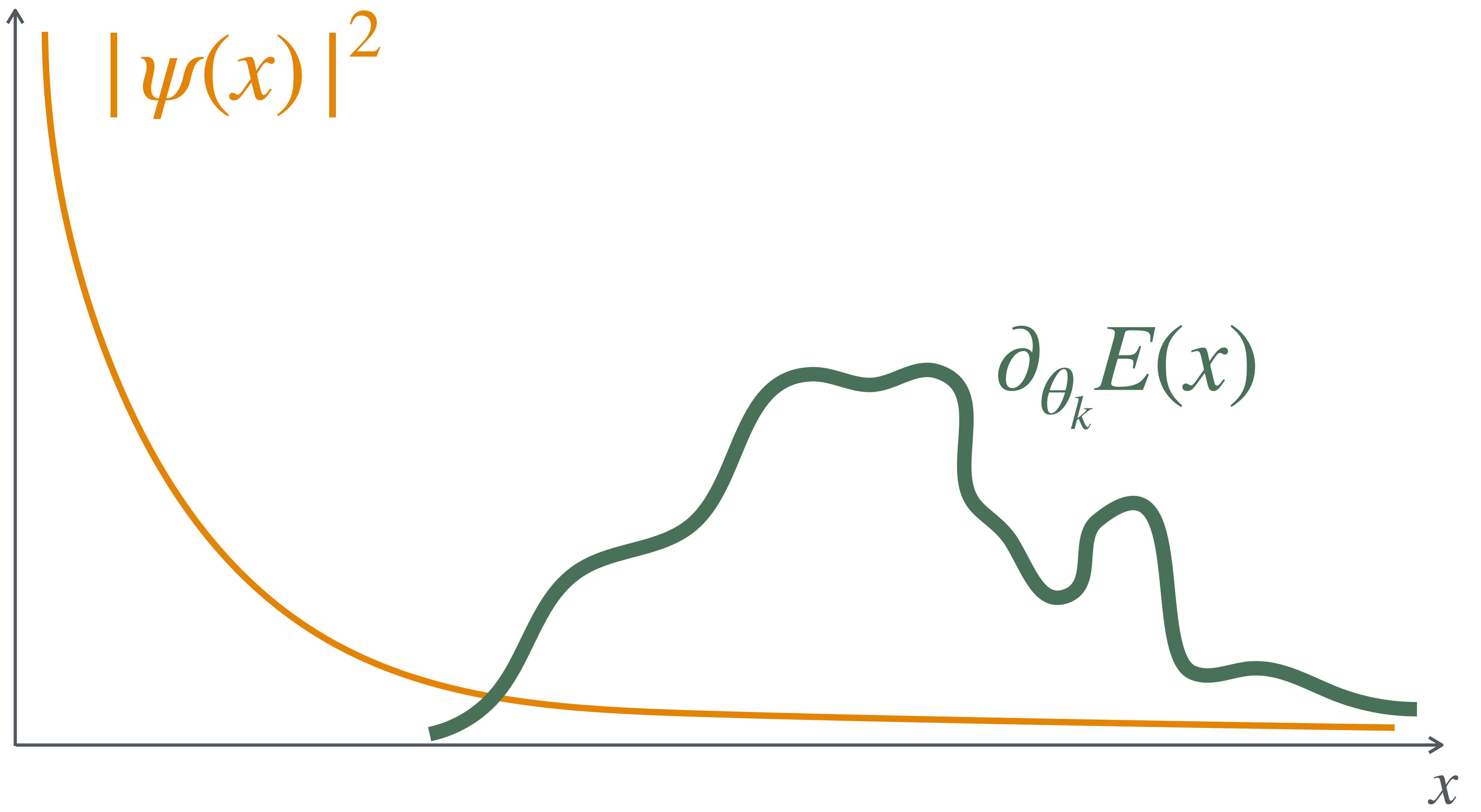


Why sampling from the Born probability fails

Molecular $|\psi(x)|^2$ peaked on a few determinants



The gradient of the loss lives in low-probability regions

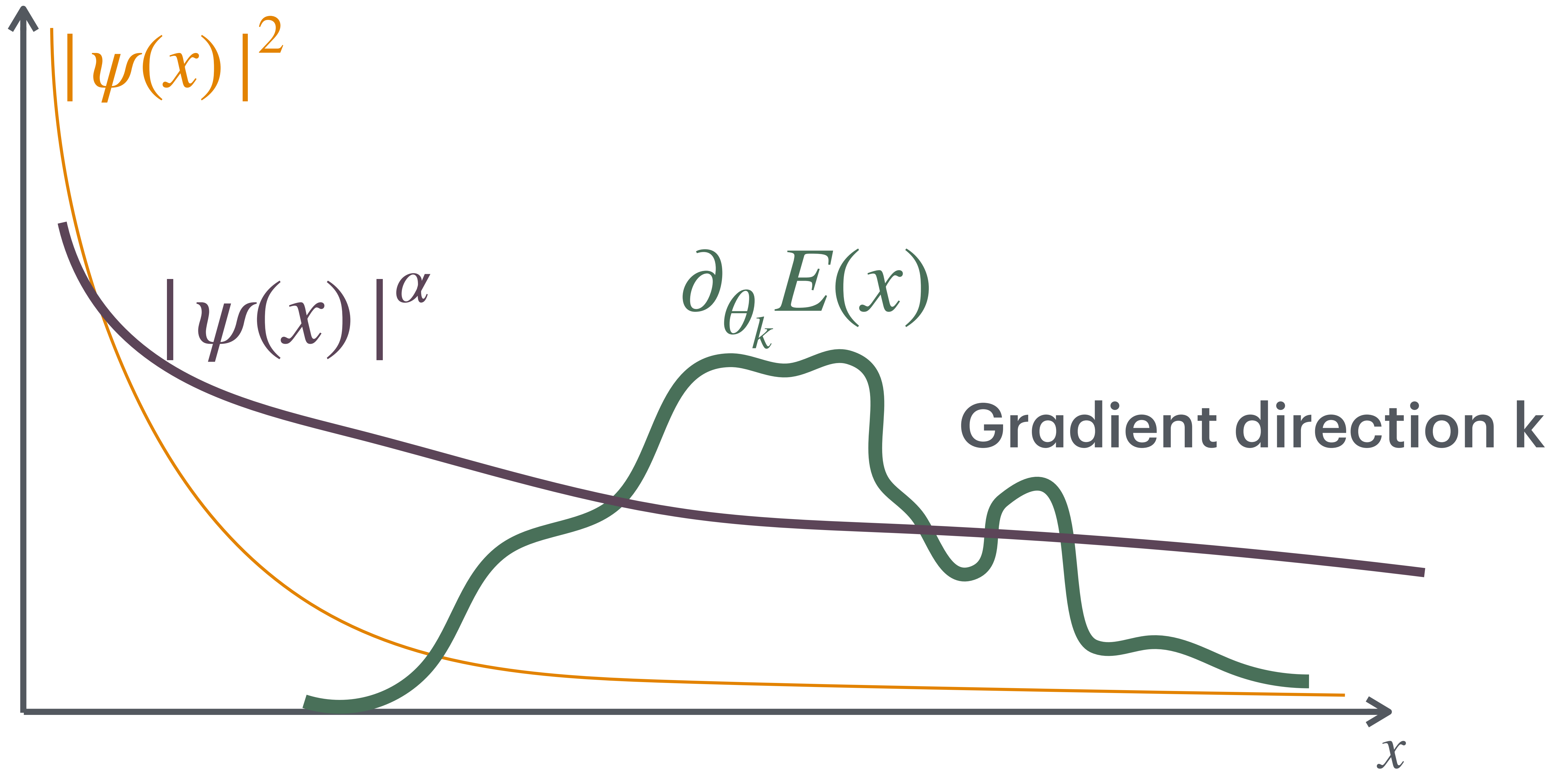


Importance Sampling

Goal Sample where gradient matters

$$q_\alpha(x) \propto |\psi(x)|$$

$\alpha < 2$ broader distribution
(Over dispersed sampling)



Optimal sampling distribution

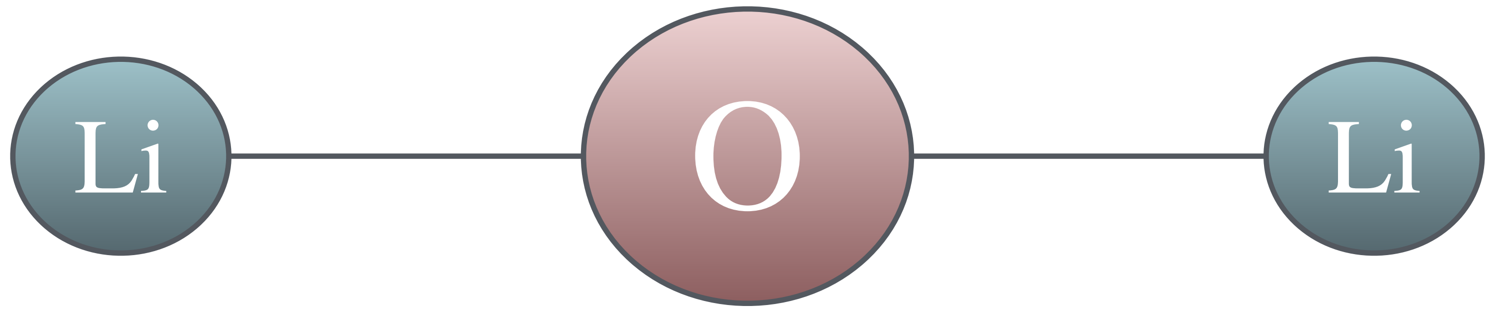
$$\mathscr{L}_{\mathrm{IS}} = \frac{1}{N_{\mathrm{p}}} \sum_{k=1}^{N_{\mathrm{p}}} \mathrm{SNR}_{q_\alpha}[\partial_{\theta_k} E]$$

$$\alpha' = \alpha + \eta \partial_\alpha \mathscr{L}_{\mathrm{IS}}$$

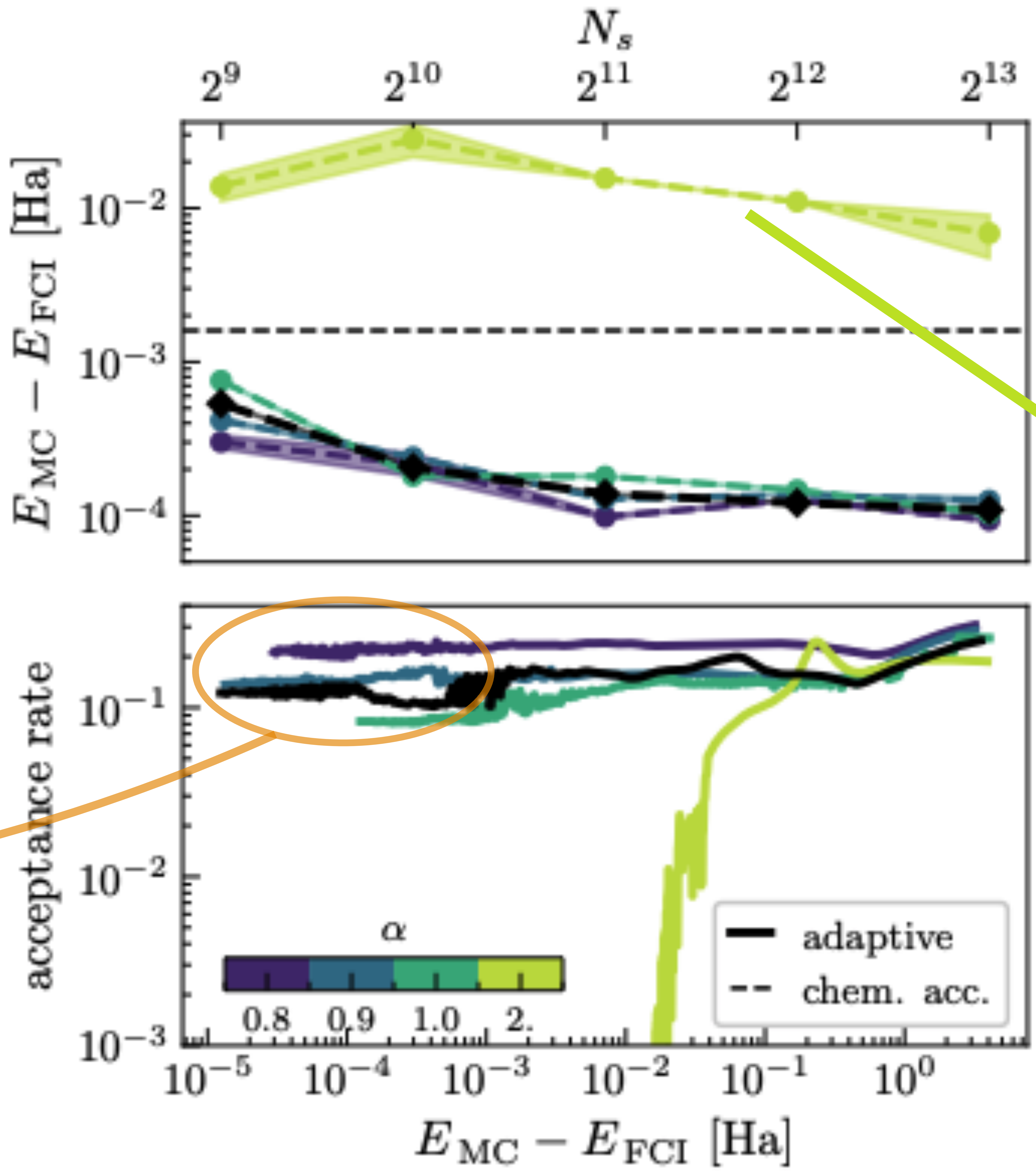
Optimize the Signal to Noise ratio of the gradient $\longrightarrow$ improved variance less samples

$$q_{\vec{\alpha}} = f(x; \overrightarrow{\alpha})$$

Over dispersed Sampling



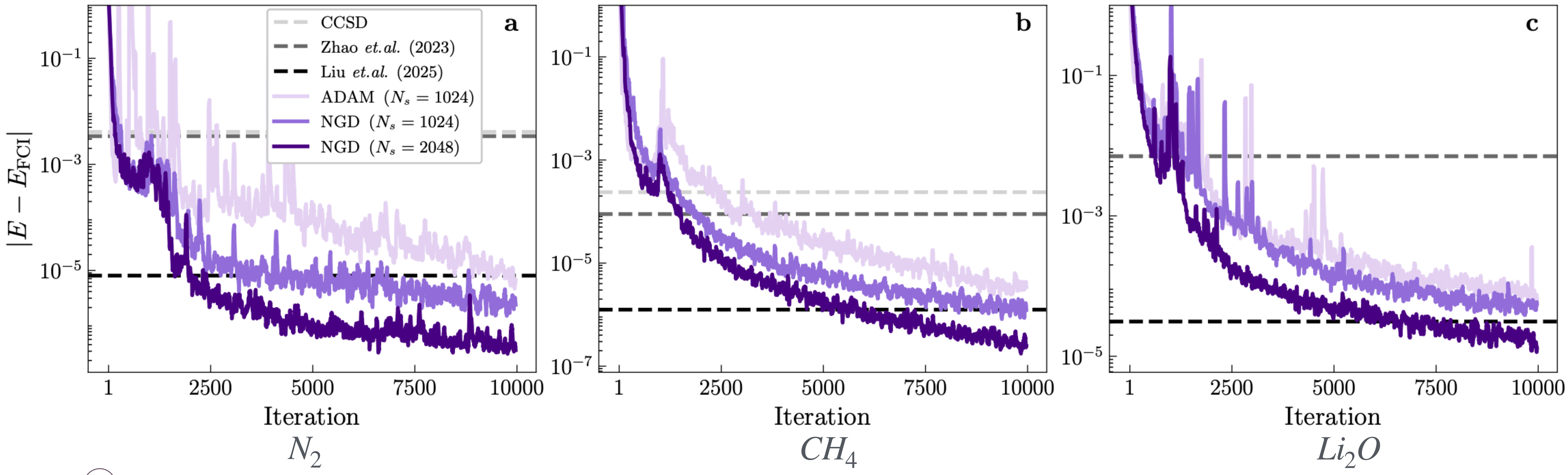
$$q_\alpha = |\psi(x)|^\alpha$$

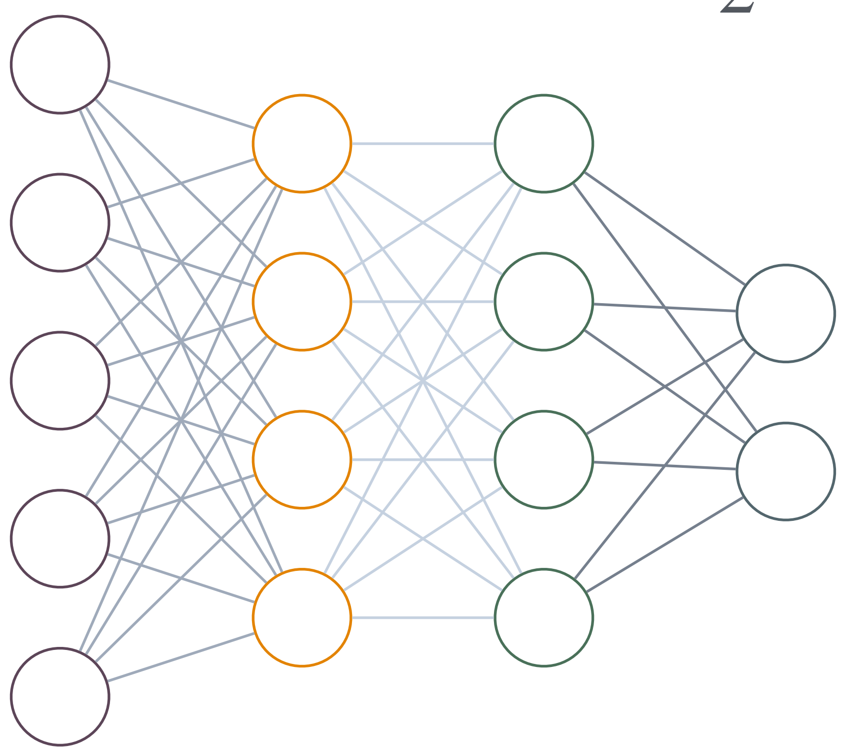


Sampled from Born distribution

Importance sampling chemical accuracy

Neural Network Sampling (preliminary)





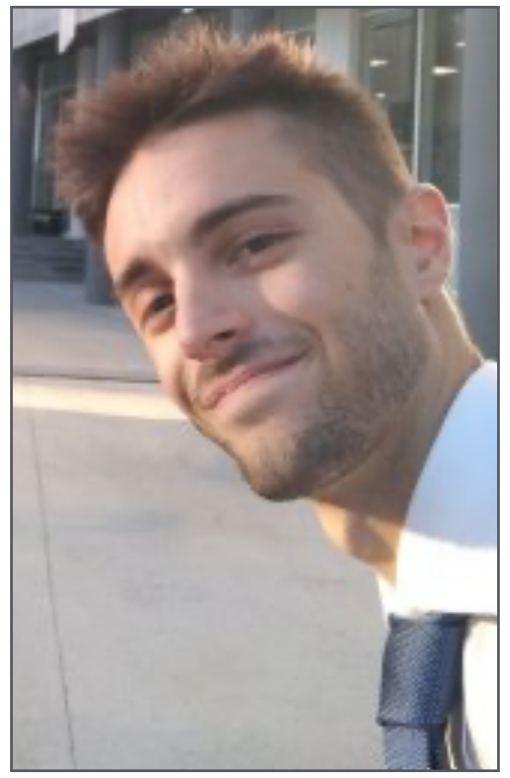
$$q_{\vec{\alpha}}(x) = \mathrm{NN}(\mathrm{x}; \overrightarrow{\alpha})$$

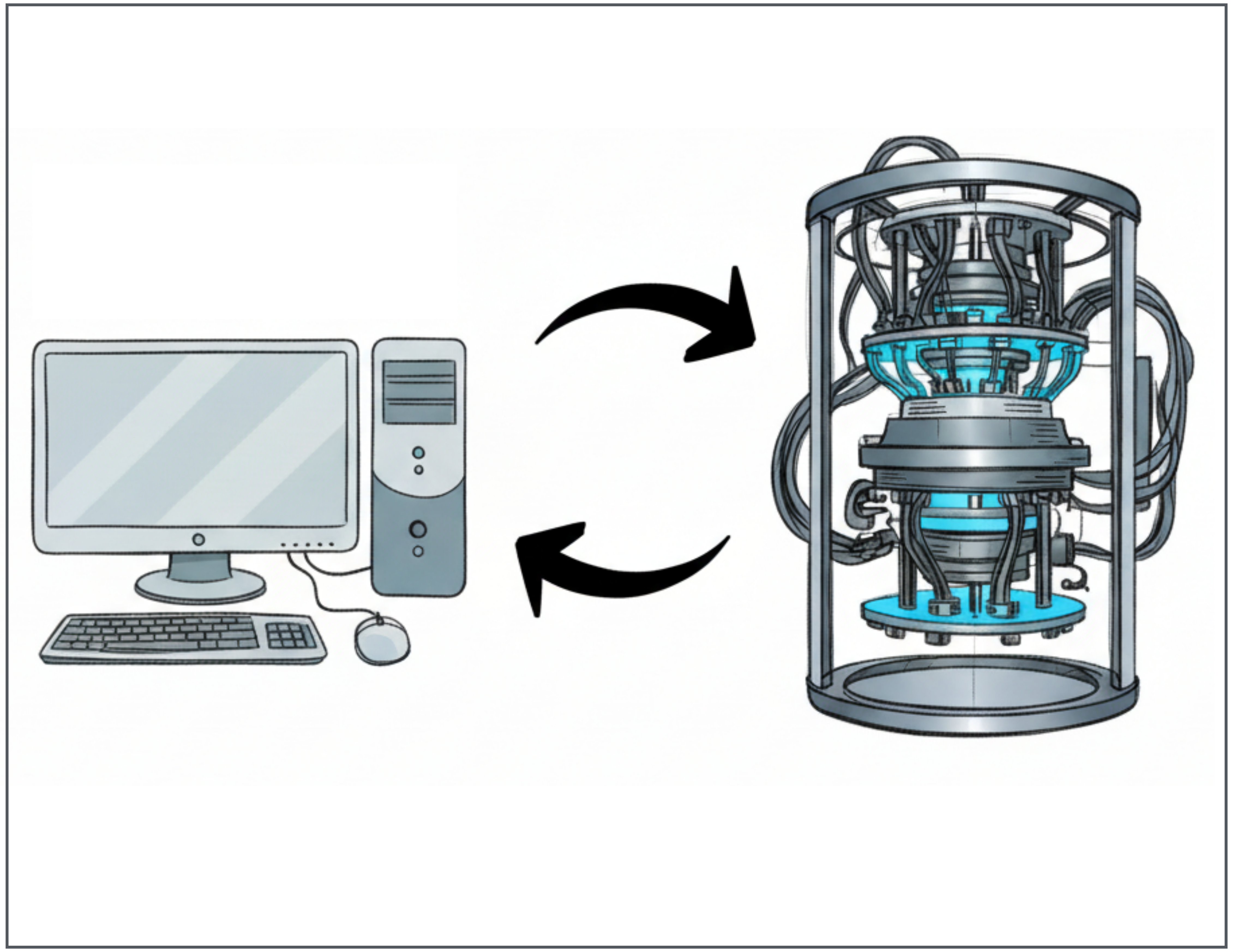
Hybrid subspace algorithm

Classically Prepared, Quantumly Evolved:
Hybrid Algorithm for Molecular Spectra

AS, S. Barison, F. Vicentini

arXiv preprint *arXiv:2510.24911*



Hybrid subspace algorithm

	Classical techniques	Quantum Hardware
Variational Ground State	😎	🥺
Variational Dynamics	🥺	🥺
Brute Force Dynamics	🥺	😎

Hybrid subspace algorithm

	Classical techniques	Quantum Hardware
Variational Ground State	😎	🥺
Variational Dynamics	🥺	🥺
Brute Force Dynamics	🥺	😎

Back to Spectroscopy

$$G_A(t) = \langle \psi_0 | \hat{A}^\dagger(t)\hat{A} | \psi_0 \rangle$$

Let us suppose to have a $|\psi_A\rangle = A|\psi_0\rangle$ representation with VMC

... Dynamics is still a problem $$G_A(t) = e^{iE_0 t}\langle A^\dagger A \rangle_0 \boxed{\langle \psi_A | \hat{U}(t) | \psi_A \rangle}$$

Back to Spectroscopy

$$G_A(t) = e^{iE_0 t}\langle A^\dagger A\rangle_0 \mathbb{E}_{y\sim|\psi_A(y)|^2}\left[\sum_x \frac{\psi_A^*(x)}{\psi_A^*(y)}\langle x\,|\,\hat{U}(t)\,|\,y\rangle\right]$$

1. Sample $|y\rangle$ from $|\psi_A(y)|^2$

2. Evolve it on a quantum computer and measure it

3. Use the measured basis $\mathcal{S}_y$ to project the propagator $\hat{U}(t)$

$$\hat{U}(t) \longrightarrow \mathrm{P}_{\mathcal{S}_y}\hat{U}(t)\mathrm{P}_{\mathcal{S}_y} \approx \exp(-i\mathrm{P}_{\mathcal{S}_y}\hat{H}\mathrm{P}_{\mathcal{S}_y})$$

When the hybrid subspace algorithm work

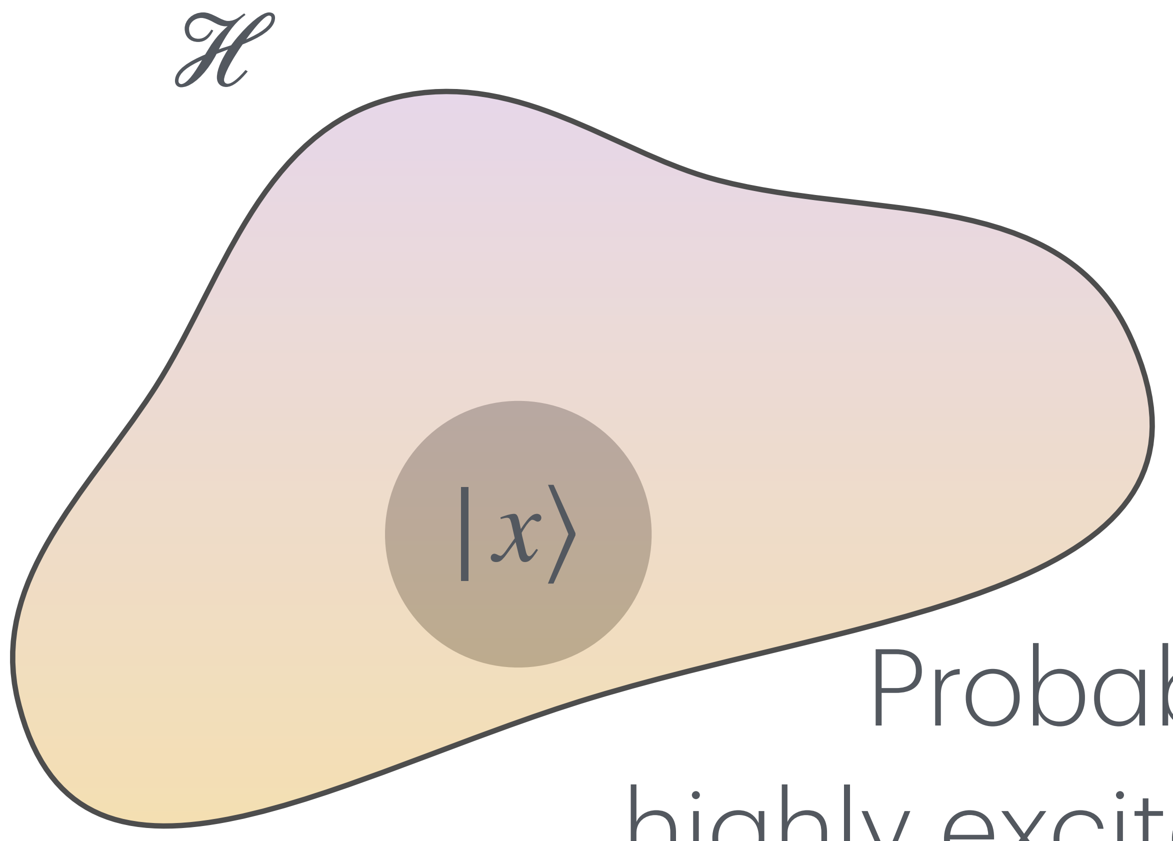
Ground state classically tractable

Quantum dynamics stays confined in $U|x\rangle$

Subspace effective dimension tractable with ED

Hilbert space fragmentation

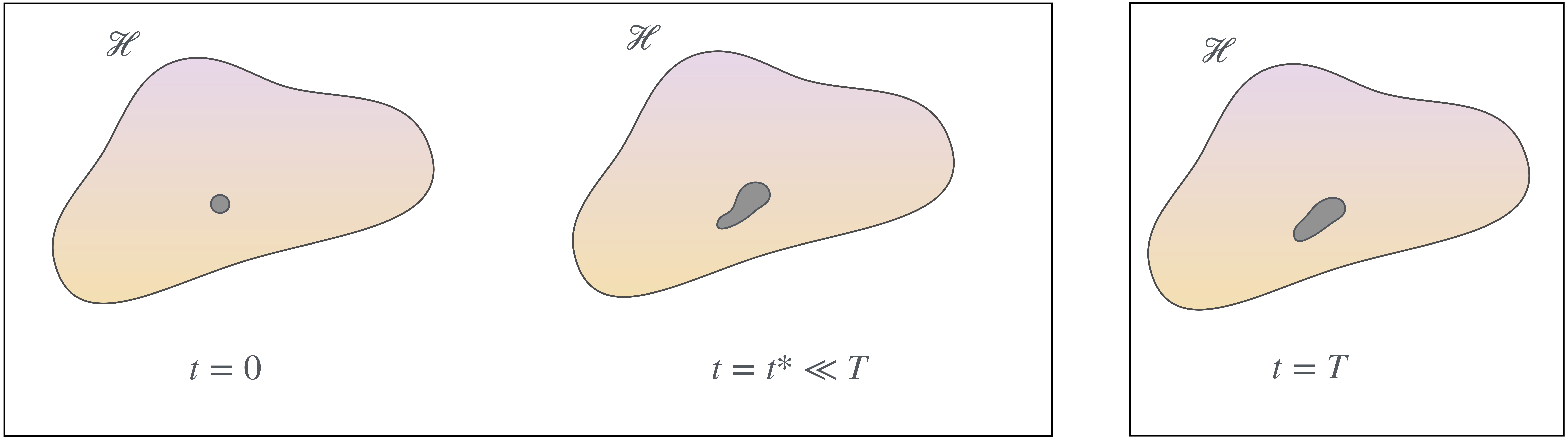
$$\#\, \langle x | \psi(t \ll T) \rangle \approx \#\, \langle x | \psi(T) \rangle$$



$$E_0 = \langle x | H | x \rangle$$

Probability of jumping to highly excited states is suppressed

Effective thermalization in a subspace

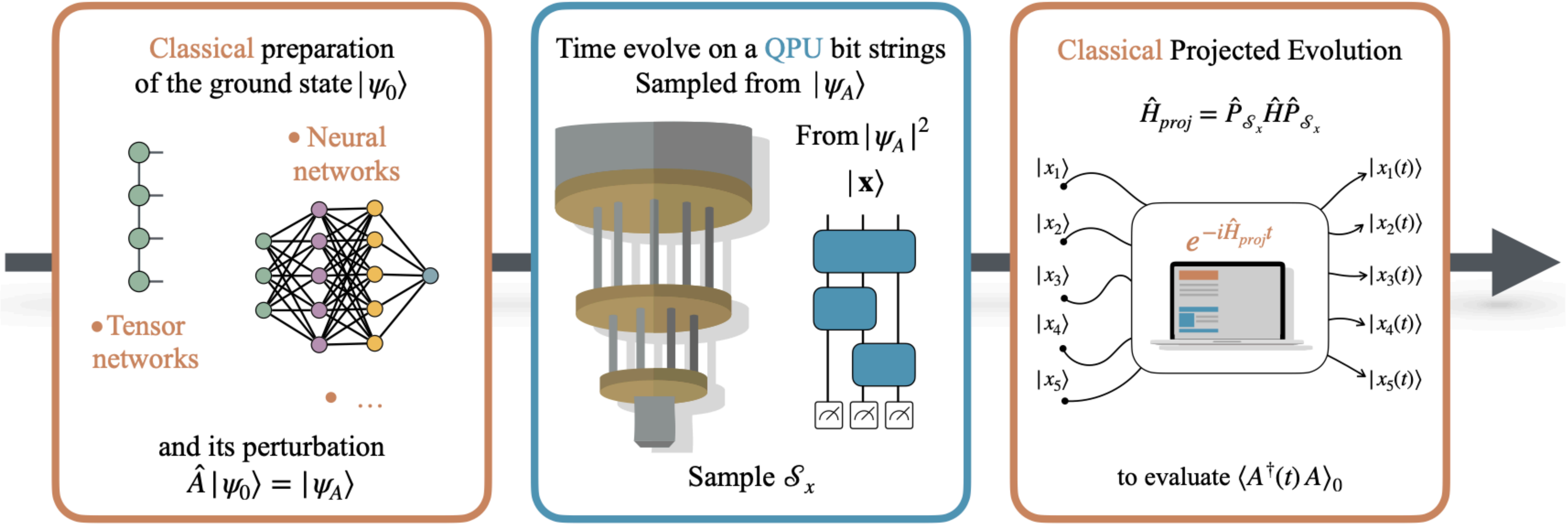


Small time **quantum hardware**

Large time to resolve small gaps

Subspace evolution extrapolates to large times

Hybrid Quantum Classical Algorithm



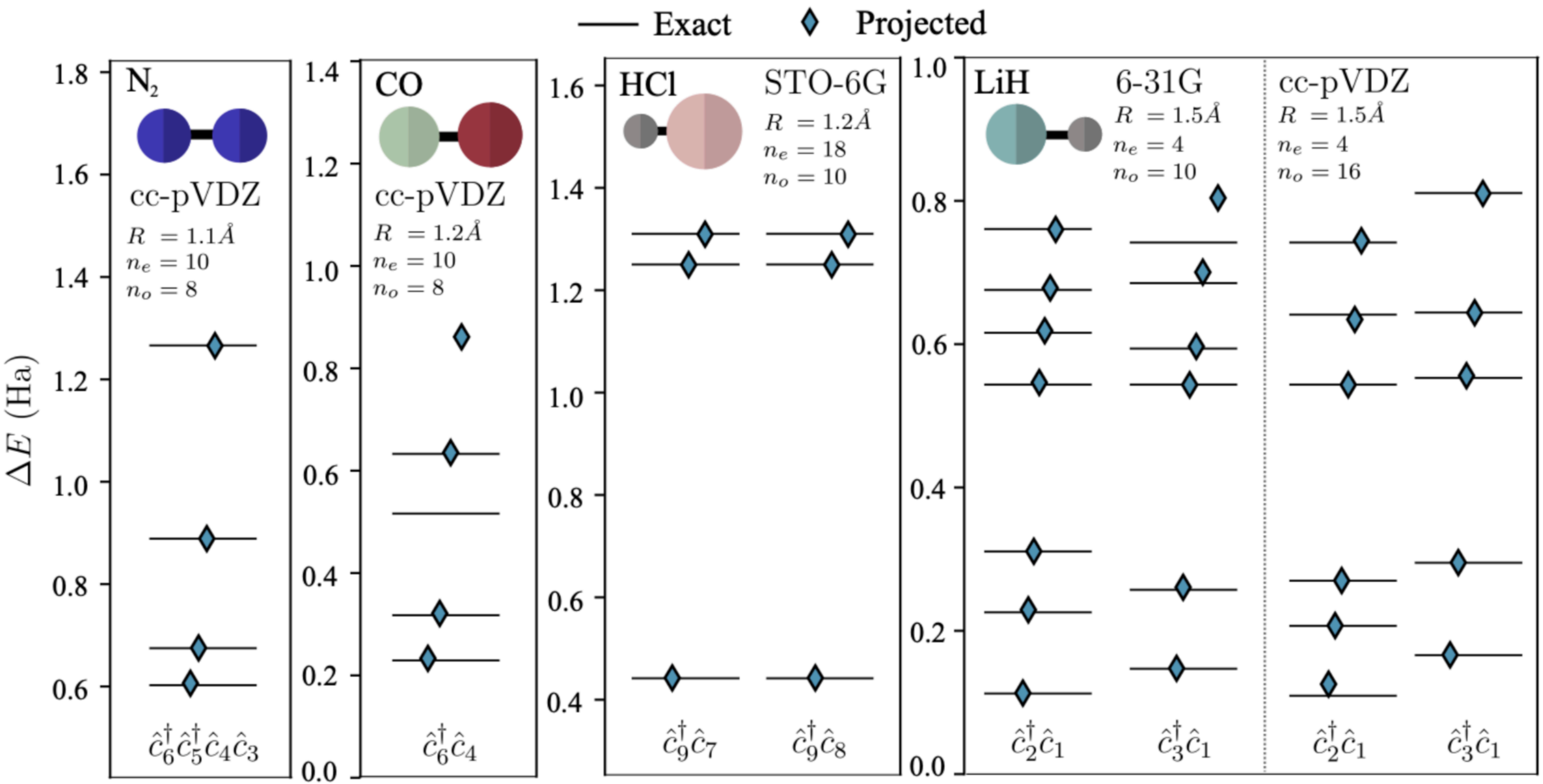
QPU friendly

- No ground state preparation
- Shallow quantum circuits

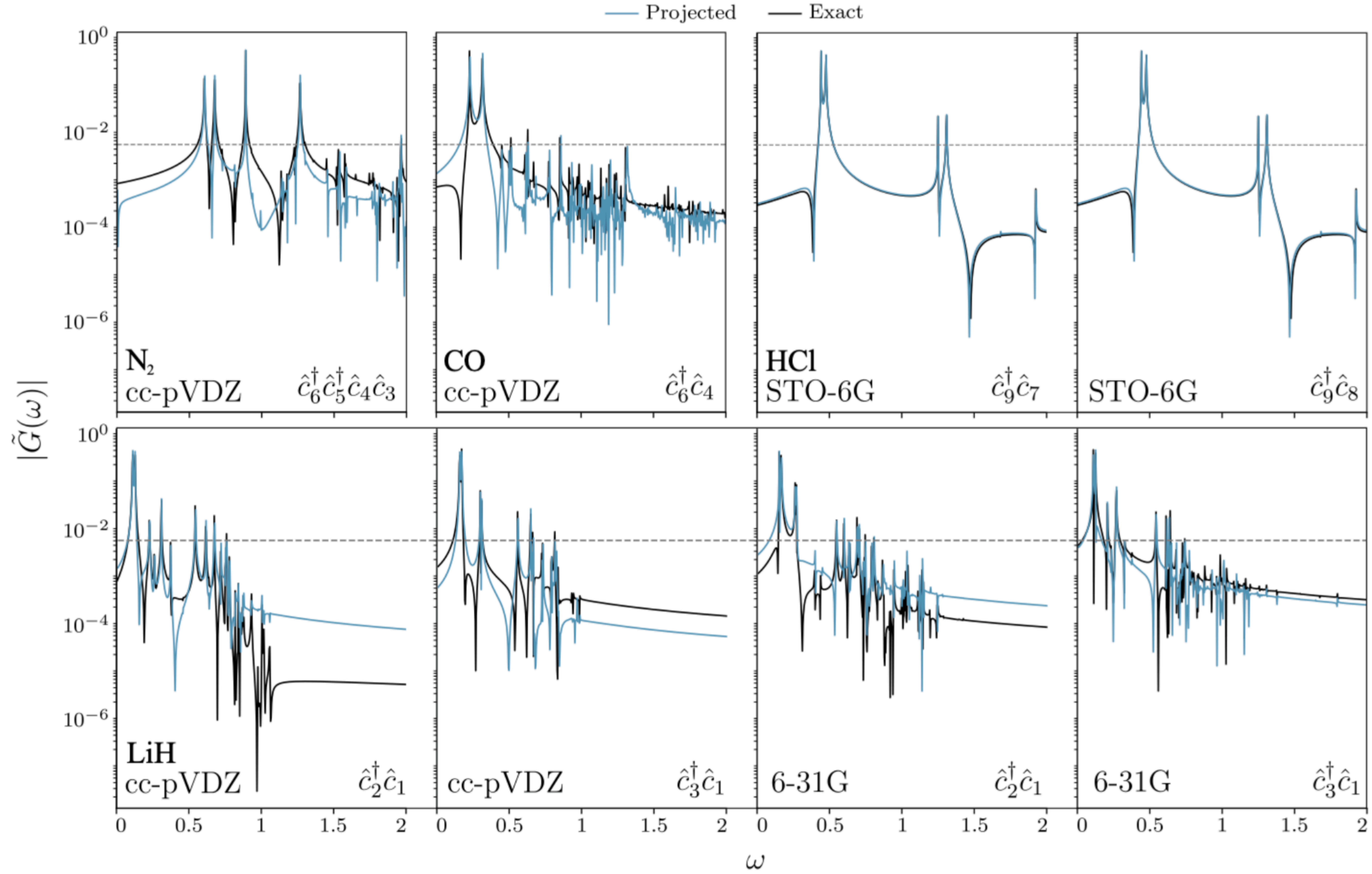
Result: accurate spectra

Molecule	n_o	n_e	R	Basis	Perturbation	Max dim $[\mathcal{S}_x]$
N_2	8	10	1.1	cc-pvdz	$\hat{c}_6^\dagger \hat{c}_5^\dagger \hat{c}_4 \hat{c}_3$	341
HCl	10	18	1.2	STO-6G	$\hat{c}_9^\dagger \hat{c}_7$	8
HCl	10	18	1.2	STO-6G	$\hat{c}_9^\dagger \hat{c}_8$	8
CO	8	10	1.2	cc-pvdz	$\hat{c}_6^\dagger \hat{c}_4$	821
LiH	10	4	1.5	6-31G	$\hat{c}_2^\dagger \hat{c}_1$	331
LiH	16	4	1.5	cc-pvdz	$\hat{c}_2^\dagger \hat{c}_1$	1421
LiH	10	4	1.5	6-31G	$\hat{c}_3^\dagger \hat{c}_1$	298
LiH	16	4	1.5	cc-pvdz	$\hat{c}_3^\dagger \hat{c}_1$	1007

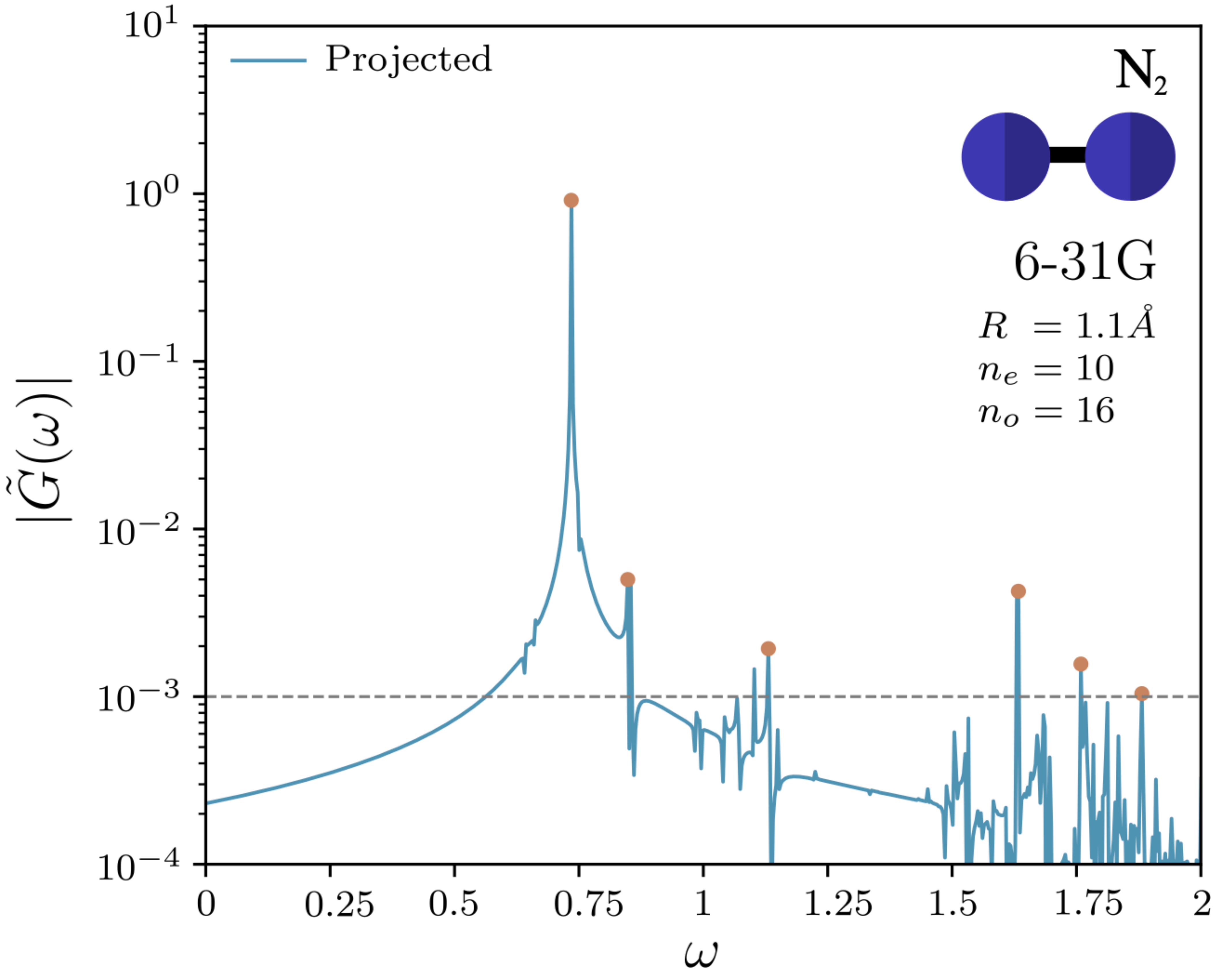
Result: accurate spectra



Result: accurate spectra



Tensor Network dynamics



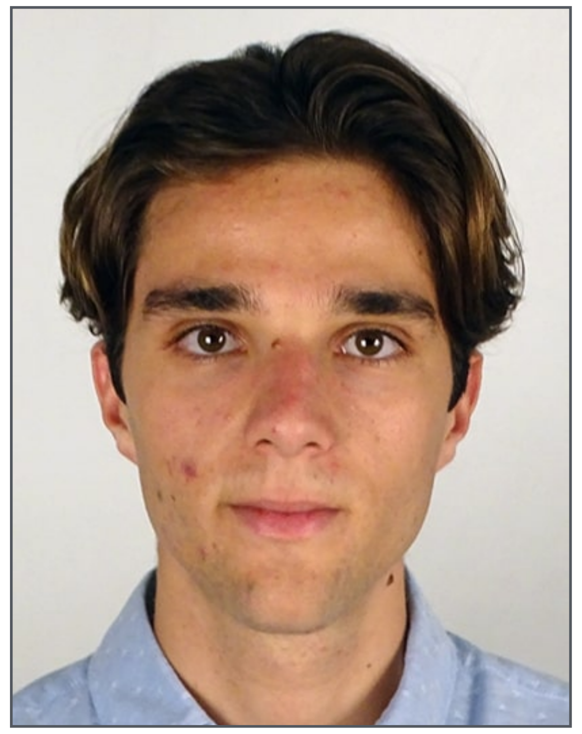
- TN algorithm simulates the quantum computer behavior

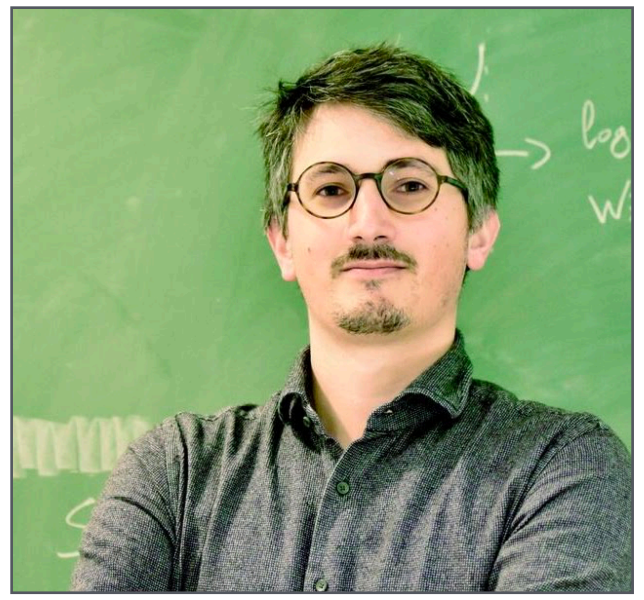
Subspace reduction

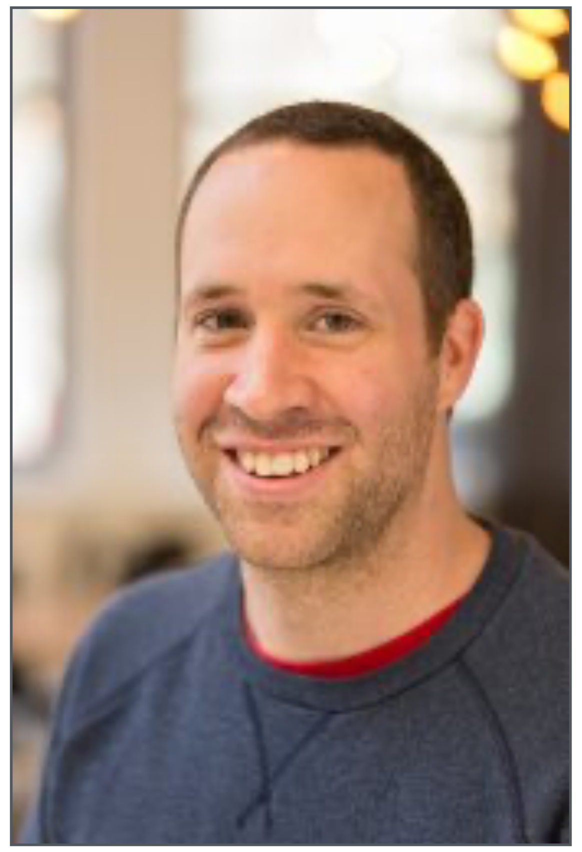
$$\bigcup_x \mathcal{S}_x \approx \frac{1}{256} \dim \mathcal{H}$$

Extension to impurity models

N. Moumique, **AS**, M. Ferrero, F. Vicentini, T. Ayral



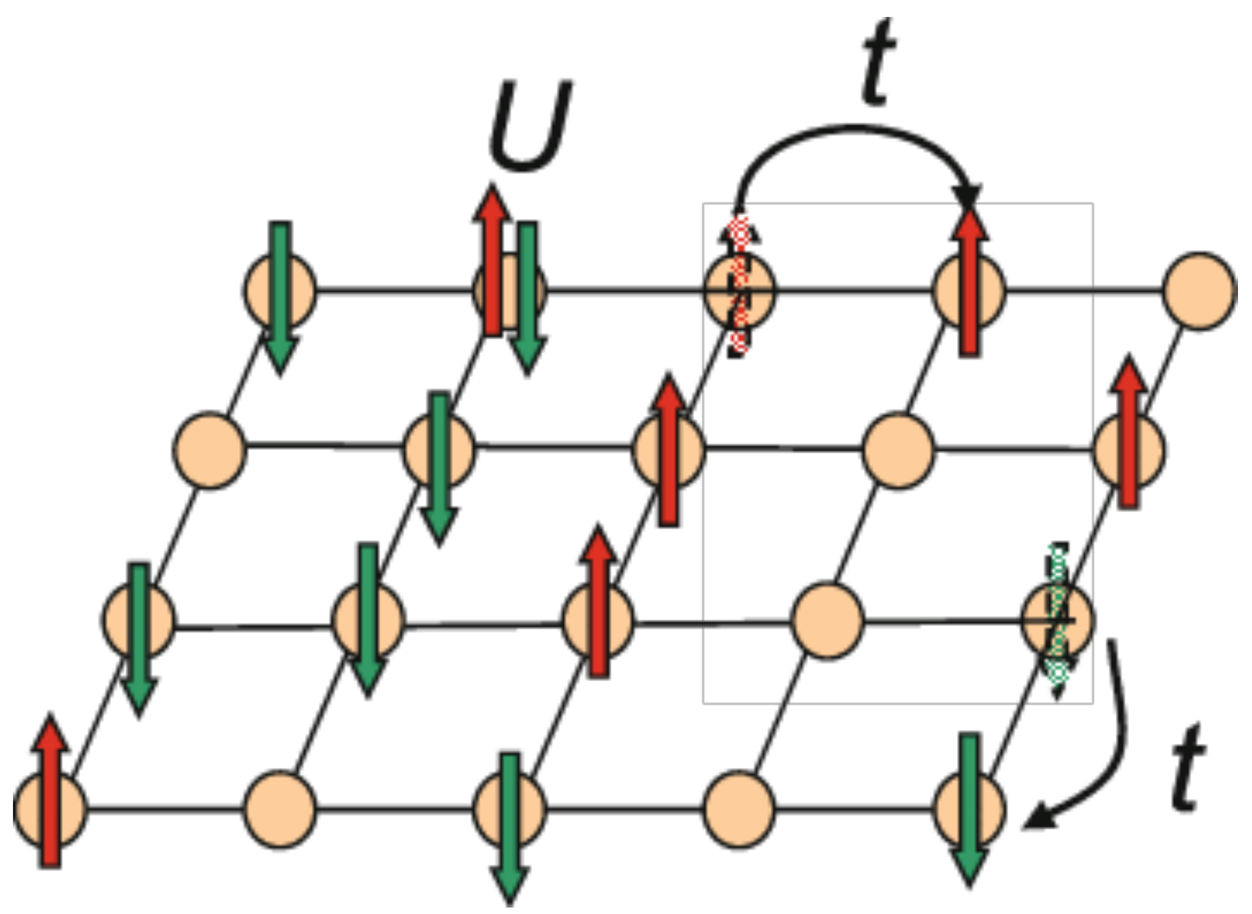




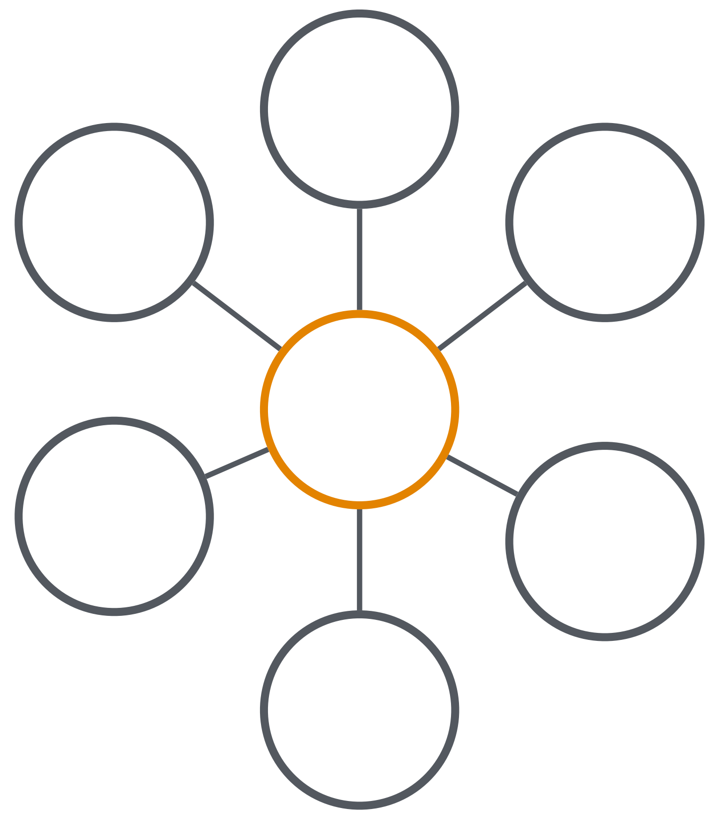
Anderson Impurity Problem

Same idea

classical ground state + quantum dynamics + subspace evolution



Embedded impurity problem



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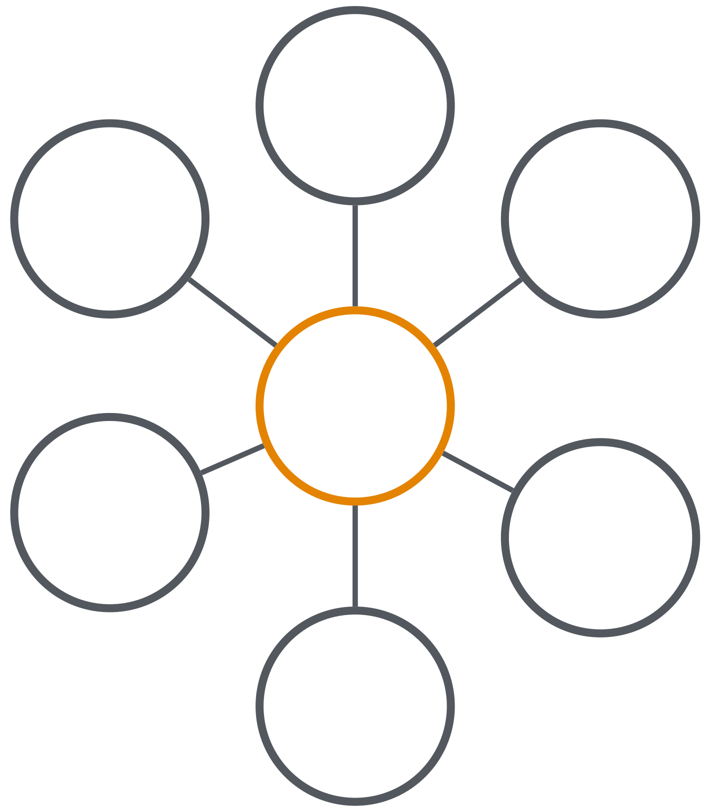
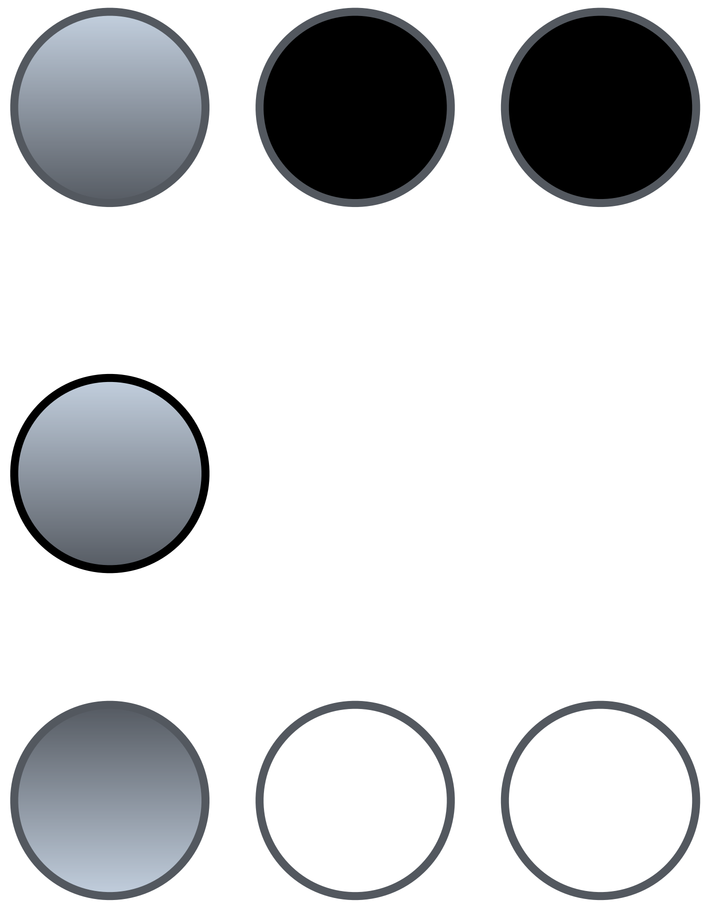


$$\vec{\tilde{c}} = M\vec{c}$$

Natural Orbital (NO) basis

$$M^{\dagger}\langle\psi|\vec{c}\vec{c}^{\dagger}|\psi\rangle M = \mathrm{diag}(\vec{\eta})$$

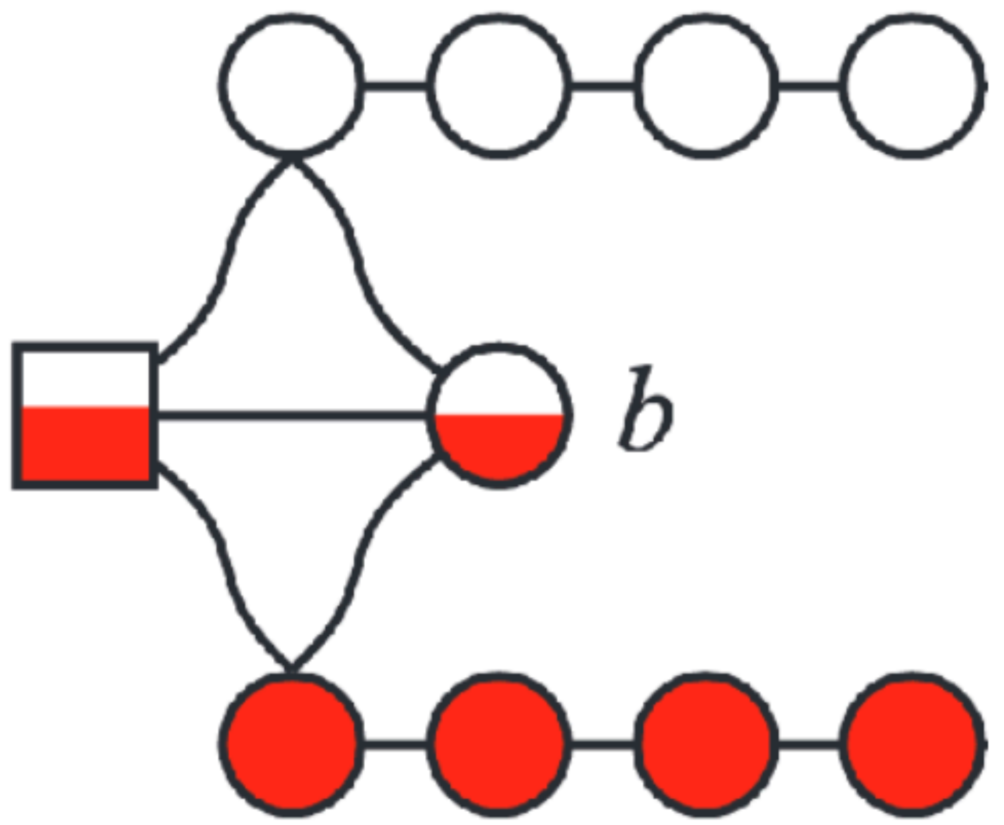


Filled orbitals

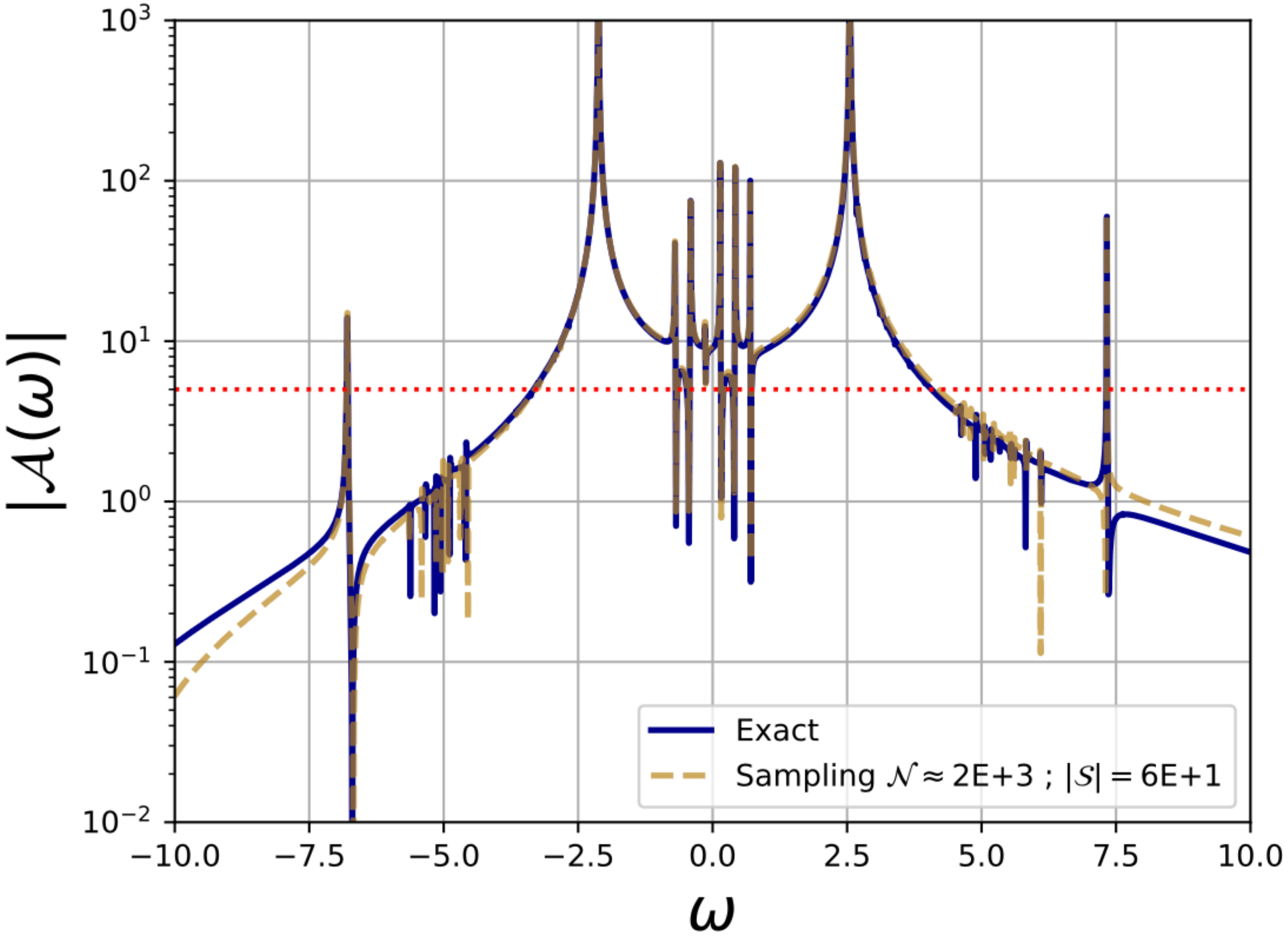
Empty orbitals

Anderson Impurity Problem

NO basis perturbed state $c^{\dagger}_{\text{impurity}}\,|\psi_0\rangle$



$U = 1$



Summary

- Improved VMC with importance sampling from trained importance sampling distribution
- Introduced a Hybrid method to compute spectral functions on QC with subspace expansion
- We generalize the method, thanks to the NO technique, to impurity models
- **Outlook:** try the method on the quantum hardware

Thanks for your attention

Looking elsewhere: improving variational Monte Carlo gradients by importance sampling
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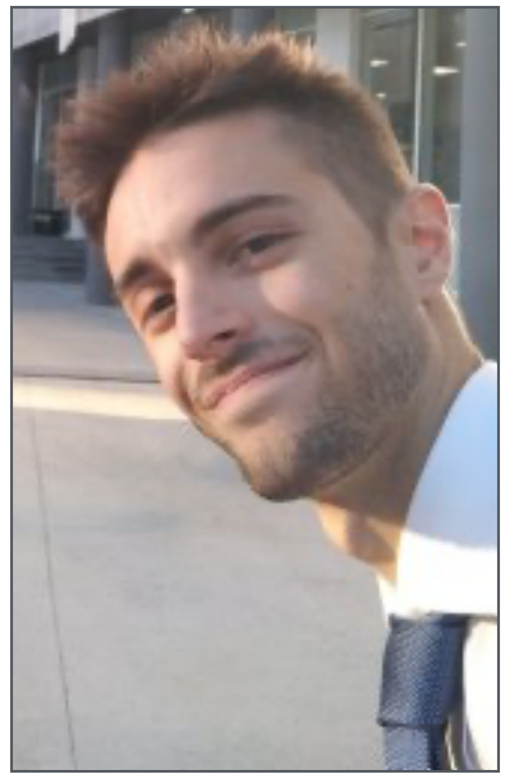
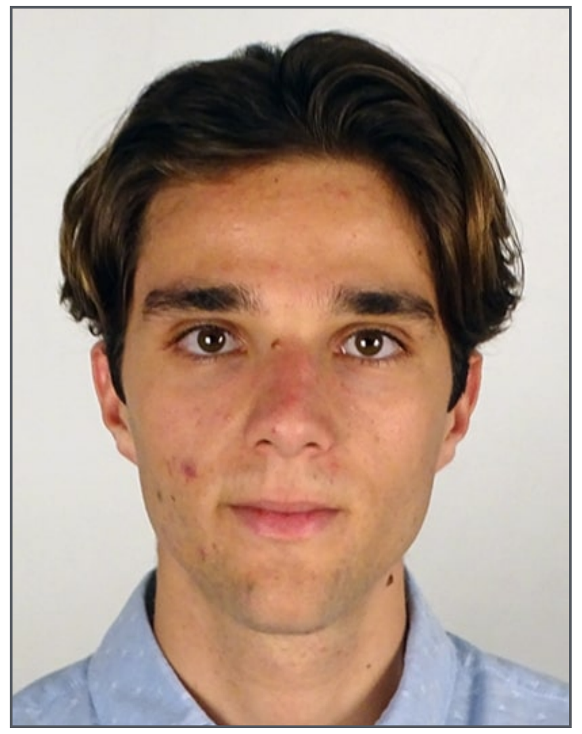
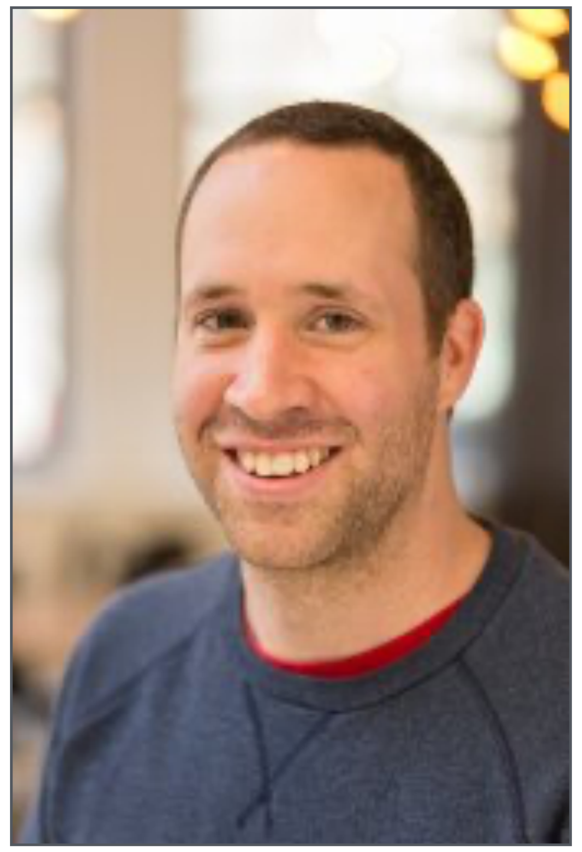
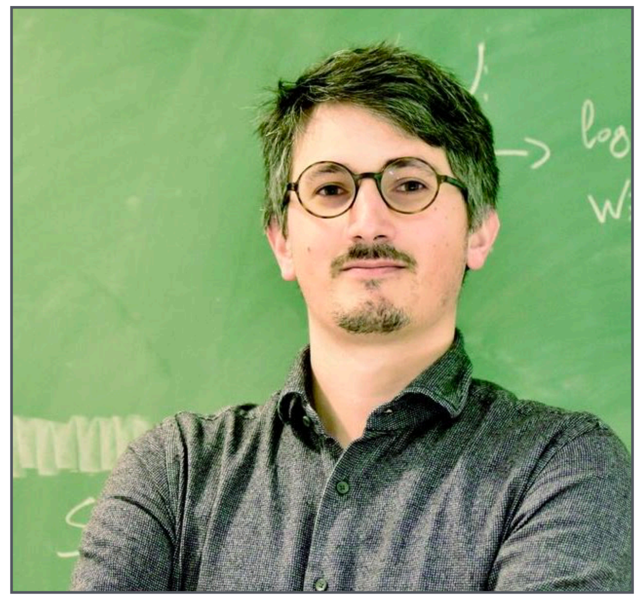
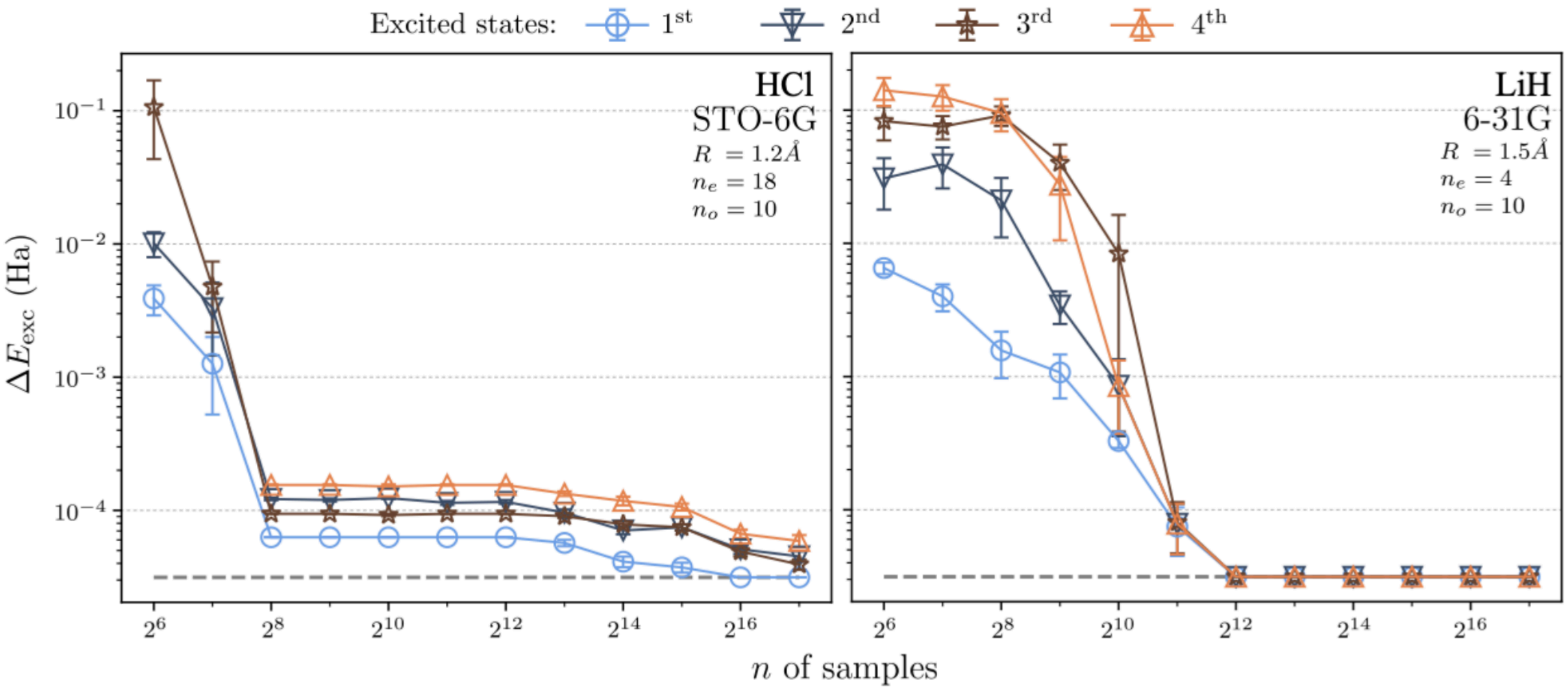


Scaling with the number of samples



Energies with NN sampling

Name	MF	n	$N_\uparrow + N_\downarrow$	K	HF Energy	CCSD	Ours	FCI
Hydrogen	H2	4	1+1=2	15	-1.06610864	**-1.101150**	**-1.101150**	-1.101150
Lithium Hydride	LiH	12	2+2=4	631	-7.76736213	-7.784455	**-7.784460**	-7.784460
Water	H2O	14	5+5=10	1390	-74.9644475	-75.015409	**-75.015511**	-75.015530
Methylene	CH2	14	5+3=8	2058	-37.4846329	-37.504411	**-37.504419**	-37.504435
Beryllium Hydride	BeH2	14	3+3=6	2074	-14.4432411	-14.472713	**-14.472922**	-14.472947
Ammonia	NH3	16	5+5=10	4929	-55.4547926	-55.520931	**-55.521037**	-55.521150
Methane	CH4	18	5+5=10	8480	-39.7265817	-39.806022	**-39.806170**	-39.806259
Diatomic Carbon	C2	20	6+6=12	2239	-74.2483215	-74.484727	**-74.486037**	-74.496388
Fluorine	F2	20	9+9=18	2951	-195.638041	**-195.661086**	-195.661067	-195.66108
Nitrogen	N2	20	7+7=14	2239	-107.498967	-107.656080	**-107.656763**	-107.660206
Oxygen	O2	20	9+7=16	2879	-147.631948	-147.747738	-147.749953	-147.750235
Lithium Fluoride	LiF	20	6+6=12	5849	-105.113709	-105.159235	**-105.165270**	-105.166172
Hydrochloric Acid	HCl	20	9+9=18	5851	-455.135968	**-455.156189**	**-455.156189**	-455.156189
Hydrogen Sulfide	H2S	22	9+9=18	9558	-394.311379	-394.354556	**-394.354592**	-394.354623
Formaldehyde	CH2O	24	8+8=16	20397	-112.354197	-112.498567	**-112.500944**	-112.501253
Phosphine	PH3	24	9+9=18	24369	-338.634114	-338.698165	**-338.698186**	-338.698400
Lithium Chloride	LiCL	28	10+10=20	24255	-460.827258	-460.847580	**-460.848109**	-460.849618
Methanol	CH4O	28	9+9=18	52887	-113.547027	**-113.665485**	**-113.665485**	-113.666485
Lithium Oxide	Li2O	30	7+7=14	20558	-87.7955672	-87.885514	**-87.885637**	-
Ethylene Oxide	C2H4O	38	12+12=24	137218	-150.927608	-151.120474	**-151.120486**	-
Propene	C3H6	42	12+12=24	161620	-115.657941	-115.885123	**-115.886571**	-
Acetic Acid	C2H4O2	48	16+16=32	461313	-224.805400	**-225.050896**	-225.0429767	-
Sulfuric Acid	H2O4S	62	25+25=50	1235816	-689.262656	-689.498410	**-689.505237**	-
Sodium Carbonate	CNa2O3	76	26+26=52	1625991	-575.016102	-575.299810	**-575.299820**	-