

Downfolding II: Systematically improvable, non-perturbative downfolding including interactions

Summary

1

Divide into high and low energy parts

Born-Oppenheimer

Diagonalize H_{KS} , choose bands

2

Find states within low-energy sector

Quantum chemistry

Diagonalize H_{KS}
(already did it)

3

Compress Hamiltonian within each sector

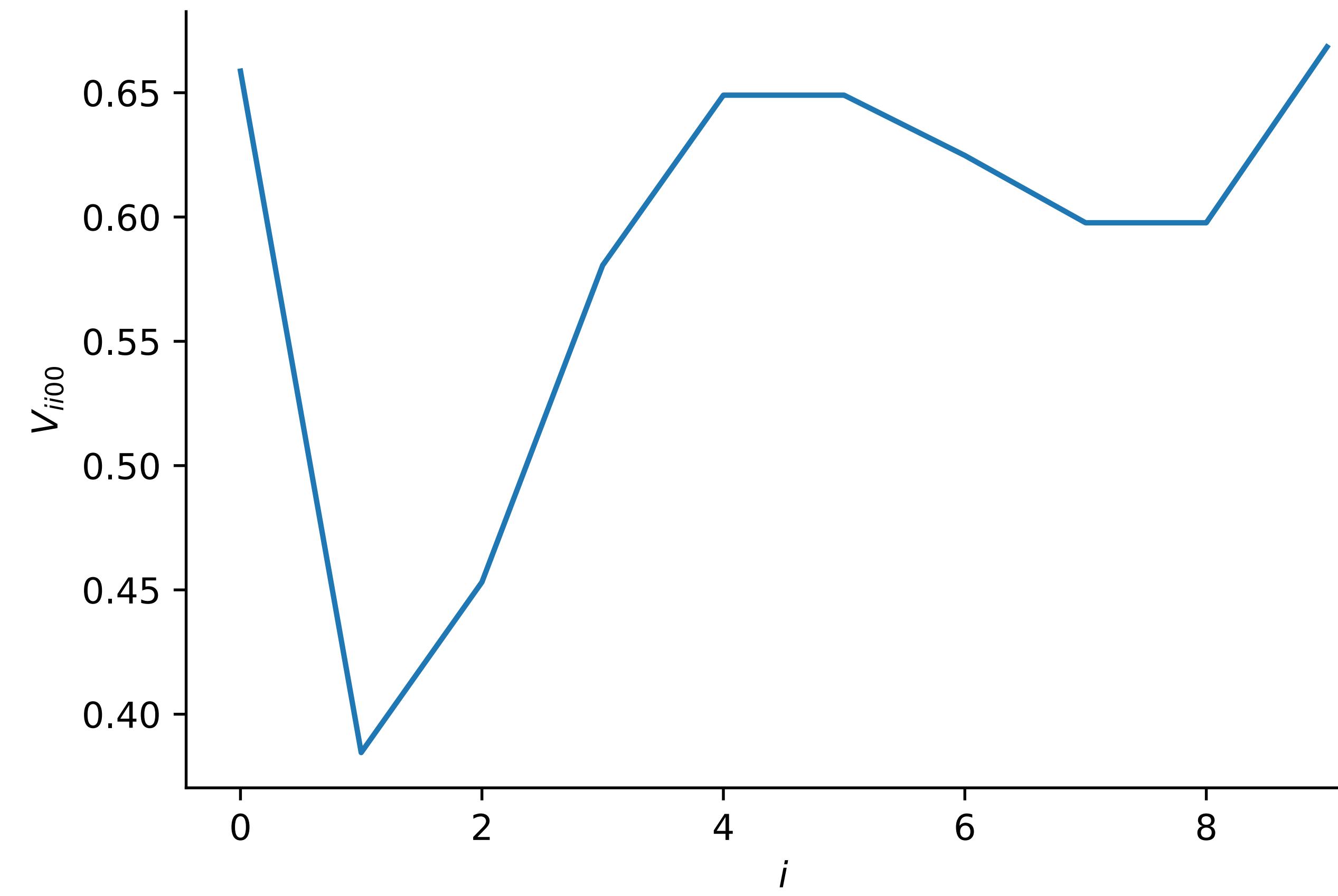
Fit to $V(x)$

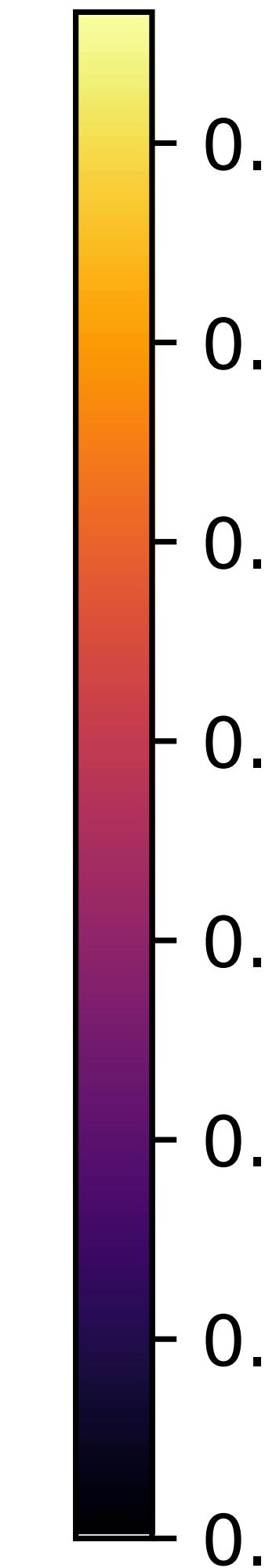
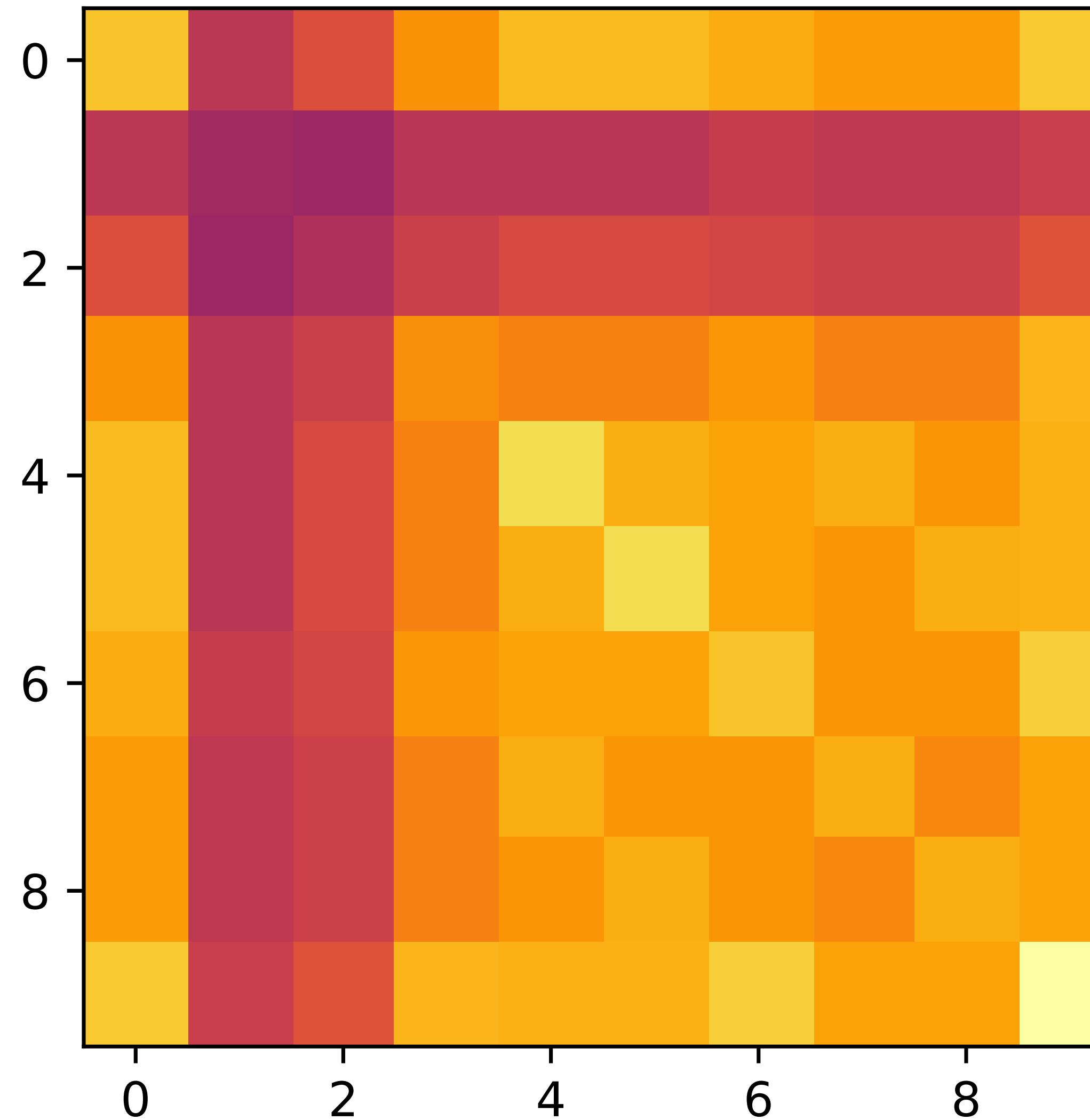
Rewrite in localized basis

Single determinants are not eigenstates of the hamiltonian

Proof:

$$H|00\rangle = 2\epsilon_0|00\rangle + \sum V_{ij00} c_i^\dagger c_j^\dagger c_0 c_0 |00\rangle = 2\epsilon_0|00\rangle + \sum V_{ij00} |ij\rangle$$





V_{iijj} is very non-diagonal \sim Hamiltonian for H2

How to divide into high and low energy parts? They are incredibly coupled.

Many ways to try to decouple them perturbatively:

- * Schreiffer-Wolf

- * CRPA

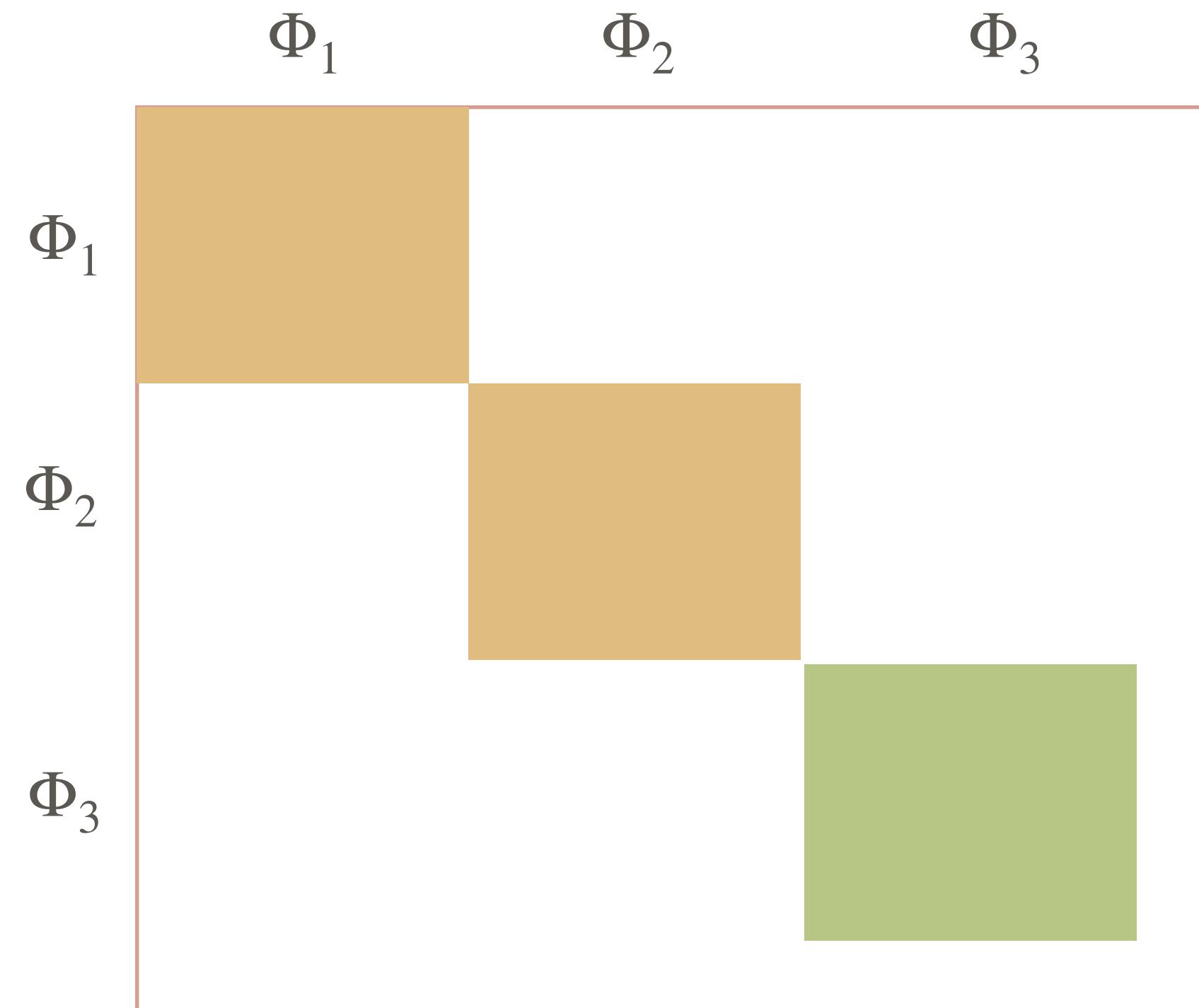
- * See also embedding methods

The need for brute-force methods



Zero energy mode

The brute force strategy



If we can find low-energy many-body eigenstates, then we can separate out the low energy and we have a representation of the Hamiltonian:

$$H_{eff} = \sum_i^N |\Phi_i\rangle E_i \langle\Phi_i|$$

Density matrix downfolding

Fundamental idea: find H_{eff} such that $|H_{ab-initio} - H_{eff}|^2$ is minimized (Frobenius norm)

Perfect effective Hamiltonian:

$$\langle i | H | j \rangle = \langle i | H_{eff} | j \rangle$$

How to compute, assuming a two-body effective Hamiltonian (not guaranteed):

$$\langle i | H_{eff} | j \rangle = E_0 \delta_{ij} + \sum_{ab} t_{ab} \langle i | c_a^\dagger c_b | j \rangle + \sum_{abcd} V_{abcd} \langle i | c_a^\dagger c_b^\dagger c_c c_d | j \rangle$$

A diagram illustrating the components of the effective Hamiltonian. Three red arrows originate from the terms $E_0 \delta_{ij}$, $\sum_{ab} t_{ab} \langle i | c_a^\dagger c_b | j \rangle$, and $\sum_{abcd} V_{abcd} \langle i | c_a^\dagger c_b^\dagger c_c c_d | j \rangle$ respectively, and point to the text "Fitting parameters" located at the bottom right.

Simple example

Outline:

- 1) Solve H₂ molecule
- 2) Understand the states, make a decision about which many-body states we want to describe.
- 3) Choose descriptors (by guessing here)
- 4) Fit to descriptors
- 5) Check the model versus ab initio

Discussion: how could we improve our model?

Some notes:

In general it is not guaranteed that the effective Hamiltonian will be just one-and two-body.

On the other hand, for many materials, band structure is unreasonably effective—one body only.

Moving to more complex materials

FeSe molecule.

Generate a model with 3d, 4s, 3p.

21 allowed terms in the effective Hamiltonian

How do we avoid overfitting?

$$\begin{array}{lll} \epsilon_s n_s, & \epsilon_{\pi,\text{Se}}(n_{p_x} + n_{p_y}), & \epsilon_z n_{p_z}, \\ \epsilon_{z^2} n_{d_{z^2}}, & \epsilon_{\pi,\text{Fe}}(n_{d_{xz}} + n_{d_{yz}}). & \epsilon_\delta(n_{d_{xy}} + n_{d_{x^2-y^2}}) \end{array}$$

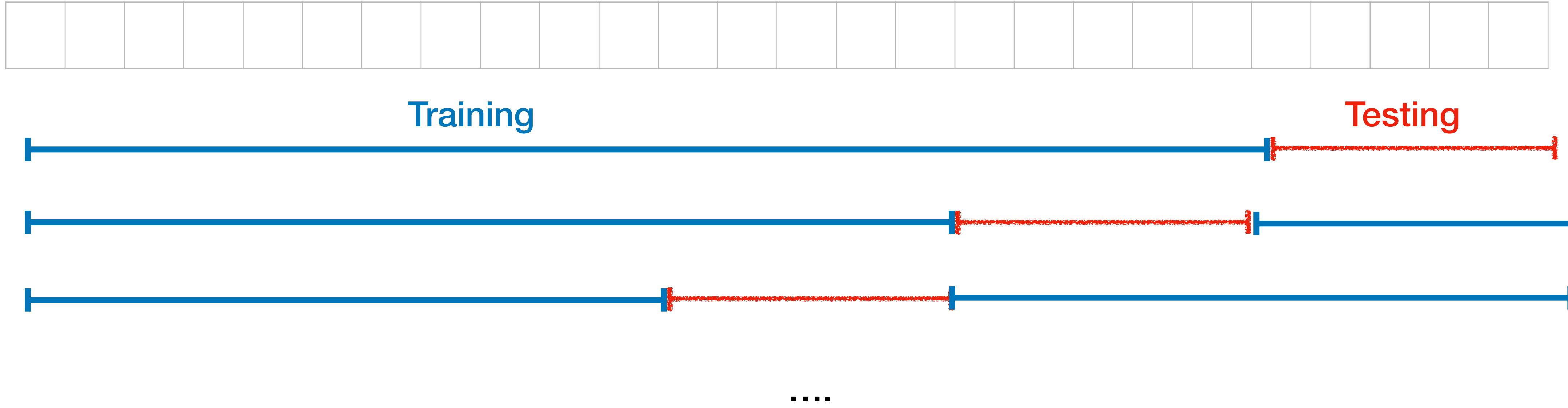
$$t_{\sigma,d} \sum_{\eta} \left(c_{d_{z^2},\eta}^\dagger c_{p_z,\eta} + \text{h.c.} \right), \quad t_{\sigma,s} \sum_{\eta} \left(c_{s,\eta}^\dagger c_{p_z,\eta} + \text{h.c.} \right), \quad t_{\pi} \sum_{\eta} \left(c_{d_{xz},\eta}^\dagger c_{p_x,\eta} + c_{d_{yz},\eta}^\dagger c_{p_y,\eta} + \text{h.c.} \right)$$

$$\begin{array}{ll} U_p \sum_{i \in p} n_{i,\uparrow} n_{i,\downarrow}, & U_{d,\delta} \sum_{i \in \{d_{xy}, d_{x^2-y^2}\}} n_{i,\uparrow} n_{i,\downarrow}, \\ U_d \sum_{i \in d} n_{i,\uparrow} n_{i,\downarrow}, & U_{d,\pi} \sum_{i \in \{d_{xz}, d_{yz}\}} n_{i,\uparrow} n_{i,\downarrow}, \quad U_{d_{z^2}} n_{d_{z^2},\uparrow} n_{d_{z^2},\downarrow} \end{array}$$

$$\begin{array}{lll} J \sum_{\substack{i \neq j \\ i,j \in d}} S_i \cdot S_j, & J_\delta S_{d_{xy}} \cdot S_{d_{x^2-y^2}}, & J_{\delta,d_{z^2}} (S_{d_{xy}} + S_{d_{x^2-y^2}}) \cdot S_{d_{z^2}}, \\ J_\pi S_{d_{xz}} \cdot S_{d_{yz}}, & J_{\pi,d_{z^2}} (S_{d_{xz}} + S_{d_{yz}}) \cdot S_{d_{z^2}}, & J_{\pi,\delta} (S_{d_{xz}} + S_{d_{yz}}) \cdot (S_{d_{xy}} + S_{d_{x^2-y^2}}) \end{array}$$

$$V \sum_{i \in p, j \in d} n_i n_j$$

Cross-validation



Fit the model on the training set and test on the testing set.

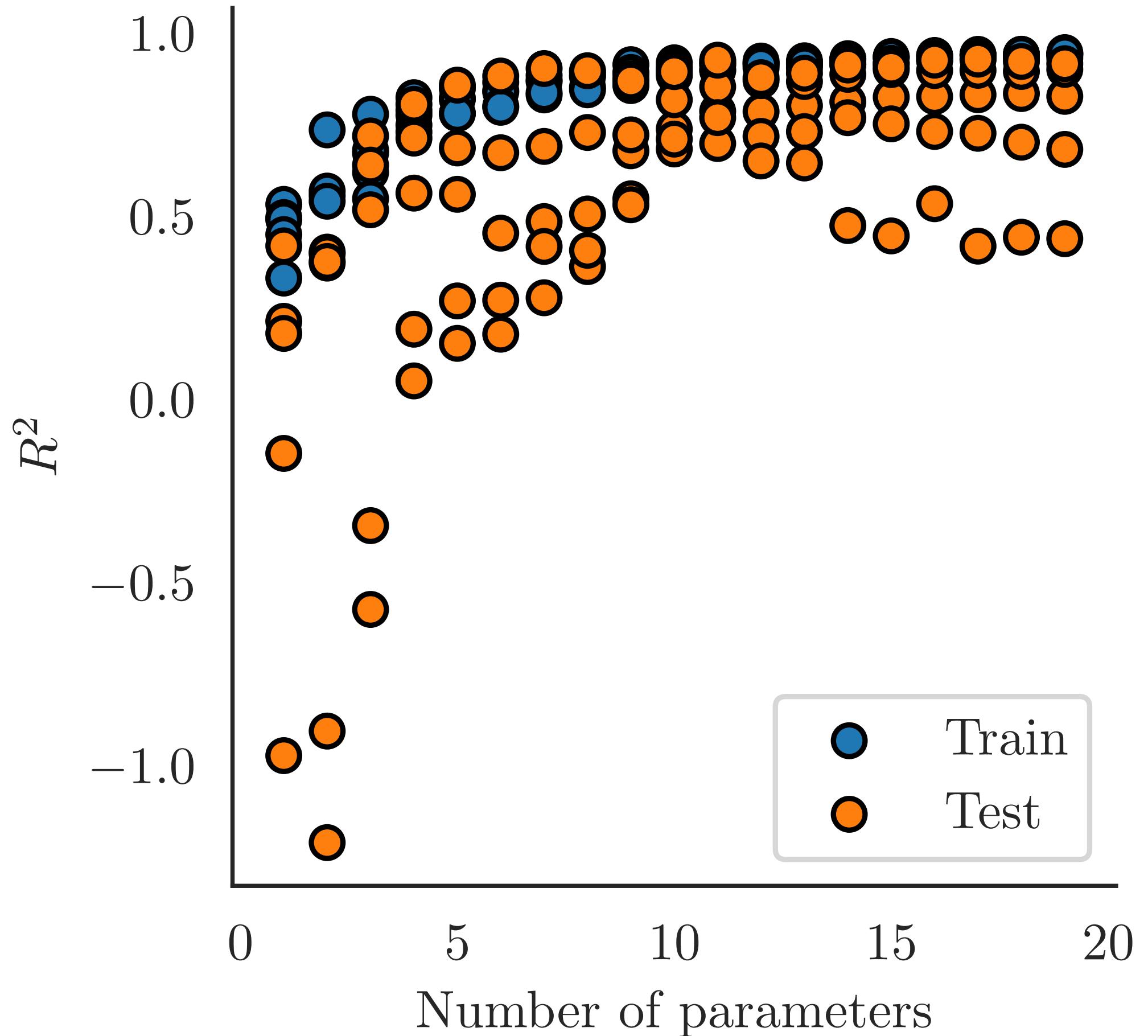
If not overfit, then expect the performance to be the same.

Orthogonal matching pursuit

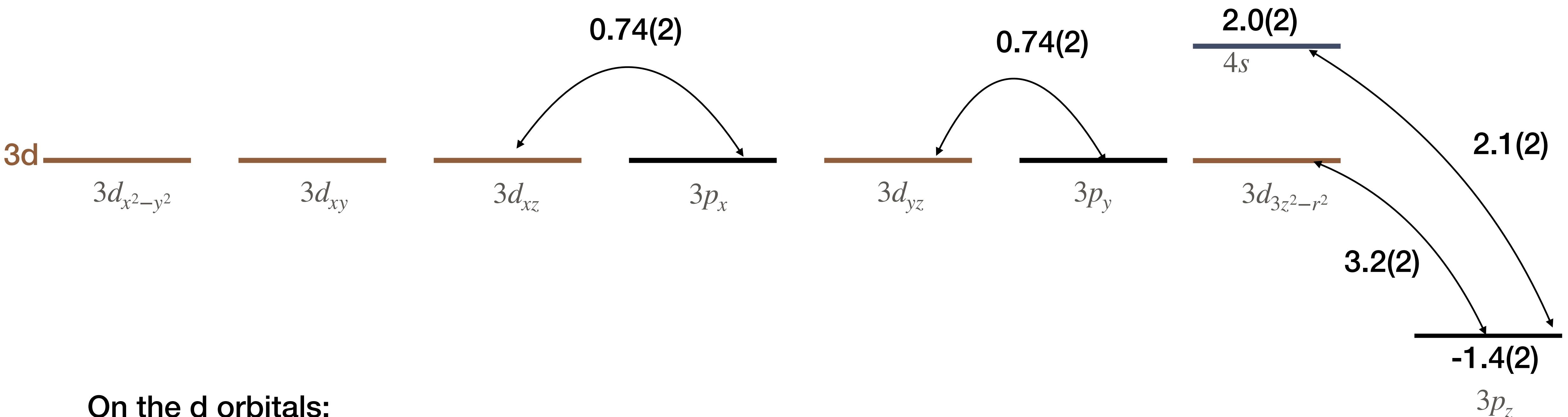
On the training set:

- 1) Choose the descriptor with largest correlation with energy.
- 2) Fit the parameter value to best reproduce the data.
- 3) Choose next descriptor with the largest correlation with energy.
- 4) Fit all selected descriptors, return to 3 unless maximum descriptors selected.

Then check vs the testing set.

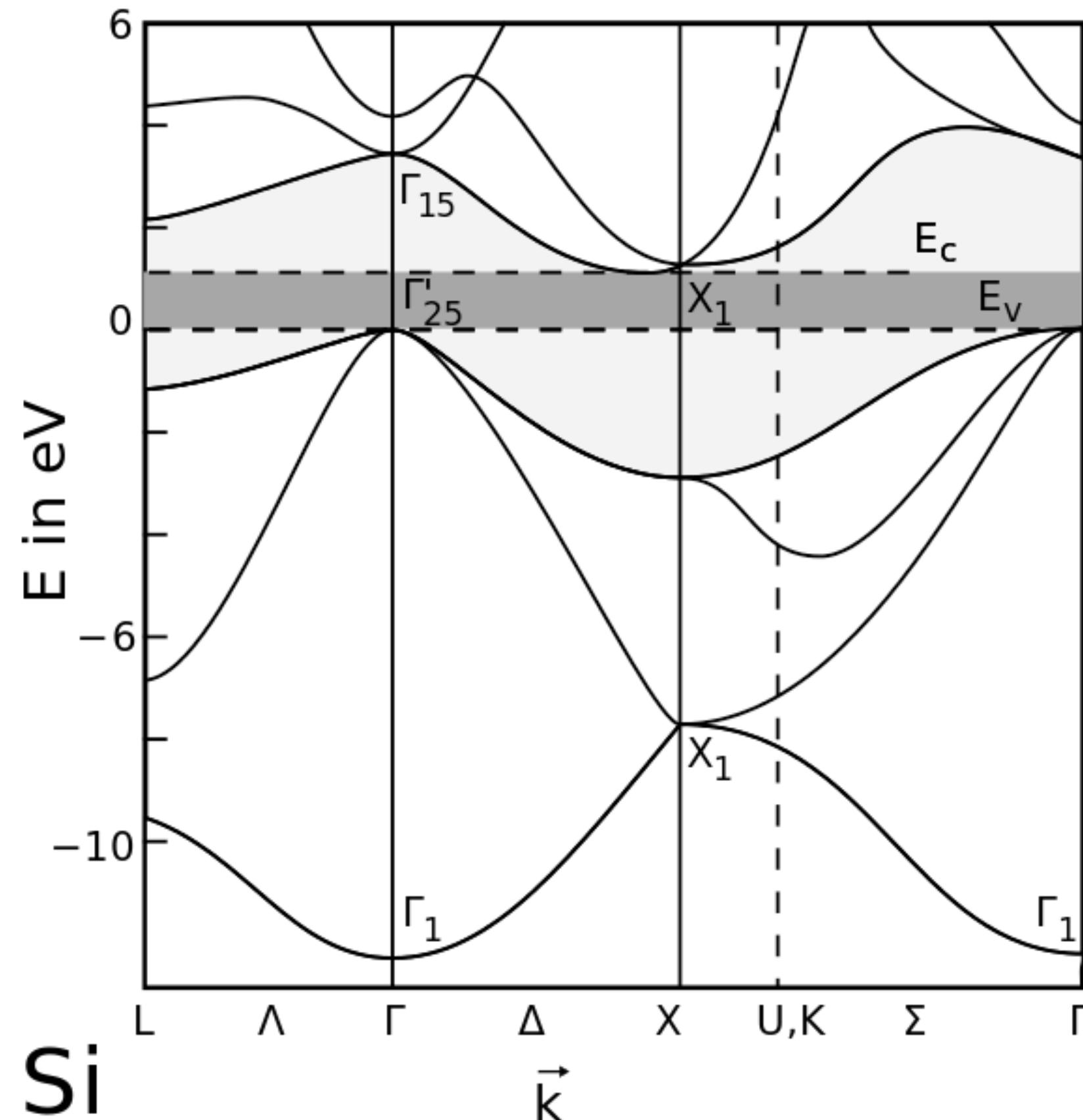


Resulting model



On the d orbitals:
Hunds J: -0.80(4)
Hubbard U: 2.4(2)

The importance of good references



Gap in Hartree-Fock from first principles, ignoring correlations: ~ 6 eV

Gap in reality: ~ 1.1 eV

In first principles, silicon looks like a strongly interacting, strongly correlated material.

The effective low-energy model looks like a non-interacting, uncorrelated material, but good underlying solver is necessary to get an accurate (simple) model.

Generating higher quality (and scalable) low-energy wave functions

Variational Monte Carlo

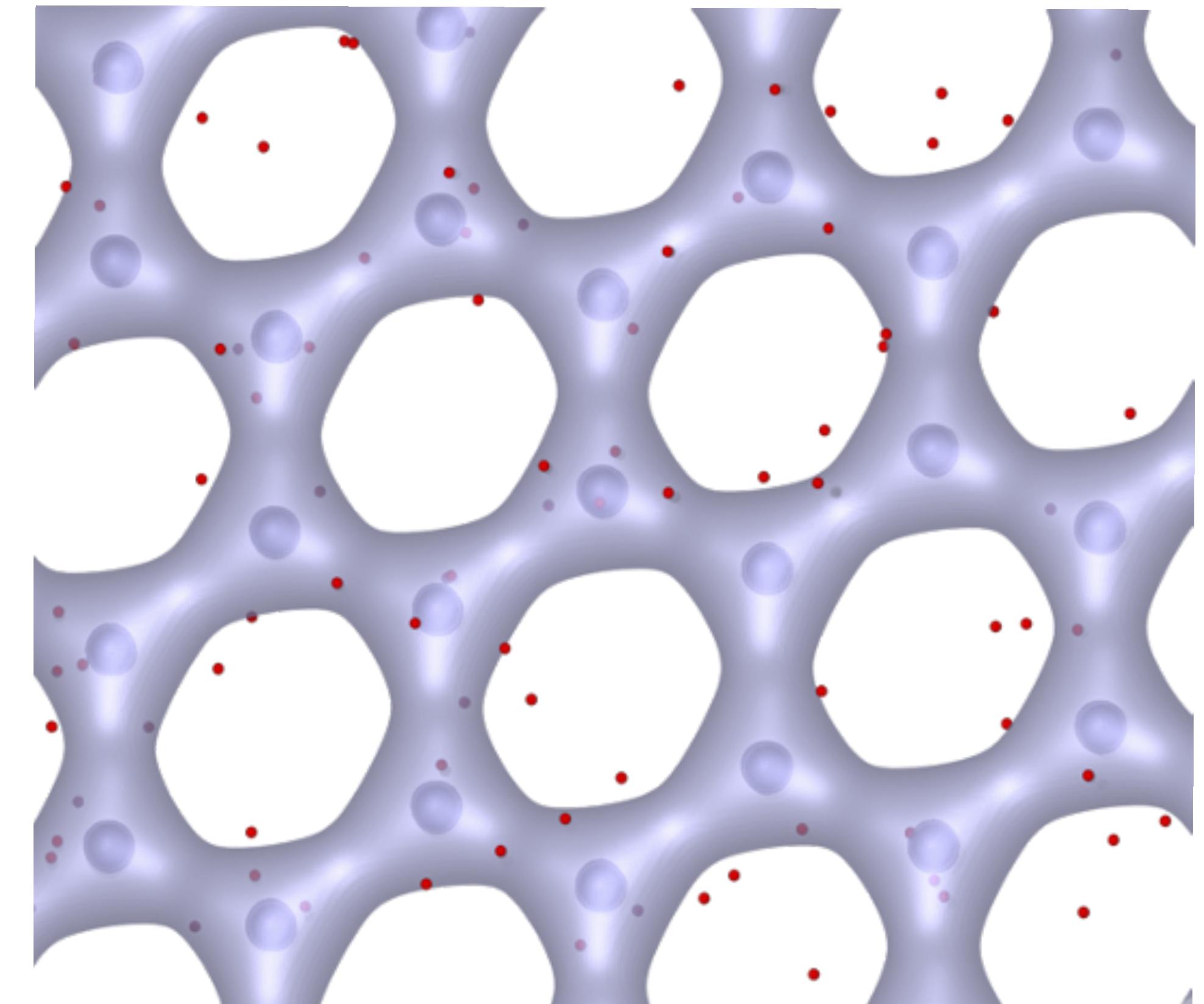
$$\frac{\langle \Psi | \mathcal{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int \langle \Psi | R' \rangle \langle R' | \mathcal{O} | R \rangle \langle R | \Psi \rangle dR dR'}{\int |\langle R | \Psi \rangle|^2 dR}$$

If \mathcal{O} is semi-local (doesn't need to be!):

$$\int \frac{\langle R | \mathcal{O} | \Psi \rangle}{\langle R | \Psi \rangle} \frac{|\langle R | \Psi \rangle|^2}{\int |\langle R | \Psi \rangle|^2 dR} dR$$

$\mathcal{O}_L(R)$ $\rho(R)$

$$\langle \mathcal{O}_L(R) \rangle_{R \sim \rho}$$



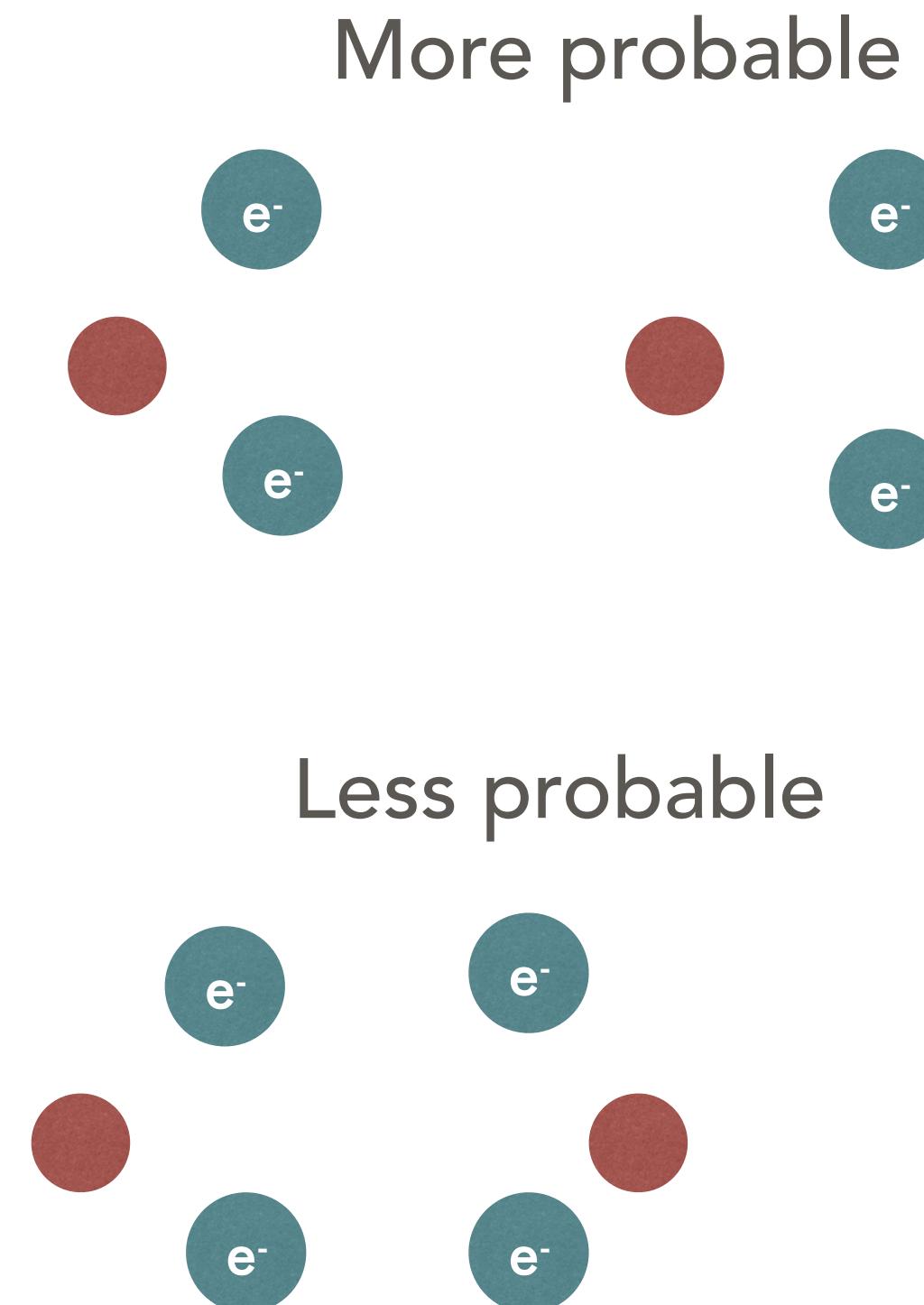
Sample **electronic coordinates**,
average local energy

The Slater-Jastrow wave function

$$\Psi(r_1, r_2, r_3, \dots) = \exp(U) \text{Det}^{\uparrow} \text{Det}^{\downarrow}$$

$$U = \sum_{ij} f(r_i, r_j, r_i - r_j)$$

Encodes the correlation



Fixed node diffusion Monte Carlo

$$\lim_{\tau \rightarrow \infty} e^{-H\tau} |\Psi\rangle = |\Phi_0\rangle$$

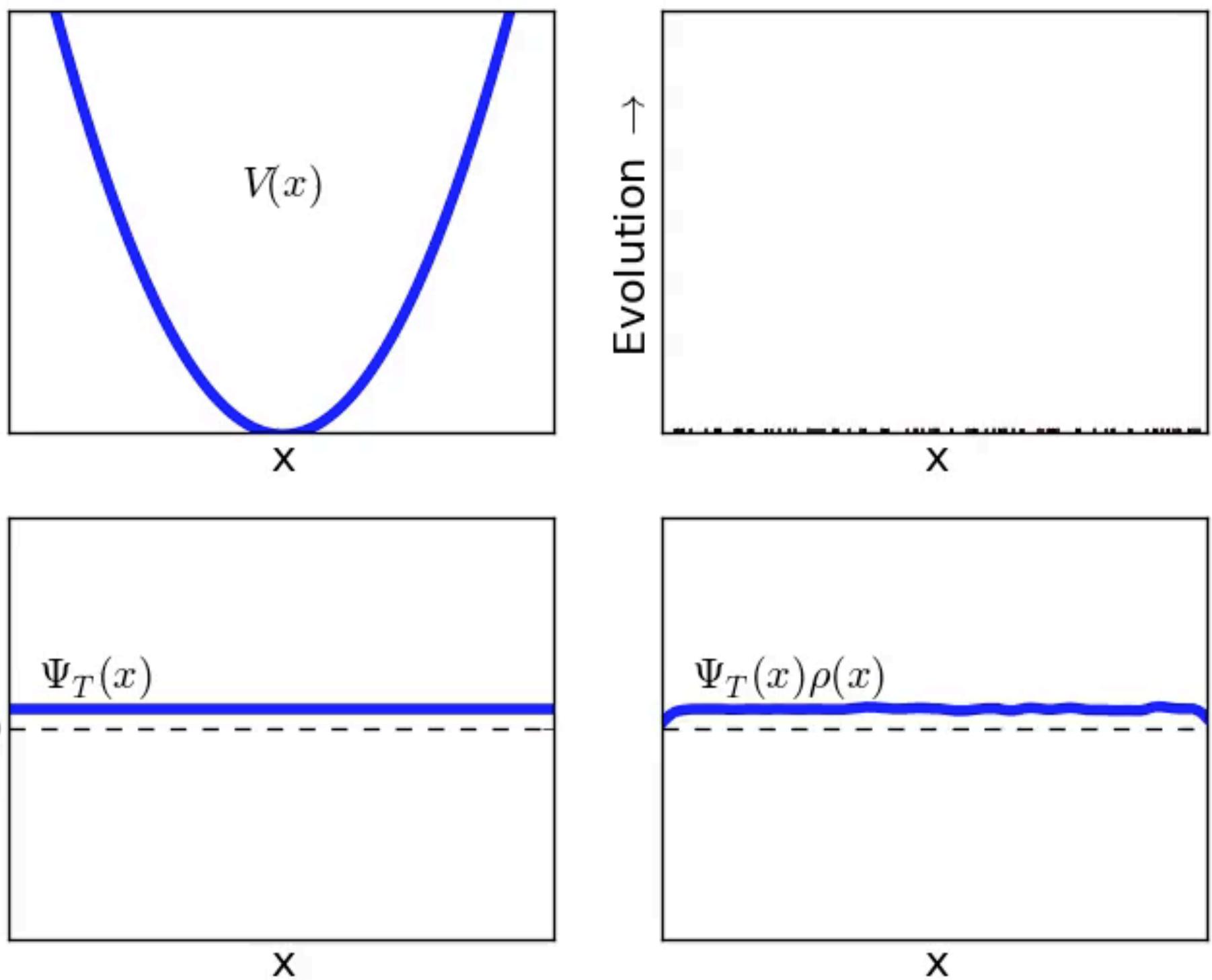
$$E_0 = \frac{\langle \Psi | e^{-H\tau} \mathbf{H} | \Psi \rangle}{\langle \Psi | e^{-H\tau} | \Psi \rangle} = \frac{\int \langle \Psi | R \rangle \langle R | e^{-H\tau} | R' \rangle \langle R' | \mathbf{H} | \Psi \rangle dR dR'}{\int \langle \Psi | R \rangle \langle R | e^{-H\tau} | R' \rangle \langle R' | \Psi \rangle dR dR'}$$

Path integral!

Sign problem: When τ is large, $\langle \Psi | R \rangle$ is uncorrelated with $\langle R' | \Psi \rangle$ and the ratio goes to 0/0.

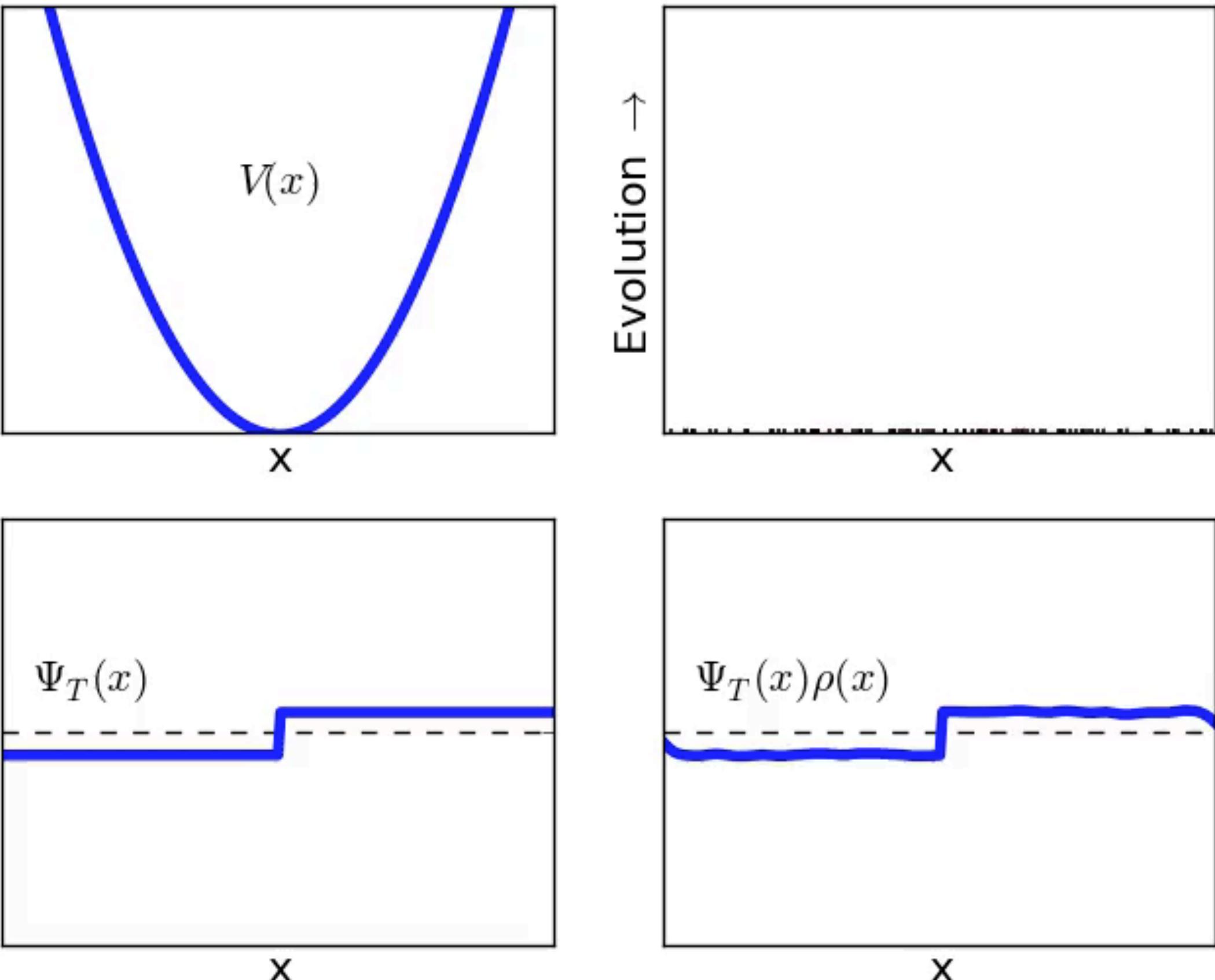
Fixed node: Set

$$\langle R | e^{-H_{FN}\tau} | R' \rangle = \begin{cases} \langle R | e^{-H\tau} | R' \rangle & \text{if } \langle R | e^{-H_{FN}\tau} | R' \rangle \geq 0 \\ 0 & \text{otherwise} \end{cases}$$



Fixed node DMC properties

- 1) Energy is an upper bound to the exact ground state energy.
- 2) If the wave function nodes correspond to the ground state nodes, then will obtain the exact ground state energy.
- 3) If the wave function nodes correspond to an excited state, then under some conditions you obtain the exact excited state.



Ceperley and Alder. J. Chem. Phys. **81** 5833 (1984)

Foulkes, Hood, and Needs. PRB **60** 4558 (1999)

Multi-Slater-Jastrow

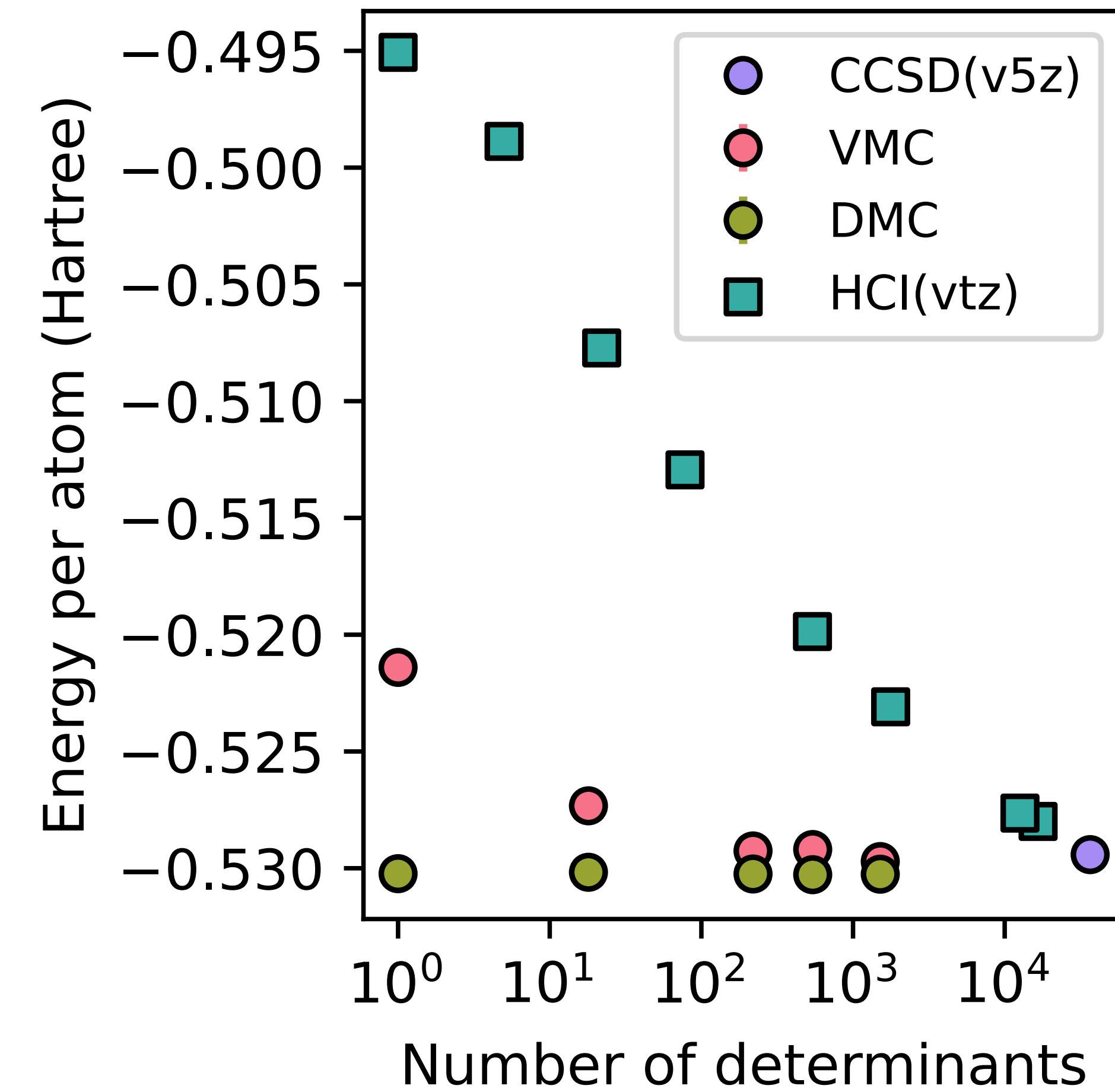
Only include determinants necessary for physics!

$$\Psi = e^U \sum_i c_i D_i$$

Fully optimize orbital coefficients, CI coefficients and Jastrow factor.



Shunyue Yuan



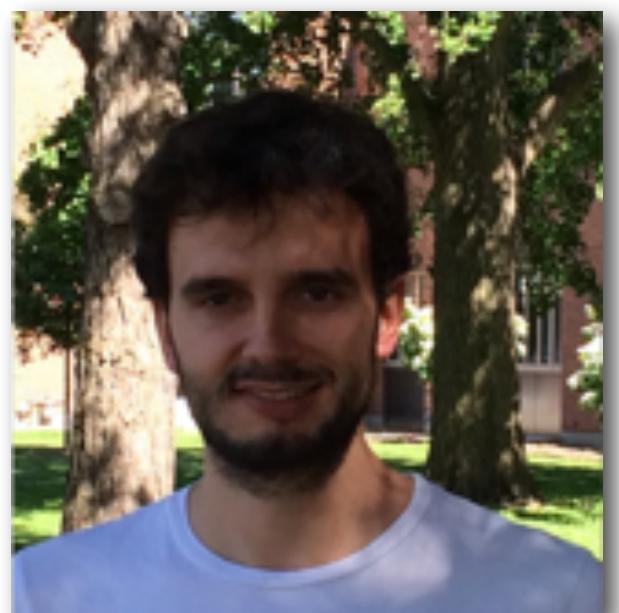
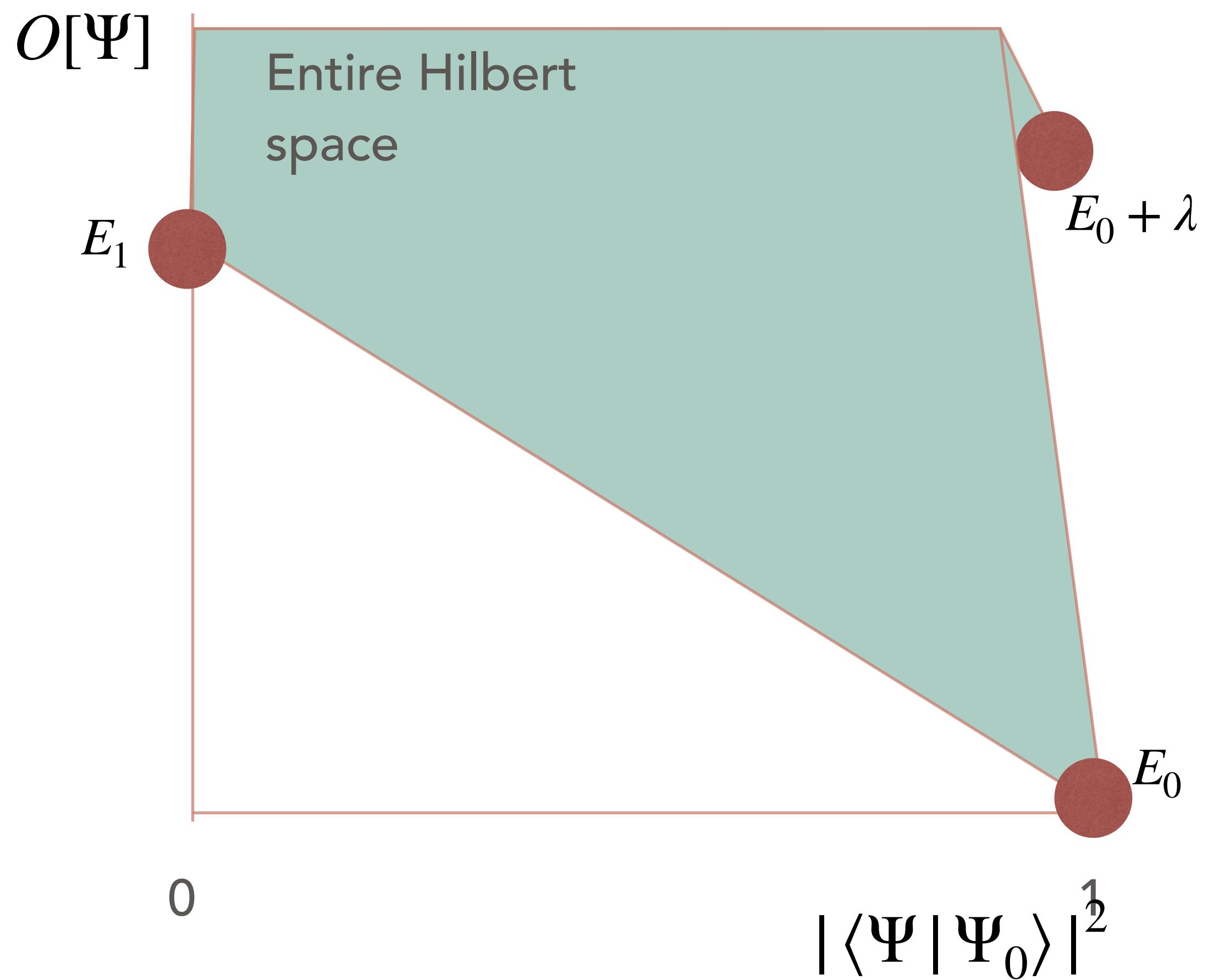
Getting excited states in VMC: Penalty method

$$O[\Psi] = E[\Psi] + \lambda |\langle \Psi_0 | \Psi \rangle|^2$$

If $\lambda > E_1 - E_0$ then the minimum is the first excited state.

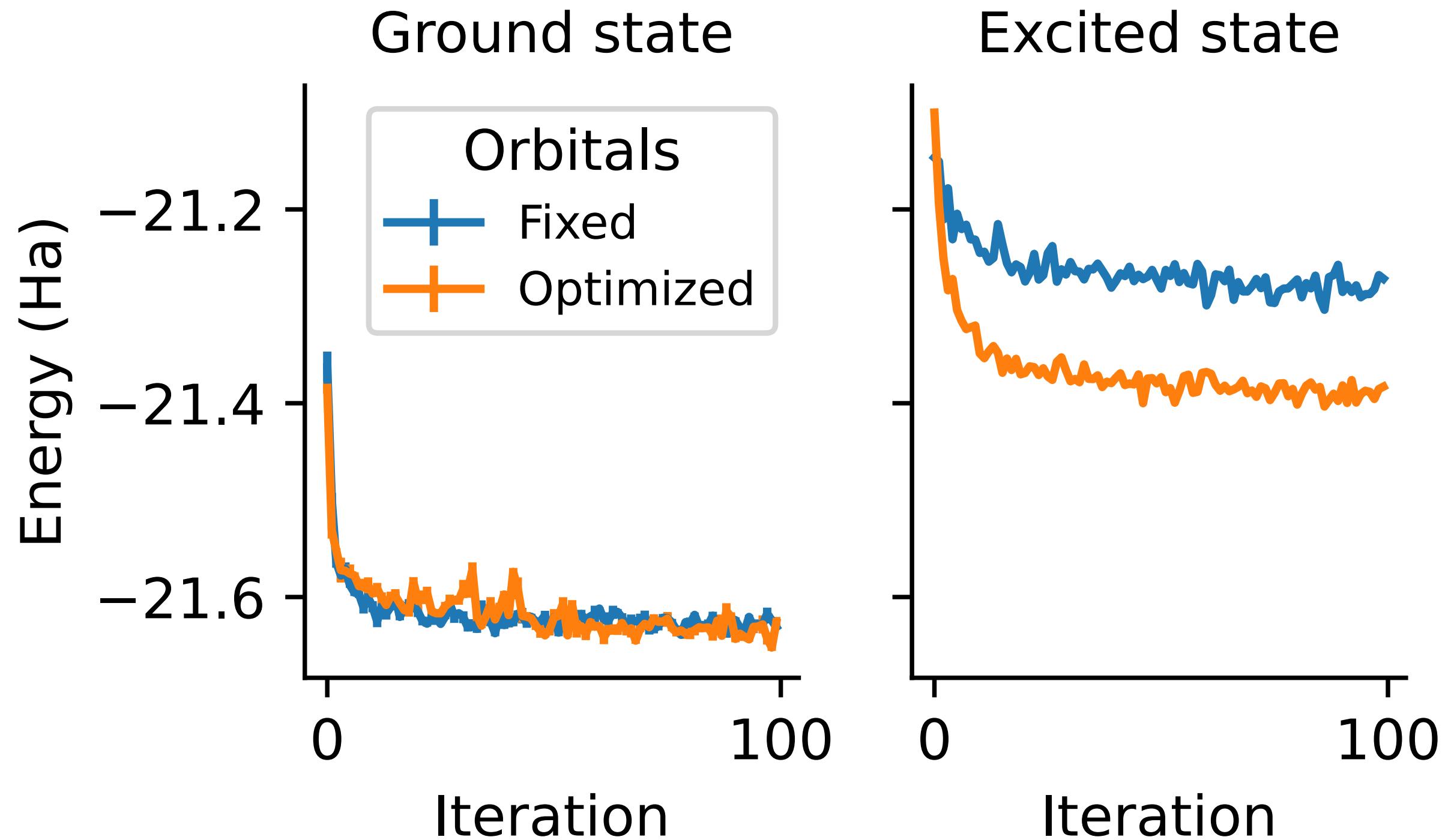
This method has been used in DMRG calculations.

There are technical issues with implementation in VMC, which we overcame.



Pathak, Busemeyer, Rodrigues, Wagner.
J. Chem. Phys. 154 034101 (2021)

Accurate and compact excited states



CO molecule—optimizing orbitals can give you 0.2 eV with the same wave function

$$\Psi = e^U \sum_i c_i D_i$$

Fully optimize orbital coefficients, CI coefficients and Jastrow factor.



Kevin Kleiner

Accurate excited states on benzene

Method	Parameters	$\Delta E_j = E_j(\text{m}) - E_j(\text{CC3})$	
		mean (eV)	RMS (eV)
CASPT2		-0.38	0.42
TTDFT-PBE0		-0.33	0.50
VMC	None	0.34	0.46
VMC	$\vec{\alpha}, \vec{c}$	0.12	0.35
VMC	$\vec{\alpha}, \vec{c}, \vec{\beta}$	0.19	0.35
DMC	None	0.24	0.35
DMC	$\vec{\alpha}, \vec{c}$	0.18	0.31
DMC	$\vec{\alpha}, \vec{c}, \vec{\beta}$	0.15	0.24

Improve accuracy by around 30% by optimizing orbitals.

Very compact wave functions.

Coupled cluster and DMC ‘handshake’ to within about 0.1-0.2 eV.

Errors smaller than nuclear quantum effects!

pyqmc: simple access to QMC methods



```
import numpy as np
class DipoleAccumulator:
    def __init__(self):
        pass

    def __call__(self, configs, wf):
        return {'electric_dipole':np.sum(configs.configs, axis=1) }

    def shapes(self):
        return {"electric_dipole": (3,)}

    def avg(self, configs, wf):
        d = {}
        for k, it in self(configs, wf).items():
            d[k] = np.mean(it, axis=0)
        return d

    def keys(self):
        return self.shapes().keys()

import pyqmc.recipes
pyqmc.recipes.VMC("h2o.hdf5", "dipole.hdf5",
                   load_parameters="h2o_sj_800.hdf5",
                   accumulators={'extra_accumulators':{'dipole':DipoleAccumulator()}})
```

Define your own
accumulator in-line

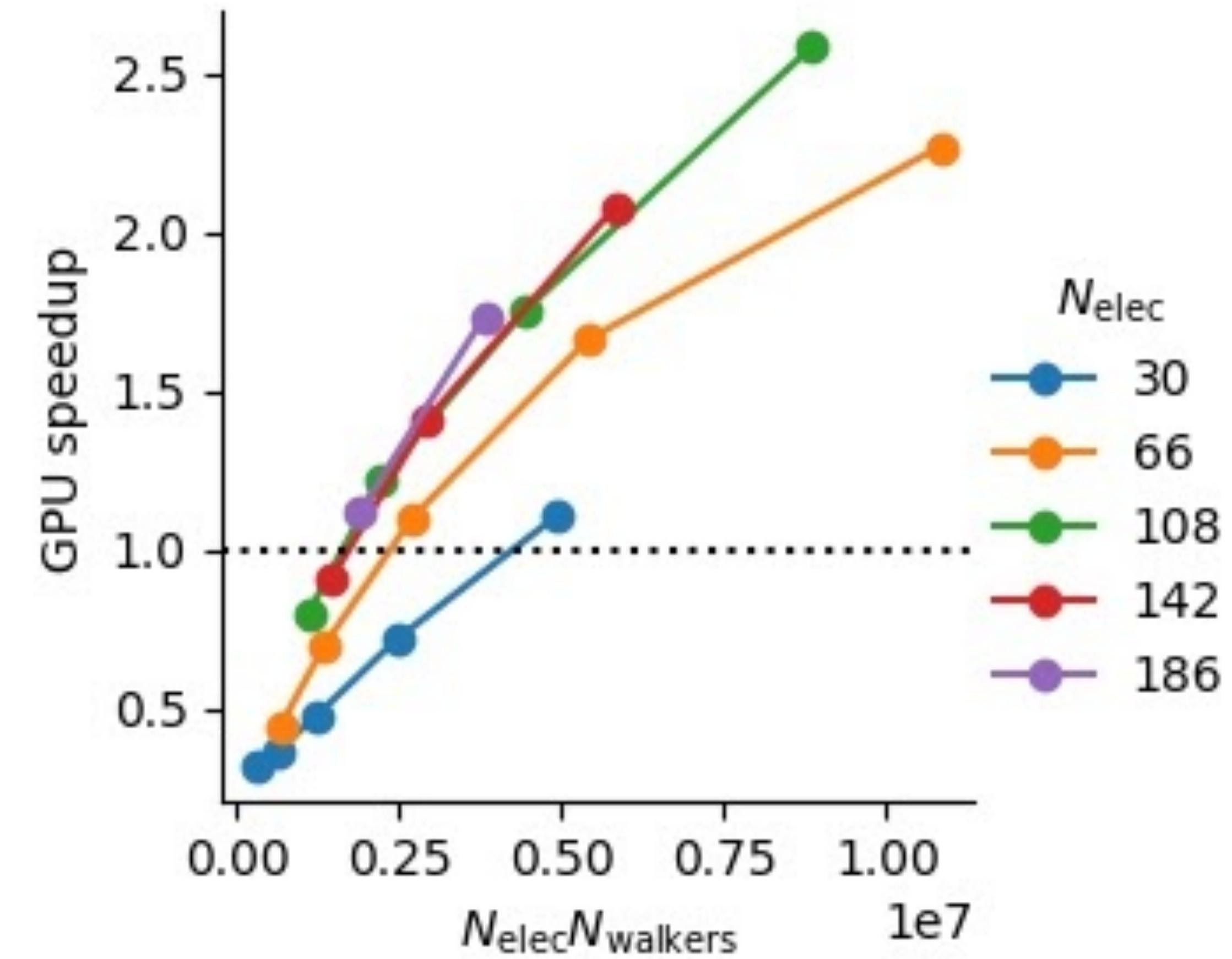
Pass it into the code

pyqmc GPU performance

6 GPUs vs 42 cores.

Once there are enough electrons, the product of electrons and walkers determines whether there's enough work for the GPUs to be efficient.

GPU improvements for systems > 100 electrons or so.



Application areas