Derivation of model Hamiltonians using Quantum Monte Carlo

QMC workshop 11/16/2021

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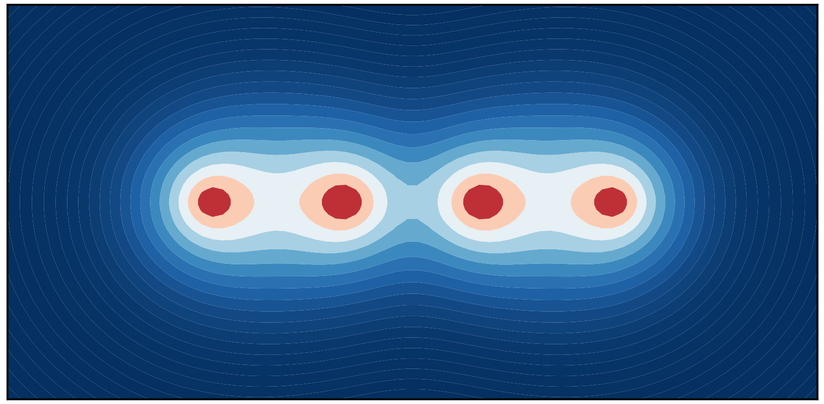

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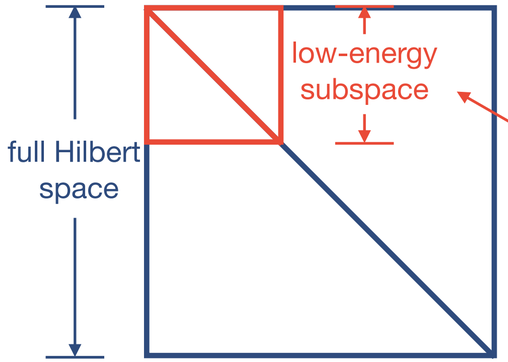
Why do we want to derive model Hamiltonians?

Models provide simple descriptions of the low energy physics.

- Low energy physics: find and analyze the eigenstates
- Simple descriptions: find a small basis, compress the full Hilbert space to a small subspace, downfold to a sparse model Hamiltonian

ab-initio Hamiltonian

$$H_{ab} = \underbrace{-\frac{1}{2}\sum_i \nabla_i^2}_{\text{kinetic}} + \underbrace{\frac{1}{2}\sum_{i,j\neq i}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{e-e interaction}} + \underbrace{\sum_{iI} V_{\text{ext}}\ (\mathbf{r}_i - \mathbf{a}_I)}_{\text{e-i interaction}}$$

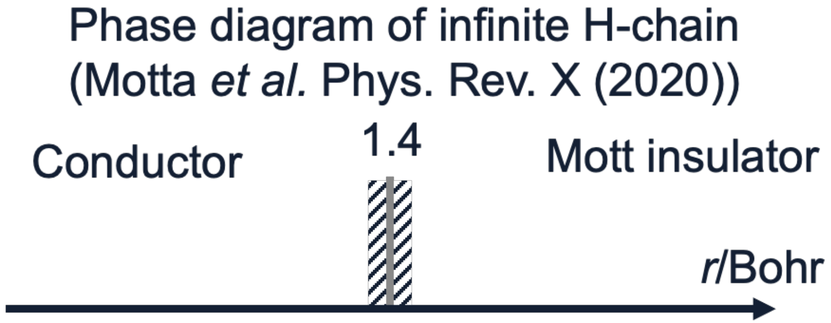


effective model Hamiltonian

$$H_{\text{eff}} = E_0 + \sum_{ij} t_{ij}\left(c_i^\dagger c_j + \text{ h.c. }\right) + \sum_{ijkl} V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l$$

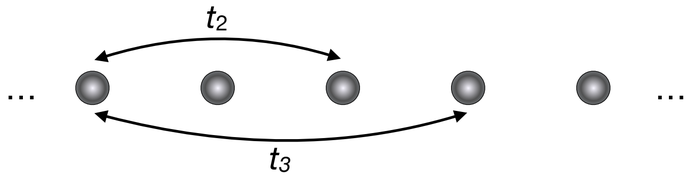
Zheng *et al.* Front. Phys. 6, 43 (2018)

Hydrogen chains model fitting problem

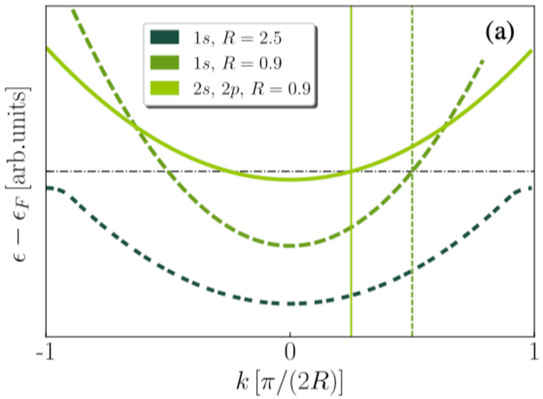


What is the minimal model that can explain the metal-insulator transition in H-chains?

- Long-range hoppings/interactions



- Multiple bands



Overlap between 1s and 2s, 2p bands leads to metallic state.

Figure from Motta *et al.* Phys. Rev. X 10, 031058 (2020).

- Both?
- Neither?

Strategy for deriving model Hamiltonians using QMC

To simplify the problem, we start from the simplest possible system:

H4 chain, equally spaced, with open boundary conditions
Effective core potential: ccecp
Basis: ccecpccpvtz

1. **Eigenstates:**
   Find the eigenstates using QMC.
   Analyze the eigenstates.

2. **Get the data and derive the model Hamiltonian:**
   Find a small basis that describes the low-energy subspace of interest.
   Sample this subspace, obtain the data (energies, one-body and two-body density matrices) for the sampled wave functions.

   Compress to the low-energy subspace and downfold to the model Hamiltonian.

Hydrogen chains: find the eigenstates

Obtain the ground state wave function

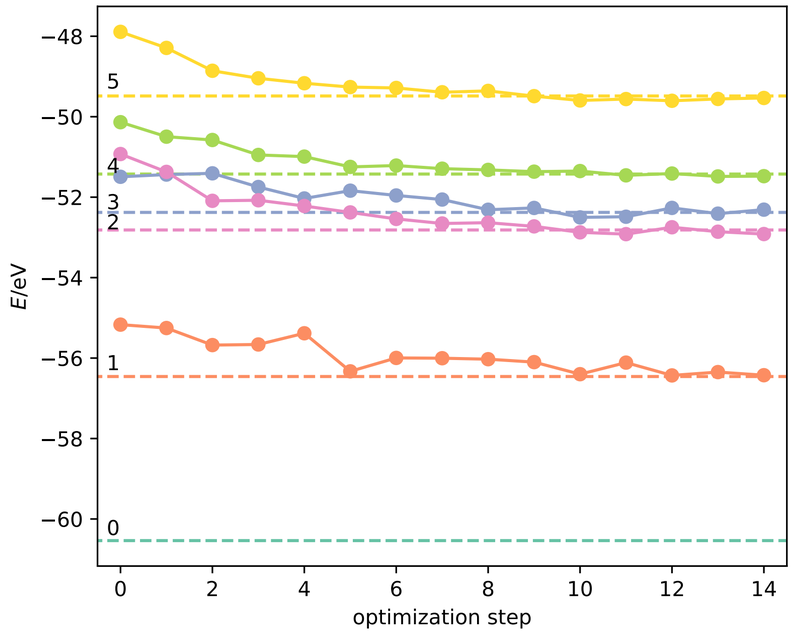
Generate trial wave functions using CASSCF(4, 4) (state-averaged)

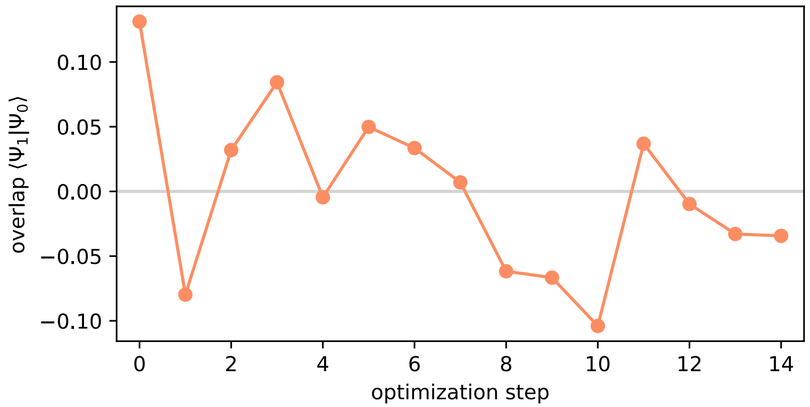
↓

Use VMC to optimize the MO coefficients, CI coefficients, and Jastrow factor to get a better approximation of the ground state wave function Ψ_0

Obtain the excited state wave functions

Use orthogonal optimization to get the excited state wave functions $\Psi_i (i = 1, 2, 3, \cdots)$

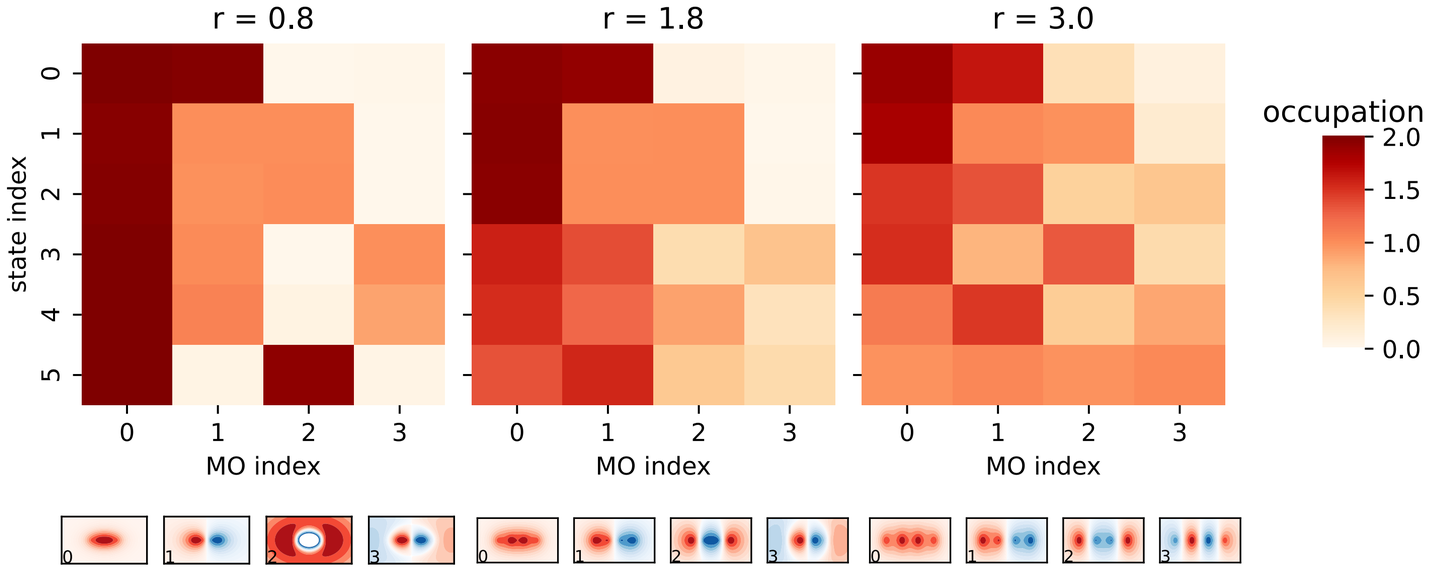




More on orthogonal optimization: Pathak *et al.* J. Chem. Phys. 154, 034101 (2021).

Hydrogen chains: analyze the eigenstates

MO occupations of the optimized eigenstate wave functions:



- ***r* = 0.8:** weakly correlated, almost all the occupations are integers, eigenstates are well represented by one or two determinants
- ***r* = 1.8:** intermediate correlated regime
- ***r* = 3.0:** strongly correlated, many occupations are not intergers, eigenstates may contain many determinants

Hydrogen chains: find a small basis, sample the low-E subspace

Find a small basis ($c_i^\dagger$) that conserves $\mathrm{Tr}(\rho)$

We want to start from a small basis (e.g. a truncated MO basis), such that the trace of the one-body reduced density matrix (OBDM) computed in this basis = the total number of electrons

Generate the energies and reduced density matrices of all the sampled wave functions

Construct linear superpositions of the first few eigenstates: $\Psi = \sum_i c_i \Psi_i$

Compute the OBDMs and TBDMs using VMC or FN-DMC sampled wave functions

For each sampled wave function Ψ, we compute:

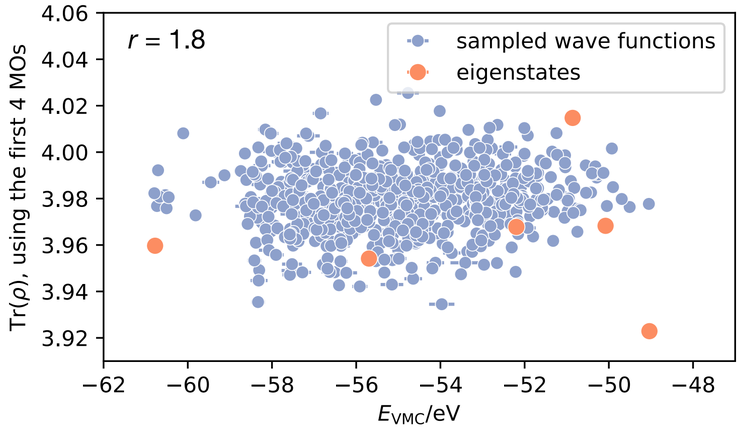
Energy $\langle \Psi | H_{ab} | \Psi \rangle$

OBDM $\left\langle \Psi \middle| c_{i\sigma}^\dagger c_{j\sigma} \middle| \Psi \right\rangle$

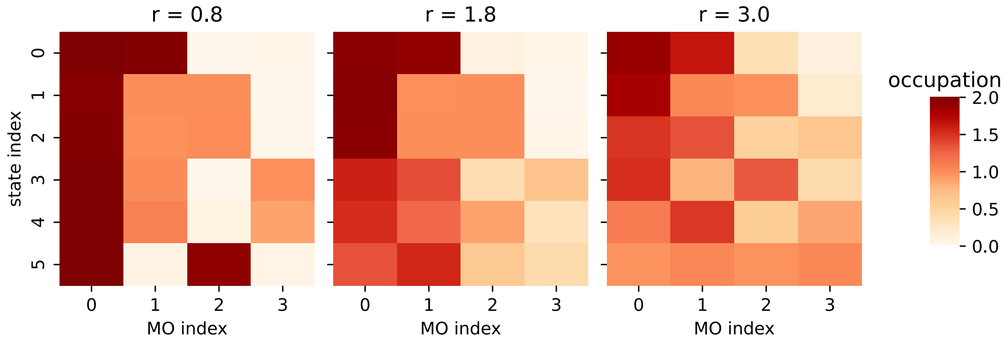
TBDM $\left\langle \Psi \middle| c_{i\sigma}^\dagger c_{k\sigma'}^\dagger c_{l\sigma'} c_{j\sigma} \middle| \Psi \right\rangle$

A slice of the data set that we generate:

For each *r,* we sampled about 800 wave functions:



Diagonals of the OBDMs:

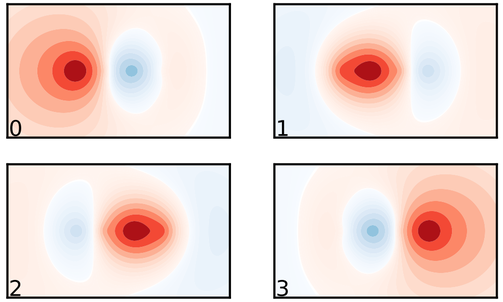


More on density matrix downfolding: Zheng *et al.* Front. Phys. 6, 43 (2018).

Hydrogen chains: compress and downfold to the model Hamiltonian

***r* = 1.2**

Basis: localized orbitals of the first 4 MOs



Descriptors:

$d(t_1)$: $\sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+1\sigma} + \text{h.c.} \right\rangle$

$d(t_2)$: $\sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+2\sigma} + \text{h.c.} \right\rangle$

$d(t_3)$: $\sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+3\sigma} + \text{h.c.} \right\rangle$

$d(U)$: $\sum_i \langle n_{i\uparrow} n_{i\downarrow} \rangle$

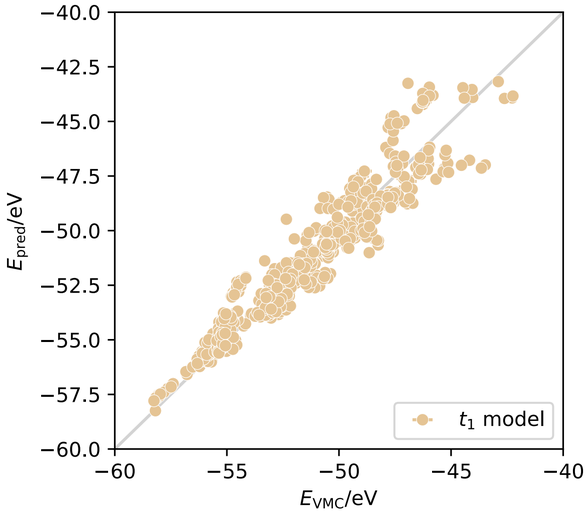
$d(V)$: $\sum_i \langle n_i n_{i+1} \rangle$

t_1 model:

$$E_{\text{VMC}} = t_1 \sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+1\sigma} + \text{h.c.} \right\rangle + E_{\text{lat}}$$

$r^2 = 0.913$

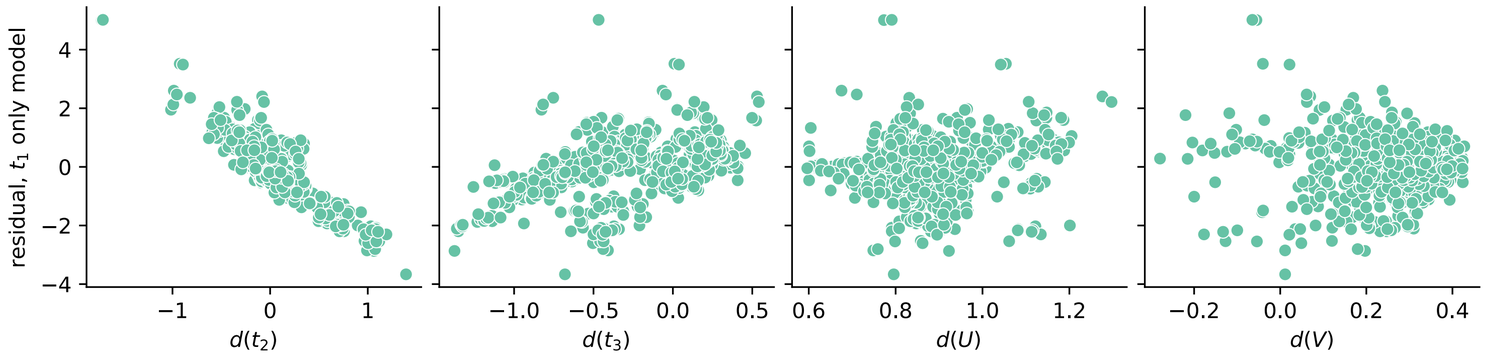
rms error = 0.959 eV



Hydrogen chains: compress and downfold to the model Hamiltonian

***r* = 1.2**

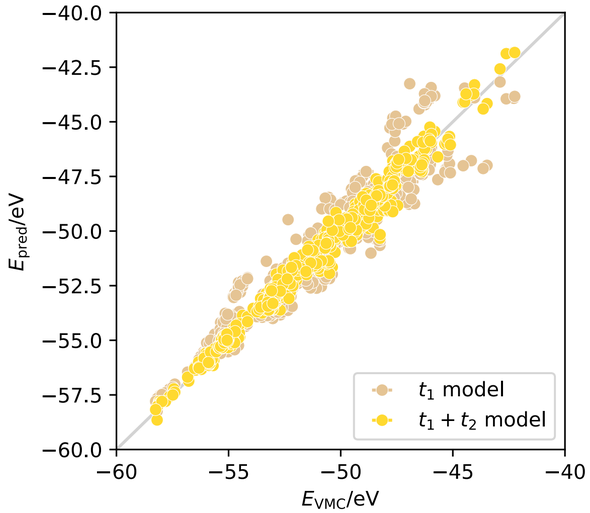
The residual of the t_1 model correlates with descriptors $d(t_2)$ the most.



$t_1 + t_2$ model:

$$E_{\mathrm{VMC}} = t_1 \sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+1\sigma} + \mathrm{h.c.} \right\rangle + t_2 \sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+2\sigma} + \mathrm{h.c.} \right\rangle + E_{\mathrm{lat}}$$

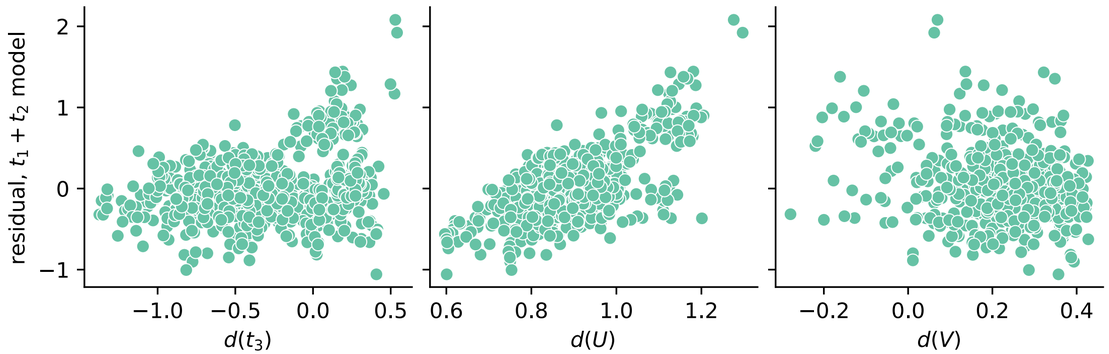
$r^2 = 0.984$
rms error = 0.406 eV



Hydrogen chains: compress and downfold to the model Hamiltonian

***r* = 1.2**

The residual of the $t_1 + t_2$ model correlates with descriptors *d*(*U*) the most.

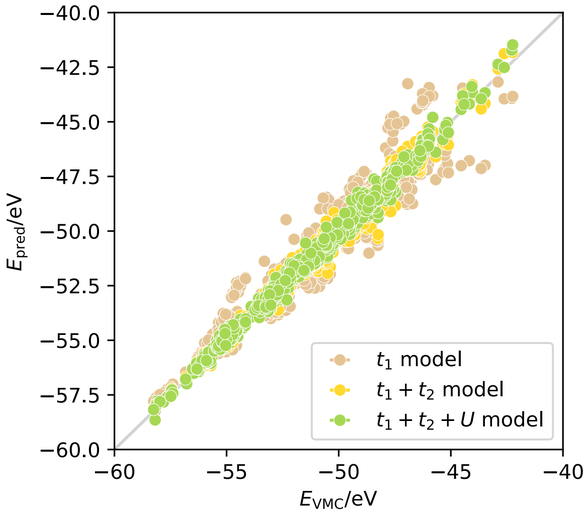


***t*₁ + *t*₂ + *U* model:**

$$E_{\mathrm{VMC}} = t_1 \sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+1\sigma} + \mathrm{h.c.} \right\rangle + t_2 \sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+2\sigma} + \mathrm{h.c.} \right\rangle + U \sum_i \langle n_{i\uparrow} n_{i\downarrow} \rangle + E_{\mathrm{lat}}$$

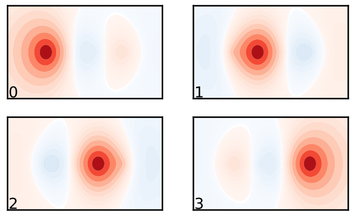
$r^2 = 0.992$

rms error = 0.292 eV

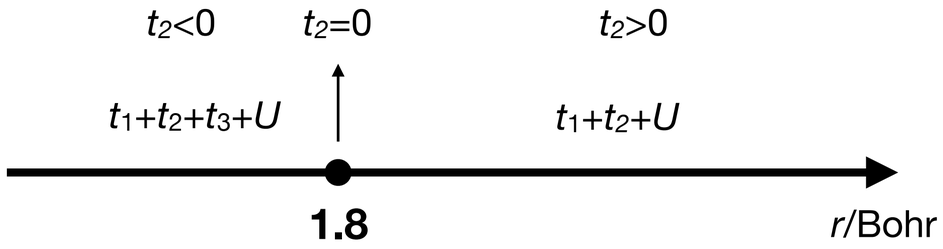


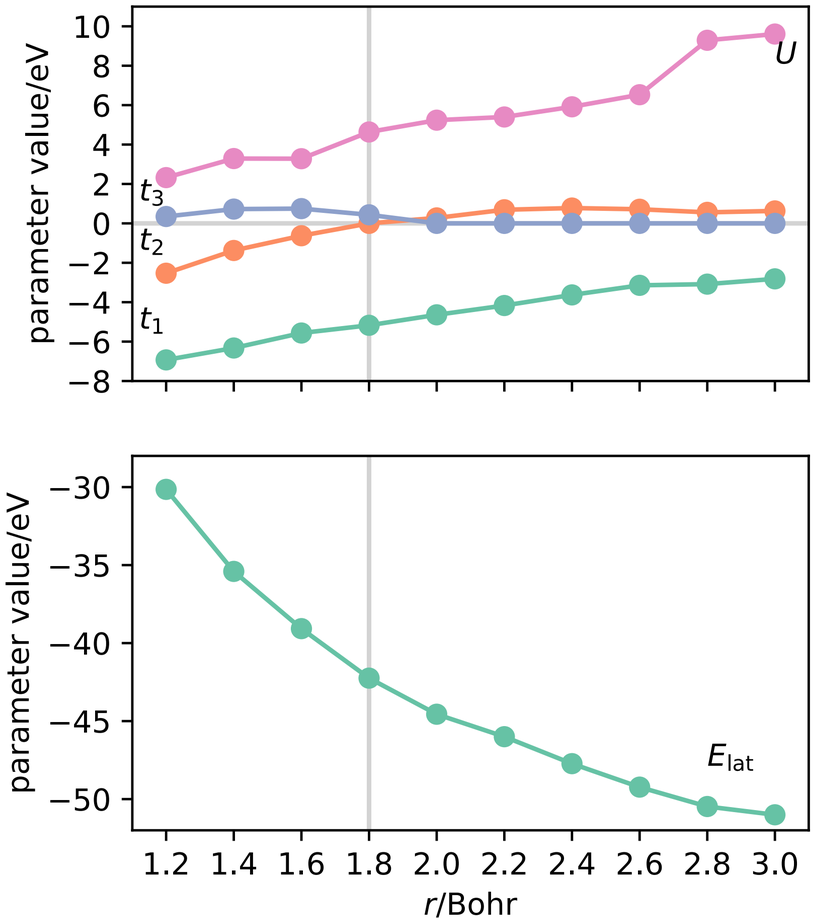
Hydrogen chains: the best models for different bond lengths

For our H4 system, the best model depends on the bond length *r*



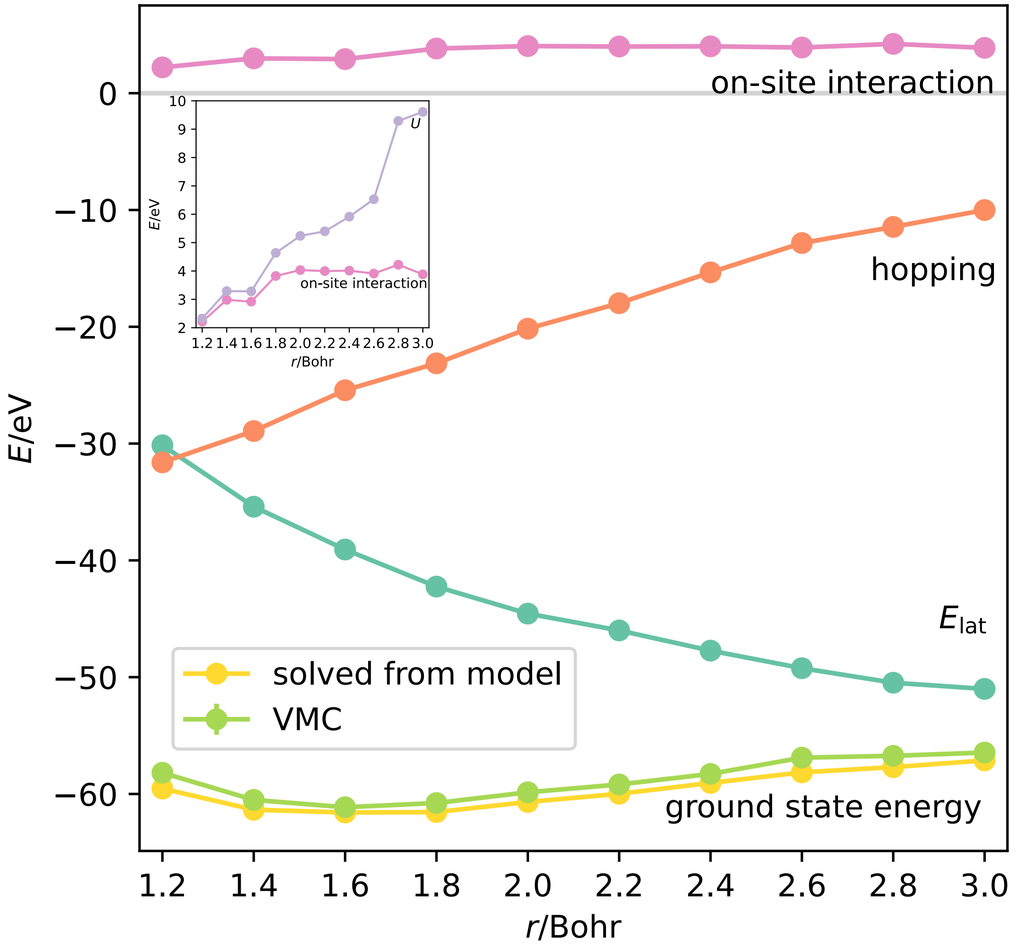
basis: IAO
(localized in real space)





Hydrogen chains summary

Energy contributions of different terms by solving the model Hamiltonians:



$$E_{\mathrm{VMC}} = \underbrace{t_1 \sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+1\sigma} + \mathrm{h.c.} \right\rangle + t_2 \sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+2\sigma} + \mathrm{h.c.} \right\rangle + t_3 \sum_{i\sigma} \left\langle c^\dagger_{i\sigma} c_{i+3\sigma} + \mathrm{h.c.} \right\rangle}_{\mathrm{hopping}}$$

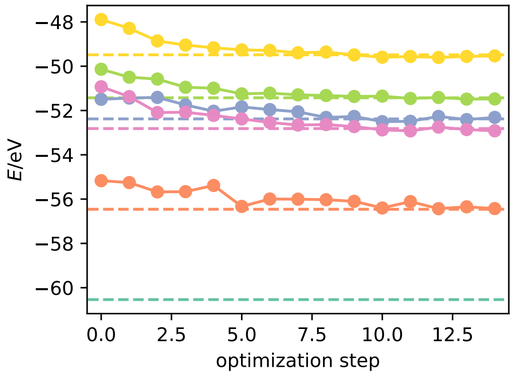
$$+ \underbrace{U \sum_i \langle n_{i\uparrow} n_{i\downarrow} \rangle}_{\mathrm{on-site\ interaction}} + E_{\mathrm{lat}}$$

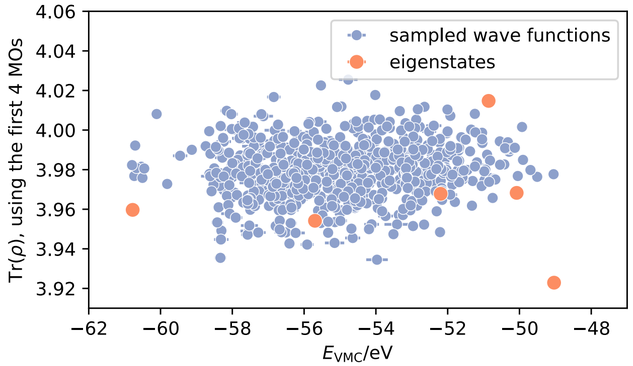
- As *r* increases, the on-site repulsion parameter *U* also increases, but the ground state double occupancy decreases, so the overall contribution from the on-site interaction does not increase much.

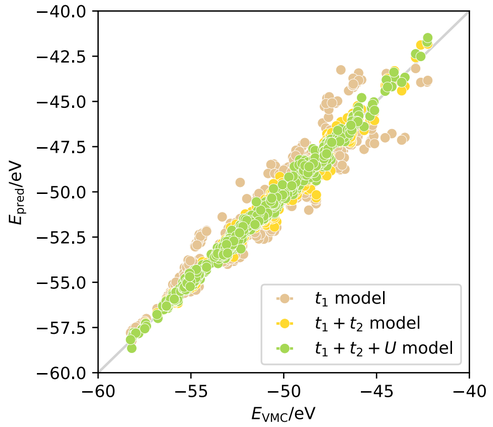
- As we go to TDL, one can make the same figure and study how the different terms contribute to the order parameter.

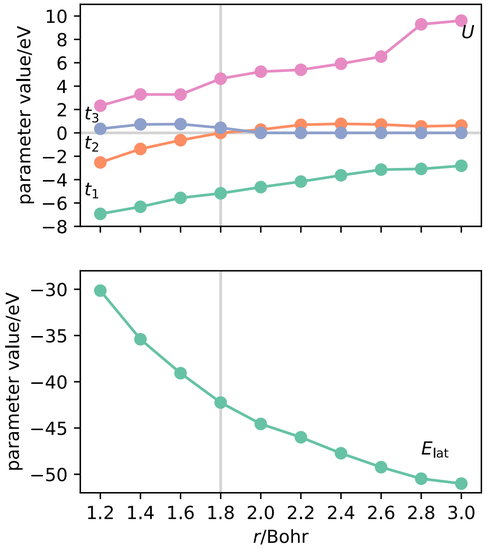
Summary

- **Derivation of the model Hamiltonian using QMC**
  - use QMC to find and analyze the eigenstates
  - sample the low-energy subspace, compress and downfold to model Hamiltonians









- **With density matrix downfolding based on QMC, one can derive model Hamiltonians treating all the one-body and two-body terms on the same footing, without double counting error.**

This framework can be generalized to more complex systems…