A GENERALIZED HYBRID FRAMEWORK FOR CRYSTAL STRUCTURES USING KOHN-SHAM ORBITALS AND WANNIER FUNCTIONS

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QuantiCoM

QUANTUM COMPUTING FOR MATERIALS SCIENCE AND ENGINEERING

QCi

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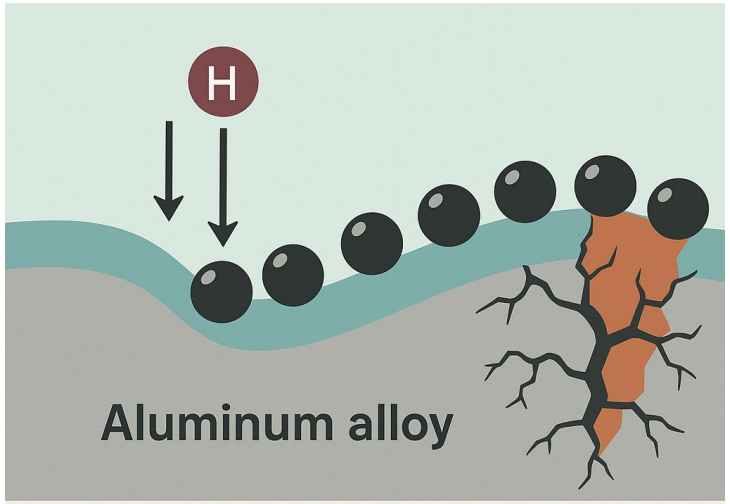
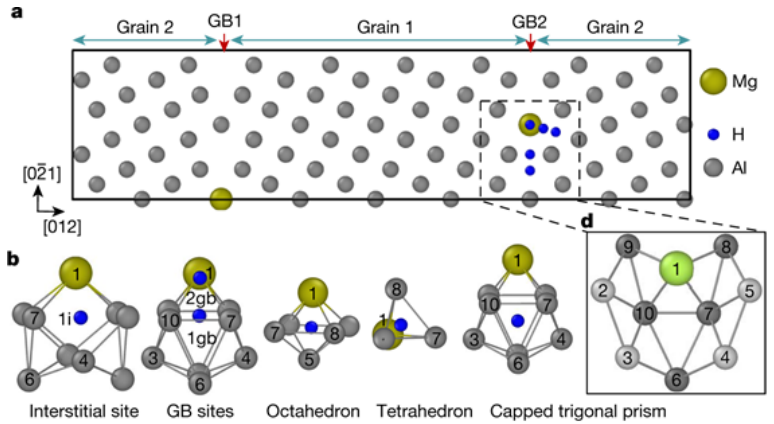
aufgrund eines Beschlusses des Deutschen Bundestages

DLR

Introduction



Hydrogen embrittlement:
after diffusion, hydrogen reacts with its surrounding to form brittle compounds.

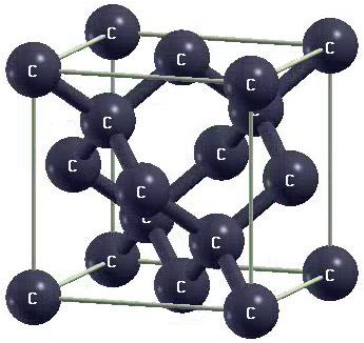


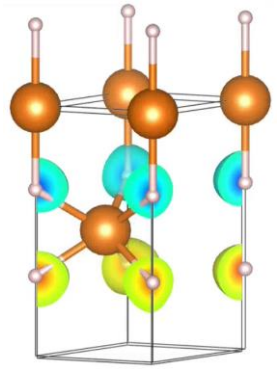
We aim to characterize crystal structure properties during/after hydrogen diffusion and especially hydrogen embrittlement using quantum computing

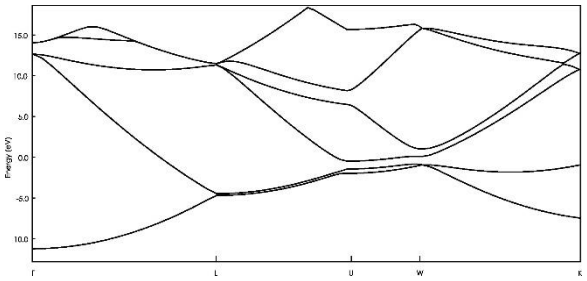
Figures: Gujarati, Tanvi P., et al. "Quantum computation of reactions on surfaces using local embedding." *npj Quantum Information* 9.1 (2023): 88.

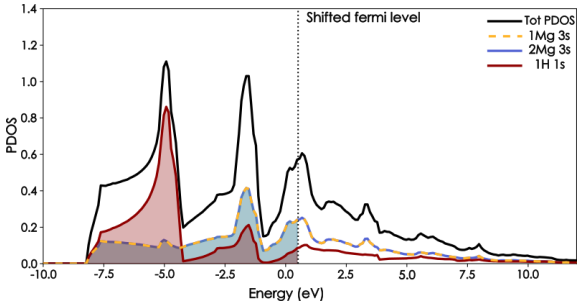
Introduction

What can we do with classical *ab initio* codes?



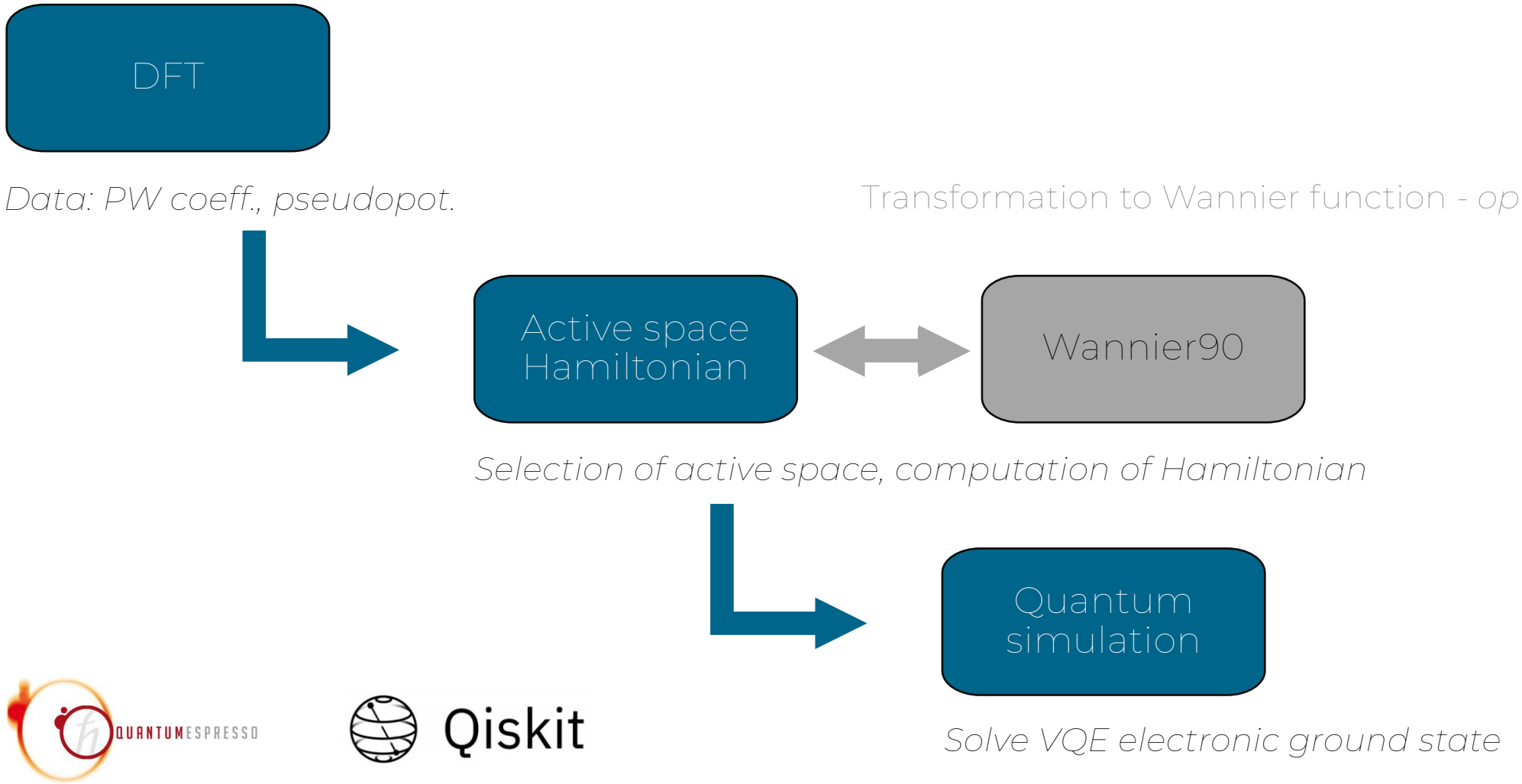






We cannot access to such data with quantum *ab initio* codes

A framework from Quantum ESPRESSO to Qiskit



A framework from Quantum ESPRESSO to Qiskit

DFT

Data: PW coeff., pseudopot.

What are the DFT condition we must fulfil?

- Close-shell
- Single k-point or following a k-path
- Norm-conservative pseudopotential

Active space Hamiltonian ⟷ Wannier90

Selection of active space, computation of Hamiltonian

Quantum simulation

Solve VQE electronic ground state

QUANTUMESPRESSO

Qiskit

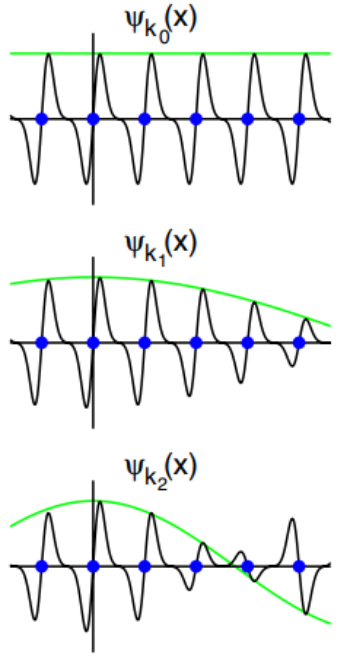
Theoretical insight: plane-waves and Wannier functions

Bloch expansion:

$$\psi_{j\mathbf{k}}(\boldsymbol{r}) = u_{j\mathbf{k}}(\boldsymbol{r})e^{i\mathbf{k}\cdot\boldsymbol{r}}$$

$$\psi_{j,\mathbf{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \sum_{\substack{\mathbf{G}\in\mathrm{BZ} \\ |\mathbf{G}|<\mathrm{G}_{max}}} C_{j,\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\boldsymbol{r}}$$

- $e^{i(\mathbf{k}+\mathbf{G})\cdot\boldsymbol{r}}$ plane-wave component



We consider p-like orbitals centered on each atom and the band is isolated.

Figure: Marzari, Nicola, et al. "Maximally localized Wannier functions: Theory and applications." *Reviews of Modern Physics* 84.4 (2012): 1419-1475.

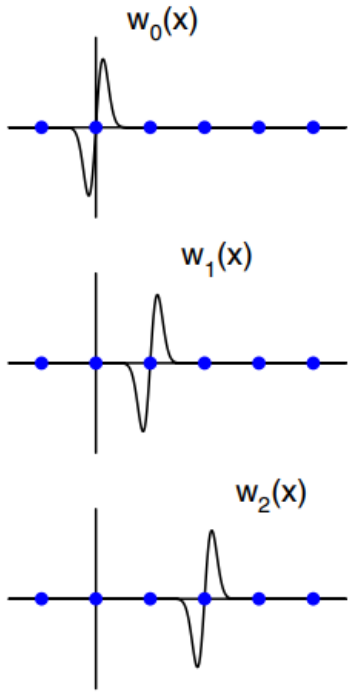
Theoretical insight: plane-waves and Wannier functions

Wannier functions:

$$w_j(\boldsymbol{r}-\boldsymbol{R}) = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} e^{-i\mathbf{k}\cdot\boldsymbol{R}}\psi_{j\mathbf{k}}(\boldsymbol{r})\,d\mathbf{k}$$

Transformation:

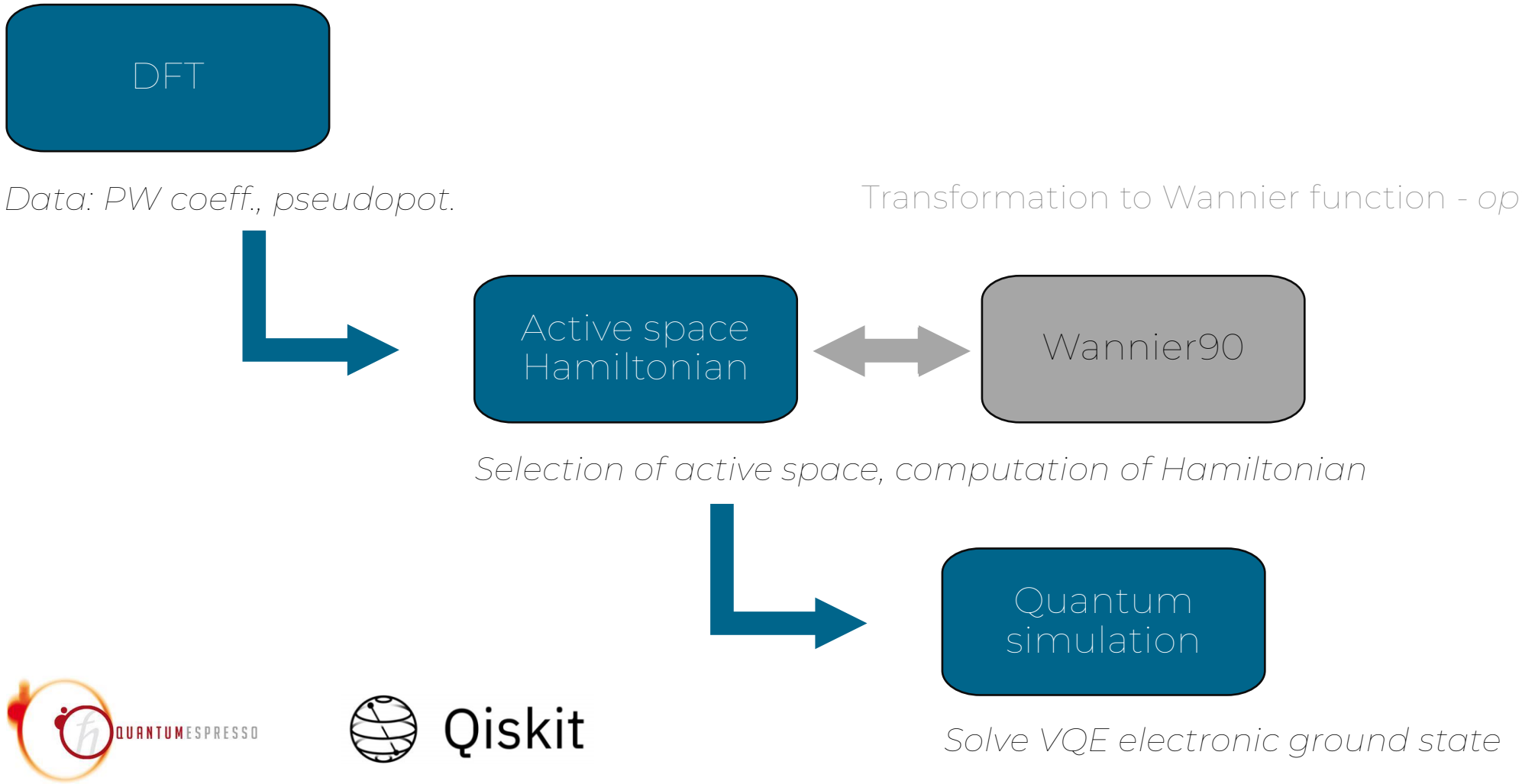
$$w_j(\boldsymbol{r}) = \sum_m U_{mj}(\mathbf{k})\psi_{j,\mathbf{k}}(\boldsymbol{r})$$



A Wannier function is the Fourier transform of a Bloch expansion

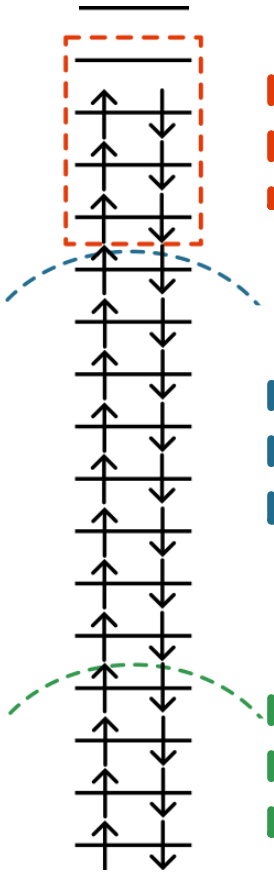
Figure: Marzari, Nicola, et al. "Maximally localized Wannier functions: Theory and applications." *Reviews of Modern Physics* 84.4 (2012): 1419-1475.

A framework from Quantum ESPRESSO to Qiskit



Evaluation of the electronic Hamiltonian

$$\hat{H}_{elec} = \hat{V}_{\mathrm{e-e}} + \hat{V}_{\mathrm{e-nu}} + \hat{T}_{\mathrm{e}} = -\sum_i \sum_{j,i\neq j} \frac{e^2}{4\pi \left\| \mathbf{r}_i - \mathbf{r}_j \right\|} - \sum_i \sum_I \frac{e^2 Z_I}{4\pi \left\| r_i - \mathbf{R}_I \right\|} - \sum_i \frac{\hbar^2 \nabla^2_{\mathbf{r}_i}}{2m_{\mathrm{e}}}$$



Determination of an active space

We determine the i_{max} and j_{max}

$$\hat{H}_{elec} = \sum_{i,j} h_{ij} \hat{a}_i^\dagger \hat{a}_j + \sum_{i,j,k,l} h_{ijkl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l$$

Frozen core approx.

Calculated as in [1]

How can we obtain $\boldsymbol{h_{ij}}$ and $\boldsymbol{h_{ijkl}}$?

Pseudopotential

Calculated as in [2]

[1]: Yalouz, Saad, et al. "A state-averaged orbital-optimized hybrid quantum–classical algorithm for a democratic description of ground and excited states." *Quant. Sc. Tech.* 6.2 (2021): 024004.
[2]: Hamann, D. R. "Optimized norm-conserving Vanderbilt pseudopotentials." *Phys. Rev. B* 88.8 (2013): 085117.

Evaluation of the electronic Hamiltonian

$$\hat{H}_{elec} = \sum_{i,j} h_{ij} \hat{a}_i^\dagger \hat{a}_j + \sum_{i,j,k,l} h_{ijkl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l$$

We express $\boldsymbol{h_{ij}}$ and $\boldsymbol{h_{ijkl}}$ in the reciprocal space

$$h_{ij} = \sum_{\mathbf{p}} \frac{|\mathbf{p}|^2}{2} C_{i,\mathbf{p}}^* C_{j,\mathbf{p}} + \sum_{\substack{\mathbf{p},\mathbf{q} \\ \mathbf{p}\neq\mathbf{q}}} \sum_I \frac{4\pi Z_I}{V} \cdot \frac{e^{i(\mathbf{p}-\mathbf{q})\cdot \boldsymbol{R}_I}}{|\mathbf{p}-\mathbf{q}|^2} C_{i,\mathbf{q}}^* C_{j,\mathbf{p}}$$

$$h_{ijkl} = \sum_{\mathbf{p},\mathbf{q},\mathbf{r},\mathbf{s}} \frac{4\pi}{V} \cdot \frac{1}{|\mathbf{p}-\mathbf{r}|^2} C_{i,\mathbf{p}}^* C_{j,\mathbf{q}}^* C_{k,\mathbf{r}} C_{l,\mathbf{s}}$$

$$\psi_{j,\mathbf{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{G}\in \mathrm{BZ}} C_{j,\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot \boldsymbol{r}}$$

Evaluation of the electronic Hamiltonian

$$\hat{H}_{elec} = \hat{V}_{\mathrm{e-e}} + \hat{V}_{\mathrm{e-nu}} + \hat{T}_{\mathrm{e}} = -\sum_i \sum_{j,i\neq j} \frac{e^2}{4\pi \left\| \mathbf{r}_i - \mathbf{r}_j \right\|} - \sum_i \sum_I \frac{e^2 Z_I}{4\pi \left\| r_i - \mathbf{R}_I \right\|} - \sum_i \frac{\hbar^2 \nabla^2_{\mathbf{r}_i}}{2m_{\mathrm{e}}}$$

h_{ij} and h_{ijkl} are calculated in the BZ

$$\psi_{j,\mathbf{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{G}\in \mathrm{BZ}} C_{j,\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot \boldsymbol{r}}$$

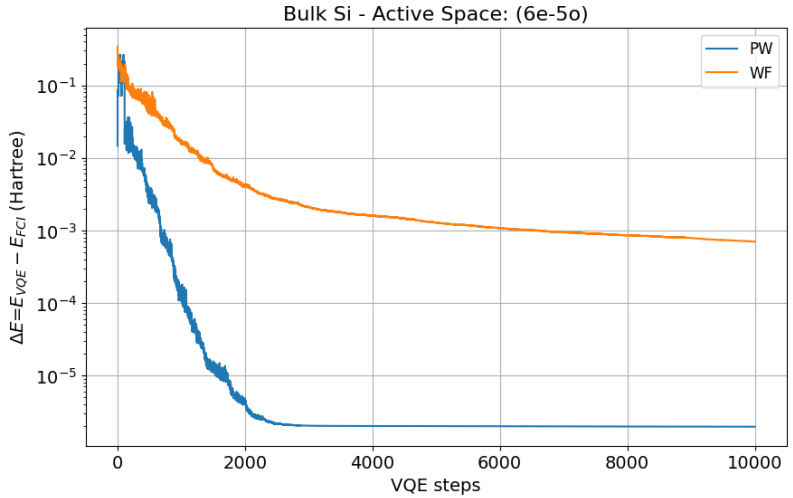
$$\hat{H}_{elec} = \sum_{i,j} h_{ij} \hat{a}_i^\dagger \hat{a}_j + \sum_{i,j,k,l} h_{ijkl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_l$$

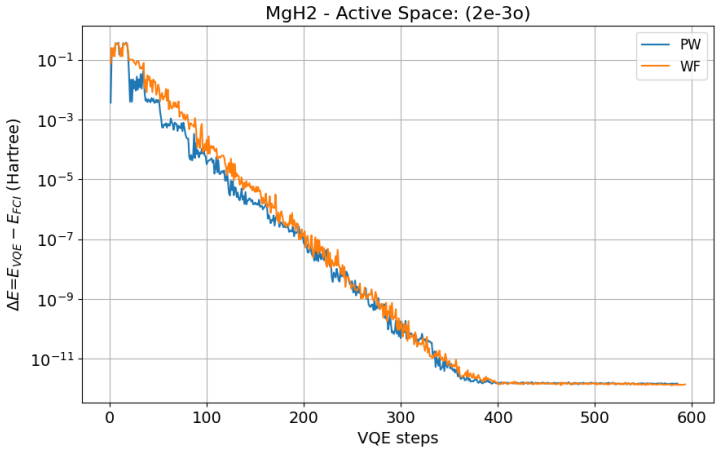
Jordan-Wigner mapping
UCCSD ansatz

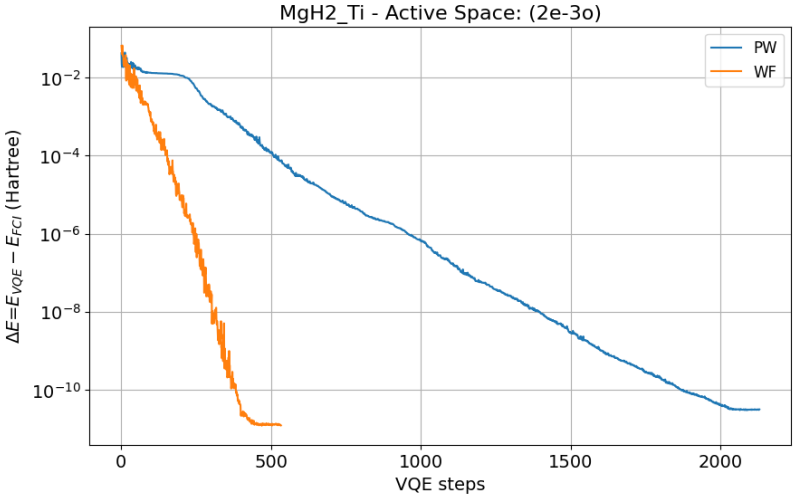
$$a_p^{(\dagger)} \rightarrow \frac{1}{2} \left(\bigotimes_{k<p} Z_k \right) \otimes \left(X_p \, {}_{(-)}^{+} \, iY_p \right)$$

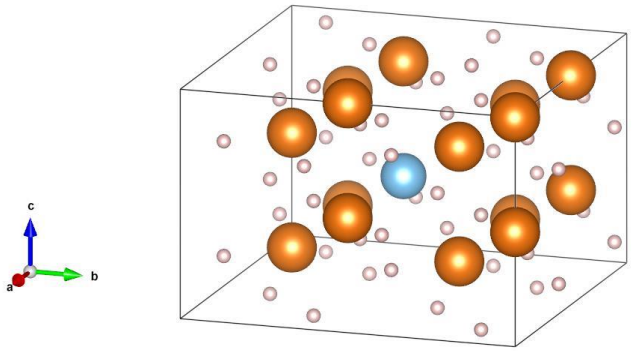
$$\hat{H}_{elec} = \sum_i p_i \hat{P}_i$$

Convergence test on a supercell









Supercell 2x2x2 MgH_2

Conclusion

- We obtain a faster convergence with plane-waves rather than Wannier functions for bulk materials.
- The convergence speed for systems with defect seems to be basis set dependent.
- Processing of the electronic wave-function to get a quantum Bader charge:

$$\rho^{\mathrm{VQE}}(\boldsymbol{r}) = \sum_i n_i^{\mathrm{VQE}} \left|\varphi_i^{\mathrm{DFT}}(\boldsymbol{r})\right|^2$$

Perspective

Open-shell:
Extension of the code to odd number of electrons

Pseudopotential:
Expansion of the code to various pseudopotentials

Geometry relaxation:
Gradient and Hessian calc. in a quantum simulation with finite difference

Orbitals optimization:
VQE does not optimize the orbitals but only the occupancy of the configurations

Imprint

Topic: A generalized hybrid framework for crystal structures using Kohn-Sham orbitals and Wannier functions

Date: 2025-04-01

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Institute: Institute of Materials Research (DLR-WF)

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