Infusing Self-Consistency into Density Functional Theory Hamiltonian Prediction via Deep Equilibrium Models

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Outline

Introduction

Method

Conclusion

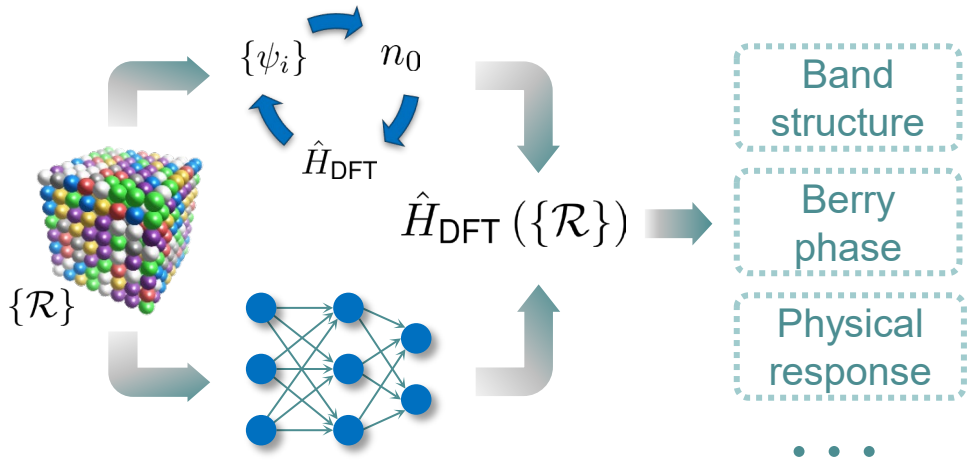
Preliminary

- Schrödinger equation under non-orthogonal basis

$$H(\boldsymbol{k})v_{n\boldsymbol{k}} = E_{n\boldsymbol{k}}S(\boldsymbol{k})v_{n\boldsymbol{k}}$$

where $H_{i\alpha,j\beta} = \langle\phi_{i\alpha}|\hat{H}|\phi_{j\beta}\rangle$ and $S_{i\alpha,j\beta} = \langle\phi_{i\alpha}|\phi_{j\beta}\rangle$.

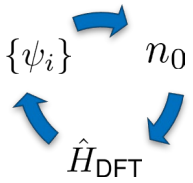
- DFT Hamiltonian as a function of molecular structure $\{\mathcal{R}\}$



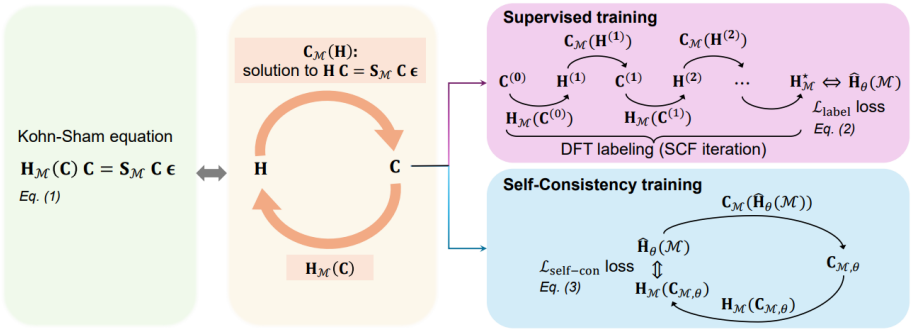
Related works

- SchNOrb, PhiSNet, DeepH, DeepH-E3, QHNet, …
- Additional properties of DFT Hamiltonian:

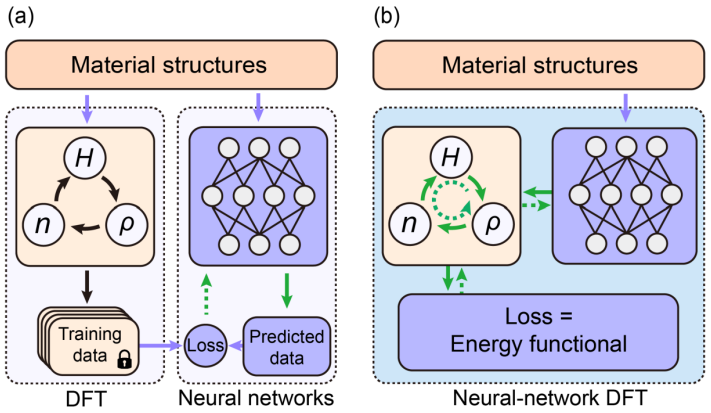
  Self-consistency



- Incorporate self-consistency:
  - SC Loss



  - AI2DFT

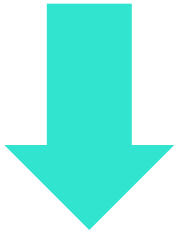


Schütt, *et al*. Nat. Commun. 2019.
Unke, Oliver, *et al*. NeurIPS 34 (2021): 14434-14447.
Li, He, *et al*. Nat. Comput. Sci.2.6 (2022): 367-377.
Gong, Xiaoxun, et al. Nat. Commun.14.1 (2023): 2848.
Yu, Haiyang, et al. ICML. PMLR, 2023.
Zhang, He, *et al*. ICML 41
Li, Yang, *et al*. Phys. Rev. Lett., 133(7):076401, 2024.

Motivation

Intertwining **DFT computations** with the **loss function** during.

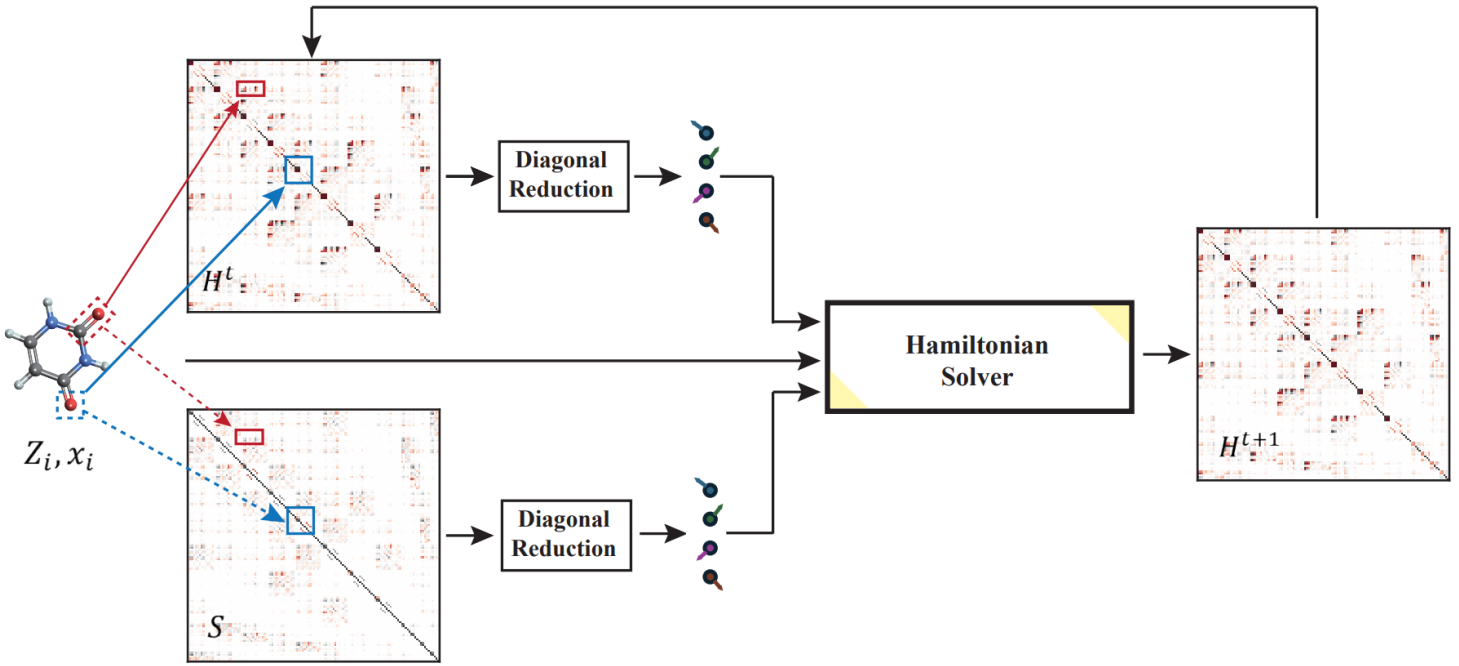
Incorporate self-consistency bypassing DFT ???



Model architecture

DEQH

- **Deep equilibrium model (DEQ):** $z^* = f(x, z^*)$
- **Hamiltonian solver** rather than **Hamiltonian predictor**
  - **Hamiltonian predictor:** $\boldsymbol{H = f(Z, R)}$
  - **Hamiltonian solver:** $\boldsymbol{H^* = f(Z, R, H^*)}$



Injection of Hamiltonian and overlap matrix

- Diagonal reduction
  - Matrix element between atom i and j of single-electron operator represented in the atomic orbitals {Φ} is $\mathbf{T}_{i\mu,j\nu} = \langle \Phi_i^\mu | \hat{\mathcal{O}} | \Phi_j^\nu \rangle$
  - Wigner–Eckart theorem $\langle jm|T_q^{(k)}|j'm'\rangle = \langle j'm'kq|jm\rangle \langle j \parallel T^{(k)} \parallel j' \rangle$ ensures that there exists a set of T-independent coefficients Q, s.t. $\mathbf{h}_A^l := \sum_{\mu,\nu} T_{AA}^{\mu,\nu} Q_{nlm}^{\mu,\nu}$ is injective and satisfy equivariance.

$$\begin{aligned}\tilde{Q}_{nlm}^{\mu,\nu} &:= \tilde{Q}_{nlm}^{n_1,l_1,m_1;n_2,l_2,m_2} \\ &= \int_{\mathbf{r}\in\mathbb{R}^3} (\Phi_A^{n_1,l_1,m_1}(\mathbf{r}))^* \Phi_A^{n_2,l_2,m_2}(\mathbf{r}) \tilde{\Phi}_A^{n,l,m}(\mathbf{r}) d\mathbf{r}\end{aligned}$$

Results

- MD17

Dataset	Model	H $[10^{-6}E_h]\downarrow$	ϵ $[10^{-6}E_h]\downarrow$	ψ $[10^{-2}]\uparrow$
Water	QHNet	**10.79**	**33.76**	**99.99**
	DEQHNet	36.07	335.86	**99.99**
Ethanol	QHNet	20.91	**81.03**	99.99
	DEQHNet	**18.73**	106.94	**100.00**
Malonaldehyde	QHNet	21.52	**82.12**	**99.92**
	DEQHNet	**17.97**	93.79	99.90
Uracil	QHNet	20.12	113.44	**99.89**
	DEQHNet	**15.07**	**107.49**	**99.89**

- QH9

Dataset	Model	H $[10^{-6}E_h]\downarrow$ diagonal	non-diagonal	all	ϵ $[10^{-6}E_h]\downarrow$	ψ $[10^{-2}]\uparrow$
QH9-stable-id	QHNet	111.21	73.68	76.31	**798.51**	95.85
	DEQHNet	**96.43**	**58.75**	**61.42**	4383.10	**99.84**
QH9-stable-ood	QHNet	111.72	69.88	72.11	**644.17**	93.68
	DEQHNet	**81.01**	**51.66**	**53.23**	5657.07	**99.80**
QH9-dynamic-geo	QHNet	149.62	92.88	96.85	**834.47**	94.45
	DEQHNet	**84.97**	**60.04**	**62.14**	1864.06	**99.92**
QH9-dynamic-mol	QHNet	416.99	153.68	173.92	9719.58	79.15
	DEQHNet	**210.76**	**97.18**	**105.80**	**4625.88**	**99.80**

Conclusion

- The Hamiltonian's iterative qualities are often neglected by standard machine learning approaches for its direct prediction. Our approach integrates **DEQ**s with off-the-shelf ML frameworks, leveraging node features derived from the Hamiltonian and overlap matrix to harness these **iterative** aspects.

- Traditional machine learning models primarily serve as Hamiltonian predictors, and while recent self-consistency integrating frameworks aim to refine training, they incur high computational costs. DEQH model distinguishes itself by acting fundamentally as a **solver**, iteratively determining the Hamiltonian with the deep equilibrium model's fixed-point capabilities. This intrinsic **self-consistency and computational efficiency** render DEQH model a scalable approach for precise quantum state prediction without a significant increase in complexity.

- We have benchmarked DEQHNet against the MD17 and QH9 datasets, demonstrating that the incorporation of Hamiltonian self-consistency can significantly enhance predictive accuracy.

- We conduct an ablation study on DEQHNet, and present conjectures regarding the efficacy of networks that incorporate DEQs for the task of learning Hamiltonians.

Thank You!