Electric polarization and interatomic force from neural network-based quantum Monte Carlo

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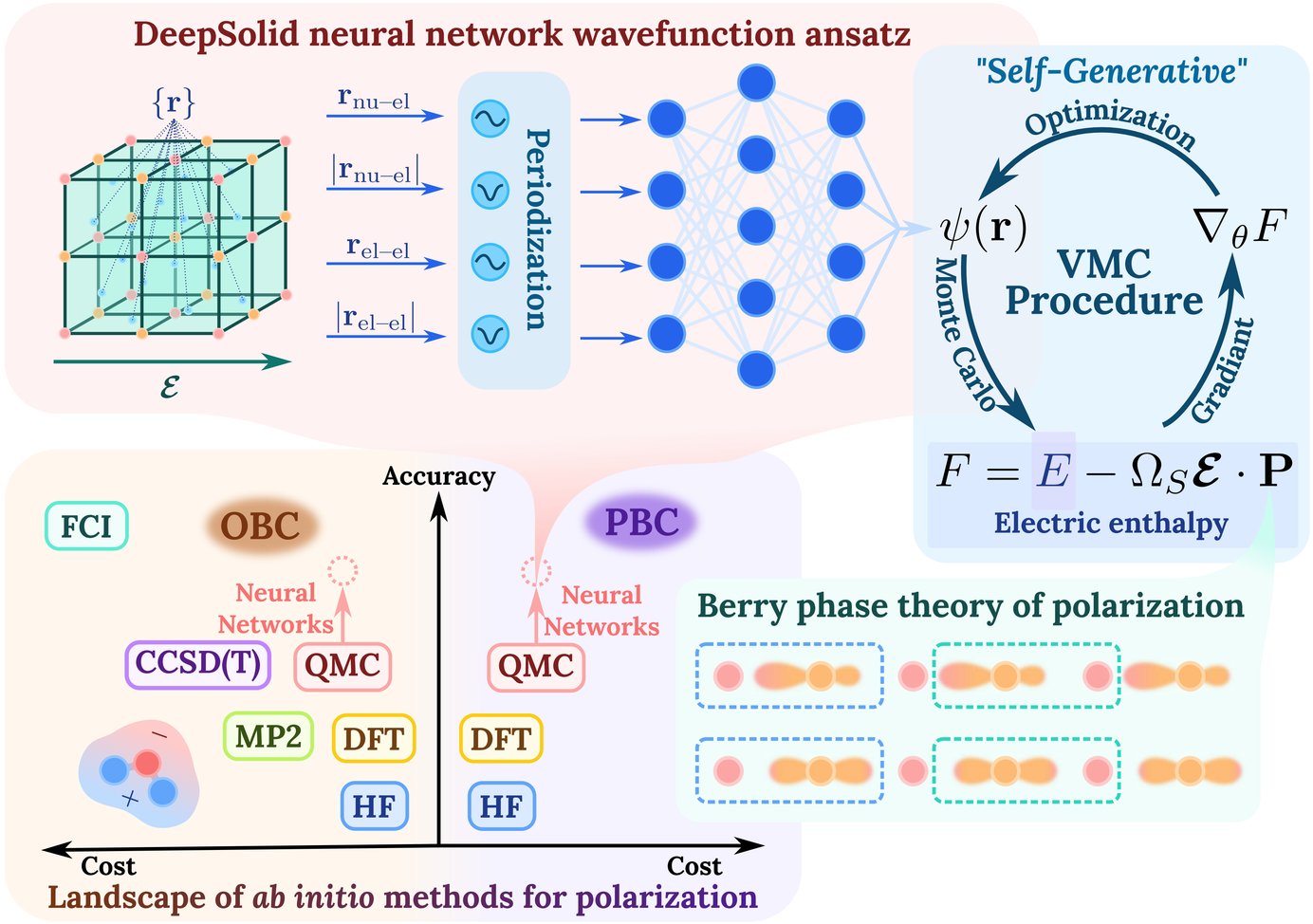


Introduction

- Neural networks are powerful ansatz for variantional Monte Carlo
- For energy, DMC or CCSD(T) level of accuracy or beyond can be reached
- Many observables are much easier to calculate in VMC than DMC
  - e.g. electric polarization & interatomic force
  - VMC could not be used in the past because it was inaccurate

Theory of polarization

Difference of polarization matters!

$$\Delta\mathbf{P} = \int \mathrm{d}t \frac{1}{V_{\mathrm{cell}}} \int_{\mathrm{cell}} \mathrm{d}\mathbf{r}\, \mathbf{j}(\mathbf{r}, t)$$

Regarding $\mathbf{j}$ as the adiabatic current, $\mathbf{P}$ is related to the *Berry phase*!

$$\mathbf{P} = \frac{e}{(2\pi)^3} \mathrm{Im} \sum_n \int \mathrm{d}\mathbf{k} \, \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle$$

We can use *single point Berry phase* for many-body wavefunction (1D example):

$$P = -\frac{e}{\Omega} \frac{L}{2\pi} \mathrm{Im} \ln \langle \psi | \mathrm{e}^{\mathrm{i}G\hat{X}} | \psi \rangle$$

Interatomic force

Coulomb force has infinite variance.

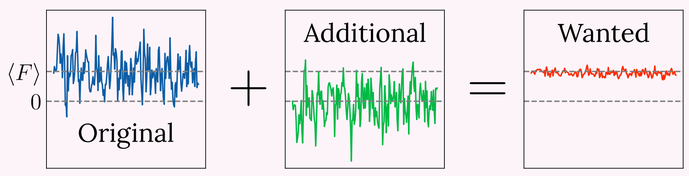


Fig. 4: Find estimators to reduce variance

For example,

$$\widetilde{\mathbf{F}}_A = \frac{\mathrm{d}\langle E_L \rangle}{\mathrm{d}\mathbf{R}_A} = -\frac{\partial}{\partial \mathbf{R}_A} E_L + 2(\langle E_L \rangle - E_L) \frac{\partial}{\partial \mathbf{R}_A} \log(|\psi_T|)$$

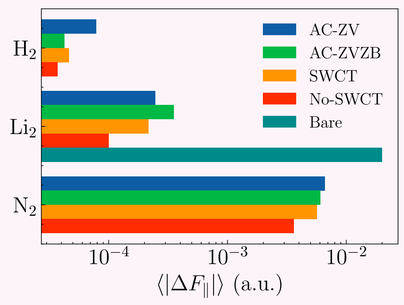


Fig. 5: Average force error over bond lengths

A better neural network gives better wavefunction, and the error and variance of interatomic force can be *improved with a better neural network*.

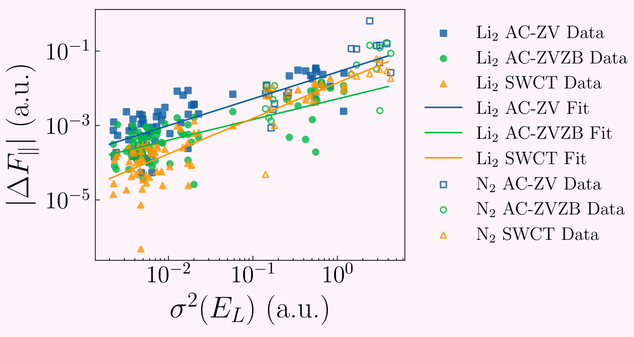


Fig. 6: Force error on Li_2 and N_2 with different qualities of neural network

Polarization calculations

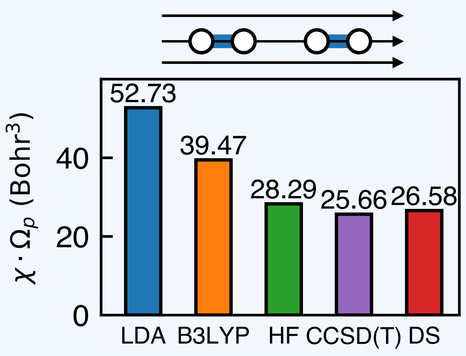


Fig. 1: Susceptibility of hydrogen chain

- Conventional *DFT overestimates* the dielectric constant.
- Our method (DS) is *efficient and accurate* on atoms, chains, slabs, cubes, and graphene
  - Agrees well with CCSD(T) and experimental results.
  - CCSD(T) results are extrapolated from OBC results, and are expensive.
- Out-of-plane dielectric constant for bilayer graphene.
  - Agrees with previous calculations, and verified $\epsilon_\infty^\perp(d)$ around equilibrium.

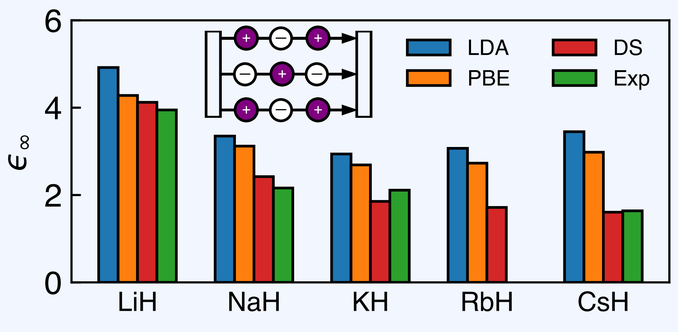
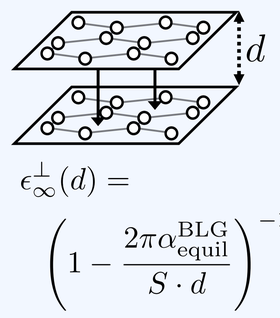


Fig. 2: High-frequency dielectric constant ϵ_∞ of alkali metal hydrides



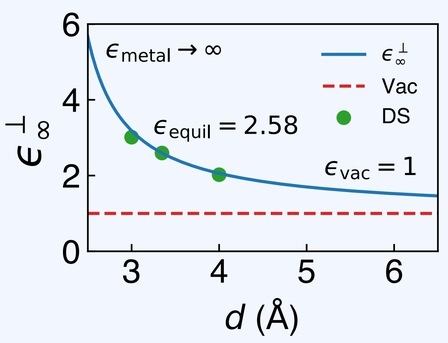


Fig. 3: Dielectric constant for bilayer graphene

Conclusion

- We proposed an *efficient and accurate method* for electric polarization.
- We *implemented and tested* different estimators for force calculation.
- Neural networks **boost** QMC:
  - Filling the gap of high-accuracy electric polarization calculation.
  - Benefit interatomic force by having a better wavefunction.

References

[1] Y. Qian, W. Fu, W. Ren, and J. Chen, Interatomic Force from Neural Network Based Variational Quantum Monte Carlo, The Journal of Chemical Physics 157, 164104 (2022).
`TheChenGroup/ferminet-force`

[2] X. Li, Y. Qian, and J. Chen, Electric Polarization from Many-Body Neural Network Ansatz, arXiv:2307.02212.

[3] X. Li, Z. Li, and J. Chen, Ab Initio Calculation of Real Solids via Neural Network Ansatz, Nat Commun 13, 1 (2022).
`bytedance/DeepSolid`

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