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

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PRL work!

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!

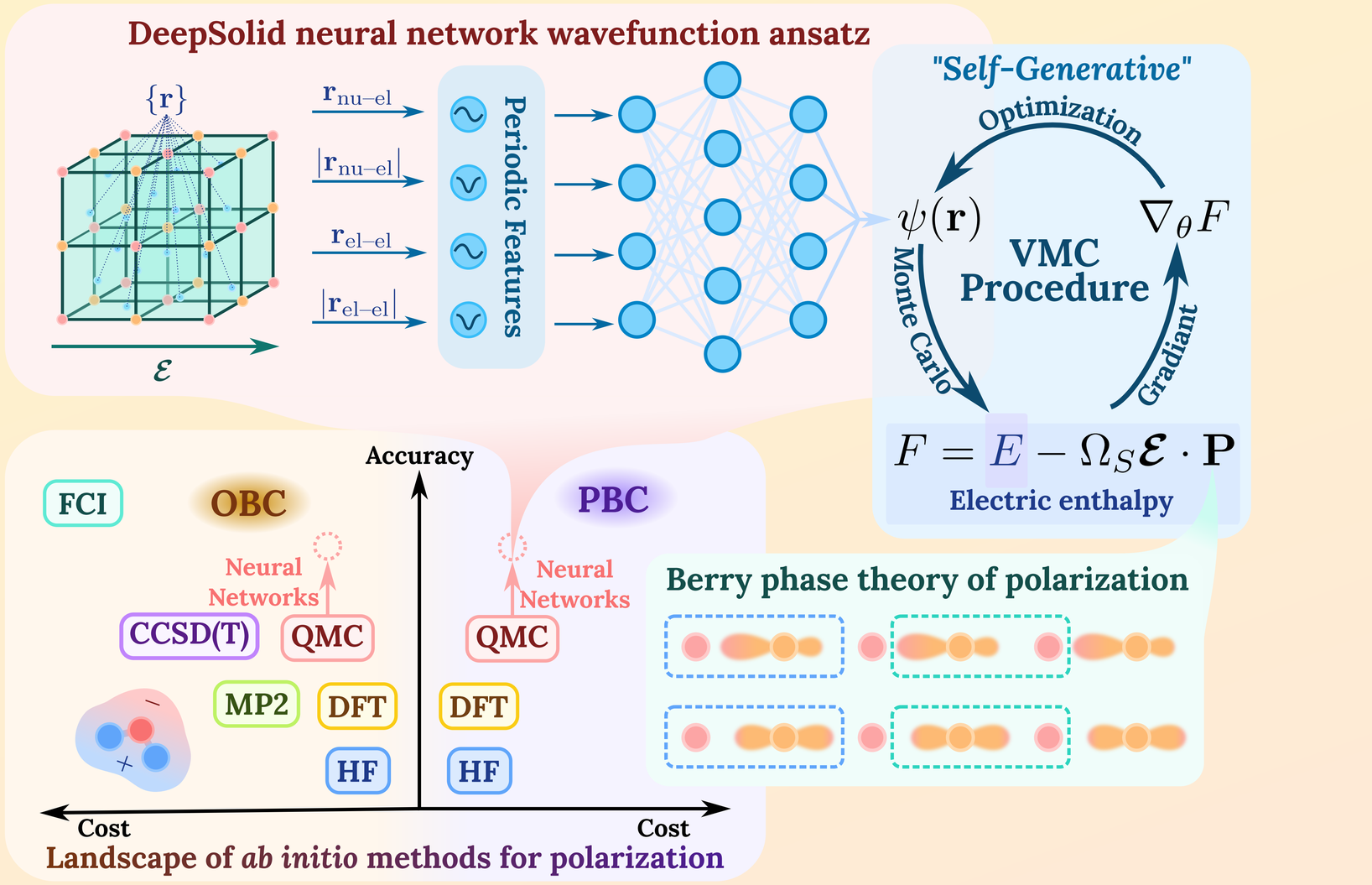
$$\Delta\mathbf{P} = \int \mathrm{d}t \frac{1}{V_{\text{cell}}} \int_{\text{cell}} \mathrm{d}\mathbf{r}\, \mathbf{j}(\mathbf{r}, t)$$

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

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

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

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



Polarization

- Conventional *DFT overestimates* the dielectric constant.
  - That is because electron correlation is approximated.
- Our method can **accurately** describe the correlation.
  - Consistent with extrapolated CCSD(T) & experiments.
  - It is the *only* high-accuracy method for dielectric properties in periodic systems.

Some computational results (our method markds as "DS"):

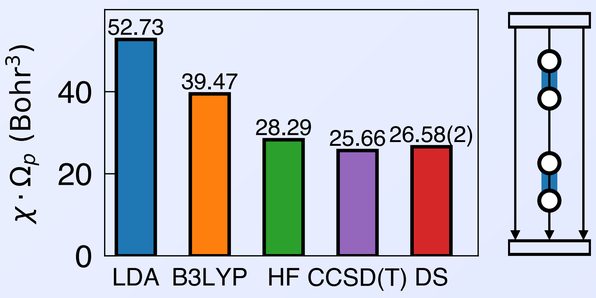


Fig. 3: Susceptibility of hydrogen chain

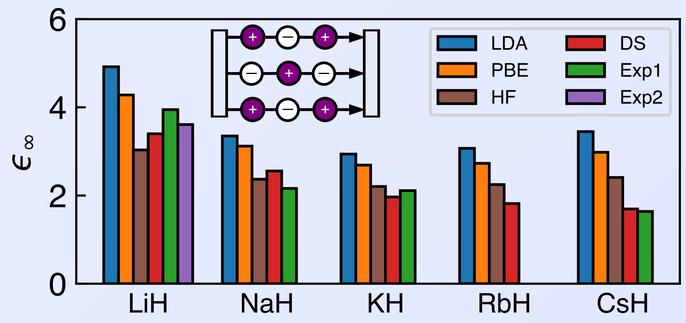


Fig. 4: High-frequency dielectric constant ε_∞ of alkali metal hydrides

Interatomic force

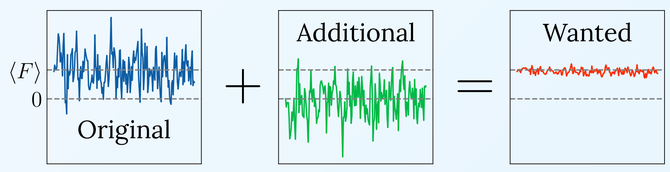
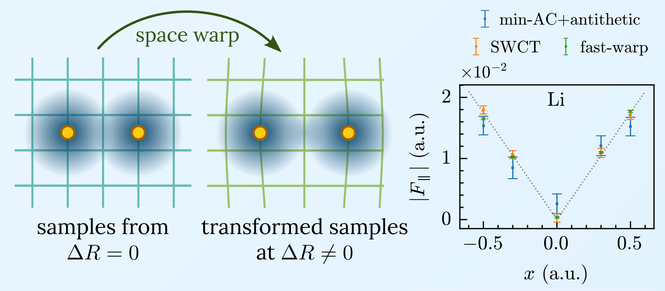


Fig. 1: Find estimators to reduce variance

- Coulomb force has infinite variance.
- Good force estimators can reduce variance.

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

- Traditional estimators works for neural network QMC, but are not the best.
- A *new force estimator* is proposed.
  - Based on space warp (SWCT) estimator.
  - It is more **accurate** and more **efficient**.
  - *100 times more efficient* than SWCT!



$$\frac{\mathrm{d}E_L}{\mathrm{d}\mathbf{R}_I} = \partial_{\mathbf{R}_I} E_L^{\mathrm{p}} + \frac{(\hat{H} - E_L)\partial_{\mathbf{R}_I}\psi_T}{\psi_T}$$

without warp

evaluation accelerated $(\hat{H} - E_L) \to -2 \operatorname{Im} E_L$

variance reduced

$$+ \sum_i \omega_I(\mathbf{r}_i) \partial_{\mathbf{r}_i} E_L^{\mathrm{p}} + \sum_i \frac{(\hat{H} - E_L)\omega_I(\mathbf{r}_i)\partial_{\mathbf{r}_i}\psi_T}{\psi_T} + \frac{1}{2}\frac{\left[\nabla_i^2 \omega_I(\mathbf{r}_i)\right]\partial_{\mathbf{r}_i}\psi_T}{\psi_T} + \frac{(\nabla_i \omega_I(\mathbf{r}_i))(\nabla_i \partial_{\mathbf{r}_i}\psi_T)}{\psi_T}$$

warp terms

Fig. 2: Fast-warp force estimator

Conclusion

- By better describing *correlation*, **accurate** dielectric properties can be obtained.
- Fast-warp is an **efficient and accurate** estimator for interatomic force.
- Neural networks **boost** QMC:
  - Filling the gap of high-accuracy electric polarization calculation.
  - Benefit interatomic force by having a better wavefunction.

References

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