Applying Harmonic Analysis to Predict Quantum Energies and Forces

Nikhil Shankar, Matthew Hirn, Yue Qi

Department of CMSE - Michigan State University

Introduction

- The majority of problems in computational chemistry depend upon finding the energy and forces of atomic systems:
  - Drug development
  - Materials research
  - Battery technology
- Simulation methods must trade off the accuracy of density functional theory (DFT) based approaches with the speed of force field calculations.
- Machine learning methods potentially offer DFT accuracy with substantial savings in computation time.
- We present a learning model which efficiently uses data to concurrently predict the energy and forces of an atomic system. The model's design is informed by physics and has the additional bonus of being relatively interpretable.

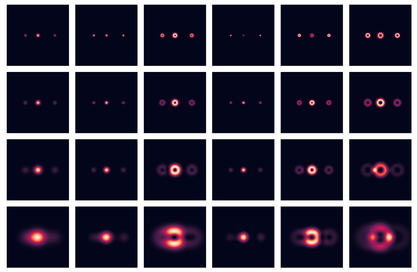

Fig. 1: Features prior to integration. Varying (n, ℓ) across and j vertically.

Data Sets

We have two data sets of DFT calculations:

- 625 LiOLi molecules at various bond lengths
- 80,000 Li-Si periodic crystals at various concentrations

We've built our model for the simpler molecular LiOLi data set. We hope to transition towards the more complex Li-Si crystal structures in the future.

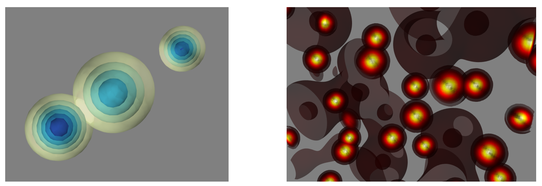

Fig. 2: LiOLi (left) and Li-Si (right) example systems

Mathematical Background

Since these are physical systems, our data is well behaved. That is, energy and forces are:

1. Invariant and covariant, respectively, to isometric displacements
2. Invariant to atom re-indexing
3. Continuous under deformations of atom positions

Let $\mathbf{R}$ be a system, a set of atoms and their positions. We would like a feature vector $\vec{\phi}$ which represents $\mathbf{R}$, and additionally respects the physical laws above. Learning on $\vec{\phi}$ will be more efficient and more likely to succeed. Below is an element of $\vec{\phi}$:

$$\phi_\lambda(\mathbf{R}) = \int_{\mathbb{R}^3} \left(\sum_{m=-l}^{l} \left| \rho_{\mathbf{R}} * \Psi^m_{n,l,j} \right|^2 \right)^{q/2}$$

In the above equation $\lambda = (n, \ell, j, q)$ represents paramaters, $\rho_{\vec{R}}$ is a pseudo electron density, and $\Psi^m_{n,l,j}$ is a wavelet characterized by a radial function and a spherical harmonic. [1]

We can think of a feature in the following manner: ϕ represents some interaction(s), j scales size, q scales range, and (n, ℓ) correspond to a specific electron orbital.

Learning Model

A linear regression over the features $\vec{\phi}(\mathbf{R})$ returns accurate energies [2]. Since force is the gradient of energy, we expect that the same linear regression over $\nabla\vec{\phi}$ would return forces:

$$E \approx \tilde{E} = \sum_\lambda w_\lambda \phi_\lambda \implies F = \nabla E \approx \tilde{F} = \nabla \tilde{E} = \sum_\lambda w_\lambda \nabla \phi_\lambda$$

In this case, a linear regression is a robust and simple solution:

- Non-linearities in the the features calculation give our model a high learning capacity
- Greedy regression techniques offer sparse, interpretable results
- A simple model is easily and cheaply differentiable

We used 240 features and evaluated the test error via $C = \frac{1}{M} \sum_{i=1}^{M} \|F(\mathbf{R}_i) - \tilde{F}(\mathbf{R}_i)\|_1$

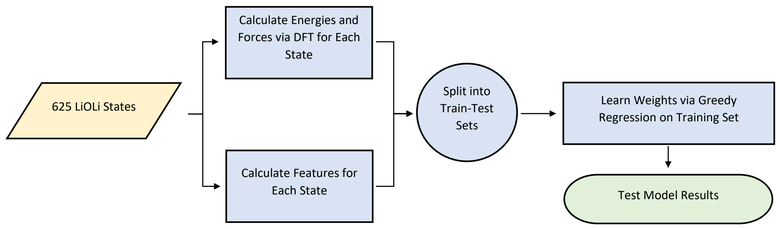

Fig. 3: Model Flowchart

Results and Discussion

We are able generalize well while training on forces. Using 309 training points and 100 features our MAE on the testing set is 0.51 eV/Å. This error is summed over 9 force directions, however, the model accurately predicts that 6 direction have 0 force (within machine precision).

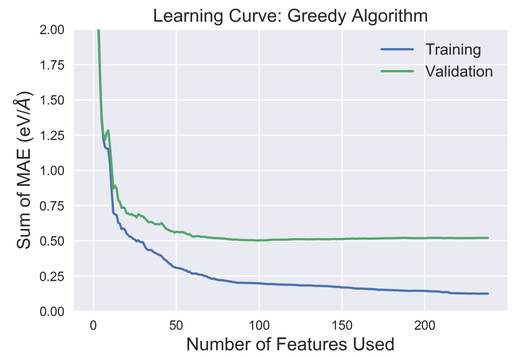

Fig. 4: Model Performance on LiOLi Data

The benchmark we will be working towards is a maximum error of 0.02 eV/Å per direction. This benchmark represents a common cutoff at which DFT simulations are said to have converged. Currently our model has a maximum directional error of 0.28 eV/Å on Oxygen.

Testing the model requires evaluating ill-conditioned transformations. We are working to alleviate this issue and believe a fix could lead to significant improvements.

Acknowledgements

We acknowledge support from the MSU ACRES REU program, which is supported by the National Science Foundation through grant ACI-1560168.
Special thanks to the CEDAR and MSCE teams for their advise and mentorship throughout the project.

References

[1] M. Hirn, S. Mallat, and N. Poilvert, Multiscale Model. Simul. **15**, 827 (2017).

[2] M. Eickenberg, G. Exarchakis, M. Hirn, S. Mallat, NIPS **30**, 6543 (2017).