Quantum Mechanical Properties of Atoms in Molecules via Machine Learning

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Overview

Problem
Computational cost of numerical approximations limits uses of electronic structure theory

Goal
Combining quantum mechanics with machine learning to handle larger systems, longer simulations, more systems, and higher accuracy

Approach
Interpolation between reference calculations across geometries and compositions
Idea of QM/ML models

- QM/ML = quantum mechanics + machine learning
- exploit redundancy in a series of QM calculations
- interpolate between QM calculations using ML

Kernel ridge regression

model \( \hat{f}(x) = \sum_{i=1}^{n} \alpha_i k(x_i, x) \)

optimization problem \( \arg\min_{\alpha \in \mathbb{R}^n} \sum_{i=1}^{n} (\hat{f}(x_i) - y_i)^2 + \lambda \alpha^T K \alpha \)

solution \( \alpha = (K + \lambda I)^{-1} y \)

with \( k \) positive definite, \( K_{ij} = k(x_i, x_j) \), regularization strength \( \lambda \in \mathbb{R} \).

Kernel ridge regression example

Weighted basis functions placed on training samples $x_i$

Example:
- $f(x) = \cos(x)$
- training samples
- Gaussian basis functions
- prediction $\hat{f}$

Local environments

Local properties of atoms in molecules

Local environments

Local atom-centered coordinate systems.

atomic Coulomb matrix

\[
M_{I,J}^{(Q)} = \begin{cases} 
\frac{1}{2} Z_I^2 & I = J \\
\frac{Z_I Z_J}{\|R_I - R_J\|} & I \neq J 
\end{cases}
\]

principal component coordinates

\[
\left( \frac{1}{n} X^T X \right) v_\ell = \lambda_\ell v_\ell 
\]

augmented by \( Z_I \)

Representations sorted by distance to atom \( Q \).

Data set and properties

- 9 k small organic molecules
- C, N, O, H; 7–9 non-H atoms
- subset of GDB9
- forces: 100 conformations for each of 168 \( \text{C}_7\text{H}_{10}\text{O}_2 \) isomers
- nuclear chemical shifts
- core level excitations
- forces

Calculations at DFT/PBE0/def2TZVP level using Gaussian

## Results

<table>
<thead>
<tr>
<th>Property</th>
<th>Ref.</th>
<th>Range</th>
<th>MAE</th>
<th>%</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C $\delta$/ppm</td>
<td>2.4</td>
<td>6 – 211</td>
<td>3.9 ± 0.28</td>
<td>1.9</td>
<td>0.988 ± 0.001</td>
</tr>
<tr>
<td>$^1$H $\delta$/ppm</td>
<td>0.11</td>
<td>0 – 10</td>
<td>0.28 ± 0.01</td>
<td>2.8</td>
<td>0.954 ± 0.005</td>
</tr>
<tr>
<td>1s C $\delta$/m$E_h$</td>
<td>7.5</td>
<td>-165 – -2</td>
<td>4.9 ± 0.12</td>
<td>3.0</td>
<td>0.971 ± 0.002</td>
</tr>
<tr>
<td>$F_C$/m$E_h$ $a_0^{-1}$</td>
<td>1</td>
<td>-99 – 96</td>
<td>3.6 ± 0.10</td>
<td>1.8</td>
<td>0.983 ± 0.002</td>
</tr>
<tr>
<td>$F_H$/m$E_h$ $a_0^{-1}$</td>
<td>1</td>
<td>-43 – 43</td>
<td>0.8 ± 0.02</td>
<td>0.9</td>
<td>0.996 ± 0.003</td>
</tr>
</tbody>
</table>

MAE = mean absolute error, $R$ = correlation coefficient

Linear scaling

Prediction of chemical shifts

Conclusions

Machine learning can be used to interpolate between quantum mechanical reference calculations to enable larger systems, longer simulations, more systems, higher accuracy.