Applications of Gaussian Process Model in Molecular Dynamics

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• Efficient Non-Parametric Fitting of PES for Polyatomic Molecules with Gaussian Processes, Jie Cui and RK, arXiv: 1509.06473
Outline

Two major problems in molecular dynamics

- Uncertainties of PESs
- Numerical complexity of quantum calculations

Gaussian Process Model as a tool for interpolation in multi-dimensional spaces

Applications of the GP model in molecular dynamics:

- Efficient fitting of PESs
- Obtaining scattering observables as functions of individual PES parameters
- Obtaining scattering observables averaged over PES variations
- Using classical trajectories to interpolate quantum results
- Obtaining converged results from unconverged calculations
- Extrapolation of scattering observables from one molecule to another
Can quantum dynamical calculations be quantitatively predictive?

Can quantum dynamical calculations be quantitatively predictive?

Dynamical calculations are sensitive to potential energy surfaces.

Potential energy surfaces are inherently inaccurate.

How to deal with this problem?

Average the results over variations of PES.
Relative probability of elastic scattering and spin depolarization – a very important question for experiments on cooling molecules
Average over variations of the PES

Error bars are obtained by simple scaling of PES

But this does not account for errors in anisotropy

Required:

- analysis of the scattering observables as functions of strength and topology of PES

Molecule – molecule collisions in a magnetic field
But this is a difficult task ...

Even for simple systems, PES is parametrized by tens of parameters.

It is impossible to compute the dynamical observables as functions of all PES parameters.

We propose to use the Gaussian Process model to solve this problem.

Gaussian Process = Gaussian Random Function
Gaussian Process Model

Input variable

Dynamical observables
Gaussian Process Model

Random functions vs. Input variable
Gaussian Process Model

- Constrained random functions

Input variable

Constrained random functions
Gaussian Process Model – how does it work?

\[ \Omega = \Omega(\mathbf{x}) \quad \text{with} \quad \mathbf{x} = (x_1, x_2, \cdots, x_q)^\top \]

Step 1. Calculate the observable at a few points of this multi-dimensional space

Step 2. Estimate correlations between the calculated points

Assume some mathematical form for the correlations, e.g.,

\[
R(\mathbf{x}, \mathbf{x'}) = \prod_{i=1}^{q} \left( 1 + \frac{\sqrt{5}|x_i - x'_i|}{\omega_i} + \frac{5(x_i - x'_i)^2}{3\omega_i^2} \right) \exp\left( -\frac{\sqrt{5}|x_i - x'_i|}{\omega_i} \right)
\]

and find the maximum likelihood estimates of the unknown coefficients.

We do this by minimizing the log-likelihood function:

$$\log \mathcal{L}(\omega | Y^n) = -\frac{1}{2} \left[ n \log \hat{\sigma}^2 + \log(\det(A)) + n \right]$$

with

$$A = \begin{pmatrix}
1 & R(x_1, x_2) & \cdots & R(x_1, x_n) \\
R(x_2, x_1) & 1 & \cdots & \\
& \ddots & \ddots & \\
R(x_n, x_1) & \cdots & 1
\end{pmatrix}$$

$$\hat{\sigma}^2(\omega) = \frac{1}{n} (Y^n - \beta)^\top A^{-1} (Y^n - \beta)$$

$$\hat{\beta}(\omega) = (I^\top A^{-1} I)^{-1} I^\top A^{-1} Y^n$$

Gaussian Process Model – how does it work?

Step 3. Make a prediction of the observable at any desired point \( x_0 \)

\[
\Omega(x_0) = \beta + A_0^\top A^{-1}(\Omega - \beta)
\]

where

\[
A_0 = (R(x_0, x_1), R(x_0, x_2), \cdots, R(x_0, x_n))^\top
\]

No analytical fitting of data needed

We are using the maximum likelihood estimates of the correlations to make a prediction at a new point of space

Obtaining multi-dimensional potential energy surfaces

Gaussian Process Model of multi-dimensional PES

\[ \Omega = \Omega(\mathbf{x}) \quad \text{with} \quad \mathbf{x} = (x_1, x_2, \cdots, x_q)^\top \]

Observable

Internal coordinates of molecule

Ab initio calculations

Jie Cui and RK, arXiv: 1509.06473
### Six-dimensional PES for N4

<table>
<thead>
<tr>
<th>Number of ab initio points</th>
<th>RMSE at energy &lt; 100 kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES from [1]</td>
<td></td>
</tr>
<tr>
<td>16421</td>
<td>1.8 %</td>
</tr>
<tr>
<td>GP model</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>6.39 ± 1.77</td>
</tr>
<tr>
<td>480</td>
<td>4.19 ± 1.56</td>
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<tr>
<td>720</td>
<td>2.96 ± 0.78</td>
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<tr>
<td>960</td>
<td>2.58 ± 0.67</td>
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<tr>
<td>1200</td>
<td>2.26 ± 0.49</td>
</tr>
<tr>
<td>1800</td>
<td>1.81 ± 0.46</td>
</tr>
<tr>
<td>2400</td>
<td>1.50 ± 0.37</td>
</tr>
</tbody>
</table>

Gaussian Process Model of multi-dimensional PES

Six-dimensional PES for N4

Obtained with only 240 ab initio points!

No fitting of ab initio data with analytical functions needed!

Jie Cui and RK, arXiv: 1509.06473
Obtaining scattering observables as functions of potential energy surface parameters
Gaussian Process Model – how does it work?

\[ \Omega = \Omega(\mathbf{x}) \quad \text{with} \quad \mathbf{x} = (x_1, x_2, \cdots, x_q)^\top \]

Collision energy, internal energy and PES parameters are treated on an equal footing as variable parameters.

A **10 dimensional problem**: Collision lifetimes of C6H6 with Ar

100 scattering calculations used to train the model

100 calculations enough to interpolate in 10 dimensional space

... can be used to compute observables with error bars

![Graph showing lifetime (ps) vs collision energy (cm⁻¹)]

... can be used to analyze sensitivity to individual PES parameters

Interpolating quantum results with classical trajectory calculations

Interpolating quantum results with classical trajectory calculations

Quantum calculations are expensive

Classical calculations are cheap

Can correlations between classical and quantum results be used to interpolate quantum results?

Interpolating quantum results with classical calculations

For this, we use a two-step Gaussian Process model

\[ E(\cdot) = \rho F(\cdot) + G(\cdot) + \varepsilon \]

Gaussian Process to model the classical results

Gaussian Process to model the difference between the quantum and classical results

Interpolating quantum results with classical calculations

Collision energy (cm$^{-1}$)

Cross section (a.u.)

Figure 1: GP models (solid curves) of quantum scattering cross sections (symbols) for C$_6$H$_6$-He collisions. Blue dashed line: quantum calculations are used directly to train the GP model (?). Red solid line: A combination of classical and quantum results is used in a hybrid GP model (?). The CT results stabilize the GP model predictions of the quantum calculations. The models are trained by the points represented by squares. The circles are used to illustrate the accuracy.

Red line: GP model trained by a combination of classical and quantum results

Extrapolation of dynamical observables from one molecule to another

Extrapolation of dynamical observables

Consider two molecules

benzene

benzonitrile

Extrapolation of dynamical observables

What is the effect of the $-H \rightarrow -CN$ substitution?

Can we answer this question without computing the PES for benzonitrile?

Extrapolation of dynamical observables

\[
PES_{\text{benzonitrile}} = PES_{\text{benzene}} + f(\alpha)
\]

\[
\alpha = (\alpha_1, \alpha_2, ..., \alpha_q)
\]

unknown parameters

Collisions of benzonitrile with He

Conclusions

Gaussian Process model is an excellent tool for interpolation in multi-dimensional spaces

Multiple parameters

Observable

Can be used to obtain the dependence of the observable on each of the input parameters

- Very easy to implement
- No need to fit any data with analytical functions
- Can be applied to systems with up to 100 parameters
Conclusions

Enormous potential for applications in molecular dynamics

Makes constructing (>10-50)-dimensional PES easy

Can potentially elevate quantum scattering calculations to become fully predictive (with error bars)

Can be used for the inverse scattering problem

Can be used to analyze the role of individual atoms in determining the encounter of complex molecules