A machine-learning approach for determining the best potential surface with the least number of *ab initio* points and solving the inverse scattering problem for quantum reaction dynamics

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A quantum description of a chemical reaction requires the knowledge of an accurate potential energy surface. For typical reactive systems of three atoms or more, such potential energy surfaces are constructed by computing the potential energy at thousands of points in the configuration space and fitting the computed points by an analytical function or a neural network. Computing and fitting the potential energy points is a very laborious and time-consuming task. Here, we demonstrate that accurate potential energy surfaces for quantum reactive scattering calculations can be obtained with a very small number of potential energy points and without analytical fits. We show that accurate results for the reaction probabilities in a wide range of energies can be obtained with only 30 ab initio points for the three-dimensional $H + H_2 \rightarrow H_2 + H$ reaction and 290 ab inito points for the six-dimensional $OH + H_2 \rightarrow H_2O + H$ reaction. To obtain these results, we represent the scattering observables and the potential surfaces by Gaussian Processes, which are trained by the results of rigorous quantum scattering calculations and optimized by means of Bayesian optimization producing and trying hundreds of surfaces. In this approach, the construction of the surfaces is completely automated. This work demonstrates that a combination of machine learning with quantum dynamics calculations allows one to ask new questions, such as: What is the least number of *ab initio* points sufficient to describe quantum dynamics of polyatomic systems with desired accuracy?

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Solving a quantum reaction dynamics problem requires a potential energy surface, which describes the interaction energy between all atoms participating in the reaction as a function of the atomic coordinates. Such potential energy surfaces (PES) are usually obtained by computing the potential energy of the reaction complex at a large number of relative atomic coordinates and fitting the computed energy points with some analytical function. The number of the energy points and the complexity of the analytical functions required for obtaining an accurate PES increases quickly with the number of atoms in reacting molecules. One reason for this is because one typically aims to obtain a global PES as accurately as possible in the entire range of the atomic coordinates. However, not all parts of a PES are equally important for determining the outcome of a chemical reaction. The difficulty is that it is not *a priori* known which parts of the PES are more or less important for the chemical dynamics process. Here, we propose an approach that, instead of obtaining a globally accurate PES, aims to determine the best PES, which describes most accurately specific observables in a given range of energies with the least number of potential energy points. The approach is based on Bayesian optimization [1, 2] of a two-tiered Gaussian Process model [3] giving scattering observables as functions of the positions of the *ab initio* points directly. We show that this approach produces a PES yielding an accurate description of quantum reaction probabilities with only 30 *ab initio* points for a three-dimensional (3D) reaction and about 300 points for a six-dimensional (6D) reaction system. This approach can be used for finding the PES yielding the best prediction of the experimentally measured observables, i.e. solving the inverse scattering problem of paramount importance in chemical reaction dynamics [4–6].

Any quantum dynamics calculation of molecular collision observables involves three steps: (i) computing the potential energy points for a wide range of relative atomic coordinates; (ii) fitting or interpolating these energy points to construct a PES; (iii) integrating the Schrödinger equation for the motion of the atomic nuclei on this PES. Step (i) can be very time consuming for polyatomic molecules if one requires extremely high accuracy of the potential energy calculations. Minimizing the number of potential energy calculations is therefore important for applications requiring high precision. Quantum dynamics calculations are further complicated by step (ii) above, i.e. finding the best analytical representation of the PES. While much progress has been recently made to develop efficient methods for fitting PES [7–11], almost any fitting technique is significantly laborious, requiring hours to months of research time. A more serious problem with the conventional approach to computing PES is that the energy points thus obtained are always affected by the errors of quantum chemistry calculations. These errors become more significant for heavier atoms

and are often unknown. Therefore, it would be ideal to develop an approach that bypasses quantum chemistry calculations altogether or that corrects the errors of the *ab initio* calculations. This could be achieved by deriving the empirical PES from the experimental data [4–6]. For collisions of atoms at ultracold temperatures, which are extremely sensitive to interatomic potentials, this is the only viable method of obtaining potential energy curves, which could be used in calculations for *quantitative* predictions [12]. However, it is generally unfeasible to construct accurate empirical PES from the experimental data on reaction dynamics for reaction systems of more than three atoms.

To obtain the PES yielding the best description of the experimental dynamical results, one could start with a rough PES based on a small number of ab initio calculations and systematically improve the surface by one of the following two iterative procedures:



In the first approach, one would compute and add more *ab initio* points to the PES at each iteration, thus placing an emphasis on the parts of the configuration space most relevant for the dynamics. In the second approach, one could attempt to solve the inverse scattering problem by first computing the global PES and then modifying the fit of the PES through an iterative procedure. Given that each cycle of these iterations requires refitting of the PES and that each quantum dynamics calculation (step iii above) takes minutes to hours of computer time, it is easy to see that such optimization of the PES is generally unfeasible. Here, we show that such optimization cycles can be implemented by means of a two-tiered Gaussian Process (GP) regression. In particular, we show that our approach produces a statistical model, which gives the results of (iii) as explicit functions of the locations and magnitudes of the *ab initio* energy points, eliminating step (ii) in the above optimization cycles and drastically reducing the number of quantum dynamics calculations required to construct the best surface.

GP regression is a non-parametric statistical learning technique, which, given a set of data, can be used to interpolate the data. In previous work, we used GP regression to construct PES for polyatomic molecules [13] and compared the efficiency of GP regression with another popular machine-learning method for constructing PES based on Neural Networks (NN) [14]. We found that GP regression is more efficient (i.e. requires fewer *ab initio* points) for interpolation of PES than NNs. Importantly, compared to most other fitting methods, including those based on NNs, GP regression can be much more easily automated since it does not suffer from overfitting. Most importantly for the present work, GP regression produces not only the value of the potential energy at a given point but also the prediction uncertainty. This uncertainty can be used for Bayesian optimization (described in the Supplementary Information and used below) to avoid the trapping in local minima of the function under minimization.

In the present work, we consider two chemical reactions:

$$H + H_2 \rightarrow H_2 + H \quad (1)$$

$$OH + H_2 \rightarrow H_2O + H \quad (2)$$

We compute the reaction probabilities using the time-dependent wave packet dynamics approach described in Ref. [15–18], explicitly accounting for all three (for reaction 1) or six (for reaction 2) degrees of freedom. The basis sets of the reaction dynamics calculations are chosen to ensure full convergence of the dynamical results.

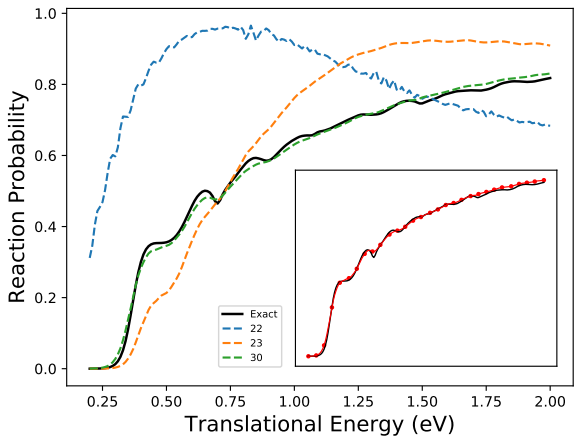
Both of these chemical reactions have been studied before [19, 21]. For reaction (1), Su et al computed the reaction probabilities using the PES from Ref. [19]. For reaction (2), Chen et al computed the reaction probabilities using the PES from Ref. [21]. In Ref. [20], the 3D PES for H_3 was constructed using an analytical fit to 8701 *ab initio* energy points. The 6D PES from Ref. [21] was constructed using NN fits to ∼17 000 *ab initio* calculations.

The first goal of this work is to illustrate that the reaction probabilities can be computed *without* analytical fits of the PES and using orders of magnitude fewer *ab initio* points. To do this, we first sample a small number of points ($n = 20$ for the 3D surface and $n = 200$ for the 6D surface) from the original PES for the reaction system under study and construct an approximate PES by GP regression, as described in our previous work [13] and with details relevant here in the Supplementary Information. We denote the GP model of the surface thus obtained by $\mathcal{G}(n)$. This model is likely to be highly inaccurate. Any quantum dynamics calculation with this surface is expected to produce highly inaccurate results.

Given $\mathcal{G}(n)$, we then ask the following question: if one *ab initio* point is added to the original sample of few points, where in the configuration space should it be added to result in the maximum improvement of the quantum dynamics results based on the surface model $\mathcal{G}(n+1)$? In principle, this question could be answered by a series of quantum dynamics calculations based on $\mathcal{G}(n+1)$ with the added point moved around the configuration space. It is obvious, however, that such an approach would be completely unfeasible as it would require about $10^{\mathcal{N}}$ dynamical calculations for each added *ab initio* point, where $\mathcal{N}$ is the dimensionality of the configuration space.

To overcome this problem, we introduce another GP, hereafter denoted by $\mathcal{F}$, representing the reaction probabilities as functions of the location of the added *ab initio* point. This GP model is trained by approximately $15 \times \mathcal{N}$

quantum dynamics calculations. We thus obtain the explicit function of the reaction probabilities $\mathcal{F}[\mathcal{G}(n+1,\boldsymbol{r})]$, where $\boldsymbol{r}$ is the $\mathcal{N}$-dimensional vector denoting the position of the added *ab initio* point in the configuration space. By training $\mathcal{F}$, we also obtain $\Delta\mathcal{F}[\mathcal{G}(n+1,\boldsymbol{r})]$, representing the uncertainty of $\mathcal{F}$ at $\boldsymbol{r}$, as the conditional standard deviation of the GP [13]. We next propose three approaches.



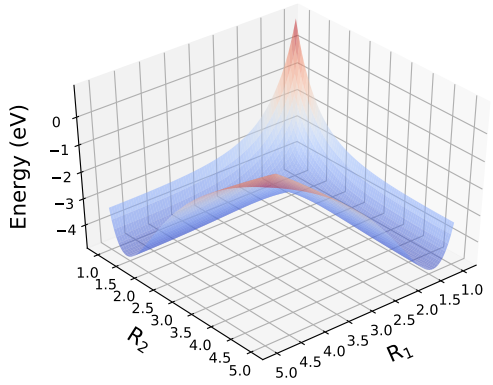


FIG. 1. Upper panel: the reaction probability for the $H_2 + H \rightarrow H + H_2$ reaction as a function of the collision energy. The black solid curve – accurate calculations from Ref. [20] based on the surface constructed with 8701 *ab initio* points. The dashed curves – calculations based on the GP PES obtained with 22 *ab initio* points (blue); 23 points (orange), 30 points (green) and 37 points (inset). The RMSE of the results with 37 points is 0.009. Lower panel: The GP model of the PES for the H_3 reaction system constructed with 30 *ab initio* points. This surface yields the quantum dynamics results shown by the green curve in the upper panel.

(1) Fitting known quantum dynamics results. If the reaction probabilities are known, either from a calculation with the full surface or from an experiment, one can minimize the difference between $\mathcal{F}[\mathcal{G}(n+1,\boldsymbol{r})]$ and the known results, to obtain the optimal value of $\boldsymbol{r}$. This minimization can then be iterated by setting $n+1 \Rightarrow n$, until n becomes large enough to produce an accurate surface $\mathcal{G}$.

In order to make such iterative minimization procedure feasible, we apply Bayesian optimization (BO) [1, 2]. For this application, instead of working directly with reaction probabilities, we train a GP model $\mathcal{R}[\mathcal{G}(n+1,\boldsymbol{r})]$, representing the root-mean-square (RMS) deviation of the reaction probabilities from the known results. The error of this model $\Delta\mathcal{R}$ allows one to apply BO to find the global minimum with minimal computation effort [1, 2]. In the current implementation, BO amounts to minimizing the following function:

$$\mathcal{R} + \kappa\Delta\mathcal{R}, \tag{3}$$

with $\kappa = 0.005$. After a local minimum of $\mathcal{R}$ is reached, the second term directs the minimization algorithm towards the parts of the configuration space where $\mathcal{R}$ is less known, thus sampling the entire configuration space in search of the global minimum [1, 2], as discussed in the Supplementary Information. With this procedure, the minimization of $\mathcal{R}$ for each value of n requires about 35 quantum dynamics calculations for H_3 and 60 calculations for OH_3.

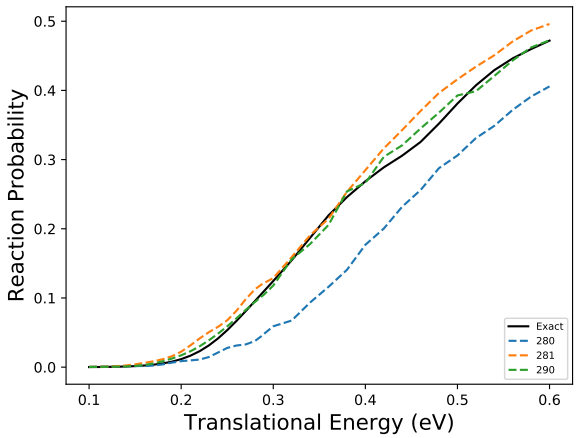


FIG. 2. The reaction probability for the $OH + H_2 \rightarrow H + H_2O$ reaction as a function of the collision energy. The black solid curve – accurate calculations from Ref. [21] based on the surface constructed with ∼17000 *ab initio* points. The dashed curves – calculations based on the GP PES obtained with 200 *ab initio* points (blue); 280 points (orange) and 290 points (green). The RMSE of the 290-point result is 0.0076.

Figure 1a illustrates the performance of this algorithm in search of the best PES for reaction (1). As can be seen, the starting model $\mathcal{G}$ of the PES based on 22 *ab initio* points produces highly inaccurate results, but the BO scheme converges to the correct PES after only 8 iterations, yielding accurate results for the reaction probabilities (green dashed line) with the GP model $\mathcal{G}$ of the

PES trained by only 30 *ab initio* points. Figure 1b shows the model $\mathcal{G}$ of the PES obtained with $n = 37$ *ab initio* points, illustrating that the GP regression produces a physical and accurate surface.

Figure 2 illustrates the performance of this algorithm for the 6D reaction (2). As the dimensionality of the configuration space increases, so does the number of points required to represent acurately the PES. Nevertheless, the BO algorithm introduced here produces accurate results for the reaction probabilities (green dashed line) with the GP model $\mathcal{G}$ of the PES trained by only 290 *ab initio* points. The root-mean-square error of the green dashed curve thus obtained is 0.0076. Note that, as any supervised learning technique, the algorithm presented here is guaranteed to become more accurate when trained by more *ab initio* points, so continuing to add more points in the surface would further improve the quantum dynamics results.

(2) Obtaining the best surface without known dynamical results. If accurate quantum dynamical results are not available, we propose to *maximize* the absolute difference of the reaction probabilities computed in two successive iterations:

$$\sqrt{\{\mathcal{F}[\mathcal{G}(n+1,\boldsymbol{r})] - \mathcal{F}[\mathcal{G}(n)]\}^2}, \qquad (4)$$

while restricting $\boldsymbol{r}$ to be within a physically reasonable range. This is justified by the observation that $\mathcal{G}(n \to \infty)$ must produce the best surface so the maximum improvement of the surface at each iteration is achieved when $\boldsymbol{r}$ corresponds to the maximum of Eq. (4).

To illustrate the validity of this assumption, we show in Figure 3 a series of computations as functions of n, showing the convergence of the iterative calculations to the accurate results (black solid curve). We emphasize that the accurate results were not used in any way in this calculation.

(3) Towards the inverse scattering problem. In the previous sections, we sampled the energy points from known *ab initio* PESs with the goal of reproducing the quantum dynamics results already obtained in calculations with the full surfaces constructed elsewhere. Here, we show that the same approach can be used to obtain a new PES that reproduces the dynamical results, which cannot be reproduced with the original surface. This is an approach one would follow to construct the best surface yielding the most accurate description of experimental results, i.e. solving the inverse scattering problem.

Here, we assume that an ensemble of energy points is known from some (not necessarily accurate) quantum chemistry calculation. As before, this ensemble of energy points will serve as a starting point for the model $\mathcal{G}$ of the PES. However, in order to allow for the improvement of the PES, we now allow the energy of each point of the PES to be a variable $\varepsilon(\boldsymbol{r})$. This variable is a function of $\boldsymbol{r}$ and allows the model $\mathcal{G}$ to sample from an interval of energies centered about the points of the initial rough

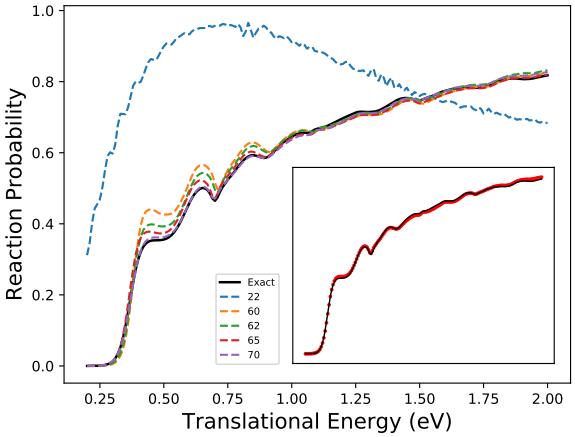


FIG. 3. The reaction probabilities for the H_2 + H → H + H_2 reaction as functions of the collision energy. The black solid curve – accurate calculations from Ref. [20]. The dashed curves – the results of iterative calculations maximizing the difference between the reaction probabilities in subsequent iterations. The black curve is **not used** for these calculations. The inset shows the agreement between the reaction probabilities (red symbols) based on the GP approach after 48 iterations (total of 70 *ab initio* points) and the exact results.

PES. The results of the scattering calculations are now used to train the model $\mathcal{F}[\mathcal{G}(n+1, \varepsilon(\boldsymbol{r}), \boldsymbol{r})]$, effectively increasing dimensionality of the variable space to $\mathcal{N}+1$. with $\mathcal{N}$ dimensions for the configuration space and the added dimension for the energy variation of the PES.

To illustrate that this approach works, we modify the exact scattering results of Figure 1 by shifting the black curve along the energy axis. This produces the dot-dashed curve in Figure 4 and the PES depicted in the lower panel of Figure 4. The dot-dashed curve extends the interval of energies, where the reaction probability is zero, which means that the PES for this reaction must have a higher reaction barrier.

The reaction probabilities given by the dot-dashed curve cannot be obtained with the original PES for H_3 because the departure of the reaction probabilities from zero is determined by the magnitude of the reaction barrier and, when the original surface is used, always occurs where the solid black curve in Figure 4 departs from zero. On the other hand, the approach introduced in this section produces the green dashed curve, yielding an accurate representation of the modified reaction probabilities if trained by 52 *modified ab initio* points. Figure 4b illustrates how this algorithm modifies the original PES in order to obtain an accurate description of the modified reaction probabilities.

Conclusion. We have shown that accurate quantum dynamics results for chemical reaction probabilities can be obtained with PES based on a very small number of *ab initio* points: 30 for the 3D H + H_2 → H_2 + H reaction

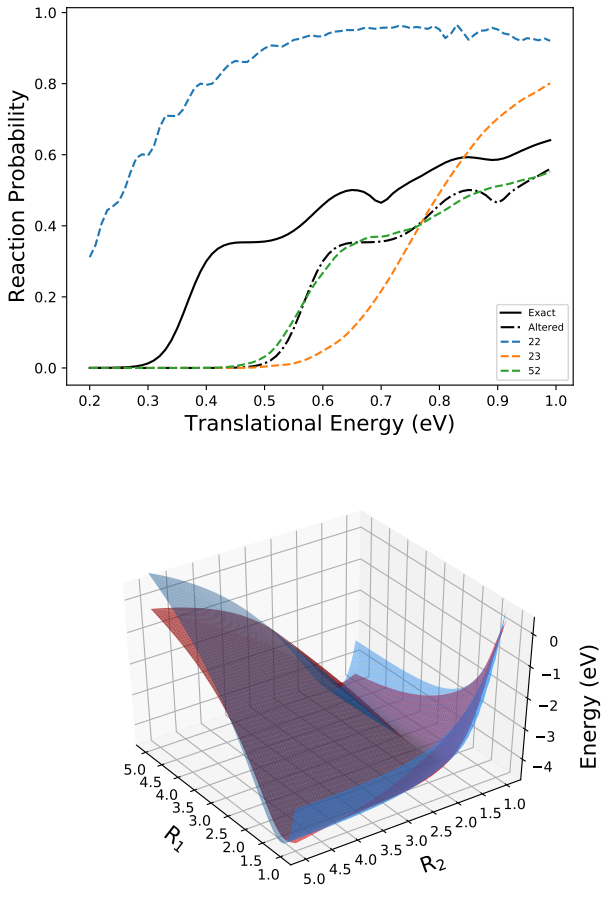


FIG. 4. Upper panel: The reaction probabilities for the modified $H_2 + H \rightarrow H + H_2$ reaction as functions of the collision energy. The black dot-dashed curve is obtained by a modification of the previous results (black solid curve) involving a translation along the energy axis. The machine-learning models are trained to obtain the PES that would describe the new reaction probabilities. The green dashed curve is a results of such training after 30 iterations, resulting in a surface constructed with 52 *ab initio* points. Lower panel: Comparison of the original PES (blue) with the new PES (red) found by the BO algorithm. The new PES yields the reaction probabilities described by the green dashed curve in the upper panel. The RMSE of the results shown by the green dashed curve is 0.016.

and 290 for the 6D $OH + H_2 \rightarrow H + H_2O$. That chemical reaction probabilities can be computed with such a small numer of *ab initio* points opens the possibility of generating highly accurate PES for quantum dynamics.

For practical applications, the locations of these few points in the configuration space can be determined as described in sections (1) or (2) above with a low-level *ab initio* method for the potential energy calculations and an approximate dynamical approach (for example, a coupled channel method with one of many decoupling approximations). Once the positions of the points are known, this small number of *ab initio* points can be calculated with extremely high precision. This makes the approach proposed here very useful for applications where high accuracy is required.

Furthermore, we have demonstrated that quantum dynamics calculations of probabilities for atom - molecule and molecule - molecule reactions can be performed in an automated procedure without explicitly fitting the PES, which allows for iterative improvement of PES, starting from statistical models of PES obtained with a very small number of energy points. The PES in this approach is represented by a Gaussian Process model, which is automatically morphed towards a better surface as the number of *ab initio* points increases. We have introduced a two-tiered GP model, which gives the reaction probabilities as explicit functions of the position of an added *ab initio* point. This allows one to apply Bayesian optimization in order to find the most optimal location for each *ab initio* point added in the sample for training the PES model.

We have also shown that the conditions on the placement of the energy points determining the molecular interactions can be relaxed to obtain the PES yielding solutions of the Schrödinger equation, which accurately represent arbitrary reaction dynamics probabilities. We believe this is an important step towards developing a general approach for obtaining the empirical PES from the experimental data on chemical reaction dynamics.

Finally, this work demonstrates that a combination of machine learning with quantum dynamics calculations allows one to ask questions generally considered unfeasible. Three examples illustrated here are: What is the least number of *ab initio* points sufficient to describe quantum dynamics of polyatomic systems with desired accuracy? Given an approximate PES, where in the configuration space should a single *ab initio* point be added to improve quantum dynamics the most? Given a specific modification of the quantum dynamics observables, what is the corresponding change of the potential energy surface?

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