Gaussian Process Regression for Geometry Optimization

Alexander Denzel\textsuperscript{1} and Johannes Kästner\textsuperscript{1}

\textit{Institute for Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany, kaestner@theochem.uni-stuttgart.de}

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We implemented a geometry optimizer based on Gaussian process regression (GPR) to find minimum structures on potential energy surfaces. We tested both a two times differentiable form of the Matérn kernel and the squared exponential kernel. The Matérn kernel performs much better. We give a detailed description of the optimization procedures. These include overshooting the step resulting from GPR in order to obtain a higher degree of interpolation vs. extrapolation. In a benchmark against the L-BFGS optimizer of the DL-FIND library on 26 test systems, we found the new optimizer to generally reduce the number of required optimization steps.
INTRODUCTION

Geometry optimization is one of the most essential tasks in theoretical chemistry. Thereby, one has to reduce the amount of evaluations of the potential energy surface (PES) as much as possible. This is because energy evaluations can be quite costly, depending on the chosen electronic structure method. Nevertheless, most geometry optimizers are gradient-based: The gradient gives a good first estimate of the direction in which one can find, for example, a minimum. Most simply one can go in the opposite direction of the gradient, following the steepest descent. More frequently employed methods are subspace methods, often using the Krylov subspace, like the conjugate gradient method.\(^1\) Second-order optimizers, like Newton’s method, converge much faster; but the necessary generation of Hessians is often too costly in quantum chemistry. Quasi-Newton methods use only gradient information, but try to build up an approximation of the inverse Hessian matrix during the optimization procedure, which results in a considerable speedup. Maybe the most popular variant of these methods is the Limited-memory Broyden–Fletcher–Goldfarb–Shanno (L-BFGS) algorithm.\(^2–8\)

The main goal in the development of new geometry optimizers is to limit the number of energy/gradient evaluations further and further. With increasing popularity of machine learning methods like neural networks\(^9\), and kernel methods\(^10–12\) in theoretical chemistry, the question arises whether these methods can be exploited to increase the efficiency of geometry optimizers. For example, the nudged elastic band method\(^13,14\) was improved recently through the kernel-based methodology of Gaussian process regression (GPR).\(^15\) Furthermore, the method was used to fit multipole moments,\(^16\) polarizable water,\(^17\) predicting kinetic energies,\(^18\) and many other chemical properties.\(^19–21\) In this paper we present a new gradient-based geometry optimizer that employs GPR to find minimum structures. For that we build a machine learned surrogate model for the PES that is improved on the fly. A similar approach was suggested previously to perform molecular dynamics calculations.\(^22\) The resulting algorithm of our optimizer is implemented in the open-source optimization library, DL-FIND\(^23\). Therefore, it may be used in ChemShell.\(^24,25\) It will be made available to the scientific community.

This paper is organized as follows. We give a short introduction to the theory of GPR in Section II A. In Section II C we explain the implementation of our new optimizer, show the
difficulties in the endeavor of using GPR for geometry optimization, and how to overcome them. We also present benchmarks to compare our GPR optimizer to the well established L-BFGS optimizer of DL-FIND in Section III.

All properties in this paper are expressed in atomic units (Bohr for positions and distances, Hartree for energies), unless other units are specified.

II. THEORY

GPR is a kernel-based machine learning technique that uses the methodology of statistical/Bayesian inference. In this section we give a short introduction to this method. A set of so called training points at which we calculated the energy, and gradient of the PES, is interpolated to infer the shape of the PES in the vicinity of these points. We will first consider GPR by only using energy values. The inclusion of gradient information will be done in Section II B. Subsequently, we discuss the applicability for geometry optimization, and present the key elements of our GPR optimizer.

A. Gaussian process regression

To clarify what a Gaussian process is, we will first define the more general term, stochastic process: A stochastic process is a collection of random variables. If we want to represent a PES as a stochastic process, we can assign every point, i.e. every molecular geometry, in the configuration space a random variable. This random variable will take on the value of an energy. Giving the joint probability distribution for every finite subset of these random variables, specifies the stochastic process. If these distributions are multivariate Gaussian distributions, the stochastic process is called a Gaussian process (GP). Given the fixed energy values at some training points, this yields a probability distribution over the energy value at any point in configuration space. From that distribution we can estimate the most probable energy value at this point, and also how likely this value is. One can use arbitrary coordinate systems for GPR, but the coordinate system will influence the resulting parameters and accuracy.

Initially we restrict ourselves to the task of interpolating a PES from some given energy values. A GP is uniquely defined by a so called prior mean function, and the covariance
The prior mean function is a guess of the PES before one has included any training points in the scheme. It can be a sophisticated estimate of the PES, but often one simply uses zero, or the constant average value of all energy values in the training set as the prior mean.

The covariance function, $k(\vec{x}, \vec{x}')$, describes the covariance between the two random variables specified by the coordinates, $\vec{x}, \vec{x}' \in \mathbb{R}^d$, of a $d$ dimensional system. These can be the $d = 3n$ Cartesian coordinates of the $n$ atoms in a molecule. We also call the covariance function kernel, although not every kernel has to be a covariance function. It is not mandatory for a kernel to describe a covariance of random variables. But in the framework of GPR one wants to keep the interpretation of the covariance; therefore, one must choose a covariance function as a kernel. A kernel is a valid covariance function if and only if it is symmetric, i.e. $k(\vec{x}, \vec{x}') = k(\vec{x}', \vec{x})$, and

$$\sum_{i=1}^{N} \sum_{j=1}^{N} c_i k(\vec{x}_i, \vec{x}_j) c_j$$

is non-negative for all $N \in \mathbb{N}$, all $\vec{x}_i, \vec{x}_j \in \mathbb{R}^d$, and all coefficients $c_k \in \mathbb{R}$ for $k = 1, ..., N$.

Here we consider only two specific covariance functions. These are stationary isotropic, i.e. they only depend on $r = |\vec{x} - \vec{x}'|$ which we will interpret as the Euclidean distance between the two points $\vec{x}$ and $\vec{x}'$. Furthermore, the closer/distant a training point is the larger/smaller its influence on the estimate of the energy should be. This influence is represented by the covariance function. Consequently, the covariance function should decrease with increasing distance, $r$.

We consider the squared exponential covariance function

$$k_{SE}(r) = \sigma_f^2 \exp \left( -\frac{r^2}{2l^2} \right)$$

and a form of the Matérn covariance function

$$k_M(r) = \sigma_f^2 \left( 1 + \sqrt{5r} \frac{r}{l} + \frac{5r^2}{3l^2} \right) \exp \left[ -\sqrt{5} \frac{r}{l} \right]$$

both of which we implemented. The functions are depicted in Fig. 1. The parameter $\sigma_f$ could be used to maintain numerical stability by scaling up the value of covariances, but it will have no influence on the analytical solution. We simply chose it to be 1 in our algorithm. The parameter $l$ defines a certain characteristic length-scale of the GP. It will have the biggest influence on the obtained interpolant since it defines the sphere of influence that a training point will have in the GP. The presented two covariance functions are especially
FIG. 1. The squared exponential covariance function from Equation (2) and the Matérn covariance function from Equation (3) with parameters $l, \sigma_f = 1$.

interesting because they guarantee a PES that is in the $C^2$ class, i.e. two times continuously differentiable. The squared exponential covariance function implies that the PES is also in the $C^\infty$ class. We usually assume this to be true in theoretical chemistry, but our tests show that the presented Matérn covariance function yields better results. This is because the high constraint that the smoothness of $k_{SE}$ implies on the GP leads to overshooting and oscillation, especially in the close extrapolation regime. Additionally, in our experiments we found that one should choose a larger $l$ for the Matérn kernel than for the squared exponential kernel.

To model a PES with a GP we take a training set including $N$ configurations of the molecule $\vec{x}_1, \vec{x}_2, ..., \vec{x}_N$, and the respective energies at these points $E_1, E_2, ..., E_N$, so that the calculated electronic structure yields the energy $E_m$ given the configuration $\vec{x}_m$ of the atoms. Note that the points $E_m$ are the energy values within the used electronic structure method. Consequently, the energies may be noisy. In GPR one assumes a normally distributed noise on the values $E_m$ with its variance given by a parameter $\sigma_e^2$.

We also introduce the prior mean function $E_{\text{prior}}(\vec{x})$ which is our estimate of the PES before we have included any training points. Consequently, GPR only learns the error of $E_{\text{prior}}(\vec{x})$ rather than the PES directly. The prior mean function can also be considered as a bias that mostly affects the regression scheme away from the training points.

A GP yields a posterior mean function $E(\vec{x})$, which is the most probable value of the energy at the position $\vec{x}$ in the stochastic GP framework; therefore, also the prediction of
the GPR-PES. It is given by

\[ E(\vec{x}) = \sum_{n=1}^{N} w_n k(\vec{x}, \vec{x}_n) + E_{\text{prior}}(\vec{x}) \]  

(4)

in which \( \vec{w} = (w_1 \ w_2 \ ... \ w_N)^T \) is the solution of the linear system

\[ \sum_{n=1}^{N} K_{mn} w_n = E_m - E_{\text{prior}}(\vec{x}_m) \]  

(5)

for all \( m = 1, 2, ..., N \) and

\[ K_{mn} = k(\vec{x}_m, \vec{x}_n) + \sigma_e^2 \delta_{mn} \]  

(6)

are the entries of the so called covariance matrix \( K \) which contains the covariances between the training data and \( \delta_{mn} \) which is the Kronecker delta. The parameter \( \sigma_e \) arises from the already mentioned, normally distributed noise in the \( E_m \) with variance \( \sigma_e^2 \). If we use a kernel that is a covariance function, the covariance matrix \( K \) is positive semi-definite, which follows from the properties of the covariance as a positive semi-definite symmetric bilinear form. Note that the computationally most demanding step is to solve the linear system of Equation (5). In our code this is carried out via a standard Cholesky decomposition. The computational effort to solve such a linear system scales cubically with the number of training points.

B. Including derivative information

Derivation is a linear operation. Therefore, the derivative of a GP is again a GP.\(^{27}\) Random variables in the stochastic process can, therefore, also take on the values of a derivative of the energy instead of the energy itself. Let us consider a Gaussian process with an arbitrary kernel function, \( k(\vec{x}, \vec{x}_n) \). The interpolant (in our case for example the energy, \( E \)) is calculated according to Equation (4). Since the kernel function is the only dependency on \( \vec{x} \) we can use learned derivative information in GPR. For example, the expression

\[ \tilde{E}^i(\vec{x}) = \sum_{n=1}^{N} v_n^i \frac{dk(\vec{x}, \vec{x}_n)}{dx_n^i} \]  

(7)

is also the prediction of a Gaussian process with a different covariance function \( \frac{dk(\vec{x}, \vec{x}_n)}{dx_n^i} \), that exploits information about the derivative at the training point \( \vec{x}_n \) for inference. We use the notation \( \frac{d}{dx_n^i} \) as the derivative with respect to the variable \( \vec{x}_n \) in the direction of the
unit vector in the \( i \)-th dimension. Combining learned energies and gradients, the inferred GPR-PES is

\[
E(\vec{x}) = \sum_{n=1}^{N} w_n k(\vec{x}, \vec{x}_n) + \sum_{n=1}^{N} \sum_{i=1}^{d} v_n^i \frac{d}{dx_n^i} k(\vec{x}, \vec{x}_n) + E_{\text{prior}}(\vec{x})
\]

(8)

with new parameters \( v_n^i \). Our GPR optimizer is based on this equation. The \( k \)-th element of the gradient on this GPR-PES can also be obtained analytically.

\[
\frac{d}{dx^k} E(\vec{x}) = \sum_{n=1}^{N} w_n \frac{d}{dx^k} k(\vec{x}, \vec{x}_n) + \sum_{n=1}^{N} \sum_{i=1}^{d} v_n^i \frac{d^2}{dx^k dx_n^i} k(\vec{x}, \vec{x}_n)
\]

\[
+ \frac{d}{dx^k} E_{\text{prior}}(\vec{x})
\]

(9)

The weights \( w_n \) and \( v_n^i \) will be obtained by solving a larger linear system with a covariance matrix of the following form.

\[
K = \begin{bmatrix}
k(\vec{x}_m, \vec{x}_n) + \sigma_e^2 \delta_{mn} & \frac{d}{dx_m^i} k(\vec{x}_m, \vec{x}_n) \\
\frac{d}{dx_m^i} k(\vec{x}_m, \vec{x}_n) & \frac{d^2}{dx_m^i dx_n^j} k(\vec{x}_m, \vec{x}_n) + \sigma_e^2 \delta_{mn} \delta_{ij}
\end{bmatrix}
\]

(10)

The parameter \( \sigma_g \) describes the variance of the assumed normally distributed noise on the input gradient entries. This is equivalent to \( \sigma_e \) for the energy values. The linear system of Equation (5) will become

\[
K \begin{bmatrix} w_1 \\ \vdots \\ w_N \\ v_1 \\ \vdots \\ v_N \end{bmatrix} = \begin{bmatrix} E_1 \\ \vdots \\ E_N \\ \vec{g}_1 \\ \vdots \\ \vec{g}_N \end{bmatrix} - \begin{bmatrix} E_{\text{prior}}(\vec{x}_1) \\ \vdots \\ E_{\text{prior}}(\vec{x}_N) \\ \vec{\nabla} E_{\text{prior}}(\vec{x}) |_{\vec{x} = \vec{x}_1} \\ \vdots \\ \vec{\nabla} E_{\text{prior}}(\vec{x}) |_{\vec{x} = \vec{x}_N} \end{bmatrix}
\]

(11)

in which \( E_m \) is the energy and \( \vec{g}_m \) is the gradient at point \( \vec{x}_m \), and \( \vec{\nabla} E_{\text{prior}}(\vec{x}) |_{\vec{x} = \vec{x}_m} \) is the gradient of the prior mean function at the point \( \vec{x}_m \), and \( \vec{v}_m = [v_1^i \ldots v_N^i]^T \) contains the coefficients from above. Note that the covariance matrix in this linear system has the size \( N(d+1) \times N(d+1) \). Therefore, the required CPU time to solve Equation (11) formally scales with \( O([N(d+1)]^3) \), if we solve the linear system exactly. To overcome this obstacle we will introduce an approach that uses multiple GP layers to bring the scaling down, see Section II C 4. Iterative solution of the linear system, does not easily give a good enough solution since the covariance matrix is not necessarily diagonally dominant. To see how to use GPR with second order derivatives we provide additional information in the supplementary material.
The GPR optimization

The basic idea of our GPR optimizer is to use already obtained energy and gradient information of the PES to build a GP surrogate for it, the GPR-PES. Then we search for a minimum on this GPR-PES to estimate a minimum on the real PES. This process is repeated until we consider the optimizer to be converged. So far, this is similar to other optimizers with different surrogate models based on Taylor expansions instead of GPR.\(^{28,29}\)

We first explain the optimization procedure in detail. In Section II C 2 we show an example for the resulting algorithm in one dimension.

In order to define convergence for our optimizer we use the standard convergence criteria of DL-FIND for the step size and the gradient: The Euclidean norm of the step vector, and the gradient vector, as well as the maximum entry of both vectors have to drop below a certain threshold. The step vector is simply the vector that points from the last estimate to the new estimate of the minimum, and describes the proceeding of the optimization run. Given a single tolerance value, \(\delta\), the convergence criteria in DL-FIND are

\[
\begin{align*}
\max_i (g_i) &< \delta_{\max(g)} := \delta \\
\frac{|\vec{g}|}{d} &< \delta_{|\vec{g}|} := \frac{2}{3}\delta \\
\max_i (s_i) &< \delta_{\max(s)} := 4\delta \\
\frac{|\vec{s}|}{d} &< \delta_{|\vec{s}|} := \frac{8}{3}\delta
\end{align*}
\]

where \(|\vec{g}|\) (\(|\vec{s}|\)) is the Euclidean norm of the gradient (step vector), and \(\max_i (g_i)\) (\(\max_i (s_i)\)) its maximum entry. If these four criteria are fulfilled, the algorithm is considered to be converged. Note that convergence is tested for the gradient on the underlying ab-initio data rather than the GPR fit.

In the first step the GPR-PES is built by the energy, and the gradient at one single starting point \(\vec{x}_0\). In later steps we use all the obtained energies, and gradients to build the GPR-PES. We then find the minimum \(\vec{x}_N^{\text{GPRmin}}\) on our GPR-PES with the already obtained \(N\) training points. The GPR-PES is very cheap to evaluate, especially compared to the evaluation of the PES via electronic structure calculations. Therefore, the search for \(\vec{x}_N^{\text{GPRmin}}\) can be carried out very fast with an arbitrary optimization method. In our case we use a L-BFGS optimizer\(^{7}\) for that matter. We usually start the search for a minimum on the
GPR-PES at the last training point. If the direction along the optimization is changed by more than a 90 degree angle, or if the absolute value of the gradient gets larger, we search for a minimum, starting at each of the 10% of training points with lowest energies. The lowest minimum found is the next \( \vec{x}_{N}^{\text{GPmin}} \). The obvious optimization step \( \vec{s}_{N}' \) after one has obtained \( N \geq 1 \) training points would be to take the step vector to position \( \vec{x}_{N}^{\text{GPmin}} \) as the next guess for our minimum on the PES.

\[
\vec{s}_{N}' = \vec{x}_{N}^{\text{GPmin}} - \vec{x}_{N-1}
\]  

(16)

The first training point \( \vec{x}_0 \) is defined as the starting point of the optimization, and \( \vec{x}_{N-1} \) is then the last estimate of the PES minimum when \( N - 1 \) additional training points were obtained. This yields already a functional optimizer, but its performance is rather poor. This arises from a well known problem: GPR and other machine learning techniques are highly capable in interpolation, but often perform quite poorly in extrapolation. An iterative optimization as described above is obviously largely based on extrapolation. To represent the problem in a way that we mostly interpolate, rather than to extrapolate, we overshoot the estimated minimum on purpose: The first optimization step is carried out as described by Equation (16), and we define the first step as \( \vec{s}_1 = \vec{s}_1' \). From the second step onward, however, we determine the cosine of the angle between the last optimization step \( \vec{s}_{N-1}' \) and the estimated new step \( \vec{s}_N' \)

\[
\alpha_N = \frac{\langle \vec{s}_{N-1}', \vec{s}_N' \rangle}{||\vec{s}_{N-1}'|| ||\vec{s}_N'||}
\]  

(17)

with \( \langle \cdot, \cdot \rangle \) being the Euclidean dot product. The closer \( \alpha_N \) is to 1, the smaller the angle becomes. If \( \alpha_N \) is smaller than 0, the direction of the optimization is changed by more than a 90 degree angle. If it is close to \(-1\), the direction is completely inverted. As soon as

\[
\alpha_N > 0.9
\]  

(18)

we scale up the initially estimated \( \vec{s}_N' \) to obtain the next optimization step

\[
\vec{s}_N = \lambda(\alpha_N)\vec{s}_N'
\]  

(19)

for \( N \geq 2 \) and introduce the scaling factor

\[
\lambda(\alpha_N) = 1 + (\lambda_{\text{max}} - 1) \left( \frac{\alpha_N - 0.9}{1 - 0.9} \right)^4
\]  

(20)
FIG. 2. The scaling factor for overshooting the step, see Equation (20), with \( \lambda_{\text{max}} = 10 \) is plotted against \( \alpha_N \).

with a maximum scaling factor of \( \lambda_{\text{max}} \) so that \( 1 \leq \lambda(\alpha_N) \leq \lambda_{\text{max}} \). This scaling factor is depicted in Fig. 2.

To avoid large overshooting in the area around the actual minimum on the PES we only apply this scaling factor, if the estimated step \( \vec{s}'_N \) does not satisfy the convergence criteria of the maximum step entry in Equation (14). Close to convergence we also limit the maximum scaling factor through

\[
\lambda_{\text{max}} = \left( 1 + \tanh \left( \beta^2 - 1 \right) \right) \frac{\tilde{\lambda}_{\text{max}} - 1}{2} + 1 \tag{21}
\]

in which

\[
\beta = \max_i (s'_i) / \delta_{\text{max(s)}} \tag{22}
\]

is the ratio of the maximum entry of \( \vec{s}' \) and \( \delta_{\text{max(s)}} \), the convergence criterion for the maximum step entry from Equation (14). The variable \( \beta \) indicates how close the algorithm is to convergence with respect to the maximum entry of the step vector. If \( \beta \leq 1 \), the convergence criterion is met. No scaling will occur in this region. We plot \( \lambda_{\text{max}} \) against \( \beta \) in Fig. 3.

To some extent, the limitation of the highest possible scaling factor \( \tilde{\lambda}_{\text{max}} \) to \( \lambda_{\text{max}} \) via Equation (21) is intended to guarantee a smooth transition into the region of convergence. However, keeping at least \( \tilde{\lambda}_{\text{max}}/2 \) at the point where the convergence criterion is met does not seem to hinder convergence. Consequently, we keep \( \lambda_{\text{max}} \approx \tilde{\lambda}_{\text{max}}/2 \) in the area of convergence. The value of \( \tilde{\lambda}_{\text{max}} \) is chosen to be 5 at the beginning of the optimization. It is increased by 5\%, if we observe that we do more than one overshooting according to Equation (20) in a row, i.e. that the criteria of Equation (18) are satisfied for two consecutive steps in the optimization procedure. At the end of each optimization step, the estimated
FIG. 3. The limitation of the scaling factor, see Equation (21), is plotted against the variable $\beta$, see Equation (22). The upper limit of $\lambda_{\text{max}}$ is set to $\tilde{\lambda}_{\text{max}} = 10$.

step size $|\vec{s}_N|$ is limited by the maximum step size $s_{\text{max}}$ we set externally for the optimization procedure.

1. Separate dimension overshooting

In several tests we observed that usually only a few dimensions seem to converge very slowly, while the convergence in the other dimensions is already accomplished. This is especially the case in longer optimization runs. We assume that the reason for this may be that we use only one length scale parameter $l$ in Equation (3), and do not assume different length scales for different dimensions. On the other hand, it is not easy to find suitable parameters for every dimension, and introducing more parameters lets the optimizer become more prone to chance. Instead we make use of the fact that we can overshoot the correct solution to our optimization problem quite a bit, and introduce an additional separate dimension overshooting: We consider every dimension independently of the others. If we observe that the optimizer has monotonically changed the value of the coordinate in this dimension over the last 20 optimization steps, we build up a one dimensional GP to represent the optimization along this single coordinate. It approximates the value of the corresponding coordinate with respect to the number of steps taken: The position of the training points for this GP is simply the number of the step along the optimization procedure. The value that is interpolated is the value of the considered coordinate at that step. On this GP we search for the next maximum/minimum assuming it could be a good guess for the dimension’s value.
at the real minimum of the PES. Thereby, we ignore coupling of the different coordinates. To give the optimization procedure time to explore the omitted coupling, we suspend the separate dimension overshooting for 20 optimization steps after we performed it. To restrict the overshooting to a reasonable regime, we limit the separate dimension overshooting by a factor of 4 compared to the originally estimated step without any overshooting. Furthermore, we only apply the separate dimension overshooting, if it suggests higher overshooting than the scaling factor in Equation (20), and if the convergence criterion for the maximum step entry from Equation (14) is not satisfied. Also this overshooting procedure is finally limited by the maximum step $s_{\text{max}}$ allowed for the optimization procedure.

2. The algorithm in one dimension

We explain the overall optimization process in a simple one-dimensional example PES $E(x)$ illustrated in Fig. 4.

- **Step 1**: At the start, the GPR-PES is built with the energy and gradient information from the starting point. We find the minimum on the GPR-PES shown by the star symbol. This is our next estimate for the PES minimum, and we calculate the energy and gradient of the PES at that position, indicated by the arrow.

- **Step 2**: After evaluating the energy and gradient at the estimate from the last step, we build up the next GPR-PES with now two training points. The new minimum of the GPR-PES, however, leads us in the same direction as in the last step. Therefore, we scale up the estimated step size in the overshooting procedures described above. The overshooting to a more distant point is indicated by the tilted arrow, which points to the next estimate at which we calculate the energy and the gradient. If the estimated step size is now larger than the externally set maximum step size $s_{\text{max}}$, we scale the step down to a step size of $s_{\text{max}}$.

- **Step 3**: The minimum on the new GPR-PES with now three training points, leads to a step in the opposite direction of the last step. Therefore, no overshooting is performed.
Step 4: The next estimate for the minimum is close enough to the last estimated minimum, so the convergence criteria for the step size are satisfied. Calculating the gradient at estimate 4, will also show that the convergence criteria for the gradient are satisfied. The optimizer is completely converged.

FIG. 4. The basic idea of the GPR optimizer in the case of a Lennard–Jones potential as a simple example for a PES.

The limitation of the step size, called $s_{\text{max}}$, lies roughly between 0.5 and 1 a.u. This prevents the overshooting process from shooting in a region outside of the domain in which the chosen electronic structure calculations are valid.

3. Parameters

For all results presented in this paper we used the Matérn covariance function of Equation (3). We chose the parameter $\sigma_f = 1$ since it does not influence the result. The only other parameter in the covariance function is $l$. We chose $l = 20$ at the beginning of the optimization. Then we chose a dynamic approach: Every step along the optimization on which the gradient has become larger, instead of smaller, we increase $1/l^2$ by 10% of its
This leads to a shrinking characteristic length scale along the optimization, which means that the steps predicted by the GPR optimizer will become smaller, the training points closer. A smaller characteristic length scale is also advisable towards the end of an optimization procedure, since we often need more careful steps as we approach the minimum. The noise parameters $\sigma_e$ and $\sigma_g$, see equations (6) and (10), are chosen to be $\sigma_e = \sigma_g = 10^{-7}$ which is a compromise between the smallest possible value, and numerical stability we found by using cross validation on several systems. It may change for different electronic structure methods or codes. We also found that the Matérn covariance function is rather insensitive to changes of the $\sigma$ parameters. One can also use the maximum likelihood principle\textsuperscript{27} to optimize the parameters. Still, in our test cases we found it to be less useful than cross validation, and less successful than our dynamic approach.

We also include an offset in the form of the prior mean function, see Equation (4). Away from any training point the GPR-PES will slowly converge to that value. This is a fact we exploit in our optimizer: The prior mean is chosen to be a constant that is much higher than the energy values observed in the system. This will restrict the optimization to a reasonable area around the observed training points, and guarantees that a minimum on the GPR-PES can be found at any time. The prior mean for our minimization procedure is chosen to be

$$E_{\text{mean}} = \max_i E_i + 10$$

The value of $E_{\text{mean}}$ can change with an increasing amount of training points and is reevaluated, if new training points are added to the GPR-PES.

Just like in L-BFGS optimizations, the maximum step size $s_{\text{max}}$ is the only parameter which has to be specified by the user. The parameters in the overshooting schemes were chosen to provide reasonable performance on the Baker test set we show in Section III. The sensitivity of the performance on these parameters is small.

4. **Multi-level GPR**

In GPR one needs to solve a linear system with the covariance matrix. If we include gradient information, the size of the covariance matrix is approximately $Nd \times Nd$, see Equation (10). $N$ is the number of points at which we have gradient and energy information, $d$
The number of degrees of freedom of the system. The size of the matrix results from the fact that every entry of the gradient is considered to be a new training point. The solution of the linear system with the covariance matrix is carried out via Cholesky decomposition. Therefore, the required CPU time to solve the linear system scales with \( O(N^3d^3) \). In high dimensional systems and long optimization runs this can become computationally more demanding than density functional theory (DFT) calculations. To overcome this problem one can restrict the GPR to, e.g., the last 50 training points which leads to a formal scaling of \( O(d^3) \). That is independent of the length of the optimization history.

We found that it is more efficient to use the neglected training points to build up another GP. The other training points are then used to minimize the error of that GP. In our code we build up a hierarchical multi-level GP: As soon as the number of training points reaches \( N_{\text{max}} \), we take the oldest \( m \) of them to build a GP, called \( GP_1 \). The remaining \( N_{\text{max}} - m \) elements of the training set are used to learn the error of \( GP_1 \) to give a new surface \( GP_0 \). We use \( GP_1 \) as the prior mean function for \( GP_0 \). Along the optimization procedure new training points are added to \( GP_0 \). As soon as their number reaches \( N_{\text{max}} \) again we rename \( GP_1 \) to \( GP_2 \). We use the \( m \) oldest training points of \( GP_2 \) to build up a new \( GP_1 \), that uses \( GP_2 \) as its prior mean function. The remaining \( N_{\text{max}} - m \) training points of \( GP_0 \) are used to build a new surface \( GP_0 \), that uses \( GP_1 \) as its prior mean function. This process is repeated by increasing the number of levels as soon as the number of training points in \( GP_0 \) reaches \( N_{\text{max}} \). The last \( GP_q \), with the highest \( q \), uses the usual offset of Equation (23). Only the \( E_i \) included in this \( GP_q \) are used to calculate this offset.

The multi-level approach decreases the accuracy of the regression compared to full GPR near the training points that are not included in \( GP_0 \). However, the most relevant information for an optimizer is most likely encoded in the last few training points which are still included in \( GP_0 \). We found it to be sufficient to set \( N_{\text{max}} = 60 \), and \( m = 10 \), to keep relatively good performance whilst requiring much lower computational cost than the DFT method. We set these values in all the presented test cases in this paper.
III. APPLICATIONS

We apply our optimization algorithm to several test cases. We chose a set of 25 test systems suggested by Baker.\textsuperscript{30} The starting points of the optimization were chosen following Ref. 30 close to a transition state on the Hartree–Fock level. In contrast to Ref. 30 we use the semi-empirical AM1\textsuperscript{31} method for the electronic structure calculations. The resulting minimum structures are shown in Fig. 5. These tests are in the following referred to with IDs 1 to 25. Note that the structures with ID 23 and 24 start at different geometries, but end up in the same minimum.

Additionally, we set up a more realistic test case: We use a part of a previously investigated molybdenum amidato bisalkyl alkylidyne complex\textsuperscript{32} that includes 41 atoms, see Fig. 6. Electronic structure calculations are carried out with the BP86 functional\textsuperscript{33,34} in the def2-SVP basis set.\textsuperscript{35} We give the optimization runs on this molybdenum system the IDs 26, 27, and 28. We chose a different starting point for the optimization in run 27 than in the other two. Runs 26 and 28 begin at the same starting point and only differ in the chosen convergence criteria: The convergence criteria were chosen according to equations (12 – 15) with $\delta = 4.5 \cdot 10^{-4}$ for the run on the molybdenum system with IDs 26 and 27. We chose
FIG. 6. The minimum structure of the molybdenum amidato bisalkyl alkylidyne complex found by our GPR optimizer in the run with ID 26. Molybdenum is depicted in golden brown, nitrogen in blue, carbon in grey and hydrogen in white.

the stricter criterion $\delta = 1 \cdot 10^{-4}$ for the run on the molybdenum system with ID 28, and we set $\delta = 3 \cdot 10^{-4}$ for the Baker systems with IDs 1 to 25.

The maximum step size was set to 5 $a.u.$ (never reached) for L-BFGS since it yields the best performance like that. The maximum step size for our GPR optimizer was set to 0.5 $a.u.$ for the Baker systems, and 1 $a.u.$ for the molybdenum system runs. The number of steps in the L-BFGS memory is chosen to be 50 for the molybdenum system, and equal to the number of dimensions in the Baker systems. The L-BFGS optimizer in DL-FIND employs a variable trust radius based on energy decrease.$^{23}$

We performed all the presented calculations in Cartesian coordinates. The GPR optimizer is in principle able to handle other coordinates, but the adaptations of the algorithm needed to perform well with these is not trivial. Especially the optimal length scale parameter $l$ may be different in every dimension. Our implementation is not able to do that yet.
Comparison to L-BFGS

Rigorously proving the convergence order of our optimizer is rather difficult, if not impossible. Instead we present a comparison to the super-linearly converging L-BFGS algorithm that is implemented in DL-FIND. In table I we show a comparison between the GPR and the L-BFGS optimizer in DL-FIND for the different test systems. We compare the number of steps both optimizers take until convergence and we compare the obtained minima according to their energy and the RMSD value of their geometries. In the supplementary material we show a further comparison to the steepest descent and the conjugate gradient methods, which perform much worse than L-BFGS. We also show the optimization runs on the Baker test set using DFT instead of AM1.

The GPR optimizer yields quite good results. In most cases it is faster than the L-BFGS optimizer. Some qualitative differences can be observed. In the case of system 16 the GPR optimizer finds a different minimum than L-BFGS. One of these two different minima represents the reactant, the other one the product of this system. This happens because the optimization starts in the vicinity of the transition structure. System 3 and 9 show high RMSD values between the structures while their energy differences vanish: These are bimolecular reactions in which the minimum region of the separated molecules is flat using AM1. In the case of the molybdenum system with ID 26 and 27 the GPR optimizer finds a minimum that is higher in energy, and a little closer to the starting point. The minima look similar with slightly different torsions in the aliphatic groups. For the molybdenum system with ID 28 we applied stricter convergence criteria: the GPR optimizer is significantly faster, but again finds a minimum that is a little higher in energy. Towards the end of the optimization the convergence of L-BFGS is mostly hindered by larger predicted step sizes. All obtained minima look chemically plausible and (except for system 16) similar comparing the results of L-BFGS and the GPR optimizer.

For some of the test cases, we show the convergence rates as the Euclidean norm of the gradient versus the number of steps taken: We depict the convergence rate of four of the biggest test cases from the Baker test set in Fig. 7. We also show the convergence rates of the runs on the molybdenum system with IDs 26 and 27, that have two different starting
TABLE I. A comparison of the L-BFGS and the GPR optimizer in our test systems, sorted by the number of dimensions $d$ in the system. The number of steps required until convergence is given for L-BFGS and the GPR optimizer, $\Delta$steps is their difference, $\Delta$energy is the energy difference between the minima in Hartree, RMSD denotes the root-mean-square deviation of their atomic positions in Ång.

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FIG. 7. The Euclidean norm of the gradient with respect to the number of steps taken by the L-BFGS and the GPR optimizer in 4 of the biggest systems from the Baker test set.

points in Fig. 8. The higher fluctuations of the GPR optimizer compared to the L-BFGS optimizer are due to the overshooting procedures, see Sections II C and II C 1. They are not necessarily a sign for bad performance of the algorithm. The high overshooting is intentional, and decreases the overall number of steps needed in almost all cases. The convergence criteria concerning the step size are usually fulfilled later than the ones concerning the gradient. This explains the large amount of steps that L-BFGS uses in the molybdenum system, although, the convergence criterion for the gradients are already met. Also the L-BFGS optimizer discards a lot of steps when the energy increases along the optimization, especially at the end. This can be seen when the norm of the gradient stays constant for some time: No actual step is taken. The discarding of steps is not necessary for the GPR optimizer.

B. Timing

The GPR optimizer is more demanding in terms of computational power per step. The Cholesky decomposition of the matrix scales with the third power of the dimension, and the amount of training points. We formally eliminate the scaling with respect to the number of training points by the GPR multi-level approach, see Section II C 4. Nevertheless, the optimizer takes more time per step than the L-BFGS optimizer. This can best be seen in our biggest test case, the molybdenum system (IDs 26 to 28): The GPR optimizer took about
10% of the overall computational time. The L-BFGS optimizer procedures take around 1%. Omitting the multi-level approach will result in only slightly faster convergence of the GPR optimizer. This is in terms of number of optimization steps. Nevertheless, the time needed for the optimizer procedures will be almost equal to the time consumption of the DFT calculations. The additional overhead of approximately 9% using the multi-level approach is easily compensated by the faster convergence in our test case. In the run with ID 26, the GPR optimization took around 48 minutes in total, while the L-BFGS optimization took around 88 minutes. The runs were all performed on an Intel i5-4570 quad-core CPU. If we chose more accurate electronic structure methods than the DFT method we used here, and look at correspondingly smaller systems, we expect only a negligible overhead from the GPR optimizer.

IV. DISCUSSION

We presented an algorithm to use GPR to find minima on the PES using Cartesian coordinates. Different coordinate systems that intrinsically incorporate translational and rotational invariance, and invariance to permutations of identical atoms can improve the efficiency of machine learning methods.\textsuperscript{9,11,12,20} The incorporation of those would possibly require different characteristic length scale in the covariance function for the different coor-
We prefer Cartesian coordinates because of their simplicity.

We tested only two covariance functions for our algorithm. Combinations of those, or inclusion of other covariance functions might improve the efficiency of the algorithm.

Generally, it is known that machine learning methods like GPR are best in learning small errors of the energy between different methods, rather than learning the exact energy directly. Therefore, one could use a fast estimate of the PES using e.g. a simple force field method as a prior of the GPR just like we did with the higher levels in our multi-level approach. This could further improve the performance, and the additional overhead may pay off for high-precision calculations.

In higher dimensional systems GPR is less promising since the covariance matrix can become sparse. In our investigated systems no such indications were found. Even in the 123-dimensional molybdenum system GPR performs well. On the other hand, due to the high scaling of its computational effort with the number of dimensions GPR is recommended mainly for small systems in any case. Furthermore, the fixed number of 60 training points in the last level of our multi-level approach may have to be increased for larger systems.

The overall result of our benchmark indicates a good performance of the new GPR optimizer. The big advantage of the GPR optimizer compared to traditional optimizers is that it can do comparably large steps: If a step overshoots the minimum, or even yields a higher energy structure than before, this generally improves the performance of the optimizer. It can easily use the obtained information from an overestimated step to build a more conservative step later. This results in the possibility of doing large steps without compromising the efficiency of the optimizer. The possibility to do large steps like this can speed up the optimization procedure as we have seen in our largest test case.

V. CONCLUSIONS

We presented a new optimizer for finding minima on potential energy surfaces using GPR. It outperforms the super-linearly converging L-BFGS optimizer. Using only one external parameter, a step size limit, it is easy to apply. It is included in DL-FIND and hence, usable in ChemShell. We will further investigate possibilities for improvement, some mentioned in Section IV, and try to extend the optimizer to saddle point searches.
Supporting Information: Derivations for including second derivatives, results of the Baker set for conjugate gradient and steepest descent optimizers, as well as with DFT, are provided as supporting information.

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Squared exponential
Matérn

$k(r/l)$

$r/l$

0 0.5 1 1.5 2 2.5 3