Minima Hopping Accelerated Path Search: An Efficient Method for Finding Complex Chemical Reaction Pathways

Bastian Schaefer, Stephan Mohr, Maximilian Amsler, and Stefan Goedecker

1) Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland
2) Laboratoire de simulation atomistique (L$	ext{Sim}$), SP2M, UMR E CEA/UJF-Grenoble 1, INAC, F-38054 Grenoble, France

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Based on Minima Hopping and its capabilities of exploring potential energy surfaces we have developed Minima Hopping Accelerated Path Search (MHAPS) which is a novel algorithm for efficiently finding the reaction paths of complex chemical reactions by sampling collections of energetically low-lying minima and first order saddle points of potential energy surfaces. For this new reaction path search method we developed a highly reliable approach for computing saddle points which is based on the idea of a bar rolling downwards the potential energy landscape. For Lennard-Jones benchmark systems, Minima Hopping Accelerated Path Search was compared to a known mode-following based approach for sampling collections of minima and first order transition states. Although we used a stabilized mode-following technique that reliably allows to follow distinct directions that are defined by the eigenvectors of the Hessian matrix, we observed that Minima Hopping Accelerated Path Search is far superior in finding lowest-barrier reaction paths. By applying Minima Hopping Accelerated Path Search to 75-atom and 102-atom Lennard Jones systems we found previously unknown reaction paths that connect the two lowest minima of the 75-atom system. Compared to previously known paths, the new paths contain a smaller number of intermediate transition states and the highest energy along the paths is significantly lower in energy. In case of the 102-atom system Minima Hopping Accelerated Path Search found a previously unknown energetically low-lying funnel.

I. INTRODUCTION

The exploration of potential energy landscapes requires two important aspects to be considered. On the one hand, the geometries of stable ground-states are of large importance. For this reason powerful global optimization methods such as several genetic algorithms, Basin Hopping and Minima Hopping (MH) have been developed during the last two decades. On the other hand, processes like protein folding, catalysis, chemical reactions in solutions and surfaces or the formation of stable phases in solids often force the reacting systems to undergo rarely occurring complex transformations between long-lived states. Actively stabilizing or destabilizing long-lived states by inhibiting or promoting reaction paths responsible for certain events allows to synthesize new materials or substances with specifically tailored properties. Unfortunately, the sole knowledge of the global minimum and a collection of local minima provided by global optimization methods is not sufficient for being able to influence reaction paths specifically. Instead, an accurate knowledge of the atomistic details of reaction paths is needed. For this reason, in addition to local minima also transition states and the information which minima are connected by which transition states are of great importance. As soon as this data is available, various methods like the master equation approach, the discrete path formulation of Discrete Paths Sampling or Kinetic Monte Carlo allow to compute dynamic properties. Using graph-theoretic methods it is possible to extract reaction pathways from databases containing the just mentioned data. Since paths with energetically high barriers have a vanishingly small contribution to properties like rate constants, it is important not to investigate just any paths but to sample preferably those that have low overall barriers.

As shown by existing methods, such sampling can in principle be accomplished by means of one-sided saddle searches coupled to an energy feedback which introduces a driving force towards the low energy region of the system. However, in a study by Doye et al. a systematic sampling approach was considered not to be able to find at least one single path connecting both lowest lying minima of the 75-atom Lennard-Jones system within a feasible computation time. Instead of using a completely unbiased search, they had to use a method which optimizes an initially given input path. The method of constructing an initial path which connects two states of interest and subsequently finding lower energy paths by perturbing the initial path has been used and refined in various ways in later studies conducted by Wales et al.. Apparently, this approach seems to be an efficient procedure for constructing reaction paths since, in a nutshell, this is the method of choice in the often applied Discrete Path Sampling approach.

A further method that has been widely applied to calculate dynamical properties and pathways of processes is Transition Path Sampling (TPS) which generalizes importance sampling to trajectory space. However,
as has been shown by Miller and Predescu, TPS with shooting and shifting moves becomes trapped in high-energy structures of LJ\textsubscript{38} and thus fails to find the global minimum funnel of this system. They thus developed a double-ended transition path sampling method, named Sliding and Sampling, which could find paths between both funnels\textsuperscript{29} However the main drawbacks of their method are the non-ergodicity of their simulation for LJ\textsubscript{38} and the high computational cost. Miller and Predescu reported that 10\textsuperscript{6} CPU hours were required for their LJ\textsubscript{38} computations.

In this work we re-examine the systematic sampling approach based on one-sided transition state searches using a stabilized mode-following method. In accordance with previous investigations\textsuperscript{19,20}, we also conclude that in general this approach is not optimal and occasionally fails even for moderately sized systems like LJ\textsubscript{38}. We therefore introduce a completely novel Minima Hopping Accelerated Path Search (MHAPS) approach. Using MHAPS we mapped out the energy surfaces of LJ\textsubscript{75} and LJ\textsubscript{102}. Despite numerous published investigations of the Lennard-Jones clusters, we were able to detect many paths that are significantly lower in energy and shorter with respect to the integrated path length and number of intermediate transition states than previously known paths for LJ\textsubscript{75}\textsuperscript{31} For LJ\textsubscript{102} we found a third, previously unknown and energetically low-lying funnel at the bottom of which a new structural motif is located. The paths found between both lowest minima of LJ\textsubscript{102} are also significantly shorter in terms of the number of intermediate transition states and in terms of the integrated path length when compared to previously presented paths\textsuperscript{31}.

II. METHODS

A. Lennard-Jones Potential

All interactions in this study were modeled by the Lennard-Jones (LJ) potential\textsuperscript{13–15}

\[ E = 4\epsilon \sum_{i<j} \left\{ \frac{(\sigma/r_{ij})^12}{2} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right\}, \]

where \( \epsilon \) defines the pair-well depth and \( 2^{1/6}\sigma \) is the pair-well equilibrium distance. All energies and distances are reported in units of \( \epsilon \) and \( \sigma \), respectively.

B. Transition states, their connectivity and stationary point databases

We follow the usual definition of a transition state being a first order saddle point of the energy function.\textsuperscript{13–15} Steepest descent paths connect transition states to two stationary points. In most cases these stationary points are local minima. We adapt the terminology of Wales\textsuperscript{13–15} and denote sequences of minima and transition states connected by steepest descent paths as ‘discrete paths’. A collection of local minima, transition states and the information which transition states connect which minima is called a ‘stationary point database’\textsuperscript{13–15}.

Building stationary point databases requires the identification or distinction of atomic configurations with or from each other. For this purpose we utilized the recently developed fingerprints which are based on the eigenvalues of a s-orbital overlap matrix.\textsuperscript{35} For the calculation of the fingerprints, we used \( 2^{1/6}\frac{\pi}{2} \) as the covalent radius of the LJ atoms. We considered two conformers to be identical if their energy difference was smaller than \( 10^{-5}\epsilon \) and their fingerprint distance less than \( 2 \times 10^{-4} \).

Extracting from a stationary point database all lowest-barrier paths with the least number of intermediate transition states between two given minima poses a problem that is closely related to the so called shortest-widest\textsuperscript{13} path problem. This can be solved by applying Dijkstra’s algorithm\textsuperscript{36} twice.\textsuperscript{35} In the first step Dijkstra’s algorithm searches for all paths that connect both minima with the lowest possible energy barrier \( E_{\text{bar};\text{lowest}} \). The stationary point database then is truncated by removing all transition states with energies higher than \( E_{\text{bar};\text{lowest}} \). Next, Dijkstra’s algorithm passes through the truncated database and searches for the path with the smallest possible number of intermediate transition states.

To determine the connectivity in all sampling approaches presented below, we stepped away from a transition state by adding to and subtracting from the transition state one-100th of the normalized Hessian eigenvector that corresponds to the negative curvature. Using Euler’s method with a maximum step size of \( 10^{-2}\sigma \), approximate steepest descent paths were computed until the Euler integrator entered the quadratic region surrounding a minimum. In this Euler integration scheme steps were rejected and the step size was decreased if either the angle between the gradients of two successive steps was larger than 60 degree or if the energy increased. Inside the quadratic region the Euler method was replaced by the fast inertial relaxation engine (FIRE)\textsuperscript{37} in order to speed up the geometry optimization. For the FIRE integrator itself it is not of any relevance whether it operates inside the quadratic region or not. However, compared to non-quadratic regions it seems less likely that inside the quadratic region the FIRE method will converge to a different minimum than Euler’s method. Because dynamic properties computed from stationary point databases are unlikely to depend strongly on whether the connectivity of the potential energy surface is established by using approximate steepest descent paths or paths from advanced minimization algorithms\textsuperscript{11,12} like for example FIRE or BFGS\textsuperscript{38–42}, the time used for relaxations to local minima could have shortened significantly when omitting the Euler integration and using advanced minimization algorithms throughout. However, because we introduce a new reaction path search method, we decided to use the
conservative Euler integration approach in order to sample connectivity information that is in accordance with the connectivity defined by the widely accepted intrinsic reaction coordinate.\textsuperscript{13} Although we do not report any results based on FIRE-only minimization, we compared the differences of paths obtained from FIRE-only and Euler integration plus FIRE optimization. We only observed changes in the number of intermediate transition states. In all cases the energetically lowest transition state between two states found by FIRE-only runs was identical to the lowest transition state found by connections established by approximate steepest descent paths.

In addition to the conservative combination of Euler’s method and FIRE, all new paths explicitly reported in this study (Figures 7 and 8) were double-checked in a post-processing step. In order to obtain quasi-exact intrinsic reaction paths, steepest descent paths were recomputed using only Euler’s method with a maximum displacement of $10^{-6}\sigma$ in each integration step. Before this steepest descent relaxation the structures had been pushed away from the transition state one-10,000th of the normalized eigenvector belonging to the negative Hessian eigenvalue.

It has to be emphasized that, similar to all commonly used global optimization algorithms, the methods presented in this work do not rigorously guarantee that an optimal solution has been found. That is, all presented structures and lowest-barrier paths should be denoted as ‘putative lowest structures’ or ‘putative lowest-barrier paths’. However, for convenience we sometimes omit the word ‘putative’.

C. Disconnectivity graphs

Disconnectivity graphs introduced by Becker and Karplus\textsuperscript{16} and frequently used by Wales et al.\textsuperscript{14,16,45,46} can be used to visualize stationary point databases of multidimensional potential energy landscapes. They therefore allow to obtain a rough, intuitive insight into dynamic properties. In this section we briefly recapitulate the theory of disconnectivity graphs.

Disconnectivity graphs illustrate which minima are convertible into each other by following reaction paths without ever exceeding a given threshold energy. Such mutually accessible regions are called ‘superbasins’.\textsuperscript{16} The number of superbasins depends on the threshold energy. The vertical axis of a disconnectivity graph is partitioned into a predefined and freely chosen number of energy thresholds. At each threshold energy the superbasins are represented by nodes on the graph and are arranged along the horizontal axis. At threshold energies at and above which superbasins are mutually accessible, the corresponding nodes below this threshold energy are connected by lines. Finally all the single minima at the bottoms of the superbasins are represented separately by drawing lines down to the energy of each minimum. The horizontal position of the nodes and minima is arbitrary. Typically there are too many minima to visualize, hence only the lowest $n$ minima are usually plotted. Nevertheless, all minima and transition states contained in the underlying stationary point database contribute to the superbasin and barrier analysis.

The number and positions of the chosen threshold energies can heavily influence the appearance of a disconnectivity graph and hence these parameters have to be well chosen in order to obtain a suitable trade-off between a detailed and coarse grained visualization of the topological information contained in the underlying stationary point database.\textsuperscript{16}

The plots of all disconnectivity graphs in this work were generated using the disconnectDPS\textsuperscript{45,46} software.

D. A stabilized mode-following method

As the name suggests, the basic idea of mode following methods is to find the path from a minimum to a first-order saddle point by following an eigenmode of the Hessian. In practice the determination of the eigenmodes via a diagonalization is too costly and one therefore has to resort to iterative methods, meaning that the mode to be followed is found by a minimization problem.

In our approach the Hessian eigenmodes are found using a version of the dimer method.\textsuperscript{16} The dimer consists of two images $\mathbf{R}_1$ and $\mathbf{R}_2$ in the $3N$-dimensional search space, separated by a short distance $2\epsilon$:

\begin{align*}
\mathbf{R}_1 &= \mathbf{R}_0 + \epsilon \hat{\mathbf{N}} \\
\mathbf{R}_2 &= \mathbf{R}_0 - \epsilon \hat{\mathbf{N}}
\end{align*}

where $\hat{\mathbf{N}}$ is the normalized dimer direction and $\mathbf{R}_0$ is the dimer midpoint. The dimer method first rotates the dimer in order to align it with a Hessian eigenmode and then translates it along this mode. This procedure is repeated until the transition state is reached.

1. Rotating the dimer

The essential point of the dimer method is to find an efficient prescription for the rotational part. The quantity that has to be minimized is the curvature along the dimer direction, $C_{\mathbf{R}_0}(N) = \hat{\mathbf{N}}^T \mathbf{H}_{\mathbf{R}_0} \hat{\mathbf{N}}$, where $\mathbf{H}_{\mathbf{R}_0}$ is the Hessian evaluated at the dimer midpoint. Since the computation of the exact Hessian is in general too costly, the curvature is approximated using finite differences computed from the forces that act on the two images of the dimer:

\[
C_{\mathbf{R}_0} = \frac{(\mathbf{F}_2 - \mathbf{F}_1) \cdot \hat{\mathbf{N}}}{2\epsilon}.
\]

There are ways to locally approximate the curvature by a short Fourier series and then to directly minimize this
expression. However we chose a more straightforward approach by working directly with the torsional force

\[ F^\perp = (F_1 - F_2) - \left( (F_1 - F_2) \cdot \hat{N} \right) \hat{N}. \]  

Image 1 of the dimer is now iteratively moved according to this force until the latter falls below a given threshold; at each step the position of the image has to be adjusted to keep the dimer separation constant. In order to reduce the number of force evaluations, the force acting on image 2 is approximated by using the force acting on the dimer midpoint, \( F_0 \) i.e. \( F_2 = 2F_0 - F_1 \), in this way leading to

\[ F^\perp = 2(F_1 - F_0) - 2 \left( (F_1 - F_0) \cdot \hat{N} \right) \hat{N}. \]

Since the value of \( F_0 \) does not change during the rotation, only one force evaluation per iteration is required.

For the current purpose it is crucial to have the ability to find systematically many different transition states leading out of a given minimum. This means that one has to be able to follow many different modes. For the mentioned dimer method – and as well for other related mode following methods – this is not the case. The reason for this is very simple. As is shown in Appendix A only the lowest mode is a stable one, meaning that the curvature has a local minimum there. All other modes represent saddle points (except for the highest mode which is a maximum). This implies that, as soon as the search mode deviates from an exact eigenmode of the Hessian – which will inevitably happen during a mode following process due to the finite step size for the translation – there is a strong tendency that the re-determination of the exact eigenmodes will lead to the lowest one, even though one might initially have been aligned along another one. In other terms, it is very likely that searches started along different modes of a given minimum will lead to the same saddle point and thus the efficiency of exploring the potential energy surface and finding lowest-barrier reaction paths is degraded.

This problem can be circumvented by a very simple modification, namely by using DIIS to perform the rotation of the dimer. Since DIIS has the tendency to find the closest stationary point, the iterative procedure to come back to the exact eigenmode will not lead to the lowest mode, but rather to the one which has the largest overlap with the previous one. In this way the dimer method is stabilized and it is possible to systematically follow different modes out of a given minimum. In order to avoid any instabilities related to the DIIS procedure, it is required that the starting point does not lie too far away from the exact eigenmode. This is achieved by keeping the step size for the translation reasonably small. A comparison of the stabilized mode following technique using DIIS and a standard approach using steepest descent for the rotations is shown in Fig. 1.

However, as one is searching first-order saddle points, it is necessary that one finally ends up on the lowest mode, no matter which mode one has started with. It turns out that the order of the mode usually decreases as one moves away from the minimum, but in order to safely reach a saddle point it is still necessary to abandon the initial mode at some point and to follow the lowest mode instead – a simple criterion to do so is when the second derivative of the energy with respect to the number of iterations becomes negative. In our implementation the lowest mode was determined by using the Lanczos method, as presented in Ref. [49].

2. Translating the dimer

In contrast to the rotation of the dimer, the translation is rather straightforward, following the approach

\[ F^\perp = (F_1 - F_2) - \left( (F_1 - F_2) \cdot \hat{N} \right) \hat{N}. \]
If the saddle point search was started from a local minimum, then there are two cases to distinguish. First the dimer has to be brought out of the convex region around the minimum. To this end it is moved upwards along the dimer direction using the most convex region around the minimum. To this end it is advisable to switch to a convergence accelerator; in our case we were using DIIS, an approach which is also employed in ART nouveau.\cite{ref:47}

Using our new stabilized one-sided transition state search method, the potential energy surface was mapped out by utilizing the algorithm outlined in Ref.\cite{ref:13}. Based on the used method for the transition state search, we henceforth will denote this algorithm as the eigenvector following exploration (EFE) method. Concisely spoken, the walker of the EFE method starts at a local minimum and follows the lowest Hessian eigenvector until a transition state is found. If this transition state leads to a minimum with an energy that is less than or equal to the energy of the current minimum, the new minimum is accepted and a new transition state search is initiated from this minimum. If a transition state leads to a minimum that is higher in energy, or if the transition state is not connected to the current minimum, the move is discarded and a further transition state search is begun at the current minimum, either by following the negative direction of the just followed mode, or if this already has been done, by following the direction of the eigenvector belonging to the next higher Hessian eigenvalue. For each minimum, only a maximum number of transition state searches is performed (less or equal than 6N − 12, where N is the number of atoms). If this number is exceeded, no new transition state search is initiated from this minimum and the algorithm jumps to the minimum that is next higher in energy and for which the maximum number of transition state searches have not been accomplished yet.

**E. Generating stationary point databases using the mode-following approach**

![Trajectory of the bar starting from two initial positions on a model energy landscape](image)

FIG. 2. Trajectory of the bar starting from two initial positions on a model energy landscape $f(x,y) = (1-(x^2+y^2))^2 + (y^2)/(x^2+y^2)$. Two minima are located at (±1,0), and the saddle point is located at (0,1).

In the presence of friction, a ball released from a high altitude mountainside would roll downhill and lead to a close-by local minimum. The Bar-Saddle method presented here uses the idea that, in contrast to the rolling ball, a solid, horizontal bar would roll to the closest saddle point if its point of contact with the surface is kept at its center. In our implementation a bar is represented by two endpoints A and B at the coordinates $\mathbf{R}_A$ and $\mathbf{R}_B$ in the high-dimensional configuration space. The length of a bar is evaluated as $h = |\mathbf{R}_B - \mathbf{R}_A|$. Although the Bar-Saddle formalism derived below is formally closely related to the dimer method\cite{ref:17}, it follows a different usage paradigm. In contrast to the dimer method, the Bar-Saddle formalism can be used to find transition states connecting two given minima. To do so, it starts from a configuration that is geometrically in between the two input minima and high in energy. In principle the highest energy configuration along the linear interpolation path between two minima can be used. However in order to avoid colliding atoms we prefer the freezing string method in Cartesian coordinates for identifying a high energy geometry.\cite{ref:53} In all computations we used a new-node interpolation distance corresponding to 1/10th of the Euclidean distance of the given two minima. Perpendicular relaxations were stopped as soon as the perpendicular force fell below 5\text{e-2} or as soon as the iteration counter for the perpendicular relaxations was equal to four. Configurations in between the nodes generated by the freezing string method were interpolated using a cubic spline interpolation. A maximum energy configuration along this interpolated path was searched using Brent’s method\cite{ref:54} in between each pair of nodes and then selecting the energetically highest configuration that was found. Section\cite{sec:HTC} describes how to obtain two suitable local minima which serve as input for the freezing string method.

Having identified a suitable starting configuration from which the bar can roll down, the bar is moved iteratively such that the maximum energy along the direction of the bar is at its center (corresponding to the point of contact) and such that the energy at its center is minimized along all directions perpendicular to the bar. In each iteration, the energies and the forces are evaluated at the
bar ends. The forces are then decomposed into a component parallel to the bar \( \mathbf{F}_i^\parallel = (\mathbf{F}_i \cdot \mathbf{h}) \mathbf{h} \) and a component perpendicular to the bar \( \mathbf{F}_i^\perp = \mathbf{F}_i - \mathbf{F}_i^\parallel \), where \( i = A, B \) and \( \mathbf{h} = \mathbf{R}_{\text{EQ}} \) is the unit vector along the bar.

For the translation of the bar its energy and force along the bar is defined by a cubic interpolation at the center of the bar, such that

\[
E_{h/2} = \frac{1}{8}(4E_A + 4E_B + (f_B - f_A)h),
\]

and

\[
\mathbf{F}_{h/2}^i = \frac{6E_A - 6E_B - (f_A + f_B)h}{4h} \mathbf{h},
\]

where \( f_i = \mathbf{F}_i \cdot \mathbf{h} \).

The perpendicular force is evaluated by \( \mathbf{F}_{h/2}^\perp = \frac{1}{2}(\mathbf{F}_A^\perp + \mathbf{F}_B^\perp) \), such that the total translational forces on the bar ends result to \( \mathbf{F}_A^\text{Trans} = \mathbf{F}_B^\text{Trans} = -\gamma \mathbf{F}_{h/2}^\perp + \mathbf{F}_{h/2}^\parallel \), where \( \gamma > 0 \). In our implementation we chose \( \gamma = 2 \).

In addition, a rotational force is applied to the bar in order to approximately align it along the lowest curvature direction. This additional force is given by \( \mathbf{F}_A^\text{Rot} = \frac{1}{2}(\mathbf{F}_A - \mathbf{F}_B) \) and \( \mathbf{F}_B^\text{Rot} = \frac{1}{2}(\mathbf{F}_B - \mathbf{F}_A) \).

Finally, following a steepest descent approach, the bar ends are moved along the effective forces \( \mathbf{F}^\text{Eff} = \alpha \mathbf{F}^\text{Trans} + \beta \mathbf{F}^\text{Rot} \), where \( \alpha > 0 \) and \( \beta > 0 \) define the translational and rotational step sizes. After each step, the bar length is rescaled such that the new bar length remains the same in each iteration \( |\mathbf{R}_{\text{New}} - \mathbf{R}_{\text{EQ}}| = h \).

In comparison to Bar-Saddle, the dimer method estimates both the parallel and perpendicular components of the translational force by the arithmetic mean of the forces at the dimer endpoints. The force responsible for the rotation acts only on one endpoint in case of the dimer method and the rotation is implemented by using the parametrization of a circle in a 2-dimensional plane and rotating the dimer in a single step by an angle estimated using a modified one-dimensional Newton method.

Fig. 2 shows the trajectories of the Bar-Saddle method on a model energy landscape. Note that, although the method works most efficiently if the initial point is energetically higher than the saddle point, it will still converge when the search is started close to a local minimum.

The efficiency of the method can be improved by applying an energy or gradient feedback to the step sizes \( \alpha \) and \( \beta \). In practice we used a hybrid method where the first few iterations were obtained from steepest descent with gradient feedback, followed by a BFGS minimization with respect to the translational force \( \mathbf{F}^\text{Trans} \) only and applying the rotational forces separately in each iteration.

In our implementation we considered a Bar-Saddle computation as converged if the force norm at the center of the bar fell below \( 10^{-5} \) and the curvature in bar direction was negative. Typically, only on the order of 0.1% of all saddle computations used for the simulations reported in this study could not met these convergence criteria within 15,000 iterations.

G. Generating stationary point databases using the Minima Hopping accelerated approach

Exploring the connectivity of an energy surface requires an algorithm that moves efficiently in one or between several low energy regions. An algorithm that has proven its efficiency in exploring the low energy regions of several force-fields and quantum mechanical potential energy surfaces is MHAPS. It therefore seems natural to combine the guiding capabilities of MH with a method that connects two given minima by a series of transition states into a Minima Hopping accelerated path search technique. Fig. 3 shows a flow chart of our new MHAPS approach. Similar to MH, MHAPS begins at a local minimum and tries to escape its catchment basin by following a short, random and soft mode biased MD trajectory at the end of which a local geometry optimization is performed. The softening procedure has been described previously. The escape trials are repeated until MHAPS successfully escapes from the catchment basin of the current minimum. In order not to get trapped in the current catchment basin, the kinetic energy is increased by a factor \( \beta_0 \) after each failed escape trial. When MHAPS successfully escapes to a different minimum it either decreases the kinetic energy by a factor \( \beta_1 \) or increases it by a factor \( \beta_0 \), depending on whether the new minimum has been visited before or not. This introduces a feedback which promotes cooling down in unexplored regions and heating up in well explored regions of the potential energy surface and thus ensures that the algorithm quickly samples the bottom of a funnel and at the same time does not get trapped.

Based on a Metropolis-like criterion MHAPS decides whether it should connect the current minimum \( M_{\text{curr}} \) and the new minimum \( M \) by a discrete path. If the energy of the new minimum \( E \) is lower than the energy \( E_{\text{curr}} \) of the current minimum, a connection attempt is always made. If its energy is higher than the energy of the current minimum, an attempt is made with a probability of

\[
\exp \left( -\frac{E - E_{\text{curr}}}{E_{\text{diff}}} \right).
\]

The connections are made by recursively applying Bar-Saddle and following approximate steepest descent paths from emerging intermediate transition states. Establishing the connection between the two Bar-Saddle input minima \( M_{\text{curr}} \) and \( M \) in a recursive or iterative fashion is essential, because there is no guarantee that the two minima \( M_{\text{curr}} \) and \( M \) can be connected with each other by exactly one transition state. Hence, during a connection intermediate transition states can appear which might not be connected to one or to both of the two input
minima. In such a case the minima to which the intermediate transition states are connected also have to be connected to the corresponding Bar-Saddle input minima in order to obtain a discrete path that properly connects $M_{\text{curr}}$ and $M$.

MHAPS is not limited to using Bar-Saddle for connecting minima. In principle any double-ended saddle search method like for example the Nudged Elastic Band method\cite{58-61} or the Splined Saddle method\cite{62,63} could be used. However, we decided to use the Bar-Saddle method, because it is highly reliable for converging successfully to saddle points.

After connecting $M_{\text{curr}}$ and $M$ by a discrete path, $E_{\text{diff}}$, which enters the acceptance criterion, gets decreased by a factor $\alpha_a$. The new minimum becomes the current one and the algorithm starts a new MD trajectory at this minimum. The whole procedure is stopped as soon as a given number of distinct minima are identified. In all simulations presented in this study the standard minima hopping parameters ($\beta_S = \beta_O = 1/\beta_n = \alpha_T = 1/\alpha_a = 1.05$) were used\cite{5,64}.

### III. BENCHMARKS AND COMPARISONS

In contrast to global minimum searches, a performance analysis of stationary point database generation algorithms is not straightforward since there is no obvious stopping criterion. One possible stopping criterion can be defined by checking whether a putative lowest-barrier path between two minima has been found. Because of the computational cost of Dijkstra’s algorithm, this check is not feasible if it has to be performed between every pair of minima for a given system. Therefore, a suitable test system should contain two outstanding and well defined minima for which paths that connect them can be examined. LJ$_{38}$ is a system that fulfills these requirements and at the same time is small enough in order to perform a sufficient number of runs within a feasible amount of time.

Table I shows the results of a performance test based on 1000 independent runs for LJ$_{38}$. Each run was started using a random non-fcc structure as input geometry and, depending on what happened earlier, was either stopped as soon as the putative lowest-barrier path between the global minimum and the second lowest local minimum of LJ$_{38}$ was identified, or if $5 \times 10^5$ distinct local min-
shows the EFE method exploring the icosahedral 20
30
25
45
shows the history of all transition state ener-
15
shows the history of the 7
60
100
150
200
250
Number of transition states along accepted moves
(b)
Energy of transition state [LJ unit]
(a)
FIG. 4. History of transition states along accepted moves of the walker of both algorithms for the LJ$_{75}$ system. For both plots the runs were stopped after having performed a total of 275,000 transition states computations. The bold dashed line shows the putative lowest barrier between both funnels of LJ$_{75}$ (see section IV). For clarity, only every 10-th transition state is plotted.

TABLE I. Results of performance test for LJ$_{38}$. Averages for $\langle n_{\text{ts, diff}} \rangle$ and $\langle n_{\text{ts}} \rangle$ are taken over $1000 - n_f$ independent and successful runs.

| Method | $n_{\text{ev}}^a$ | $\langle n_{\text{ts, diff}} \rangle^b$ | $\langle n_{\text{ts}} \rangle^c$ | $n_{\text{E}}^d$ | $n_e^e$
|--------|-----------------|-----------------|-----------------|----------------|----------------|
| MHAPS  | n/a             | 9267            | 14580           | 3464           | 0              |
| EFE    | 10              | 64611           | 168688          | 3384           | 24             |
| EFE    | 25              | 72977           | 192097          | 3508           | 8              |
| EFE    | 40              | 91313           | 268422          | 3492           | 1              |

$^a$ Number of lowest eigenvectors along which transition states were searched in positive and negative direction
$^b$ Average number of distinct transition states needed to be found before identifying a lowest-barrier path.
$^c$ Average number of transition states computations needed before identifying a lowest-barrier path.
$^d$ Number of totally performed energy evaluations divided by the number of totally performed transition state computations.
$^e$ Number of runs in which lowest-barrier paths could not be found before identifying $5 \times 10^5$ distinct minima.

ima were found. For all methods and all runs the same convergence criteria for the stationary points were used.

EFE needed roughly between a factor of 12 to 18 more transition state computations than the MHAPS method before encountering a lowest-barrier path of LJ$_{38}$. Because the number of energy evaluations per transition state computation $n_{\text{E}}$ are similar for both methods, similar factors are obtained when measuring the computational cost in terms of energy evaluations.

For the EFE method we could observe a small number of runs that failed to find a lowest-barrier path at all. Since the number of failure runs decreased with increasing number of followed mode directions these failures can be explained by the limited number of search directions available to the EFE method. At maximum, the EFE method can follow 6$N$ − 12 directions per minimum for a $N$-atom system. However, the number of transition states connected to a minimum can exceed the number of 6$N$ − 12 directions by far. For example it is known that the global minimum of LJ$_{13}$ is surrounded by 535 local minima which are connected to the global minimum by 911 transition states. It is therefore possible to miss stationary points that potentially lie on the lowest-barrier path. This general restriction of mode-following methods has been mentioned before by Malek and Mousseau.

The average number of distinct transition states $\langle n_{\text{ts, diff}} \rangle$ divided by the average number of computed transition states $\langle n_{\text{ts}} \rangle$ was between 66% and 87% larger for the MHAPS method than corresponding ratios of the EFE method.

The average CPU time required before MHAPS identified the lowest-barrier paths between both lowest structures of LJ$_{38}$ was measured to be roughly 8 minutes (on a single core of an Intel Xeon E5-2665 CPU clocked at 2.40GHz). This timing should be compared to the $10^5$ CPU hours that were required for the Sliding and Sampling computations reported in Ref. 29. The MHAPS timing is in particular noteworthy when noting that Ref. 29 only presents paths that are higher in energy than the lowest known barrier path.

Fig. 4 shows the history of all transition state energies along accepted steps of the walkers for both methods in case of the 75-atom LJ-system. The runs shown in these plots were started from the second lowest local minimum which is located at the bottom of a large icosahedral funnel. The size of this icosahedral funnel in combination with the high barrier separating it from the global minimum funnel makes the icosahedral funnel difficult to escape from. Both methods were stopped as soon as 275,000 transition state computations were performed. Panel (a) of Fig. 4 shows the history of the MHAPS walker. The peaks between the 50,000th and 100,000th transition state and the peaks just before the 150,000th transition state correspond to sampling inside the global minimum funnel which is visited for the first time shortly after the 60,000th transition state along the walker trajectory is computed. The history in panel (b) of Fig. 4 shows the EFE method exploring the icosahedral funnel in a bottom-up fashion. In contrast to MHAPS the EFE method was not able to leave the large icosahedral funnel. The number of transitions states along ac-
FIG. 5. Disconnectivity graphs of LJ$_{75}$ [panel (a)] and LJ$_{102}$ [panel (b)]. Panel (a) shows the new putative lowest barrier between both funnels. The blue dashed line indicates the previously known lowest barrier connecting both funnels. Panel (b) shows a third, previously unknown, funnel with an energetically low bottom structure (minimum b.3) and a high barrier connecting it to the other two funnels. Both graphs show the 250 lowest minima that were found for each system. The bottom structures of each major funnel are labeled and highlighted using red color.

accepted moves of the walkers is a measure for the amount of the explored potential energy landscape. Therefore, panel (b) of Fig. 4 shows clearly that the EFE-walker explored a much smaller fraction of the potential energy landscape than the MHAPS-walker.

We also performed a short test run for the LJ$_{55}$ cluster which is a strong structure seeker. Despite its structure seeker character there exist two non-icosahedral minima which lie behind comparatively high barriers. The labeling of the illustrations corresponds to the labeling of panel (b) in Fig. 5.

FIG. 6. Bottom structures of the three major funnels of LJ$_{102}$. The labeling of the illustrations corresponds to the labeling of panel (b) in Fig. 5.

c) and was stopped as soon as 30,000 transition state computations were performed. The overall appearance of the disconnectivity graph containing the lowest 700 minima generated from EFE-sampling is equivalent to the graph presented in Ref. 19, however in this test run our implementation of the EFE method could not identify the lower of the two non-icosahedral minima. The other of the two mentioned non-icosahedral minima could be found by the EFE method, however the barrier connecting it to the global minimum funnel was significantly larger than the barrier found in Ref. 19. In contrast, the disconnectivity graph containing the lowest 700 minima generated from the MHAPS run contained all important features of the LJ$_{55}$ potential energy surface, including both of the above mentioned non-icosahedral minima. The barriers connecting the two non-icosahedral minima to the global minimum funnel were also reproduced in accordance with the barriers of the disconnectivity graph presented in Ref. 19.

IV. APPLICATION OF MHAPS TO LJ$_{75}$ AND LJ$_{102}$

Due to its advantages presented in section III we applied MHAPS to LJ$_{75}$ and LJ$_{102}$. Concerning the task
FIG. 7. Paths found by MHAPS connecting the bottom-structures of both LJ\(_{75}\) funnels (configurations a.2 and a.1 of Fig. 5). The dashed horizontal lines indicate the highest energy along the previously known lowest-barrier path. Panels (a), (b) and (c) show three alternative putative lowest-barrier paths. Panels (d), (e) and (f) show paths that have been obtained by successively removing the highest energy transition state along the lowest-barrier path from the stationary point database [panels (d) and (e)] or from a preliminary test run [panel (f)]. They only have slightly higher barriers than the paths of panels (a) to (c) and thus show that there exist a variety of paths lying energetically between our best results and the previously presented lowest-barrier paths for LJ\(_{75}\).

of sampling relevant stationary points, in particular LJ\(_{75}\) is known to be a very difficult system. This is explained by the frustration of its potential energy surface and the large geometrical differences of both structures located at the bottoms of two major funnels.

For each system we started 10 independent runs at the corresponding global minimum structures. For every run different random seeds were used. A run was stopped, as soon as \(2 \times 10^6\) distinct local minima were found. For the analysis of the potential energy surfaces the stationary point databases resulting from all runs were merged into a single database for each system. For LJ\(_{75}\) this procedure resulted in a stationary point database containing roughly \(12.0 \times 10^6\) distinct transition states connecting \(7.0 \times 10^6\) distinct local minima. In case of LJ\(_{102}\) we obtained by this procedure a database
FIG. 8. Putative lowest-barrier paths that were found by MHAPS for LJ$_{102}$. Panel (a) shows a putative lowest-barrier path connecting the putative global minimum (configuration b.1 of Fig. 5) to structure b.3 of Fig. 5. A lowest-barrier path connecting the second-lowest minimum of LJ$_{102}$ (configuration b.2 of Fig. 5) and configuration b.3 of Fig. 5 is shown in panel (b). The parts of the reaction paths shown in panel (a) and (b) that coincide with each other are highlighted by using dashed lines. Panel (c) shows a putative lowest-barrier path connecting the second-lowest configuration of LJ$_{102}$ (configuration b.2 of Fig. 5) to the putative global minimum (configuration b.1 of Fig. 5).

containing roughly $10.9 \times 10^6$ distinct transition states which connect $7.5 \times 10^6$ distinct local minima. The disconnectivity graphs of both systems are shown in Fig. 7 and Fig. 8 show plots of the energy along the reaction paths in dependence of the integrated path length $S$ which is defined by the arc length of the steepest descent reaction path in the $3N$-dimensional coordinate space. Numerically the integrated path length is computed by summing up all the lengths $|\Delta \mathbf{R}|$ of all steepest descent steps:

$$ S = \sum_{\text{steps}} |\Delta \mathbf{R}| . \quad (9) $$

A. LJ$_{75}$

As shown in panel (a) of Fig. 5 the largest barriers along the lowest-barrier paths connecting the two major funnels of LJ$_{75}$ that were found by MHAPS are significantly lower in energy than those of the previously known lowest-barrier paths. Using Dijkstra’s algorithm as outlined in section 115 we could identify roughly 20,000 paths all having the same highest-barrier energies of $7.51\epsilon$ and $6.30\epsilon$ and the same number of 51 intermediate transition states. Compared to this, the previously known lowest-barrier path has significantly higher highest-barrier energies of $8.69\epsilon$ and $7.48\epsilon$ and possesses 65 intermediate transition states. In order to illustrate typical differences between alternative lowest-barrier paths, the panels (a), (b) and (c) of Fig. 7 explicitly show the steepest descent reaction paths of three lowest-barrier paths. In order to check whether there might exist further paths which are energetically in between the previously known lowest-barrier path and the putative lowest-barrier paths found by MHAPS, we successively removed the highest energy transition state along the lowest-barrier path from the stationary point database and applied Dijkstra’s algorithm. Paths resulting from this removal are shown in panels (d) and (e) of Fig. 7. For the path shown in panel (d) the barriers are $7.52\epsilon$ and $6.31\epsilon$, for the path of panel (e) the barriers are $7.54\epsilon$ and $6.33\epsilon$. They are only slightly higher in energy than the highest barriers along the putative lowest-barrier path. This suggests that there exists a whole range of paths that are energetically between the putative lowest paths presented in this study and the previously known lowest path. This conjecture seems to be reinforced by the path shown in panel (f) of Fig. 7. This path was found in a preliminary single-run test in which only roughly $6 \times 10^5$ distinct local minima and roughly $9 \times 10^5$ distinct transition states were sampled. The highest barriers along this path are $7.78\epsilon$ and $6.57\epsilon$. 
B. \( \text{LJ}_{102} \)

As shown in panel (b) of Fig. 6, \( \text{MHAPS} \) could find a previously unknown funnel for \( \text{LJ}_{102} \). An illustration of the bottom structure of this funnel is given in Fig. 9. The new bottom structure possesses icosahedral elements and its surface is dominated by buckled hexagonal patches. Its has an energy of \(-568.388773 \epsilon\).

Lowest-barrier paths connecting the new structure to the global minimum and to the second lowest minimum are shown in panels (a) and (b) of Fig. 8. The lowest-barrier paths connecting this new structure and the global minimum contain 40 intermediate transition states and the highest barriers are 7.97\( \sigma \) and 7.89\( \sigma \). The highest barriers of the lowest-barrier paths that connect the second lowest minimum to the bottom of the new funnel are 7.97\( \sigma \) and 7.00\( \sigma \). These paths contain 53 intermediate transition states.

Furthermore, \( \text{MHAPS} \) could confirm the energy of the highest barrier along the putative lowest-barrier path connecting the global minimum to the second lowest minimum. However, both in terms of the number of intermediate transition states and in terms of the integrated path length, the path found by \( \text{MHAPS} \) is significantly shorter than the previously known path. It contains only 16 intermediate transition states compared to 30 transition states contained in the path published earlier. The integrated path length is roughly 11\( \sigma \) shorter (difference of paths length was estimated using the plot of Ref. 31).

V. CONCLUSION

We have compared a stabilized mode-following approach for the exploration of the potential energy surface and generation of stationary point databases with a completely new Minima Hopping accelerated path search technique. In comparison to the mode-following approach, \( \text{MHAPS} \) detects a significantly larger number of distinct transition states when performing the same number of transition state computations. Due to the excellent and unbiased guiding capabilities of the Minima Hopping method, \( \text{MHAPS} \) must perform expensive transition states computations only between minima for which visiting them is particularly promising for the purpose of the exploration of the potential energy surface. \( \text{MHAPS} \) reduces the cost of sampling stationary points and their connectivity information by one order of magnitude compared to the mode-following approach. In contrast to other methods, \( \text{MHAPS} \) could successfully find the lowest-barrier paths of \( \text{LJ}_{32} \) in all tests and due to its unbiased sampling approach does not fail to explore unforeseen and unexpected features of the potential energy surface. The efficiency of our new method is also confirmed by new results that were found for \( \text{LJ}_{75} \) and \( \text{LJ}_{102} \), systems that have been thoroughly examined for more than a decade.

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Appendix A: Stability of the modes

The curvature along an arbitrary vector \( \mathbf{x} \), evaluated at the position \( \mathbf{x}_0 \), is defined as

\[
C_{\mathbf{x}_0}(\mathbf{x}) = \frac{\mathbf{x}^T \mathbf{H}_{\mathbf{x}_0} \mathbf{x}}{\mathbf{x}^T \mathbf{x}},
\]

where \( \mathbf{H}_{\mathbf{x}_0} \) is the Hessian at \( \mathbf{x}_0 \). If \( \mathbf{x} \) was an eigenvector \( \mathbf{v}_i \), this would give the corresponding eigenvalue \( \lambda_i \). Furthermore, calculating the gradient with respect to \( \mathbf{x} \) under the constraint of normalization gives

\[
\frac{1}{2} \frac{d}{d\mathbf{x}} \left. \frac{\mathbf{x}^T \mathbf{H}_{\mathbf{x}_0} \mathbf{x}}{\mathbf{x}^T \mathbf{x}} \right|_{\mathbf{x}^T \mathbf{x} = 1} = \mathbf{H}_{\mathbf{x}_0} \mathbf{x} - (\mathbf{x}^T \mathbf{H}_{\mathbf{x}_0} \mathbf{x}) \mathbf{x}.
\]

This expression vanishes in case \( \mathbf{x} \) is an eigenvector, showing that the eigenmodes are stationary points of \( C_{\mathbf{x}_0}(\mathbf{x}) \).

The next point is to show that among all these stationary directions, only the lowest mode is actually a minimum and thus stable, meaning that rotating a slightly misaligned dimer according to its torsional force will lead back to this mode. Since the eigenvectors form a complete set, any vector can be written as a linear combination of them, i.e. \( \mathbf{x} = \sum_i c_i \mathbf{v}_i \), with the normalization condition \( \sum_i c_i^2 = 1 \). Plugging this into Eq. (A1) and using the orthonormality of the eigenvectors gives

\[
C_{\mathbf{x}_0}(\mathbf{x}) = \sum_i c_i^2 \lambda_i = c_l^2 \lambda_l + c_m^2 \lambda_m + c_n^2 \lambda_n + \sum_{i \notin \{l,m,n\}} c_i^2 \lambda_i.
\]

There are three cases to consider:

- \( m \) corresponds to the lowest eigenvalue: Eq. (A3) is minimal for the set \( \{c_l = 0, c_m = 1, c_n = 0, c_i = 0\} \), proving that the lowest mode corresponds to a minimum.

- \( m \) corresponds to the highest eigenvalue: Eq. (A3) is maximal for the set \( \{c_l = 0, c_m = 1, c_n = 0, c_i = 0\} \), proving that the highest mode corresponds to a maximum.

- \( m \) corresponds neither to the lowest nor the highest eigenvalue: assuming \( \lambda_l < \lambda_m < \lambda_n \), then choosing \( \{c_l = 1, c_m = 0, c_n = 0, c_i = 0\} \) results in \( C < \lambda_m \), whereas choosing \( \{c_l = 0, c_m = 0, c_n = 1, c_i = 0\} \) results in \( C > \lambda_m \). Together this shows that all these modes are saddle points.
