Chain-of-State Ends Pre-Optimization Using Spherical Optimization

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Abstract

Chain-of-states(COS) methods like nudge elastic band(NEB) method are robust and efficient methods with double ended, whereas two reliable ends are needed which in some cases cannot be acquired like molecule dissociation, or the two ends are too far so that more replicas are needed for convergence of minimum energy path(MEP) and transition state(TS). A method based on spherical optimization(SOPT) is presented here for pre-optimizing ends used in COS methods, in which regular geometry optimization is executed with root mean square distances(RMSD) of two ends keeping fixed. We show how this method works in two examples: (1) CHOH dissociation channel and (2) the first step of Aldol reactions. In all cases, SOPT makes MEP smoother and the convergence faster.

1 INTRODUCTION

Finding the minimum energy path (MEP) between two local minima (the initial and final states) and locating the transition state (TS) is a key topic in theoretical and computational chemistry. MEP is the highest statistically weighted path connecting the two states, and the
maximum along the path is identified as the TS, which is a first-order saddle point on the potential energy surface (PES). Once the MEP and TS are determined, the transition rate between the two states can be then estimated using transition state theory.

Various methods have been proposed to determine the MEP, and they can be generally classified into two categories: the single-ended methods and the double-ended methods, with the latter also known as the chain-of-states (COS) methods. In applying the COS methods such as the nudged elastic band (NEB) method, two end states are required beforehand, and an initial guess of states composing the chain is generated (typically by linear interpolation between the two end states, or image dependent pair potential (IDPP) method\textsuperscript{7}). Optimization routine is then executed until one image of the chain reaches the TS point. Therefore, the robustness and efficiency of the optimization algorithm and the quality of initial guess for the chain both dictate the speed of transition state search. NEB and its variations like CI-NEB,\textsuperscript{8} as one of the best COS methods, is frequently used to find MEP because of its robustness and efficiency.

Concerning the initial guess of the chain, the external degrees of freedom like translation and rotation may slow down or even prevent the convergence to MEP. A method based on quaternion algebra solved the problem by minimizing the root mean square deviation (RMSD) of atomic positions between two images\textsuperscript{9}. However, there are cases where one of the ends cannot be optimized, or the optimized geometry differs drastically from the other one. For example, the formaldehyde dissociation reaction (CHOH $\rightarrow$ CO+H\textsubscript{2}) has one end composed of two molecules barely bound by very weak interaction, which leads to a flat PES that poses a great difficulty for the geometry optimization to reach convergence. Even if it converges with loose criteria, the resulted structure is likely far too different from the other end. This means that more images and iterations are needed for MEP convergence, although the part of MEP near the one end is essentially diffusion and is uninteresting. Generally, for any MEP, the part near one or both ends are dominated by diffusion and thus is not
interesting, but the images are still needed for the convergence, and these extra images slow down the convergence significantly.

One solution is to use an artificial model structure as the end instead of a local minimum. This implies the necessity of geometry optimization for an end structure with constraints, and thus inspires us to compose a properly formulated constraint for optimizing the model end structure without increasing the distance between two ends. In the present article, we use spherical optimization (SOPT) method with the RMSD between two ends fixed. This method enables faster MEP convergence with less images needed. Although NEB is used as the MEP searching algorithm in this article for simplicity, this method is applicable to any COS methods for pre-optimizing model end structures.

2 METHODS

2.1 NEB Method and Minimize RMSD with Quaternion Algebra

NEB method is one of the most popular MEP searching methods. In practically applying the NEB method, a discrete representation of the MEP is generated initially, the elements of which are referred as “images”, \([R_0, R_1, ..., R_N]\). The NEB force on image \(i\) is modified as

\[
F_i = F_i^\parallel + F_i^\perp
\]

\[
F_i^\perp = - (\nabla E(R_i) - \nabla E(R_i) \cdot \hat{\tau} \hat{\tau})
\]

\[
F_i^\parallel = k(|R_{i+1} - R_i| - |R_i - R_{i-1}|) \hat{\tau}
\]

where \(k\) is the coefficient of stiffness and is usually 0.1 eV/Å, \(\hat{\tau}\) is the local unit tangent. A simple estimation could be
\[ \dot{\tau} = \frac{R_{i+1} - R_{i-1}}{|R_{i+1} - R_{i-1}|} \]  

(2)

Note that the external degrees of freedom including translation and rotation introduce inefficiency into the MEP searching, because part of the forces acting on the images contributes to translating and rotating the images that are chemically insignificant. This problem is solved by minimizing the RMSD between images with quaternion algebra. The square of RMSD, called residual, is defined as

\[ E = \frac{1}{N} \sum_{k=1}^{N} |\mathcal{R}x'_k + g - y'_k|^2 \]  

(3)

where \( N \) is the number of atoms of the system, \( x'_k, y'_k \) are the coordinates of atom \( k \) in two images, \( g \) and \( \mathcal{R} \) are translation vector and rotation matrix, respectively. \( g \) is simply defined as the difference between centers of mass of two images, and \( \mathcal{R} \) is calculated with quaternion algebra and the details of the algorithm are skipped here.

Additionally, as elaborated in the previous section, it is much more efficient to introduce model end structures for NEB that allow a short path with inclusion of only key images and thus enable efficient convergence, while an optimization technique is required for relaxing the internal forces without increasing the distance between two ends.

### 2.2 Spherical Optimization

Consider the case where one of the ends employs the model structure (noted as \( x, \) and the other end as \( y \)) with \( N \) atoms, with the constraint of keeping the RMSD between two ends fixed, it is converted to a constrained optimization problem, like Y. Abashkin and N. Russo
did in 1993\textsuperscript{10}

\[
\begin{align*}
\min_{\vec{x}} E &= E(x_1, x_2, \ldots, x_n) \\
\text{s.t.} \quad (x_1 - y_1)^2 + (x_2 - y_2)^2 + \cdots + (x_n - y_n)^2 &= R^2
\end{align*}
\]

where \( R \) is the initial RMSD, and \( n = 3N \) is the total degrees of freedom. To solve this optimization problem, the constraint function is rewritten by choosing an index \( q \) so that

\[
x_q = f(x_1, x_2, \ldots, x_{n-1}, R) = y_q \pm \sqrt{R^2 - \sum_{i \neq q} (x_i - y_i)^2}
\]

For numerical stability, \( q \) is chosen so that \(|x_q - y_q|\) is maximized, and the sign in Eq. 5 is carefully chosen so that it matches the reality. For simplicity, we swap \( q \) with \( n \), and energy function is rewritten by introducing the constraint into the energy function

\[
E' = E(x_1, x_2, \ldots, x_{n-1}, f(x_1, x_2, \ldots, x_{n-1}, R))
\]

Derivative of \( x_n \) over \( x_i \) is

\[
\frac{\partial x_n}{\partial x_i} = \frac{\partial f}{\partial x_i} = -\frac{x_i - y_i}{x_n - y_n}
\]

and force is rewritten as
\[ F'_i = -\frac{\partial E'}{\partial x_i} = -\left( \frac{\partial E}{\partial x_i} + \frac{\partial E}{\partial x_n} \frac{\partial x_n}{\partial x_i} \right) = F_i - F_n \frac{x_i - y_i}{x_n - y_n} \]  \hspace{1cm} (8)

where \( F \) is the force obtained from electronic structure calculation, and \( F' \) is a \( n-1 \) vector. In this way, we successfully construct an optimization problem with \( n-1 \) variables. Regular optimization techniques can be used for solving the problem, such as steepest descent, conjugate gradient, BFGS, L-BFGS. After the optimization, the internal force is relaxed while keeping the RMSD between two ends constant, making the end a perfect one for further NEB calculation, as we will see in the examples.

### 2.3 Flowcharts of Spherical Optimization

We provide flowcharts of the algorithm of spherical optimization.

1. One end is assigned as the initial state that will be optimized, and the other is assigned as the partner.
2. Use the quaternion method mentioned above to minimize the RMSD between two ends, which denoted as \( R \).
3. Calculate the force acting on each atom in the initial state.
4. Recalculate modified force with Eq. 8.
5. Perform optimization with the chosen technique.
6. Repeat 3-5 until the forces meet the criteria.

If both ends needed to be optimized, then swap the initial and final states, and repeat the procedure again. In principle, both the ends should be optimized repeatedly, but it is observed that with optimizing each end only once, the result is good enough for NEB calculation.
3 RESULTS

In the following, NEB with spherical optimization (NEB-SOPT) is applied in two examples, the CHOH dissociation channel and the first step of Aldol reaction, and regular NEB (NEB-R) are performed as well to show the validity. Both NEB-SOPT and NEB-R are performed with climbing image option. The former shows more clearly why the method is efficient. Although both ends could be optimized to minimum, they are too far from each other and thus the NEB calculation is unnecessarily slow or even fail.

In the following two examples, Gaussian 09 is used as electronic structure and force calculator, as well as for geometry optimization without constraint. B3LYP functional and 6-31G(d) with default parameters in Gaussian 09 are used in all the cases if not specified. BFGS provided in ASE is used as geometry optimizer in SOPT and NEB calculation with step size of 0.2 Å, and the maximum steps of 120 in both cases. Linear interpolation over Cartesian coordinates is used for initial NEB chain generation. The convergence max forces are all set to be 0.2eV/Å, while it is worth mentioning that max force could be set to 0.5eV/Å in SOPT to save iterations and the result is still OK.

3.1 CHOH dissociation channel

CHOH MEP searching has been one of the benchmarks for MEP and TS searching methods. In this study, the dissociation channel of CHOH (CHOH-dc) is selected as our test case, in which the CHOH molecule is dissociated into CO and H\textsubscript{2}. In applying the normal NEB method, a structure composed of CO and H\textsubscript{2} should be prepared and optimized to local minimum. However, since there is only weak interaction between CO and H\textsubscript{2}, the structure cannot be optimized with routine convergence criteria. So we start from an artificially modeled structure and optimize it with BFGS provided in ASE, and the max force is set as 0.2 eV/Å, which is higher than ordinary. The structures with from regular optimization and
spherical optimization are shown in Fig.1(b) and Fig.1(c), respectively. The energy difference between two structures is only 0.04 eV, showing the weak interaction between two molecules. But the geometry structures are quite different. As can be seen, in Fig.1(c), the distance between CO and H₂ is much shorter than that in Fig.1(b), and the structure in Fig.1(c) shows a special relative position between the two molecules which does not exist in Fig.1(b). This implies that the structure in Fig.1(c) is optimized to a neighbor of TS, indicating the validity of spherical optimization, since in regular geometry optimization, force acting on atoms could only push the two molecules apart instead of posing them to a specific position like spherical optimization, as shown in this case.

Figure 1: (a) CHO molecule as partner, (b) CO+H₂ with regular optimization, (c) CO+H₂ with spherical optimization (d) TS given by NEB3-R(Wrong)

NEB calculations are performed with 5 and 3 images, and noted as NEB5 and NEB3, respectively. The numbers of iterations needed are shown in Table 1. In NEB5, both NEB-SOPT and NEB-R calculations are converged, but the MEPs given by two methods are different in some aspects, as shown in Fig.2. The difference in activation energy is the caused by the convergence criteria and is acceptable. However, in NEB-R calculation shown in Fig.2(a), image 1 and 2 are very close, and image 4 is a shallow local minimum on MEP curve, whereas in Fig.2(b), there is no local minimum on the curve between two ends, with the images on the curve distributed evenly, and the curve by NEB-SOPT is much smoother than the by NEB-R. The length of entire reaction path is controlled no more than 1.75 Å in NEB-SOPT, whereas it goes to almost 2.0 Å in NEB-R. The spherical
optimization introduces pre-optimization of the ends, while such additional computational cost is negligible. However, the iteration numbers needed for NEB-R and NEB-SOPT are 28 and 10, respectively, which means that NEB-SOPT saves almost 60% of iterations and force calculations.

Because of the simplicity of the reaction, we also tried 3 images for NEB-R and NEB-SOPT, and the comparison is more revealing. For NEB-SOPT, only 13 iterations are needed for a correct convergence as shown in Fig.2(c), whereas NEB-R used 36 iterations, but converges to a wrong MEP and the TS is shown in Fig.2(d).

Since NEB3 could save 2/3 of force evaluations than NEB5, NEB-SOPT practically saves 85% of force calculations in this case, and the result is still correct. This shows the robustness and efficiency of the method.

![Figure 2: MEP of CHOH-dc by (a) NEB5-R (b) NEB5-SOPT (c) NEB3-SOPT](image)

Table 1: Number of iterations used by NEB-R and NEB-SOPT

| Application          | NEB-R | NEB-SOPT | Iteration saved |
|----------------------|-------|----------|-----------------|
| CHOH-dc(NEB5)        | 28    | 11       | 60%             |
| CHOH-dc(NEB3)        | 36(wrong) | 13 | -               |
| Aldol-1(NEB11)       | 111   | 33       | 70%             |
| Aldol-1(NEB5)        | fail  | 30       | -               |
For better understanding of the spherical optimization, we illustrate each image of CHOH-dc MEPs by NEB5-R and NEB5-SOPT in Fig. 3(a) and Fig. 3(b). It shows clearly that image 4 in NEB5-R is almost identical to image 5 in NEB-SOPT. This means that only 4 of 5 images are utilized in NEB5-R and the last image is only diffusion process that is uninteresting. In other words, our method removes insignificant images by a constrained geometry optimization.

3.2 The First Step of Aldol Reaction

The first step of Aldol reaction (Aldol-1) is chosen as a test case, in which formaldehyde (CHOH) and ethenol (CH₂CHOH) couple to form 3-hydroxypropionaldehyde (C₃H₆O₂). This case has also been tested by Keiji Morokuma et al. with GRRM program. In this case, PBE/6-31G(d) is used for SOPT to testify the robustness and generality of the method because it’s much cheaper than B3LYP, but the calculated force is relatively correct. This may introduce some error into the energies of end points because of the optimized geometry difference between two functionals, but the result is still OK. In NEB-R, both the ends are optimized to local minimum. NEB-R and NEB-SOPT are implemented with 5 images.
iterations are needed for NEB5-SOPT to converge with MEP shown in Fig.4(a), however, after 120 iterations, NEB5-R is still not possible to converge, and the intermediate images are broken and unphysical, even with a quite small step size of 0.05 Å. We also tried NEB-R with 7 and 9 images, and NEB-R still cannot converge. For 11 images, NEB-R converged with 111 iterations, whereas NEB-SOPT uses only 33 iterations, as listed in Table 1 and the MEPs are shown in Fig.4(b) and Fig.4(c).

In Fig.4(a), the MEP of NEB5-SOPT is quite smooth, while image 4 with energy a little lower than image 5 is the result of larger R in SOPT and PBE functional used in SOPT instead of B3LYP. The calculated TS structure agrees with that by GRRM, and the activation energy in this case is 1.64 eV, agrees well with 1.51 eV calculated by GRRM, and the difference is attributed to the fact that GRRM used 6-31G as basis sets instead of 6-31G(d) in this case.

As for the failure of NEB-R with 5/7/9 images, it is most likely originated from the rotation of CHOH molecule, because at least 5 out of 11 images are needed for molecular rotation in the MEP, as images 7-11 shown in Fig.6. This case clearly shows the efficiency of spherical optimization, which removes the rotational part of MEP, and thus enables NEB with much fewer images.

Figure 4: MEP of Aldol-1 by (a)NEB11-R (b) NEB11-SOPT (c)NEB5-SOPT
4 SUMMARY AND DISCUSSION

Large RMSD between the initial and final state used in chain-of-state methods will can slow down or even fail the convergence, and the images needed may increase. Spherical Optimization method presented here is a robust and efficient method for pre-optimizing the ends used in these methods like NEB. Instead of regular geometry optimization implemented on the ends for regular NEB calculations, constrained optimization is executed in spherical optimization, keeping the distance between two given ends fixed. Details of the algorithm is provided in section 2.3. Comparing NEB-R and NEB-SOPT, NEB-SOPT could save atmost 60% of iterations with same number of images, allow correct converge with fewer images, and even can make NEB valid in some cases like the Aldol reaction shown above, whereas NEB-R may need more images and more iterations, but the convergence may still fail. And more interestingly, spherical optimization does not introduce extra computation.
since it substitute regular geometry optimization, and lower level method like PBE or even LDA could be utilized in spherical optimization and the result is still OK. This method shows power in finding MEP of molecule association/dissociation reactions, and it is also valid in surface adsorption/desorption reactions since these reactions are the same kind. For normal MEP searching without molecule splitting, the method may not be that powerful, but is still valid.

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14
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