Nudged Elastic Band Transition State Searching and the Image-Parallel Running Mode in ONETEP

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1 NEB Method

The Nudged Elastic Band (NEB) method is a systematic approach to transition state searching. A brief overview will be provided here; for a more detailed description see [1].

1.1 Overview

Tools such as geometry optimization make determining the properties and relative energies of products and reactants relatively straightforward. Of equal importance to understanding a reaction or diffusion problem is the transition state (TS) - the highest-energy point on the minimum energy path (MEP) connecting the reactant and product in configuration space. Unfortunately determining the TS is not a simple local minimization problem, but instead it requires a determination of the MEP from the set of paths that connect the reactant and product. Several approaches that attempt to approximate the TS given a set of assumptions about the energy landscape exist, such as LST/QST. NEB attempts to offer a systematic determination of the TS through a local optimization of the MEP from an initial guess.

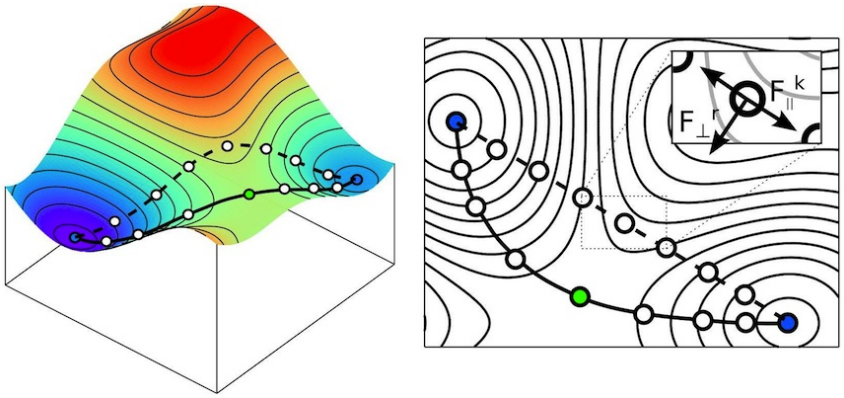

Figure 1: Cartoon of a NEB path initialization by linear interpolation and final sampling of the MEP. Each image only feels the component of the spring force parallel to the path tangent and the real force perpendicular to the path tangent. Image source & copyright [4].

1.2 Theory

An elastic band method connects the reactant and product with a chain of beads in configuration space connected to their immediate neighbors with springs of natural length 0. This chain is then relaxed with the reactant and product held fixed and each bead on the chain feeling the forces from the potential energy surface as well as the springs.

Unfortunately, this approach runs into two immediate issues. The spring force perpendicular to the path works to pull the chain away from the correct MEP, leading to a poor approximation of the TS, and the force from the potential energy surface tangent to the path pushes beads to lower energy areas, whereas the goal is to sample the highest-energy point on the path. Varying the spring constant can reduce one issue while exacerbating the other and there is no systematic way to sample the highest point of the correct MEP.

The nudged elastic band approach is to project out the problematic components of the spring and PES force, 'nudging' the chain back onto the MEP. That is, each bead feels only the component of the force due to the potential energy surface perpendicular to the path tangent and that of the spring force parallel to the path tangent. The former relaxes the chain onto the MEP and the latter evenly distributes the images along the path. Using this approach the beads will lie strictly on the MEP regardless of bead count assuming an accurate approximation to the path tangent at each point.

As with any local minimization, the final path depends on the initial guess and is not guaranteed to be the global MEP. Care should be taken in complicated reactions or diffusions - in particular a reaction passing through several stable intermediates might be broken into a number of separate NEB calculations. More control over the initial path guess may be implemented in the future.

1.3 Tangent Approximation

Because the MEP is approximated by a series of beads, the path tangent must be approximated. A number of valid approximations exist - ONETEP uses an improved-stability approximation described in [2]. This approach reduces kinks in the path that

arise in some systems and is generally stable. Equation 1 describes the tangent $\boldsymbol{\tau}_i$ approximated at bead i with energy E_i, where $\boldsymbol{\tau}_i^+ = \mathbf{R}_{i+1} - \mathbf{R}_i$ and $\boldsymbol{\tau}_i^- = \mathbf{R}_i - \mathbf{R}_{i-1}$, in cases where the neighboring beads' energies make a strictly increasing or decreasing series. If that's not the case, Equation 2 gives the tangent approximation, where $\Delta V_i^{\max} = \max\left(|V_{i+1} - V_i|, |V_i - V_{i-1}|\right)$ and $\Delta V_i^{\min} = \min\left(|V_{i+1} - V_i|, |V_i - V_{i-1}|\right)$.

$$\boldsymbol{\tau}_i = \begin{cases} \boldsymbol{\tau}_i^+, & V_{i+1} > V_i > V_{i-1} \\ \boldsymbol{\tau}_i^-, & V_{i-1} > V_i > V_{i+1} \end{cases} \tag{1}$$

$$\boldsymbol{\tau}_i = \begin{cases} \boldsymbol{\tau}_i^+ V_i^{\max} + \boldsymbol{\tau}_i^- V_i^{\min}, & V_{i+1} > V_{i-1} \\ \boldsymbol{\tau}_i^+ V_i^{\min} + \boldsymbol{\tau}_i^- V_i^{\max}, & V_{i-1} > V_{i+1} \end{cases} \tag{2}$$

1.4 Climbing-Image NEB

NEB tries to ensure that the beads are equally spaced along the path. This doesn't guarantee good sampling of the transition state, which is the most important part of the path. The TS energy can be interpolated if there are enough beads on the path, but the climbing image addition to NEB (CI-NEB) works to move a selected bead near the TS to exactly sample the TS. Once enabled, the highest-energy bead doesn't feel the NEB spring force and moves in a modified potential energy surface, where the components perpendicular to the path are essentially mirrored. This transforms a saddle point region of the PES into a basin with a minimum at the transition state. That bead is then minimized in this potential and the rest of the chain in the normal way. This is generally useful when the MEP is being sampled well, though it does make assumptions about the shape of the PES near the saddle point. More details can be found in [3].

2 Image-Parallel Implementation in ONETEP

Each NEB iteration each bead requires a local energy and force calculation, as well as knowledge of the locations and relative energies of its neighbors for spring force calculation and tangent approximation. For this reason, and for other simulations that involve multiple communicating but largely independent subsystems, an alternate running mode was developed for ONETEP that allows multiple simulations to exist in the same MPI world. Each simulation, or image, can progress independently but special communicators have been set up to allow communication between them. In the case of NEB, each ONETEP image controls one bead in the chain.

Important to note is that when running in image-parallel mode the default communicator for things like comms operations is changed from `mpi_comm_world` to `comms` mod's `pub_image_comm`, a communicator between all processes in one ONETEP image. `comms` mod's `pub_imroots_comm` is a communicator between the root processes of each image, allowing images to communicate and allowing tasks to give each image something different to do. Additionally, each image opens its own new file `{rootname}{image_num}.onetep` to write `stdout` to, with the original `stdout` being available through `image_comms` mod's `orig_stdout`. Each image similarly

maintains its own set of restart files, properties files, etc, and nothing special has to be done to restart image-parallel calculations.

Normally the number of MPI processes specified at runtime must be divisible by the number of images requested. Advanced configuration allows images to be different sizes, in case a task needs to be able to perform calculations that aren't necessarily comparable in cost.

3 Commands

3.1 NEB Keywords

NEB can be enabled by setting two input file keywords: `task : transitionstatesearch` and `tssearch_method : neb`. ONETEP must be executed with enough MPI processes to support the number of images requested. Several geometry optimization keywords will apply to NEB as the chain optimization is threaded through the geometry optimizer.

The reactant is taken from the atomic positions specified in the input file. A product section must also be provided through e.g. `%block positions_abs_product`. A guess intermediate can also be provided, in which case the NEB chain will place beads on the linear interpolation from reactant to intermediate and intermediate to product. This can be specified with e.g. `%block positions_abs_intermediate`.

Basic Usage

- `num_images: n`
  [Intermediate integer, default `1`].
  Defines the number of ONETEP instances that should run in the simulation and enables image-parallel mode. In NEB, this is also the number of beads in the chain.

- `{reactant,product}_energy`
  [Intermediate real physical, default `N/A`].
  `{reactant,product}_rootname`
  [Intermediate string, default "`NONE`"].
  Both the reactant and product energies must be known at the start of the calculation. The energy can be specified either as a raw total energy or as a rootname from which ONETEP can read the tightbox NGWF and density kernel (and, in EDFT, Hamiltonian) files from a previous calculation, or they can be calculated from scratch if neither is specified. The reactant and product energies needn't be specified in the same way.

Additional Controls

- `neb_ci_delay: n`
  [Intermediate integer, default `-1`].

Defines the number of BFGS steps the chain should take before enabling a climbing image. Negative numbers disable the climbing image entirely.

- `neb_print_summary`
  [Intermediate boolean, default `.true.`].
  If `.true.`, ONETEP will print NEB convergence information as well as a summary of the reduced reaction coordinate and relative energy of each bead after each NEB step to the original stdout.

Convergence

Currently the calculation is considered converged when each bead is individually converged. These tolerances are used instead of the geomopt ones.

- `tssearch_energy_tol`
  [Expert real physical, default `1.0e-5 Ha`].
  Convergence tolerance on change in bead energy in one NEB step.

- `tssearch_force_tol`
  [Expert real physical, default `0.005 Ha/bohr`].
  Convergence tolerance on max force on any atom.

- `tssearch_disp_tol`
  [Expert real physical, default `0.01 bohr`].
  Convergence tolerance on displacement of any atom in one NEB step.

Other Image-Parallel Keywords

- `image_sizes`
  [Expert string, default "`DEFAULT`"].
  If specified in the input file, a string of the format '`i|j|k|l|m|...`' can be used to individually size the images in an image-parallel run. The number of sections specified should be equal the number of images in the run and the sum of the image sizes should be equal the number of MPI processes specified at runtime.

References

[1] H. Jónsson, G. Mills, and K.W. Jacobsen. Classical and Quantum Dynamics in Condensed Phase Simulations Pt. II, Chapter 16: Nudged elastic band method for finding minimum energy paths of transitions.

[2] G. Henkelman, and H. Jónsson. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.*, 113, 9978 (2000).

[3] G. Henkelman, B.P. Uberuaga, and H. Jónsson. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.*, 113, 9901 (2000).

[4] Copyright P. Cordier `http://umet.univ-lille1.fr/Projets/RheoMan/en/to-learn-more-about/nudged-elastic-band.php` Accessed 21 April 2018.