Qeios

Peer Review

Review of: "Comment on ”Exploring potential energy surfaces to reach saddle points above convex regions” [J. Chem. Phys. 160, 232501 (2024)] by M.Gunde et al."

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I do not recommend this work for publication. The world is already full of low-quality articles, and we should avoid adding useless stuff on top of it.

Global impression :

In the commented paper, ARTn was used by stopping when getting back a positive Hessian lowest eigenvalue (entering a convex region) to save computational cost. This is shown to be a mistake, as it prevents the obtaining of some relevant saddle points. A solution has been proposed to extend the algorithm above the convex regions and consequently obtain these saddle points with good efficiency.

This Comment presents an already known method (following Newton trajectories) and reminds us that it does not care for convex regions to get all the saddle points. Is this Comment needed ? There are plenty of methods to get saddle points; I hope the authors will not write a comment every time someone tries to improve their own method. Sorry, by looking at their list of publications, it is exactly what they do! In my opinion, this is only showing muscles on an irrelevant 2D toy model to remind us of the existence of NTs and doing self-citations (come on, 30 self-citations in a simple comment!). The message of the comment is obvious and not impressive because any algorithm that does not follow the minimum curvature can continue through convex regions without any care. It does not contribute anything new. The two methods are different and face their own drawbacks, which is the subject of the main article but unfortunately not discussed in the Comment, summarized by «we can also do it !» without any analysis. Contrary to what is expressed in the abstract, “ARTn is not compared to NTs”. This comment is interesting but out of the scope of the initial paper and should have a better place in a review of Quapp&Bofill's works.

Here are the main problems that need to be solved before publication :

Physics : The main message of the commented article has been hidden behind useless stuff : how to efficiently reach the SP that are above convex regions or valleys branching. This is, for me, the main problem of this Comment. In fact, by using

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the 2D toy model, the comment shows that the 5 connected saddle points can be reached from the minimum by following Newton Trajectories with five directions : f=+/-(1, 1) for SP1 and SP4, f=+/-(1,0) for SP3 and SP5, and f=(0.987, 0.163) for SP2. In my opinion, this fifth red Newton trajectory is the one for which the authors are proud and find mathematically cleaner than the minimum eigenmode following trajectory (ARTn, commented paper Figure 2). However :

-As expressed in the text, the corridor for this NT is very narrow. By doing an exploration of the PES from the minimum (trying many random f, as it is a priori unknown), the probability of getting SP2 is then quite null by following NTs compared to what M. Gunde's article shows in Figure 3c. This first failure must be FAIRLY expressed, for example, by giving this probability and comparing it to the one of M. Gunde's work.

-If this corridor leading to SP2 is luckily reached, it will go through the Shoulder point Sh, where many corridors are infinitesimally close to each other. Note that this point CANNOT be detected during an exploration with only local information. In real cases (N dimensions), the time step used in the Comment (Equ. 3) must be numerically big enough to save computational cost (ab initio forces are expensive!). This implies that going through the Shoulder will inevitably lead to a change of corridor and thus losing the corridor that was already unlikely to reach. This second failure must also be fairly expressed.

-I am wondering how unlikely it will be to reach the magenta saddle point of Fig.9 of M.Gunde's paper. Even if it is still on the 2D toy model, this is a more challenging and interesting task! More generally, I am wondering how unlikely it will be to reach any SP that is above several branchings and convex regions as shown in Fig. 6 of M.Gunde's paper. Please, when you do a « Comment » to show that your method is better, comment on what the paper is claiming.

-In my opinion, what is missing in M.Gunde's work is the link between convex regions that do not contain a minimum and valley branching. Is there a link? If yes, this should deserve a comment.

-All the comments focus on an irrelevant 2D toy model instead of dealing with a real 3NatomsD system. It is claimed that it works for bigger systems «We report that NTs are calculated for the PES of Frenkel-Kontorova chains with up to 500 atoms and for medium molecules with up to 150 atoms » but there the algorithm seems to actually miss the saddle points despite a terrible computational cost. The cited works are insufficient to support the claims that their algorithm is efficient in 3D.

Definitions :

-Ridges : It seems that the authors of M.Gunde's paper have used Hoffman definitions given here https://link.springer.com/article/10.1007/BF00527704 in Fig 1, where the dashed 1D line is where the gradient is parallel to the lowest eigenvalue. A valley with a maximum of 1 negative eigenvalue, so that the 2 arrows go to the valley, ridges with at least 2 negative eigenvalues, so that the arrow escapes the ridge. It seems that what you have used as a definition of a ridge is what they define as the 'perpendicular hyperplane' (which is obviously locally a hyperplane and globally a hypersurface) where the gradient is orthogonal to Vmin. I do not see any inconsistency in their claim along the paper. So if it is only a semantic question, this paragraph is useless; if not, please precise your own definition of a valley and of a ridge.

- Valley branching : « A further gap is the distinction between 'valley branching' and VRI points » and the paragraph. Here I do not understand why you say this : when comparing their Fig.1 (and their Fig.9) with your Fig.1, we can clearly see that there is no valley branching at your VRI points Xi, but only a Newton trajectories crossing (forbidden). On the contrary, we

can clearly see that the valleys in their figures do forbidden crossing in the convex regions. I do not see any trouble in their definition of VRI : the point between a valley becomes a ridge=where the 2nd inflection takes place! Nor in their definition of a branching point (volume of forbidden crossing): the point where a valley switches into several valleys. With these definitions and the examples given in the figures, I do not see how it is possible to have the two definitions at the same point as you claim. So if it is only a semantic question, this paragraph is useless; if not, please precise your own definition of valley branching and VRI points and draw the valleys on the graph to show that their branching occurs at your X_i, which I doubt. As you confirm this later in the text «Note that there is no bifurcation of the valley of *M* at the shoulder, Sh. The corresponding bifurcation points are *X*1 and *X*5», you HAVE TO add into your Fig.1: the bottom of the valleys, the ridges, and the different regions (corridors) that lead to the same SP colored as M.Gunde's Fig.3. Your algorithms are different, so these regions must be different.

Language : The Comment is badly organized with some spelling mistakes (please use a corrector). Here are some :

-« This letter » → this comment

-« Introduction » is more like « Nts method ». A good introduction would explicitly say what the problem of the commented paper is and how the Comment solves it. Here it is only, « they use this, we use that ».

-« compare the example in Section II »→ as shown in...

-« Normally it connects »→ Precise « it »= singular Newton trajectories?. Why « Normally », sometimes not ?

- «an saddle point » → a saddle point (seen many times)

- «A second gap », → where is the first ? Gap is not the correct word; remark or correction seems better. Same for 3 and 4 gaps.

-All this definitions stuff should be elsewhere so that the NT method is linked to the PES example and not separated by definitions. Like Intro/Def/Method/Results/Conclusions.

Useless stuff : All the following stuff is irrelevant

- « A few notes in advance: To calculate the stationary points of the PES of a molecule, only $3N_{at}$-6 internal degrees of freedom (DoF) are needed. » → This is too obvious and does not add anything to the original article nor to the comment. For information, these DoF are removed for the Hessian in ARTn using a central routine, but this routine does not deserve an article.

- «A second gap is the wayward definition of a ridge on page 3. For example, at an SP of index one we have one nega... » and all this paragraph. Please give your definition of a ridge.

- « A third gap... » Without any explanation, this sentence is useless; probably it goes with the same paragraph as « A forth gap ».

- «A forth gap... » Same comment. I think it is completely out of the scope of the initial paper and of this comment and can be removed.

Sentences that need precision :

-« It (Hessian) can be updated ». Can you please specify at what cost? For example, the same authors here https://doi.org/10.1016/j.commatsci.2022.111363 show that less than 5 force calculations are needed to obtain the lowest eigenvalue above the inflection.

-« A first step from a stationary point goes in direction f ». Can you please specify how f has been chosen ? Is it random like any other algorithm ? Is it important that the starting point is stationary?

-« For example, the dashed blue curve is the singular NT through the VRI point X1 »... obtained by taking f=... Can you please specify how you have obtained the blue curves ? I suppose you first found all the SPs and then from each of them you do follow a NT, but with which f ?

- « For example, one branch of the thick black NT (direction f = 1√2 (1, 1)) connects SP1 to M via Sh, leading to SP4 », this is misleading; the reader feels that you start from SP1, fall to Sh, then to M, and then to SP4. Is my proposition correct : « From M in direction +(1,1), the NT goes to SP1 via Sh, and in direction -(1,1) to SP4. » ? Same for the sentence after.

Declarations

Potential competing interests: No potential competing interests to declare.