Replay
to the Comment by Sheppard and Henkelman on the Nudged Elastic Band Method

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In many cases the NEB method approximates the steepest descent (SD) from a saddle point (SP). That is the established experience of the last 13 years. However, it does not exclude the possibility that the projection operator

$$\mathbf{I} - \hat{\tau}_i \hat{\tau}_i^T \tag{1}$$

which is the backbone of the method, but which is also an interesting part of the gradient extremal (GE) theory [1, 2], works in the other direction, as was asked in the inquiring Letter [3] (here after labeled as QuBoLet).

The basic equations of the NEB method are given in eqs.(1) to (5) of the foregoing comment (here after labeled as SheHcom). The authors of SheHcom argue that an algorithm based on the representation of a polygonal curve under the force of their eq. (1) achieves an SD curve. This is the central point of the discussion. It should be known that the SD curves are extremal curves of an integral functional. The question was studied a time ago by the authors of QuBoLet in references [4, 5]. An important conclusion of this study is that from the theory of the calculus of variations the necessary and sufficient variational conditions until the second order to achieve the SD curve from any guessed curve are not given those by eqs. (1) to (5) of SheHcom. Equation (3) is the correct variational condition but not eq. (2). Equation (2) does not follow from the theory even until the second order. It is reasonable to think that eq. (2) perturbs during the search of the SD the correct effect of eq. (3) converging to a curve that differs with respect to

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the desired SD. The latter does not imply that the NEB equations do not converge to the SD in many cases. However, to forbid any question, we set the spring forces of eq. (2) of SheHcom to zero, by $k = 0$, in QuBoLet. Under this condition one can study the pure action of the intrinsic operator (1), the projection operator. Under $k = 0$, its work becomes manageable. There seems to be a unique meaning between SheHcom and QuBoLet on the point.

In QuBoLet, examples are reported where a first order method like the NEB, or a second order method like TASC [5], do not converge in some regions to the SD curve. No, a GE curve is approximated (which needs third order methods in the general case). We believe that this is not bad news for the NEB algorithm. The calculation of a GE is neither useless, nor bad. The GE curve is often a good reaction path representation. In other words, if the NEB algorithm constructs curves which are located in a valley floor of the PES under consideration, but different to the SD like GEs often do, what is the problem? And it may be in the past, that an obtained approximation was nearer to a valley GE, but no one has detected it, because not everybody has searched for a GE? Note: very often the GE coincides with the corresponding SD curve, or both kinds of reaction paths are very near together. For example, in Fig.3 of SheHcom, there the GE and the SD from the SP (b), as well as from SPs (a) and (c) totally coincide. The quarrel is useless, which of both curves is approximated.

In contrast, in Fig.3 of QuBoLet, repeated in Fig.1 of SheHcom, the modified NFK surface [6] is presented where both kinds of curves are quite different curves. The two curves allow the existence of two clearly different numerical solutions of methods which use the projection operator (1). To accept the fact, of course, open-mindedness is crucial. And one can look for a second numerical solution if, and only if one has a theoretical idea of its existence: "It is the theory which decides what can be observed," says A. Einstein. For the strange QuBoLet example we could demonstrate that a modified NEB method can lead to a GE [3]. Though the SD from SP is nearer to the used initial chain, the algorithm moves the chain of nodes to jump over the SD and approximates a GE. Here our replay could be finished. We presented a (singular) example which confirms our idea in an extreme case. The Fortran code of the algorithm, as well as a movie of the development of its approximation of the GE, were presented on an open web page [7] after the submission of QuBoLet. The working example is a sufficient evidence for the possibility of an approximation of a GE.

But if one treats the problem somehow more deeply, one may detect that we modified the NEB in QuBoLet only at a special entry, see the footnote 8 of SheHcom. Specifically, in a loop over the nodes, by i, the damped dynamics velocity, V, was calculated as

$$V = V + \Delta\, tF_i \tag{2}$$

where F_i is the force at the current node, and Δt is the integrator time step. The original velocity along SheHcom should be calculated for each node separately,

$$V_i = V_i + \Delta\, tF_i\ . \tag{3}$$

Now a question emerges, if the NEB method is that one which uses the damped dynamics velocities V_i of eq. (3) and which then can lead to the SD from SP, but contrary, if one uses a more coarse velocity V of eq. (2) and one can obtain a GE, why it is this contradict

anything? What is here the question? Do the velocities V or V_i emerge in the basic eqs.(1) to (5) of SheHcom? No, they do not emerge. The backbone of the NEB method is the projection operator (1). It is used in both cases. What contradicts our claim that a GE could be reached? (A matter of fact, indeed.) Or is it the other question, that it is "forbidden" to modify the holy NEB method of Prof. Dr. Henkelman? The usage of the velocity V, or contrary of the velocities V_i, is a pure technical step of the numerical method for the application of eqs. (1) to (5) of SheHcom. After some tests, and without any further theoretical reasoning, we used that V which pushes the initial chain of nodes over the SD in the example of Fig.3 of QuBoLet.

By the way, it is not only possible to obtain the SD by the step from V of eq. (2) back to the velocities V_i of eq. (3), as it is done in Fig.1 in SheHcom. One may change only the order in our initial chain of nodes: interchange beginning and end nodes, thus, start the iterations at the minimum. Then our modified NEB can not differentiate the small angle between SD and GE at the minimum, and it adheres on the SD solution, but does not jump over it. Because, the SD remains to be a solution of the method. In this case, beginning at the minimum, we also obtain the SD, well-considered with the putative "coding error" eq. (2) against eq. (3) which Sheppard and Henkelman think to have detected.

Neither from Henkelman et al., nor from others we know a uniqueness proof for the SD from SP by the NEB method. (Compare a corresponding convergence proof for valley floor GEs by TASC [8].) What one has is the numerical experience that curves emerge which could be the SD from SP, in a great many of cases. But this is never a uniqueness proof. Maybe, here a "clash of cultures" happens: mathematical against chemical thinking [9]. We propose to read the old Hamlet [10]:

"There are more things in heaven and earth, Horatio,
Than are dreamt of in your philosophy."

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