

A Comment to the Nudged Elastic Band Method

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Abstract: The minimum energy path (MEP) is an important reaction path concept of theoretical chemistry, and the nudged elastic band (NEB) method with its many facets is a central method to determine the MEP. We demonstrate in this comment that the NEB don't have to lead to a steepest descent pathway (as always assumed). In contrast, as long as it is used without spring forces, it can lead to a gradient extremal.

Key words: Potential energy surface; reaction path following; potential force; projected gradient; Newton trajectory; gradient extremal; tangent search concept

Introduction

The concept of the minimum energy path (MEP) of an adiabatic potential energy surface (PES) is the usual approach to the theoretical kinetics of larger chemical systems. It is roughly defined as a line in a coordinate space, which connects two minimums by passing the saddle point (SP) or the transition structure of a PES. The energy of the SP is the highest value tracing along the MEP. It is the minimal energy a reaction needs to take place. The idea of an MEP circumvents the dimension problem for large molecules: it is impossible to fully calculate their PES.

It is an uncertainty of the MEP definition, how a reaction path ascends to the SP: what is the direction a reaction has to start with? The usual answer is that the

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pathway is a steepest descent (SD) from SP downhill to the two adjacent minimums. It is also assumed the the NEB method[1, 2] (see also ref.[3] and references therein), will find the SD pathway. We will show that this has not to be always the case. In contrast, the potential force of the NEB can be used to calculate a gradient extremal (GE). Of course, the spring forces will often smear the character of the curve images. With an improved method,[4] one finds the SD pathway from SP, the IRC. We discuss the difference.

The Nudged Elastic Band Method

The NEB method is a chain-of-states method in which a string of images is used to describe the MEP. The images are connected by spring forces to ensure a quasi equal spacing along the pathway. The calculation is started from an initial chain which has to connect reactant and product minimums. The images along the NEB are relaxed to the MEP through a force projection scheme in which potential forces act perpendicularly to the chain, but spring forces act along the chain. To define the projection a tangent, \mathbf{t} , is used along the path. If a parameterization, s , of the reaction pathway is given $\mathbf{x}(s)=(x^1(s), \dots, x^n(s))^T$, n is the dimension of the problem, then the unit tangent is $\mathbf{t} = (d\mathbf{x}/ds)/|d\mathbf{x}/ds|$. The chain is represented by $m+1$ images, \mathbf{y}_i , $i=0,1,\dots,m$. The NEB force to every image, \mathbf{y}_i , has two independent components,[3]

$$\mathbf{F}_i^{NEB} = \mathbf{F}_i^\perp + \mathbf{F}_i^\parallel, \quad (1)$$

where \mathbf{F}_i^\perp is the component of the force perpendicular to the unit tangent,

$$\mathbf{F}_i^\perp = -P_{\mathbf{t}} \mathbf{g}(\mathbf{y}_i), \quad \text{with} \quad P_{\mathbf{t}} = \mathbf{E} - \mathbf{t}_i \mathbf{t}_i^T, \quad (2)$$

\mathbf{g} is the gradient of the PES, $P_{\mathbf{t}}$ is a projection operator constructed by a dyadic product of the tangent vector, \mathbf{E} is the unit matrix, and \mathbf{F}_i^\parallel is a spring force parallel to the band

$$\mathbf{F}_i^\parallel = k (|\mathbf{y}_{i+1} - \mathbf{y}_i| - |\mathbf{y}_i - \mathbf{y}_{i-1}|) \mathbf{t}_i, \quad (3)$$

k is the spring constant. The spring interaction between adjacent images is added to ensure continuity of the chain.

Action of potential force

First, we will treat the first force only, thus we imagine a chain without spring forces. We set the spring constant k in eq. (3) to zero. There the task emerges: find a chain which fulfills the projector equation

$$P_{\mathbf{t}} \mathbf{g}(\mathbf{y}_i) = \mathbf{0}. \quad (4)$$

Of course, every SD curve is a solution of the task, because for the SD it is defined

$$\mathbf{t}_i = \mathbf{g}(\mathbf{y}_i) / |\mathbf{g}(\mathbf{y}_i)|, \quad (5)$$

and the projection orthogonal to the gradient of the gradient itself is zero. The easy theoretical solution, on the other hand, hides a quasi-solution by a GE under a special use of the iterative devise. Note that eq.(4) is not able to decide locally which SD curve is the true intrinsic reaction coordinate (IRC), the SD coming exclusively from the SP, because every SD curve is a solution of this eq. (4). The GE, on the other hand, is a local quasi-solution. To understand the connection of an GE and of eq. (4) we have to go a small detour over Newton trajectories.

The Newton Trajectory

Another view to eq. (4) is to assume a fixed projection direction, \mathbf{r} , instead of the tangent direction \mathbf{t} of every image. This task is known as the definition of the Newton trajectories (NT).[5, 6, 7, 8, 9, 10] (A former name was reduced gradient following, RGF.) These curves can be determined uphill or downhill, and they can also be used for MEP models in many cases. We remark that the search for an appropriate MEP is not necessarily equivalent to the finding of the SD pathway from the SP,[11, 12] the IRC. It should be noted that the term MEP is rather conventional when used for NTs, in the usual case of NTs without a turning point between minimum and SP: every such NT monotonically rises in energy from the minimum to the SP (or vice versa) and fulfills the natural definition of an MEP.[13, 14]

Definition of NTs

The starting point is a geometrically defined pathway which may serve as a reaction path. Geometrically defined means that only properties of the PES are taken into account like in the definition of the SD, however, no dynamical behavior of the molecule is used. In earlier times, it was proposed to choose a distinguished coordinate along the valley of the minimum, to go a step in this direction, and to perform an energy optimization of the residual coordinates.[15] Some years ago, this method was transformed into a new mathematical form.[5, 6] The concept is that any preselected gradient direction is fixed $\mathbf{g}(\mathbf{x})/|\mathbf{g}(\mathbf{x})| = \mathbf{r}$, where \mathbf{r} is the unit vector of the search direction, and \mathbf{g} again is the gradient of the PES. The search direction may correspond to an assumed start direction of a chemical reaction. Or it may be the direction along a valley of the minimum, or any other direction. The property is realizable by a projection of the gradient onto the $(n-1)$ -dimensional subspace which is orthogonal to the one-dimensional subspace spanned by the search direction \mathbf{r} . A curve belongs to the search direction \mathbf{r} , if the gradient of the PES always remains parallel to the direction \mathbf{r} at every point along the curve $\mathbf{x}(s)$

$$\mathbf{P}_{\mathbf{r}} \mathbf{g}(\mathbf{x}(s)) = \mathbf{0} \tag{6}$$

where $\mathbf{P}_{\mathbf{r}}$ projects out of the search direction \mathbf{r} . This means $\mathbf{P}_{\mathbf{r}} \mathbf{r} = \mathbf{0}$. The projector $\mathbf{P}_{\mathbf{r}}$ in Eq. (6) “reduces” the gradient. It can be built by an $n \times n$ matrix of the dyadic product of the search direction like $\mathbf{P}_{\mathbf{t}}$ in eq. (2).

To numerically calculate a point on curve (6) one needs the tangential vector. The derivative of Eq. (6) creates the tangent vector \mathbf{x}' to the curve

$$\mathbf{0} = \frac{d}{ds}[\mathbf{P}_r \mathbf{g}(\mathbf{x}(s))] = \mathbf{P}_r \frac{d\mathbf{g}(\mathbf{x}(s))}{ds} = \mathbf{P}_r \mathbf{H}(\mathbf{x}(s)) \mathbf{x}'(s). \quad (7)$$

The matrix \mathbf{H} is the Hessian at point $\mathbf{x}(s)$. Equation (7) is a linear equation for the tangent vector at the current point. The system can be solved by QR decomposition.[16]

For the calculation of a corrector step, one may delete one dependent line of the matrix, \mathbf{P}_r , building $\widehat{\mathbf{P}}_r$, and can then augment the reduced Hessian $\widehat{\mathbf{P}}_r \mathbf{H}$, an $(n-1) \times n$ matrix, by the tangent vector to a nonsingular $n \times n$ matrix which is the so-called \mathbf{K} matrix.[16] The \mathbf{K} matrix is the coefficient matrix of a linear system of equations. The right-hand side of the system forms the negative reduced gradient, $-\widehat{\mathbf{P}}_r \mathbf{g}$, now augmented by a zero in the last, n -th entry. (For an overview to diverse correctors of the NEB method, see ref.[3])

By the way, one can also use the pure gradient part of the perpendicular force of eqs. (2) or (6). However, the resulting algorithm sometimes runs into zigzagging, see Fig. 1 of ref.[17], and the efficiency may be bad, because the SD method is known to convergent slowly in stiff systems, see also a comparison between first and second order methods.[18] Corrector steps are applied if the norm of the reduced gradient $\widehat{\mathbf{P}}_r \mathbf{g}$ of Eq. (6) is greater than a given threshold. The corrector step is a kind of a Newton-Raphson step being orthogonal to the tangent of eq. (7).[5, 6, 10]

In contrast to their geometrical definition, NTs are like molecular dynamics curves: a family of NTs to different directions go through the same SP but may fill the space between the minimum and the SP. However, in contrast to dynamical trajectories, all NTs of the same family concentrate at the same SP. It is a consequence of the definition of NTs: at the stationary points the gradient vector is the zero vector. All search directions flow into the zero vector if the gradient disappears. If one imagines the NT to be a curve of the system point driven by a force in a fixed direction, then the NT may indeed fill the gap between the IRC and dynamical trajectories.[11]

NTs have a second definition by a differential equation

$$\frac{d\mathbf{x}(s)}{ds} = \pm \mathbf{A}(\mathbf{x}(s)) \mathbf{g}(\mathbf{x}(s)) \quad (8)$$

named the Branin equation. It uses the adjoint matrix \mathbf{A} of the Hessian \mathbf{H} , which is $[(-1)^{i+j} m_{ij}]^T$, where m_{ij} is the minor of \mathbf{H} . It is $\mathbf{A} \mathbf{H} = \text{Det}(\mathbf{H}) \mathbf{E}$. The statement follows if we treat a derivation of the gradient along a solution of eq. (8)

$$\frac{d\mathbf{g}(\mathbf{x}(s))}{ds} = \mathbf{H}(\mathbf{x}(s)) \mathbf{x}' = \mathbf{H}(\mathbf{x}) (\pm \mathbf{A}(\mathbf{x}) \mathbf{g}(\mathbf{x})) = \pm \text{Det}(\mathbf{H}(\mathbf{x})) \mathbf{g}(\mathbf{x}). \quad (9)$$

Thus, the gradient proportionally changes to itself. The direction of \mathbf{g} is invariant, and eq. (6) is true.

Relation between Gradient Extremal and NT

Definition of a gradient extremal (GE): At every point the gradient of the PES is an eigenvector of the Hessian[19]

$$\mathbf{H} \mathbf{g} = \lambda \mathbf{g} \quad (10)$$

and λ is the corresponding eigenvalue. With the definition we find out:

A point \mathbf{x} where the tangent of an NT through this point is parallel to the gradient belongs to a gradient extremal.[20]

The proof: if $\mathbf{e}_1, \dots, \mathbf{e}_n$ are the eigenvectors of \mathbf{H} with eigenvalues $\lambda_1, \dots, \lambda_n$ then they are also the eigenvectors of the adjoint matrix, \mathbf{A} , but with the eigenvalues $\mu_i = \prod_{j \neq i} \lambda_j$. This is due to the equation $\mathbf{H} \mathbf{e}_i = \lambda_i \mathbf{e}_i$, and, by multiplication with \mathbf{A} from the left, we get

$$\mathbf{A} \mathbf{H} \mathbf{e}_i = \text{Det}(\mathbf{H}) \mathbf{e}_i = \lambda_i \mathbf{A} \mathbf{e}_i, \quad \text{with } \text{Det}(\mathbf{H}) = \prod_{j=1}^n \lambda_j. \quad (11)$$

The gradient is eigenvector of \mathbf{H} and also of \mathbf{A} on a GE. By hypothesis at this point the tangent of the NT is proportional to the gradient and because NTs satisfy the Branin equation it follows equation (11). The equation of GE is obtained in terms of the \mathbf{A} matrix being the proof completed. See also Fig. 9 of ref.[21] which we reproduce here in Fig. 1. The curves are calculated by Mathematica[®].

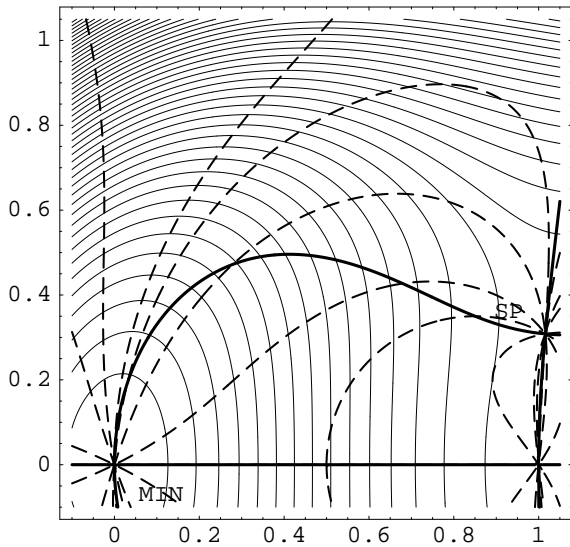


Figure 1: NTs (dotted lines) intersect the valley GE (bold line from minimum to saddle point) if they are parallel to the gradient of the PES.

The TASC method[22]

Under the following of an NT, use the current tangent at image \mathbf{y}_i for a next search direction \mathbf{r}_i ! The method is named tangent search concept (TASC).[23] After an initial step from SP or minimum, and possibly after one or two corrector steps, the method follows the streambed of the valley along the direction of the eigenvector with the smallest (absolute) eigenvalue. It results in a GE to the smallest (absolute) eigenvalue. The reason is, if one has fixed the current tangent, \mathbf{t}_i , for the search direction, the corresponding Newton-Raphson steps of the corrector converge usually very quickly. The corrector finds the (abstract) NT which fulfills $\mathbf{P}_t \mathbf{g} = \mathbf{0}$. However, the image of an NT with such a property is on a GE, see Fig.1. Note: the tangent to the GE itself usually is another direction. Nevertheless, the TASC method usually works and converges very quickly. It is because the operator (4), or (6), correspondingly, is the operator of an NT. Any image on the GE belongs to another (abstract) NT crossing the GE there. Again, TASC can operate uphill or downhill, or for a string, as well as the following of any NT.

It can be observed that the NTs concentrate in valleys (and on ridges).[8] It can be seen that the more NTs lead through a region the more the equipotential surfaces are curved. This effect will dramatically grow in higher dimensions.[24] The effect is used in the TASC method:[23] the GE following is replaced by an approximate following of the valley family of NTs where a corresponding member actually goes parallel to the gradient along the valley floor.

Proof that TASC yields a Gradient Extremal:

Instead of the definition of an NT by eq. (6) we may use the equivalent Branin eq. (8). Here the tangent, \mathbf{x}' , of the NT is given. The projector of the original NT was \mathbf{P}_r to the search direction, \mathbf{r} . We replace this constant direction at an image by the direction of the current tangent, \mathbf{t}_i , now given by the Branin eq. (8) of the current NT. Thus, the projector for the next step is constructed with the vector $\mathbf{x}'_i = \mathbf{A}_i \mathbf{g}_i$. It uses the dyadic product

$$\mathbf{P}_{\mathbf{A}\mathbf{g}} = \mathbf{E} - \frac{(\mathbf{A}\mathbf{g})(\mathbf{A}\mathbf{g})^T}{\|\mathbf{A}\mathbf{g}\|^2} . \quad (12)$$

If we search for a solution curve of (6), this becomes

$$\mathbf{P}_{\mathbf{A}\mathbf{g}} \mathbf{g} = \mathbf{0} = \mathbf{g} - \mathbf{A} \mathbf{g} \frac{(\mathbf{g}^T \mathbf{A} \mathbf{g})}{\|\mathbf{A}\mathbf{g}\|^2} . \quad (13)$$

Multiplication by the Hessian, \mathbf{H} , from the left-hand side results in

$$\mathbf{H} \mathbf{g} = \text{Det}(\mathbf{H}) \mathbf{g} \frac{(\mathbf{g}^T \mathbf{A} \mathbf{g})}{\|\mathbf{A}\mathbf{g}\|^2} . \quad (14)$$

$\text{Det}(\mathbf{H})$ can change its place to the scalar of the product $(\mathbf{g}^T \mathbf{A} \mathbf{g})$. Thus, the expression on the right-hand side, without one \mathbf{g} , is a scalar. If we denote it by $\lambda(\mathbf{x})$, we obtain the known eigenvector equation $\mathbf{H} \mathbf{g} = \lambda \mathbf{g}$, which is the eq.(10) of the gradient extremal.[19]

Example 1

An instructive mystery is Fig. 5 of ref. [4], the preceding paper. The pathway found is not an SD from MAX, however, it is the weakest descent being possible. The answer to the riddle is: the result of the NEB search (with small springs) is a ridge GE along the way TS1-MAX-TS1'. In Fig. 2 we show the GEs on the surface used.

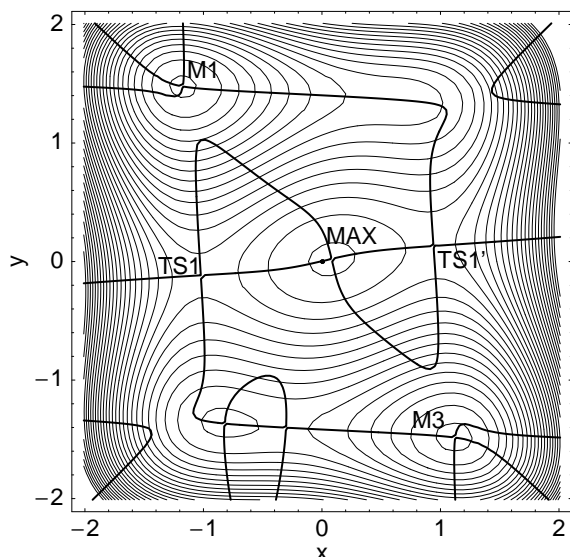


Figure 2: Gradient extremals (bold curves) on the PES of ref.[4]. The GEs are determined by Mathematica.

GEs in x -direction are the GEs to the smaller eigenvalue, in contrast to the GEs in y -direction. The ridge in question is the GE with the lowest (absolute) eigenvalue at MAX. The valley from minimum M3 to TS1' is near the TS the GE with the larger eigenvalue, in comparison to the ridge GE. The two GEs cross at TS1'. Near the minimum M3, there is a gap in the GE, at all. Consequently, an NEB procedure finds no image in the valley.[4] The similar situation is the relation between minimum M1 and TS1. There the spring force has pushed one image a small distance into the valley to M1, but again this valley is then empty.

Example 2

A toy surface for an advanced course is the modified NFK surface [25, 26]. We use it for a second example, where the NEB method finds the valley ground pathway being a valley GE. In contrast to Example 1, where the GE found is a ridge GE, here both, the SD and a valley GE, go downhill from the SP of index one. However, they go on different paths. The GE has a strong kink, and it goes far more besides than the IRC, which also is curved, and which also deviates from an initial straight line between minimum and SP. Thus, the determination of the GE should be a little more difficult, than that of the SD. An NEB method finds the GE, see Fig. 3(a). An initial chain with 50 images was used building a straight line between Min and a

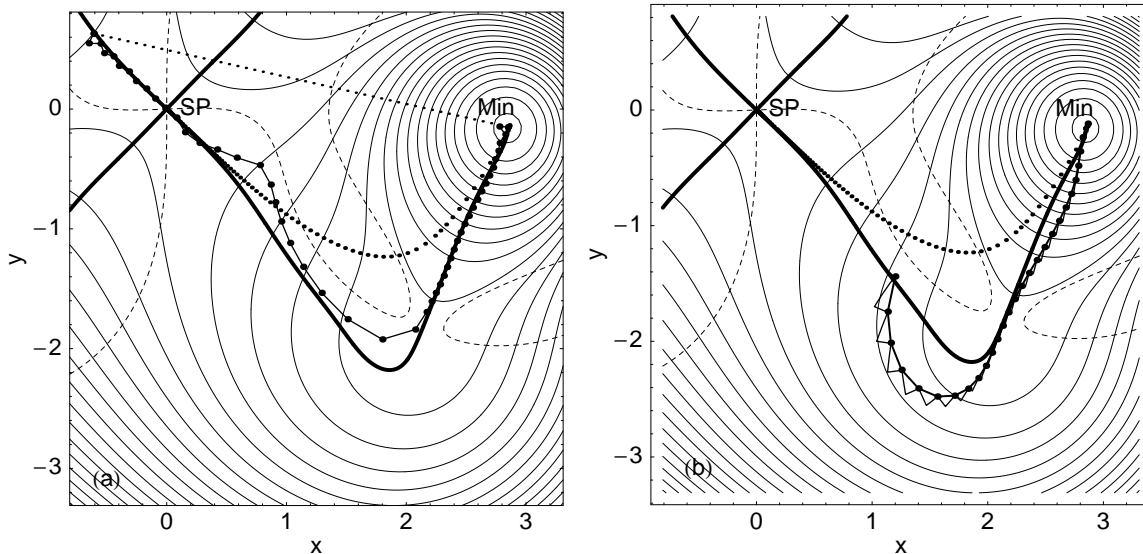


Figure 3: Gradient extremals (bold curves) across the SP, and between SP and Min, on the modified NFK-PES [26], determined by Mathematica. The bold-dotted way is the IRC from SP. Dashed curves are borders between ridge- and valley regions. (a) NEB chain (connected dots) by Euler integrator after 750 iterations. Spring constant $k=0$. Thin dots are the initial chain. (b) A growing string from Min by TASC method. Between the images are predictor- and corrector steps.

point behind the SP. We employ an Euler integrator [3]. The calculated images are the result of 750 iterations per chain, times 2 iterations per image. We used here the case of no spring constant, $k=0$, and a steplength of the Euler integrator of 0.0125 units. An approximation of the tangent vector is given by $\mathbf{t}_i = \mathbf{y}_{i+1} - \mathbf{y}_{i-1}$ where i is the current image number. The reported chain is not a convergent result. Some 100 iterations later, there bumps emerge on the part between the Min and the kink which do meander endlessly. Nevertheless, the chain meanders along the GE.

In Fig. 3(b) we show the result of TASC on this surface. Shown are predictor- and corrector images. Starting at the Min, the method finds a growing string uphill to the kink of the GE, but then it goes around and does not report the next intersection with the GE. We cut the string there. (The growing string circles further around.) The predictor steps are 0.125 units. The corrector is stopped if the norm of the reduced gradient, eq. (4), is less than 10^{-10} . The ascent away from Min is not easy for TASC, because the level lines of the surface are nearly circles. There the valley GE is difficult to localize. But the 'door' between the two noses is found. After the kink, the GE curve changes the order of the eigenvalues. Then, TASC has no chance to find the GE, because it searches the smallest eigenvalue GE only.[20] After the intersection of the growing string with the GE, the situation becomes still more difficult. The GE eigenvalue uphill becomes lower, the GE follows again the smallest eigenvalue, however, near the GE, the level lines have zero curvature. The Hessian becomes singular, there. The GE itself does not touch the zero curvature of the level lines. But TASC determines (abstract) NTs, and the NTs which cross the

GE do nearby intersect the level lines near the zero curvature. There the corrector of TASC diverges. Any try to calculate TASC uphill, or downhill from SP, diverges, anywhere near the GE curve.

The NEB, on the other hand, is a first order method, and does not suffer from a singular Hessian near the GE. Consequently, it should iterate to the GE, compare Fig. 3 (a). The message of the example could be, that we can approximate a GE by a projector method also on a very extremal surface.

Note that the example surface of the modified NFK was constructed to demonstrate that the IRC (dots) can skewly run downhill over a ridge.[26] Thus, the IRC is no valley pathway throughout. The GE from Min to SP is throughout a valley (or a cirque) GE.

Steepest descent

The good news is that operator (4) finds SD curves, as well.[4] The difference to TASC is the kind of iteration. If one applies the same operator (4) for a row of corrector steps up to convergence, it should find a GE image, see the theory above. In contrast, if one renews for every corrector step the current tangent of the iteration chain, it should find the SD[4] which fulfills explicitly the eq.(4).

Inclusion of parallel forces

The second part, eq. (3), in the NEB operator of eq.(1) is a force which should ensure quasi equal spacing of the images (along the tangent of the curve). Since the resulting curve of the orthogonal projector is a monotone valley-GE, one can leave out the part.[20, 21, 23, 27] For the SD it should also work.[28] The solution images of task (4) may be pure GE points where the criterion (4) is a local criterion. If the GE has turning points, or bifurcations, or avoided crossings,[29] thus, if it is not always a valley-GE throughout, inclusion of parallel forces with springs may result in an averaged curve between different branches of the GE, or a bridge over the gap, and we will obtain a well adapted “MEP”, cf. Fig.3 in ref.[23].

The SD case can overbridge the local character of operator (4), because, only if all tangents for all images are parallel to the current gradient, then we have an IRC, and then the operator of eq. (4) can be fulfilled for all images together. Of course, such an adaption of the tangents of all images to the IRC may need a lot of iterations. Ill-natured zigzaggings are not excluded. Additionally, spring forces act to find a shorter curve: it is often nearer to an SD than to a GE. But in principle, parallel forces are cosmetical improvements of the chain of images.

Conclusion

Since the NEB method is used without spring forces, or with weak springs only, it can localize images on a gradient extremal (GE) along the valley ground of the PES. The GE to the smallest eigenvalue is a quasi-solution of eq. (4) especially under a numerical calculation,[20] if the corrector loop is organized to converge to a (locally fixed) tangent direction for every image. In ref.[20] is outlined a convergence proof. The possibility to follow only the GE to lowest eigenvalue enforces in chemical applications the use of nonredundant, internal coordinates. Because, using Cartesians would result in six so called zero-eigenvalues of the molecules translation (three true zero), and rotation (three very small), correspondingly. The correct application of internal coordinates then also enforces the inclusion of the non-Cartesian metric of internal coordinates.[30] Often the two kinds of curves, GE and IRC, are similar, and to relate a result to one of both is useless. In contrast, if both curves are different,[21, 26] especially the SD is a solution of the projector eq. (4).[4] There the projector operator (4) has to change at every iteration step by using the current tangent.

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