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Locating transition states on potential energy surfaces by the gentlest ascent dynamics

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ABSTRACT

The system of ordinary differential equations for the method of the gentlest ascent dynamics (GAD) has been derived which was previously proposed [W. E and X. Zhou, Nonlinearity 24, 1831 (2011)]. For this purpose we use diverse projection operators to a given initial direction. Using simple examples we explain the two possibilities of a GAD curve: it can directly find the transition state by a gentlest ascent, or it can go the roundabout way over a turning point and then find the transition state going downhill along its ridge. An outlook to generalised formulas for higher order saddle-points is added.

1. Introduction

The concepts of the potential energy surface (PES) [1,2] and of the chemical reaction path are the basis for the theories of chemical dynamics. The PES is a continuous function with respect to the coordinates of the nuclei. It is an N-dimensional hypersurface if $N = 3n$ and n is the number of atoms. It must have continuous derivatives up to a certain order.

The PES can be seen as formally divided in catchments associated with local minima [1,3]. The first order saddle points or transition states (TSs) are located at the deepest points of the boundary of the basins. Two neighbouring minima of the PES can be connected through a TS via a continuous curve in the N-dimensional coordinate space. The curve characterises a reaction path. One can define many types of curves satisfying the above requirement. The reaction path model widely used is the steepest descent (SD).

There exist a large number of proposed methods that in principle reach a TS when the minimums associated to the reactant and product are known. See Ref. [4] and references therein. There are also methods that find the TS when only one minimum is known. In this case, the problem is much more cumbersome because the initial data are just the geometry coordinates of the minimum, however, the direction of the search is open. As in the first case many algorithms have been developed for this type of problem [4]. A great number of these algorithms are based in a generalisation of the Levenberg–Marquardt method [5–7] that basically consists of a modification of the Hessian matrix to achieve both, first the correct spectra of the desired Hessian at the stationary point, and second to control the length of the displacement during the location process. The first proposed algorithm within this philosophy is due to Scheraga [8] and from than up to now the list is very large [9–20]. None of the methods are foolproof, each of them has some problems. Recently E and Zhou [20] have proposed an approach called the 'gentlest ascent dynamics' method. This method can be seen as a new reformulation of the method proposed some time ago by Smith [12,13] under the name 'image function'. The method is based on the generation of an image function that is a function which has its minima at exactly the points where the original PES has its TSs and moreover by an application of a minimum search algorithm to this image function. The converged point should correspond to a TS in the actual PES. Helgaker [14] modified the algorithm by the trust radius technique. Sun and Ruedenberg [21] analysed the method concluding that image functions do not exist for general PES so that a plain minimum search is inappropriate for them. A nonconservative field gradient of the image function exists. The global structure of the image gradient fields is considerably more complex than that of gradient fields of the original function. However, the image gradient fields appear to have considerably larger catchment basins around TSs. Besalú and Bofill [18] showed that the Smith algorithm is a special type of the Levenberg–Marquardt method.

In this Letter we show the connection between the Smith method [12,13] and that described by E and Zhou [20] to find TSs, and additionally, the mathematical basis of this algorithm is discussed. Finally, some examples are reported.

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2. Background of the method

Let us denote by $V(\mathbf{q})$ the PES function and by $\mathbf{q}^T = (q_1, \ldots, q_N)$ the coordinates. The dimension of the $\mathbf{q}$ vector is N. The superscript T means transposition. At every interesting point $\mathbf{q}$ the PES function admits a local gradient vector, $\mathbf{g}(\mathbf{q}) = \nabla_\mathbf{q} V(\mathbf{q})$, and a Hessian matrix, $\mathbf{H}(\mathbf{q}) = \nabla_\mathbf{q}\nabla_\mathbf{q}^T V(\mathbf{q})$. The family of image functions of $V(\mathbf{q})$, labelled by $W(\mathbf{q})$, is defined by the differential equation [21]

$$\mathbf{f}(\mathbf{q}) = \mathbf{U}_\mathbf{v}\mathbf{g}(\mathbf{q}) = \left[\mathbf{I} - 2\frac{\mathbf{v}(\mathbf{q})\mathbf{v}^T(\mathbf{q})}{\mathbf{v}^T(\mathbf{q})\mathbf{v}(\mathbf{q})}\right]\mathbf{g}(\mathbf{q}) \tag{1}$$

where $\mathbf{f}(\mathbf{q})$ is the image gradient vector, $\mathbf{U}_\mathbf{v}$ is the Householder orthogonal matrix constructed by an arbitrary vector $\mathbf{v}(\mathbf{q})$ being in principle a function of $\mathbf{q}$, and $\mathbf{I}$ is the unit matrix. The Householder orthogonal matrix is a reflection at $\mathbf{v}(\mathbf{q})$. It has the property that $\mathbf{U}_\mathbf{v} = \mathbf{U}_\mathbf{v}^T$, and it is the result of the difference between the projectors $(\mathbf{I} - \mathbf{P}_\mathbf{v})$ and $\mathbf{P}_\mathbf{v}$, because it holds trivially $\mathbf{U}_\mathbf{v} = \mathbf{I} - 2\mathbf{P}_\mathbf{v} = (\mathbf{I} - \mathbf{P}_\mathbf{v}) - \mathbf{P}_\mathbf{v}$, being $\mathbf{P}_\mathbf{v}$ the projector that projects into the subspace spanned by the $\mathbf{v}$-vector [22]. If the derivatives of $\mathbf{v}(\mathbf{q})$ with respect to $\mathbf{q}$ are nonvanishing, the image Hessian matrix, $\mathbf{F}(\mathbf{q}) = \mathbf{U}_\mathbf{v}\mathbf{H}(\mathbf{q})$, is not obtained by the differentiation of $\mathbf{f}(\mathbf{q})$. Taking into account Eq. (1), this differentiation results in

$$\begin{aligned}\nabla_\mathbf{q}\mathbf{f}^T(\mathbf{q}) &= \nabla_\mathbf{q}(\mathbf{g}^T(\mathbf{q})\mathbf{U}_\mathbf{v}) = \mathbf{F}^T(\mathbf{q}) + \mathbf{g}^T(\mathbf{q})\nabla_\mathbf{q}\mathbf{U}_\mathbf{v} \\ &= \mathbf{F}^T(\mathbf{q}) - 2\mathbf{g}^T(\mathbf{q})\nabla_\mathbf{q}\left[\frac{\mathbf{v}(\mathbf{q})\mathbf{v}^T(\mathbf{q})}{\mathbf{v}^T(\mathbf{q})\mathbf{v}(\mathbf{q})}\right].\end{aligned} \tag{2}$$

The term in brackets is usually not zero and not symmetric, and this non-symmetry is due to the effect of the differentiation on the $\mathbf{P}_\mathbf{v}$ projector. In other words,

$$\left(\nabla_\mathbf{q}\mathbf{f}^T(\mathbf{q})\right)_{ij} - \left(\nabla_\mathbf{q}\mathbf{f}^T(\mathbf{q})\right)_{ji} = \left(\nabla_\mathbf{q}\mathbf{f}^T(\mathbf{q})\right)_{ij} - \left(\nabla_\mathbf{q}\mathbf{f}^T(\mathbf{q})\right)^T_{ij} \neq 0 \quad i \neq j. \tag{3}$$

The inequality of Eq. (3) implies that the image gradient field defined by Eq. (1) is not integrable to an 'image PES' $W(\mathbf{q})$. More explicitly,

$$W(\mathbf{q}_1) - W(\mathbf{q}_0) \neq \int_{t_0}^{t_1} \mathbf{f}^T(\mathbf{q})(d\mathbf{q}/dt)dt \tag{4}$$

where $d\mathbf{q}/dt$ is the tangent of an arbitrary curve joining the points $\mathbf{q}_0 = \mathbf{q}(t_0)$ and $\mathbf{q}_1 = \mathbf{q}(t_1)$. Due to Eq. (3), this gradient field vector should be considered as a nonconservative force field. From this fact it follows an image of the PES function does, in general, not exist [21,23].

From Eq. (3) it is easy to see that at the stationary points, where $\mathbf{g}(\mathbf{q}) = \mathbf{0}$, the inequality is transformed to an equality if the $\mathbf{v}$-vector is an eigenvector of the Hessian matrix. Note that if $\{h, \mathbf{v}/(\mathbf{v}^T\mathbf{v})^{1/2}\}$ is an eigenpair of the $\mathbf{H}(\mathbf{q})$ matrix, then $\mathbf{F}(\mathbf{q}) = \mathbf{U}_\mathbf{v}\mathbf{H}(\mathbf{q}) = (\mathbf{I} - 2\mathbf{v}\mathbf{v}^T/(\mathbf{v}^T\mathbf{v}))\ \mathbf{H}(\mathbf{q}) = \mathbf{H}(\mathbf{q}) - 2\mathbf{v}\mathbf{v}^T/(\mathbf{v}^T\mathbf{v})\ h = \mathbf{H}(\mathbf{q}) - h\ 2\mathbf{v}\mathbf{v}^T/(\mathbf{v}^T\mathbf{v}) = \mathbf{H}(\mathbf{q}) - \mathbf{H}(\mathbf{q})\ 2\mathbf{v}\mathbf{v}^T/(\mathbf{v}^T\mathbf{v}) = \mathbf{H}(\mathbf{q})\ (\mathbf{I} - 2\mathbf{v}\mathbf{v}^T/(\mathbf{v}^T\mathbf{v})) = \mathbf{H}(\mathbf{q})\mathbf{U}_\mathbf{v} = \mathbf{F}^T(\mathbf{q})$. As pointed out by Sun and Ruedenberg [21], the image functions do exist until the second order in the vicinity of its stationary points for any PES taking $\mathbf{v}$ as an eigenvector of the Hessian matrix. Due to this fact the SD curves of the quadratic image function are approximations to the gradient image curves of $W(\mathbf{q})$ being the image potential of $V(\mathbf{q})$.

With the previous analysis of the general nonexistence of an image PES, we can take the image gradient field given in Eq. (1) to define the field of SD curves as,

$$\frac{d\mathbf{q}}{dt} = -\mathbf{f}(\mathbf{q}) = -\mathbf{U}_\mathbf{v}\mathbf{g}(\mathbf{q}) = -[(\mathbf{I} - \mathbf{P}_\mathbf{v}) - \mathbf{P}_\mathbf{v}]\mathbf{g}(\mathbf{q}) \tag{5}$$

where t is the parameter that characterises the SD curve, $\mathbf{q}(t)$. If Eq. (5) is multiplied consecutively from the left by the set of $(N\text{-}1)$ linear independent orthogonal vectors to the $\mathbf{v}$-vector, we see that it corresponds to a curve which is energy descending along this set of directions on the actual PES, whereas is ascending on the $\mathbf{v}$-vector direction. This property makes the set of curves defined in Eq. (5) suitable for the location of a TS from a minimum. This observation is supported by the fact that Eq. (5) can be rewritten as

$$\begin{aligned}\frac{d\mathbf{q}}{dt} &= -[(\mathbf{I} - \mathbf{P}_\mathbf{v}) - \mathbf{P}_\mathbf{v}]\mathbf{g}(\mathbf{q}) = -(\mathbf{I} - \mathbf{P}_\mathbf{v})\mathbf{g}(\mathbf{q}) + \mathbf{P}_\mathbf{v}\mathbf{g}(\mathbf{q}) \\ &= -(\mathbf{I} - \mathbf{P}_\mathbf{v})\mathbf{g}(\mathbf{q}) + l\frac{\mathbf{v}}{(\mathbf{v}^T\mathbf{v})^{1/2}}\end{aligned} \tag{6}$$

being $l = \mathbf{v}^T\mathbf{g}(\mathbf{q})/(\mathbf{v}^T\mathbf{v})^{1/2}$, where the definition of $\mathbf{P}_\mathbf{v}$ has been used. Eq. (6) is the basic equation of the string method proposed for the location of reaction paths and TSs [24]. The $\mathbf{v}$-vector in this method is the current tangent of the path. Because we are interested to find TSs from minimums of the PES we can use the nonconservative property of the gradient image field to modify the $\mathbf{v}$-vector, during the location process. For this purpose, we first consider that at the minimum, as well as at the TS, the last term of the right hand side part of Eq. (2) is equal zero due to $\mathbf{g}(\mathbf{q}) = \mathbf{0}$. Second, at the TS, the Hessian matrix, $\mathbf{H}(\mathbf{q})$, possesses only one eigenpair with negative eigenvalue. The associated Raygleigh-Ritz quotient of this eigenpair with a negative eigenvalue is the lowest that the Hessian matrix can achieve at this point being equal to the corresponding eigenvalue [25]. The Raygleigh-Ritz quotient for a given vector $\mathbf{v}$ and matrix $\mathbf{H}$ is defined as, $\lambda(\mathbf{v}) = \mathbf{v}^T\mathbf{H}\mathbf{v}/(\mathbf{v}^T\mathbf{v})$. The structure of this eigenvector is unknown. To find the TS one should, however, ensure that during the research process the path walks through the PES (given until second order) such that the character of the surface becomes closer to a first order saddle point. Taking into account these two considerations we transform Eq. (3) imposing that $\mathbf{g}(\mathbf{q}) = \mathbf{0}$ at each point of the search and multiplying the resulting equation from the left by $(\mathbf{I} - \mathbf{P}_\mathbf{v})$ and from the right by $\mathbf{P}_\mathbf{v}$,

$$\begin{aligned}&\frac{1}{2}(\mathbf{I} - \mathbf{P}_\mathbf{v})\left[\left(\nabla_\mathbf{q}\mathbf{f}^T(\mathbf{q})\right) - \left(\nabla_\mathbf{q}\mathbf{f}^T(\mathbf{q})\right)^T\right]\mathbf{P}_\mathbf{v}\Big|_{\mathbf{g}(\mathbf{q})=\mathbf{0}} \\ &= \frac{1}{2}(\mathbf{I} - \mathbf{P}_\mathbf{v})[\mathbf{H}(\mathbf{q})\mathbf{U}_\mathbf{v} - \mathbf{U}_\mathbf{v}\mathbf{H}(\mathbf{q})]\mathbf{P}_\mathbf{v} = -(\mathbf{I} - \mathbf{P}_\mathbf{v})\mathbf{H}(\mathbf{q})\mathbf{P}_\mathbf{v}.\end{aligned} \tag{7}$$

The effect of this multiplication by the projectors, $(\mathbf{I}\text{-}\mathbf{P}_\mathbf{v})$ and $\mathbf{P}_\mathbf{v}$, is that the resulting Eq. (7), multiplied from the right by the $\mathbf{v}$-vector, is the gradient of the Rayleigh–Ritz quotient with respect to this vector. If the $\mathbf{v}$-vector is an eigenvector of the $\mathbf{H}(\mathbf{q})$ matrix then the right hand side part of Eq. (7) is equal zero because every eigenvector extremises the corresponding Rayleigh–Ritz quotient. We will denote the Rayleigh–Ritz quotient by $\lambda_\mathbf{q}(\mathbf{v})$ to indicate its dependence on $\mathbf{q}$ through the Hessian matrix. If a $\mathbf{v}$-vector makes the gradient of the Rayleigh–Ritz quotient equal zero then this vector is an eigenvector of the $\mathbf{H}(\mathbf{q})$ matrix and the value of the Rayleigh–Ritz quotient coincides with the corresponding eigenvalue of the $\mathbf{H}(\mathbf{q})$ matrix. These properties suggest that a $\mathbf{v}$-vector can be changed following the SD direction of the Rayleigh–Ritz quotient gradient with respect to $\mathbf{v}$,

$$\frac{d\mathbf{v}}{dt} = -\frac{\mathbf{v}^T\mathbf{v}}{2}\nabla_\mathbf{v}\lambda_\mathbf{q}(\mathbf{v}) = -(\mathbf{I} - \mathbf{P}_\mathbf{v})\mathbf{H}(\mathbf{q})\mathbf{P}_\mathbf{v}\mathbf{v} \tag{8}$$

Eq. (8) is also a function of $\mathbf{q}$ through the Hessian matrix. The Rayleigh–Ritz quotient of the new $\mathbf{v}$-vector obtained from, $\mathbf{v} \to \mathbf{v} + d\mathbf{v}/dt\ \Delta t$, will be lower with respect to the previous one and, in addition, Eq. (5) will give us a new energy ascent direction and a set of orthogonal $N\text{-}1$ energy descent directions. Eq. (8) searches for either the lowest positive or the single negative Rayleigh–Ritz quotient if it exists, whereas Eq. (5) determines points on the PES along the action of an increase of the energy in the $\mathbf{v}$-vector, and a decrease along the set of orthogonal directions to this vector. The specific action of Eq. (5) defines the type of points of the