



Generalisations of the Bofill Update

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| ARTICLE INFO | ABSTRACT |
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| Published online: 06 September 2023 | Some generalisation of the evolved Hessian determinants are provided within the framework of the Markovv-states model representation of the reactionpath Hamiltonian methods. New generalisations of the Bofill update are proposed. The different generalisation of the Bofill update are accorded to different Markovv landscapes considered i order to codify the information lost in the reaction-path Hamiltonian method. |
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1. INTRODUCTION

The evolution of the determinants of the Hessian matrices related to molecular dynamics reactions is studied from several points of view.

The several schematisations of the trajectories are studied in the Literature within the framework of quasi-Newtonian dynamics; as a main consequence, the constants of motion cannot be studied within this scenario.

The several approaches to the identification of trajectories as curvilinear abscissa on the potential-energy surfaces are achieved by means of functions extrapolations and truncation of polynomial expressions; the order at which the Taylor expansion is truncated has consequences on the quantity of items of information available for the description the dynamics; more in detail, the number of degrees of freedom available for the reconstruction of the dynamical processes is different.

Within the frameworks of the Markovv descriptions, several approaches are possible, in which the items of information available for the analysis of the dynamics are different.

As a main difference, it can be pointed out that even the frameworks of quasiNewtonian dynamics and that of a Newtonian-comparable one are modellised in different manners.

The aim of the present work is to define generalisations of the Bofill update according to the number of degrees of freedom available for the codification of the dynamics. The methodology is framed within the Markovv schematisations according to the number of degrees of freedom chosen, which defines a Markovvstates model.

It is demonstrated that it is possible to define the constants of motion of a virialised system within a Newtonian dynamics of each 'step'.

Each Markovv-states model is defined after the constants of motion of the virialised systems.

As a tool, the Markovv-states models for the steps of a chemical reaction are outlined; the corresponding Markovv landscapes are defined. More in detail, the Markovv landscapes are determined after a Newtonian analysis of the dynamics.

The methodology used allows one to recover (within the framework of Markovvstates models) the items of information which are lost within the approximations which qualify the reaction-path Hamiltonian method.

As a result, the divergencies of the Bofill update are analysed; the divergencies are proven to be tamed in the time evolution of the Hessian determinant at the (discretised) time intervals (so-called 'steps') in which the chemical reaction is divided.

The paper is organised as follows.

In Section 1, the properties of the curvilinear abscissa of a potential-energy surface are outlined.

In Section 2, the reaction-path Hamiltonian method is recalled; in particular, the approximation with respect to the time evolution of the Hessian determinant are reviewed.

In Section 3, the properties of the Bofill update are scrutinised.

In Section 4, the generalisations of the Bofill updates are presented. In Section 5, the properties of the generalised Bofill update for a trivial Markov landscape are studied.

In Section 6, the features of the generalised Bofill update for a shallow-valleys Markov landscape are analysed.

In Section 7, the qualities of the generalised Bofill update for a crisp Markov landscape are investigated.

In Section 8, the prospective studies are envisaged.

2. INTRODUCTORY NOTATION AND PURPOSES

The notation of [1] is here partially followed for the definition of the quantities involved in the treatment of the Hessian updates, as it is applied to manipulations of the Murtagh-Sargent update, of the Powell-symmetric Broyden update, and of the Bofill update.

2.1 The reaction-Path Hamiltonian

The Reaction-Path-Hamiltonian (RPH) method was developed in [2].

The analysis of [3] is aimed at investigation the aspects of the RPH method as far as the molecular structures are concerned. The calculated coefficients are explicit functions of the energy derivatives. As the Taylor series are expanded around the saddle point, the second and the third coefficients in the Taylor series are considered, while the third coefficient (i.e. one related to the path curvature) is disconsidered.

As a result, when the complete RPH is taken into account, the parameters depend on the third energy derivative, for which reason the same energy derivatives items of information are requested at the saddle point at non-stationary points, which comprehend the gradient, the force constants, and, finally, the components of the third derivatives along the path tangent.

The saddle point \mathbf{v} is defined after the discretised curvilinear abscissa s ; after the definition of the discretised curvilinear abscissa, \mathbf{x} is obtained as the solution of autonomous first-order ordinary differential equations

$$\mathbf{v}(s) \equiv \mathbf{v}^{(0)}(s) \equiv \frac{d\mathbf{x}}{ds} = \frac{\mathbf{g}}{c}, \quad (1)$$

where the index ⁽⁰⁾ indicates the derivative of the normalised path tangent \mathbf{v} wrt s and can in the RPH formalism be omitted. It is the aim of the present work to restore (part of) the information generalised within the framework of the RPH formalism.

The curvature vector ⁽¹⁾ is defined as

$$\mathbf{v}^{(1)} \equiv \frac{d\mathbf{v}}{ds} = \frac{d^2\mathbf{x}}{ds^2}. \quad (2)$$

This method applies for the description of a chemical reaction as from reactants and products.

In [4], new methods in the determination of the steepest descent reaction path in dynamical calculations based on the RPH are developed; in particular, the correct third order in the Taylor series is considered: this way, the higher energy derivatives are used to account for the electronic structures.

As a method, a number of different steps is used to evaluate the deviation of the computed path curvature with respect to the exact curvature; the Renormalised Multiscales Solvers (RMS) deviation of the computed transverse frequencies is adopted to obtain a comparison with the exact values, due to the consideration of the relevance of the electronic structures.

In [5], the error estimate for a polynomial is studied, with the definition of the pertinent remainder, for this formalism. The aim of the present work is to express part of the information contained in the non-expanded functions encoded in the remainder. The method of extrapolation is extended to ordinary differential equation in [6]; the upper bound and the lower one are demonstrated in [7].

A distance weighted interpolant (DWI) surface for corrector steps can be implemented: after [8], the gradient of the interpolating function is set to vanish at each data points; the potential-energy surfaces of molecular reactions is defined within this formalism for the description of the dynamics of chemical reactions in [9].

The analysis [1] descends from [3]: the intrinsic reaction coordinates are defined as the coordinates obtained after the steepest-descent method (which implies its own approximation orders), for which the coordinates are expressed as mass-weighted Cartesian coordinates through which the transition state is related at the reactants and at the products on the potential energy surface. The intrinsic reaction coordinate is in the present work chosen as starting at the *time* of the transition and going on within the path indicated after the application of the steepest-descent method as follows.

The curvilinear abscissa s of x the coordinate vector reduces as normalised wrt the gradient of the potential-energy surface g as

$$\frac{d\vec{x}}{ds} = \frac{\vec{g}(x)}{|\vec{g}(x)|}. \quad (3)$$

Furthermore,

$$E(\vec{x}) = E_0 + g_0^t \Delta x + \frac{1}{2} \Delta x^t H_0 \Delta x \quad (4)$$

with

$$g(x) = g_0 + H_0 \Delta x. \quad (5)$$

The time derivative of the curvilinear abscissa becomes

$$\frac{ds}{dt} = |g_0 + H_0 \Delta x| \quad (6)$$

from which the time derivative of the coordinate vector becomes

$$\frac{dx}{dt} = -[g_0 + H_0 \Delta x] \quad (7)$$

so that

$$x(t) = x_0 + A(t)g_0. \quad (8)$$

$A(t)$ can be defined, as well as δt .

It is the purpose of the present analysis to specify the matrix A from Eq. (8) according to the possible situations of Markov landscape of the transition within the allowed errors, where the latter are determined from both the steepest descent method and from the features of the Markov landscape. To this aim, the validity of the choices of the Markov models is checked from [10], after the controls from [11].

There exist several algorithms of controls methods of the evolution of the Hessian matrix in quasi-Newton description of geometry optimisation or of transition state search.

There exist several algorithms that allow one to reproduce the time evolution of the Hess determinant. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) update is studied for geometry optimization [12], [13] [14], [15] ;

the Powell update is suited for the transition state search [16]; further updates are presented after the Berny update (derived also from [17]), the Davidon-

Fletcher-Powell update [18], [19] , the Murtagh-Sargent-Powell update [20] , the Symmetric rank-one update [22], which are used also in computational-tolls softwares [23].

The Broyden-Fletcher-Goldfarb-Shanno (BFGS) update has found application as it allows for a compact representation [28].

3. ANALYSIS OF THE UPDATED HESSIAN MATRICES FOR LOCATING TRANSITION STRUCTURES: THE BOFILL UPDATE

The Bofill update is designed to tame the convergence of the Murtagh-Sargent (MS) update [21].

The Murtagh-Sargent (MS) update is defined as

$$\Delta H_{MS} \equiv H(t_2) - H(t_1) = \frac{(\Delta g - H(t_1)\Delta x)[\Delta g - (H(t_1)\Delta x)]^t}{[\Delta g - (H(t_1)\Delta x)]^T \Delta x} \quad (9)$$

The Powell-symmetric-Broyden (PsB) update is written as

$$\Delta H_{PsB} = \frac{[\Delta g - H(t_1)\Delta x]\Delta x^t + \Delta x[\Delta g - H(t_1)]^t}{\Delta x^t \Delta x} - \frac{\Delta x^t [\Delta g - H(t_1)\Delta x]\Delta x^t}{(\Delta x^t \Delta x)^2} \quad (10)$$

the Bofill update ΔH_B is defined as

$$\Delta H_B = \phi \Delta H_{MS} + (1 - \phi) \Delta H_{PsB}, \quad (11)$$

with the Bofill multiplier ϕ determined as

$$\phi \equiv \frac{(\Delta x^t [\Delta g - H(t_1)\Delta x])^2}{\Delta x^2 [\Delta g - H(t_1)\Delta x]^2}. \quad (12)$$

4. ASPECTS OF THE BOFILL UPDATE AND GENERALISED BOFILL UPDATES

It is the aim of the present work to study the aspects of the Bofill updates; more in detail, it is the aim of the present work to study the items of information about the molecular dynamics and those about the electron structure which escape from the accorded studied degrees of freedom, and which can be encoded in the corresponding Markov landscape; the calculations are performed through the modelisation of the Markov landscapes pertinent to particular approximations of paths on the potential-energy surface. The principal aim of the Bofill update to tame the convergence of the MS update [21] is within the present section proven to be dependent of the approximation in the expression $[\Delta g - H(t_1)\Delta x]$ from [1].

The generalisation of the Bofill update corresponds therefore to a different truncation order of rational functions which complement those analysed in Section 2; the recovery of the items of information is implemented through the analysis of the corresponding Markov landscapes. The well-posed-ness of the procedure is validated to the analysis of the errors of the Markov states models with the help of the variance Eq. (13)

$$\sigma = \int_{t'}^{t'+\Delta t} \sqrt{\sigma_i(w_i)^2} dt \simeq \bar{w} \Delta t. \quad (13)$$

It means that not all the items of information are recovered, but only those allowed after the Markov states model(s) considered.

4.1 Generalised Murtagh-Sargent update

For the purposes of the present work, the generalised Murtagh-Sargent (gMS) update is defined as

$$\Delta H_{gMS} \equiv H(t_2) - H(t_1) = \frac{(\Delta g - H(t_1)\Delta x)F_1[(\Delta g)', (H(t_1)\Delta x)']}{F_2[(\Delta g)', (H(t_1)\Delta x)']\Delta x} \quad (14)$$

with F_1 and F_2 functions to be determined. to complete the definition of the generalised Bofill update as

$$\Delta H_{gB} = \phi_{gB}\Delta H_{gMS} + (1 - \phi_{gB})\Delta H_{PsB}, \quad (15)$$

with the generalised Bofill multiplier ϕ_{gB} as

$$\phi_{gB} = \frac{\Delta x' F_3[\Delta g, (H(t_1), \Delta x)]}{F_4[\Delta g, (H(t_1), \Delta x)]\Delta x^2} \quad (16)$$

where the new functions are defined in the following.

5. TRIVIAL MARKOVV LANDSCAPE

In the case of a trivial Markovv landscape, it is possible to apply the analysis of convergence of the updates [24], in which the truncation of updates is studied according to the Newtonian features of the process investigated. In the case of $H_1 = const$ (i.e. trivial Markovv landscape $\Delta t = \delta t$), and $\Delta g = const$ (i.e. constant gradient variation):

$$\phi_{gB} = \frac{\Delta x' F_3[\Delta g, (H(t_1)\Delta x)]}{F_4[\Delta g, (H(t_1)\Delta x)]\Delta x^2} \quad (17)$$

with F_i new suitable functions.

It is straightforward computed that for the generalised Bofill update, in this case, it is consistent to truncate of the second summand in the H_{PsB} , i.e. after the definition of the truncated PsB update \tilde{H}_{PsB} as

$$\tilde{H}_{PsB} \equiv \frac{[\Delta g - H(t_1)\Delta x]\Delta x^t + \Delta x[\Delta g - H(t_1)]^t}{\Delta x^t \Delta x} \quad (18)$$

The Newtonian nature of the process in the requested time interval will be verified after the definitions.

Indeed, in this case, the trivial-Markovv generalised Bofill updates \tilde{H}_{gB} newly reads

$$\Delta \tilde{H}_{gB} = \phi_{gB}\Delta H_{gMS} + (1 - \phi_{gB})\Delta \tilde{H}_{PsB}. \quad (19)$$

The control of the Hessian update in quasi-Newton dynamics during geometry optimization or transition-state search choosing a time interval in which the constants of motion stay unaltered, for which there is no theoretical limit to the polynomial-degree expansion; expanding ΔH_{gB} in Δx ; and controlling which quantities vary in the chosen time integral.

As a result for the Taylor expansion of the generalised Bofill update in the trivial Markovv case, after posing $x = x(t)$ $\Delta x = x - x_0$, x_0 trivial, i.e. $x_0 = 0$, and $\Delta t = \delta t$ trivial, one obtains

$$\Delta \tilde{H}_{gB} = \frac{\Delta x' F_3(x_0)\Delta g[F_1(x_0) - F_2(x_0)]}{F_4(x_0)} \frac{1}{x^3} + a_{-2} \frac{1}{x^2} + a_{-1} \frac{1}{x} + a_0 + a_1 x + a_2 x^2 + a_3 x^3 + O(x^4) \quad (20)$$

The further divergence in the Bofill update is this way pointed out by refining the dynamics.

It is possible not only to eliminate directly the a_{-3} after posing $F_1(x_0) - F_2(x_0) = 0$, which is the most direct interpretation; indeed, this way, the items of information about the Markovv Landscape is lost.

It is possible to consider the ratio $[F_1(x_0) - F_2(x_0)]/F_4(x_0)$ as the needed order to recover the items of information contained in the term by adding them to the pertinent power-expansion term(s).

The Newtonian nature of the generalised Bofill update in a trivial Markovv landscape is controlled after considering for the variance Eq. (13), from a computation point of view, one digit of the clock, which is the least time interval during which the velocities and the distances of the interacting particles from the virialised system [27] allow one to define the conserved constants of motion. The issues raised in [25] and in [26] are partially solved.

6. SHALLOW-VALLEYS MARKOVV LANDSCAPE

The aim of the present Section is to investigate the behaviour of the generalised Bofill update Eq. (19) within the (intermediate) Markovv-states models of a shallow-valleys Markov landscape. In this case, the energy barrier(s) separating the valleys (i.e. the energy states by which the beginning of a transition is analytically described as from the discretisation). In this case, $H_1 = const$ (i.e. the non-trivial Markovv landscape implies a $\Delta t = t - t_0$ non-trivial), and $g = const$.

From Eq. (19) one obtains

$$\Delta \tilde{H}_{gB} = b_0 + b_1(x - x_0) + b_2(x - x_0)^2 + O((x - x_0)^3). \quad (21)$$

More in detail, one writes

$$\Delta \tilde{H}_{gB} \simeq c_{0,-5} \frac{1}{x_0^5} + c_{0,-4} \frac{1}{x_0^4} + c_{0,-3} \frac{1}{x_0^3} + c_{0,-2} \frac{1}{x_0^2} + c_{0,-1} \frac{1}{x_0} + c_{0,1} x^0 + c_{0,2} x_0^2 + \sum_{n=0}^{n=N} b_n (x - x_0)^n; \quad (22)$$

the precise terms $c_{0,-m}$, $m = -5, \dots, -1$ do not cause a divergence, because the distance x_0 is not infinitesimal, but it is determined from the molecular dynamics; i.e. the time evolution is defined after the transfer operators for the Markovv states, as it is clarified in the

following. It is interesting to specify that the definitions are chosen for a chemical reaction, in which the reactants do react, for which reason $x_0 < \infty$, i.e. the terms of order x_0 and x_0^2 do not diverge.

7. CRISP MARKOVV LANDSCAPE

A crisp Markovv landscape [10] can be analysed in order to allow one to encode the properties of the curvilinear abscissa of the molecular dynamics on the potential-energy surface to locate the transitions and to qualify it according to the properties of the transfer operators which determine the allowed time evolution. More in detail, a crisp Markovv landscape corresponds to the time at which the chemical reaction is taking place, when the reactants have a reasonably small number of (suitably-chosen) Markovv states (within the framework of a Markovv-states model) which have evolved from the initial conditions, to which the reactants themselves can locate.

According to this perspective, the action of the time evolution operators cannot be determined from the calculations Eq. (4), which, on their turn, depend on Eq. (5). For this reason, the generalisation of the functions F_i is taken in order to reproduce the effects of the possible time evolutions. Furthermore, the generalisation of the Bofill updates must comprehend the use of the complete ΔH_{PsB} update, as the (energy) barriers between the states must be one describing a 'crisp' landscape. The study of the constants of motion is here achieved to be taking place during an infinitesimal time interval $\Delta x = x - x_0$ non-trivial, as it corresponds to the time at which the chemical reaction is starting/beginning. For these purposes, one generalises the complete expression of the PsB update as From Eq. (15) and from Eq. (16), one newly writes

$$\Delta H_{PsB} = \frac{[\Delta g - H(t_1)\Delta x]\Delta x^t + \Delta x[\Delta g - H(t_1)]^t}{\Delta x^t \Delta x} - \frac{F_5(\Delta x^t)[\Delta g - H(t_1)\Delta x]F_6(\Delta x^t)}{(F_7(\Delta x^t)\Delta x)^2} \quad (23)$$

to write the new generalised Bofill update ΔH_{gB} as

$$\Delta H_{gB} = \varphi g B \Delta H_{gMS} + (1 - \varphi g B) \Delta H_{gPsB}. \quad (24)$$

The following expression of ΔH_{gB} is found

$$\Delta H_{gB} \simeq h_{0,-5} \frac{1}{x_0^5} + h_{0,-4} \frac{1}{x_0^4} + h_{0,-3} \frac{1}{x_0^3} + h_{0,-2} \frac{1}{x_0^2} + h_{0,-1} \frac{1}{x_0} + h_{0,1} x_0 + h_{0,2} x_0^2 + \sum_{n=1}^{n=N} k_n (x - x_0)^n. \quad (25)$$

As a result, it is verified that, in the time during which the chemical reaction is decided, the generalised Bofill update does not acquire any diverging term, nor any infinities. It is important to remark therefore that the generalisation of the Bofill update itself contains the items of information which are contained in the second summand of the PsB update; the two terms being functionally different, it is understood that the generalisation of the updates verifies the dynamics with respect to the degrees of freedom expressed after the full implementation of the transfer operators, allowed after the Markovv landscape, which are neglected after the approximations Eq. (4) and Eq. (5) (from the approach of the references here used).

8. OUTLOOK

In the present work, the generalisation of the Bofill update are presented within the framework of the reaction-path Hamiltonian method. More in detail, the generalisations of the Bofill update provide one with the items of information which are lost in the definition of the curvilinear abscissae used in the reactionpath Hamiltonian method. The corresponding Markovv states are analysed. The Markovv-states models obtained this way define the Markovv landscapes which contain the items of information of the various steps of the time evolution of the updates.

In the case the reactant of a chemical reaction are not reacting (yet), the Markovv landscape is defined as trivial; nevertheless, the recovery of the items of information encoded in the trivial Markovv landscape are specific enough to investigate the divergencies of the Bofill update.

The divergencies found at the initial steps of the dynamics are proven to be tamed after the implementation of the proper Markovv landscape corresponding to the chemical reaction.

In [29], a quasi-Newtonian framework is selected for the studies. Differently, in the present work, the tools to outline the Newtonian steps of the evolution of the updates are determined.

The corresponding Markovv-states models are defined.

The items of information encoded within the transfer operators are found. As a perspective study, it is possible to outline the properties of the eigenstates of the Markovv-states models, as well as the features of the transfer operators. The manuscript is organised as follows.

In Section 1, the features of the curvilinear abscissa of a potential-energy surface are described.

In Section 2, the reaction-path Hamiltonian method is revised; more in detail, the approximation with respect to the time evolution of the Hessian determinant are recalled.

In Section 3, the properties of the Bofill update are initially analysed.

In Section 4, the generalisations of the Bofill updates are provided with. In Section 5, the properties of the generalised Bofill update for a trivial Markov landscape are explored.

In Section 6, the features of the generalised Bofill update for a shallow-valleys Markov landscape are studied.

In Section 7, the qualities of the generalised Bofill update for a crisp Markov landscape are determined.

In Section 8, the prospective studies are presented.

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