



A generalized recipe to construct elementary or multi-step reaction paths via a stochastic formulation: Application to the conformational change in noble gas clusters



Srijeeta Talukder^a, Shrabani Sen^a, Rahul Sharma^b, Suman K. Banik^c, Pinaki Chaudhury^{a,*}

^a Department of Chemistry, University of Calcutta, 92 A P C Road, Kolkata 700 009, India

^b Department of Chemistry, St. Xavier's College, 30 Mother Teresa Sarani, Kolkata 700 016, India

^c Department of Chemistry, Bose Institute, 93/1 A P C Road, Kolkata 700 009, India

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ABSTRACT

In this paper we demonstrate a general strategy to map out reaction paths irrespective of the number of kinetic steps required to bring about the change. i.e., whether the transformation takes place in a single step or in multiple steps with the appearance of intermediates. The objective function proposed is unique and works equally well for a concerted or a multiple step pathway. As the objective function proposed does not explicitly involve the calculation of the gradient of the potential energy function or the eigenvalues of the Hessian Matrix during the iterative process, the calculation is computationally economical. To map out the reaction path, we cast the entire problem as one of optimization and the solution is done with the use of the stochastic optimizer Simulated Annealing. The formalism is tested on Argon clusters (Ar_N) and Argon clusters singly doped with Xenon ($Ar_{N-1}Xe$). The size of the systems for which the method is applied ranges from $N = 7 - 25$, where N is the total number of atoms in the cluster. We also test the results obtained by us by comparing with an established gradient only method. Moreover to demonstrate that our strategy can overcome the standard problems of drag method, we apply our strategy to a two dimensional *LEPS + harmonic oscillator* Potential to locate the TS, in which standard drag method has been seen to encounter problems.

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1. Introduction

The reaction path is generally presented in literature as a two dimensional plot of energy vs. reaction co-ordinate. According to the transition state theory the maximum point(s) on the plot denotes the transition state(s) (TS) and the reaction coordinate denotes the dimension along which the reaction proceeds. From statistical aspect the transition occurs from one stable state to another stable form via an energy bottleneck. If an adiabatic potential energy surface (PES) of 3N-6 dimension can be generated for a system consisting of N atoms, the stable configurations would be the minimal points on that PES. The transition path or reaction path (RP) between any two such minimal points can then be considered as the minimum energy path (MEP) on the PES, connecting the two minima. In the context of the PES, a TS represents a conformer on MEP with zero gradient norm and having a single negative eigenvalue of the Hessian matrix i.e., basically, it is a first order saddle point.

Computing RP is a non-trivial job for systems with larger dimensions. Literature for the theoretical study of RP has been enriched by several methods [1–8]. Earlier methods are mostly deterministic and need the structural information about the TS along with the reactant (R) and product (P). One way to construct the RP is to follow the eigenvector of the Hessian matrix associated with the negative eigenvalue. Quapp et al. [9–13] has made important contributions in developing theories to get RP with this concept of gradient vector. These methods may or may not involve the direct evaluation of the Hessian matrix.

The method that has also achieved high popularity is the Nudged Elastic Band (NEB). The algorithm was initially proposed by Jonsson et al. [14–16]. It requires a priori knowledge of reactant and product, but not the TS. It is a string based method and there is no need of evaluation of the Hessian matrix. The two stable states are connected by a string of replicas or images, the energy of which are minimized in order to get the MEP. A spring force is made to act on these replicas in addition to the true force obtained from the gradient of energy, which is actually directed in the direction opposite to the gradient vector. The spring force prevents the downfall during energy minimization, unless the replicas may coagulate at the two valleys rather than the region of the hump (i.e., the TS).

* Corresponding author. Tel.: +91 9830480149.

E-mail addresses: skbanik@bic.boseinst.ernet.in (S.K. Banik), pinakc@rediffmail.com (P. Chaudhury).

But the TS may be missed due to the higher extent of the spring force as the string will cut the kink in order to minimize this force. Thus a balance is needed in defining the total force acting on the string. A large amount of work [17–22] has come out with the modifications which enhance the capability of the method. This has become a much used algorithm and it is used in diverse systems.

Another formalism which must be mentioned in reviewing the methods of finding RP, is given by Dellago et. al. [23–28]. The method does not require any information about the reaction coordinate, mechanism and TS. The nature of the algorithm is a stochastic one. It follows the Monte Carlo importance sampling to sample the configurational space to obtain the transition path. The important feature of this formalism is that the computational cost is not increased intolerably with the increase in dimension of the system, which is the general characteristic of Monte Carlo sampling. Substantial work has been performed by the group of Bhattacharyya and co-workers [29–31] by casting the job of finding the TS as an optimization problem. In their strategy an objective function is defined in order to get the MEP, which is optimized by using some stochastic optimizer like Simulated Annealing (SA) [32,33] or Genetic Algorithm (GA) [34]. Only the knowledge of reactant is needed for the simulation to begin and it will generate a RP consisting of a TS of minimum energy associated with that reactant minimum. They have followed both the strategies that includes or excludes the explicit calculation of Hessian matrix. Literature are available containing further application of this algorithm in rather complicated systems of pure and also mixed noble gas clusters as well as systems with doped alkali metal ions [35–37]. Noble gas cluster system can be described by Lennard–Jones type of interaction. The number of minima touches an astronomical figure with the increase in the number of atoms of the cluster. Thus it becomes a really challenging task to identify the RP between the two conformers of such clusters.

Algorithms proposed by Wales are also very effective in exploring PES as well as RP and the given applications involve higher dimensional systems [22,38–43]. Generally most of the theoretical strategies for identifying RP which exists as such, are used to carry out treatment of reactions consisting of an elementary step only. The multi step kinetic scenario may not be followed without a priori knowledge of the intermediates. A strategy which successfully follows kinetics that involve multiple reaction steps, is Discrete Path Sampling [44–46]. The algorithm can connect a conformational change of any higher dimensional cluster system or bio-matter irrespective of that the number of TS involved in mapping out the complete path [41].

In the present communication we demonstrate a strategy to identify the RP between two minimum points, the transformation path for the said change can contain one or more first order saddle points, without the requirement any other information except the proper structures of reactant and product. The problem is cast as an optimization problem, but the objective function is constructed in a different way than what is most commonly done. The algorithm does not ask for the value of the gradient of energy or the eigenvalue of Hessian matrix and this feature makes it computationally cost effective. The formalism is applied on some sizes of pure Ar cluster and Ar cluster singly doped with Xe. Simulated Annealing is used as the stochastic optimizer during the simulation. It must be said here that for Lennard–Jones potential which describes clusters of Ar or Xe, the gradient calculations are essentially free of computational cost. A Comparison with an existing gradient only method is also done as well as an application on a two dimensional *LEPS + harmonic oscillator* Potential is made to show that the proposed method can work in the situations where standard drag method fails.

2. Method

2.1. Objective function

In a previously discussed method of stochastic construction of RP (Ref. [29,30]), the path was constructed from one of the minimum on the PES with the objective of getting a connecting first order saddle point of lowest energy, i.e., the TS. The objective function defined in those communications was,

$$F = (V - V_L)^2 + \beta \sum_i^{3N} \left(\frac{\partial V}{\partial x_i} \right)^2 + \sum_i^{3N} \eta_i e^{\rho_i \lambda_i} \quad (2.1)$$

V is the potential energy of the instantaneous system obtained during simulation and V_L is the lower bound of energy that would be controlled manually. The second term accounts for the gradient norm and the third term is defined as curvature constraint which ensures the presence of only one negative eigenvalue of the Hessian matrix for the corresponding structure (the criterion for the first order saddle point). The curvature constraint term is modulated such that if a structure with a single negative eigenvalued Hessian matrix is found, the term drastically reduces to minimize the overall F . This gives the search a proper direction towards the TS.

Starting from the R, the RP is constructed by updating the V_L value and then minimizing the objective function for each V_L . At V_L close to the saddle point the gradient norm vanishes and the minimum value of F is obtained. Once the TS is reached the rest of the path, from TS to P, may be drawn by a down hill fall from the TS to P or the upward movement from P \rightarrow TS similar to R \rightarrow TS, provided the product is known.

With the aforementioned algorithm a path with only a single TS can be constructed. But chemical transformations in most situations involve multi-step kinetics. In our present work we suggest a generalized recipe to construct the path connecting two minima on a PES irrespective of whether the concerned path involves a single or multiple first order saddle points (if a continuous path exists). The objective function for a situation like this may be defined as

$$F = \alpha V + \beta |P_c(obj) - P_c| \quad (2.2)$$

Here P_c corresponds to path co-ordinate and $P_c(obj)$ is the path co-ordinate at which the structure would be optimized. V denotes the potential energy which is the same as Eq. (2.1). α and β are the weight factors by which the effect of the two terms on the objective function is controlled. We set $\beta \gg \alpha$. Thus during the simulation the objective function F is being minimized to get the structure of lowest energy possible at a preset path co-ordinate $P_c(obj)$.

RP can be considered as the minimum energy path between two minima. The physical idea behind the objective function used for constructing RP is that, the connecting structures of minimum energy along the path co-ordinate will fall on the MEP between the two minima. The whole path may be constructed by updating $P_c(obj)$ followed by the minimization of F at those particular $P_c(obj)$'s. The algorithm does not need the information about the gradient norm and the eigenvalues of Hessian matrix of the instantaneous structures. The direction of the path is guided by the path co-ordinate. Energy minimization on a particular value of path co-ordinate thus results in a point on MEP and the said structure would not contain more than one negative eigenvalue.

2.2. Path co-ordinate (P_c)

Path co-ordinate is a well known measure for depicting the the intermediate structures along the RP. The expression of P_c is

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