

A generalized synchronous transit method for transition state location

Niranjan Govind ^{*}, Max Petersen, George Fitzgerald,
Dominic King-Smith, Jan Andzelm

Accelrys, 9685 Scranton Rd., San Diego, CA 92121-3752, USA

Abstract

This paper describes a generalized synchronous transit method for locating transition state structures or first-order saddle points. The algorithm is based on the established scheme of combining the linear or quadratic synchronous transit method with conjugate gradient refinements but generalized to deal with molecular and periodic systems in a seamless manner. We apply the method to a study of the early stage atomic layer deposition (ALD) growth of ZrO₂. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Transition state structures play a crucial role in the understanding and design of chemical reactions. Despite their fundamental significance transition state structures are very challenging to locate accurately and conventional algorithms are typically computationally demanding and are not universally applicable.

Conceptually the easiest approach to locate a transition state structure or first-order saddle point is to sample the potential energy surface (PES) and map out the minimum energy path (MEP) [1] connecting reactant and product structure. This, however, requires a reasonably accurate PES sampling. This method, though simple-minded,

becomes impractical for systems with a large number of degrees of freedom.

Over the last several years a number of methods have been proposed [2] to locate transition state structures. One good example is the first derivative based nudged elastic band (NEB) method [3]. The method uses a guess for the reaction pathway and optimizes the geometries of several images along this path simultaneously. The resulting path is the MEP. Although the NEB approach greatly reduces the computational load compared with a direct evaluation of the PES, substantial resources are still directed towards optimizing geometries at several points along the adiabatic path, even though the point of greatest interest is the transition state geometry itself.

This raises the question whether a method can be formulated where the search is still performed along a guessed path, but where the main effort is

^{*} Corresponding author.

directed towards accurately locating the transition state. A very promising attempt to solve this problem was proposed by Halgren and Lipscomb [4] in 1977 via the linear (LST) and quadratic synchronous transit methods (QST), respectively. In the LST approach a series of single point energy calculations are performed on a set of linearly interpolated structures between a given reactant and product. The maximum energy structure along this path provides a first estimate of the transition state structure. A single refinement in a direction orthogonal to the LST path is then performed, which is then used as an intermediate to define a QST pathway. This procedure yields a further refined estimate for the transition state geometry.

In this paper we propose a generalized transition state location scheme [9] where both molecular and periodic models can be treated within the same framework. Our first derivative based approach closely follows and builds upon the ideas of the traditional LST/QST method in conjunction with conjugate minimization ideas of Bell and Crighton [5] and those of Fischer and Karplus [6]. We first present the details of the method followed by an application where we investigate the reaction of ZrCl_4 with partially hydroxylated and hydrated $\text{Si}(100)$ surfaces using both periodic slab and cluster models.

2. Description of the method

2.1. Review of LST/QST

In the original LST method [4] an idealized set of structures connecting reactants and products is obtained by linearly interpolating the distances between all pairs of atoms between reactant and product in the following manner

$$r_{ab}^i(f) = (1-f)r_{ab}^R - fr_{ab}^P, \quad (1)$$

where r_{ab}^R and r_{ab}^P are the inter-nuclear distances between atoms a and b in the reactant and product, respectively, and f is an interpolation parameter that varies between 0 and 1. The number of distinct inter-nuclear separations in a molecule with N atoms is $N(N-1)/2$, which is usually greater than the $3N$ Cartesian degrees of freedom

of the system. Eq. (1), as a result over-specifies the geometry of the system. The transit path was therefore defined by using the molecular geometry with inter-atomic distances as close as possible to the idealized values obtained by minimizing the function S defined as

$$S(f) = \frac{1}{2} \sum_{a \neq b} \frac{(r_{ab} - r_{ab}^i(f))^2}{(r_{ab}^i(f))^4} + 10^{-6} \sum_{\zeta=x,y,z} \sum_a (\zeta_a - \zeta_a^i(f))^2, \quad (2)$$

where ζ_a^i is the interpolated Cartesian position of an atom and ζ_a is the actual coordinate. The function S is always greater than or equal to zero. By construction this function is minimized by the reactant and product geometries, i.e. when f is 0 or 1. Note that the transit path is constructed purely on the basis of a geometric analysis alone; no energy calculations are needed to obtain this path.

The LST maximum estimate is further improved upon by minimizing the geometry subject to constant p where

$$p = \frac{d_R}{d_R + d_P}, \quad (3)$$

d_R in the above expression is the distance between the reactant and any other geometry of the molecule defined through

$$d_R^2 = \frac{1}{N} \sum_a (\zeta_a - \zeta_a^R)^2. \quad (4)$$

A similar expression can be written for d_P . The resulting geometry, p_m , may be taken on its own as an improved guess for the transition state, or used to perform a QST calculation. In the latter case, a quadratic interpolation is performed through the reactant, the product, and p_m . The energy maximum along this quadratic path is the QST prediction for the transition state. We refer the reader to the original paper [4] for a detailed discussion.

2.2. Generalization of the synchronous transit method to periodic systems

In periodic systems idealized transit paths are defined by a straightforward generalization of

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