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Optimization of hyperplanar transition states: Application to 2D test problems

Thomas Bligaard, Hannes Jónsson [*,1]

Faculty of Science, VR-II, University of Iceland, 107 Reykjavík, Iceland

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Abstract

The implementation of the WKE two step procedure for simulating slow, thermal transitions involving (1) a transition state theory approximation and (2) dynamical trajectories starting from the transition state is discussed, in particular the optimization of hyperplanar representations of the transition state dividing surface. A test problem involving a twisted reaction path is analyzed, and it is shown that the optimal hyperplanar transition state rotates abruptly from lying along the potential energy ridge at low temperature to an entropy dominated orientation at high temperature. The construction of more complex dividing surfaces using a set of intersecting hyperplanes is also illustrated. Finally, the use of the WKE procedure to enable long time scale simulations of systems undergoing activated, rare events is discussed.

Keywords: Transition state; Rate theory; Long time scale dynamics

1. Introduction

The rate of thermal transitions in chemicals and materials, such as chemical reactions and diffusion events, is typically very low compared to the time scale of atomic vibrations. Direct simulations of atomic dynamics including the vibrational motion are, therefore, typically not useful for the study of such transitions. Alternative approaches are needed. The two-step procedure pioneered by Wigner, Keck and Eyring (WKE) [1–3] involving first a transition state theory (TST) approximation to obtain an estimate of the rate and the transition mechanism, followed by simulation of the dynamics starting from the transition state to evaluate an exact rate constant (the so-called dynamical corrections) has been highly successful. When implemented in such a way that no information about final states of transitions is input into the simulation, it can be used as the basis for simulations of the long time scale evolution of complex systems of atoms and molecules where multiple thermal transitions can take place and a delicate balance between competing events determines the morphology and chemical composition.

* Corresponding author.
E-mail address: hj@hi.is (H. Jónsson).
[1] On leave of absence from the University of Washington.

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So far, such a scheme has only been implemented within the harmonic approximation to TST [4,5]. The application to more complex systems is challenging and requires improved methods for finding optimal transition state dividing surfaces within full TST. A step in that direction has been taken by the formulation of a systematic procedure for variational optimization of a hyperplanar transition state dividing surface [6]. There, the translational and rotational force acting on the hyperplane is obtained from statistical sampling of the system confined within the dividing surface (using, for example, Monte Carlo or classical dynamics sampling). An optimization algorithm can then be applied to follow these thermally averaged forces acting on the hyperplane until a location and orientation is found that maximizes the free energy. This is analogous to the use of atomic forces to find the lowest energy configuration of atoms. The hyperplane with maximal free energy gives the smallest rate constant within transition state theory and, by the variational theorem of Keck [2], gives the best estimate of the rate constant.

It is very important to carry out this full variational optimization. The rotation of the hyperplane can reveal an unexpected transition mechanism as illustrated by the application to Al adatom diffusion on an Al(100) surface [6]. Furthermore, the second step in the WKE procedure, the calculation of the dynamical trajectory to estimate the correction to the TST approximation and to identify the product state, becomes inefficient if the transition state dividing surface is being chosen poorly.

We discuss below, in Section 2, an application of this optimization procedure to a test problem which illustrates well the large effect that a finite temperature can have on the optimal transition state. We then discuss a generalization of the hyperplanar approach to more complex systems in Section 3, and finally we sketch how a long time scale simulation algorithm based on the WKE procedure can be implemented in Section 4.

2. Twisted path example

We now present numerical results of calculations on a two-dimensional problem which has previously been studied quite extensively, both classically and quantum mechanically [7–9]. This is an interesting problem because the reaction coordinate (the minimum energy path) is highly twisted. It, in particular, represents a nice two-dimensional example of some of the problems that can arise in the search for saddle points [10]. When the optimal transition state dividing surface is found, there is an interesting competition between the energetic and entropic contributions to the free energy which leads to an abrupt rotation of the optimal dividing line at an intermediate temperature, as described below.

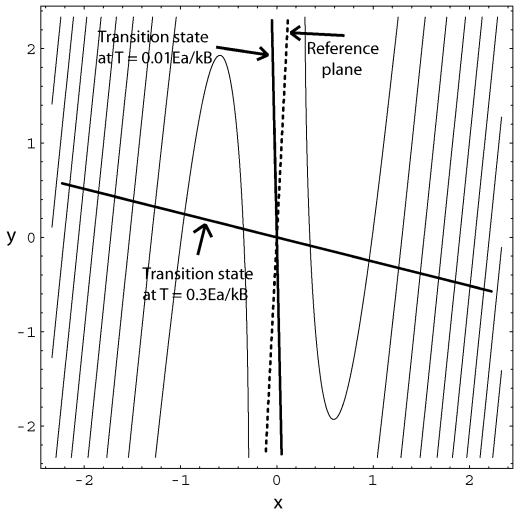

Fig. 1. A contour plot of the potential energy surface representing an Eckart barrier coupled to a harmonic oscillator.

The potential surface is generated by taking a symmetric Eckart barrier and coupling it to a harmonic oscillator to represent 'solvent' degrees of freedom. The potential surface is shown in Fig. 1 and the form of the potential is given by

$$V(x,y) = \frac{V_0}{\cosh^2(\frac{\alpha x}{2})} + \frac{1}{2}\mu\omega^2(y - Cx)^2 \qquad (1)$$

with $V_0 = 0.0156$, $\alpha = 3.97$, $\frac{1}{2}\mu\omega^2 = 1.04 \times 10^{-4}$, and $C = 10$.

The saddle point for going from the initial state to the final state is at $(x, y) = (0, 0)$ and has energy V_0. The dividing line obtained from the saddle point, i.e. the direction orthogonal to the unstable mode, makes an angle of 1.16 degrees with the vertical axis. The initial and final states are open, i.e. this represents a reactive scattering problem rather than a transition between bound states. The energy of the initial and final

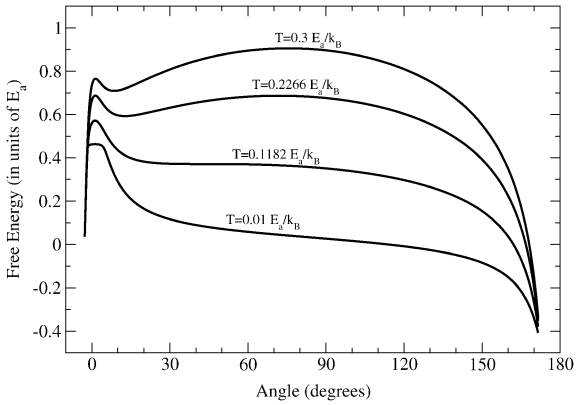

Fig. 2. The calculated free energy of a dividing line as a function of orientation. The reference line and the lines with maximum free energy at $T = 0.01E_a/k_B$ and $T = 0.3E_a/k_B$ are shown in Fig. 1.

states is zero in the asymptotic limit so the activation energy for the transition is $E_a = V_0$.

The free energy of a family of dividing lines going through the saddle point was calculated using the equations given in Ref. [6] with respect to a reference line (this line is shown in Fig. 1). The reference line was chosen to make an angle of $-\arctan(1/10)/2$ with respect to the vertical axis. The calculation was carried out by direct numerical integration over the dividing line. An adaptive algorithm was used that successively subdivides the integration range as needed, out to the walls of the enclosing parabolic part where the potential energy is up to a value of $V_0 + 22k_BT$. Numerical tests have shown this to be a reliable method for obtaining reproducible results for this potential surface.

The results of the free energy calculations are shown in Fig. 2. At the lowest temperature shown, $T = 0.01E_a/k_B$, the free energy as a function of the rotational angle peaks at 1.24 degrees. At low temperature, the influence of the potential energy ridge dominates. Sampling near the minimum energy path gives a low temperature rotational force which is entirely counter-clockwise for all angles from a couple of degrees and up to the maximally allowed angle at $\pi - \arctan(1/10)$. The free energy rises at intermediate angles as the temperature increases. This can be explained as an effect of the steep confining walls that results from the harmonic oscillator term in the potential. As the temperature increases, the potential energy ridge plays less of a role than the enveloping parabolic walls which impart a clockwise rotational force on the dividing line (when the angle made by the dividing line is within the range $[-\arctan(1/10), \pi - \arctan(1/10)]$).

At $T = 0.1182E_a/k_B$, a secondary maximum corresponding to an angle of 43 degrees has developed on the free energy curve. There are then two orientations of the dividing line that correspond to zero rotational force. As the temperature is increased further, the secondary maximum moves out to larger angles and becomes more pronounced.

At $T = 0.2266E_a/k_B$, the secondary, higher angle maximum in the free energy now located at 71.2 degrees becomes equally high to that of the low angle bump at 1.33 degrees. As the temperature is increased further, the optimal transition state dividing surface changes abruptly from the low angle to the high angle maximum. Such an abrupt change in the orientation of the optimal dividing surface had previously been noted [6,8], but can now be understood more clearly from the curves shown in Fig. 2.

The highest temperature curve in Fig. 2 corresponds to $T = 0.3E_a/k_B$. There, the low angle maximum in the free energy is located at 1.43 degrees and the high angle maximum is at 75.6 degrees. Now the steep outer walls of the harmonic oscillator term dominate over the potential energy ridge coming from the Eckart term. At extreme temperatures the outer parabolic walls, which are symmetric along the line $y = 10x$ completely control the orientation of the optimal dividing line and the maximum free energy line must be oriented perpendicular to these walls. This gives an extreme temperature optimal orientation at $\theta = \pi/2 - \arctan(1/10) = 84.29$ degrees. Such high temperatures are not relevant in the transition state approach because the transition is no longer a rare event and the basic approximations of transition state theory break down. But, already at $T = 0.3E_a/k_B$ it is evident that at high temperature the free energy barrier tends towards being perpendicular to the equipotential lines of the outer potential walls.

It is interesting to compare these results with calculations of the rate constant from using an analysis of dynamical trajectories. This is a very different approach than the free energy barrier calculation presented above and one might wonder to what extent the two give similar results. Makarov and Metiu studied classical trajectories initiated at a dividing surface line going through $(0, 0)$ and found the orientation of

the line that gives a minimum value for the rate constant within TST, as well as the corrections to TST which are related to the recrossings of the dividing surface [8]. They found that the smallest TST rate constant was obtained at $T = 0.1E_a/k_B$ with a line making a 1 degree angle to the vertical axis, while a line at a 70 degree angle gave the smallest rate constant at $T = 0.3E_a/k_B$. Our results based on free energy calculations are in very good agreement with their analysis of the classical trajectories. Interestingly, they found that some trajectories recross thousands of times at the higher temperature, but nevertheless the TST rate constant is only off by a factor of 2. This illustrates that even though there exist trajectories with multiple recrossings, the TST approximation can be quite good.

3. Rough, multichannel energy surfaces

In most cases of interest in chemistry and solid state physics, the potential energy surface has multiple minima corresponding to multiple stable arrangements of the atoms. For a given initial state there are many possible product states that a single transition can lead to. Furthermore, there can be two or more channels in the potential energy surface leading to the same product state. It is, therefore, usually not sufficient to represent the transition state dividing surface with a single hyperplane. A single hyperplane can, in general, not confine the system to the bottle neck of all channels simultaneously.

A two-dimensional example of a surface with multiple product states and thus multiple reaction channels is shown in Fig. 3. Two possibilities ways of dealing with this issue is (1) to use a curved dividing surface and (2) to use a collection of hyperplanar segments that join up to form a closed surface enclosing the initial state. Here, we have chosen the second option. The equations for the translation and rotation of a single hyperplane have been extended to such a collection of hyperplanar segments so that both the location and orientation of each segment can be optimized and a maximum free energy surface systematically obtained within this representation [11].

The result of such a calculation is shown in Fig. 3. Here, four lines are used to construct the dividing surface. The line in the lower left region does not quite trace through the high energy region and a five line representation would give a better dividing surface with somewhat higher free energy. This illustrates the kind of compromises that need to be made between complete maximization of the free energy of the dividing surface, which will in general require a large number of hyperplanes, and computational expense. It remains to be seen how many hyperplanes are needed in typical applications.

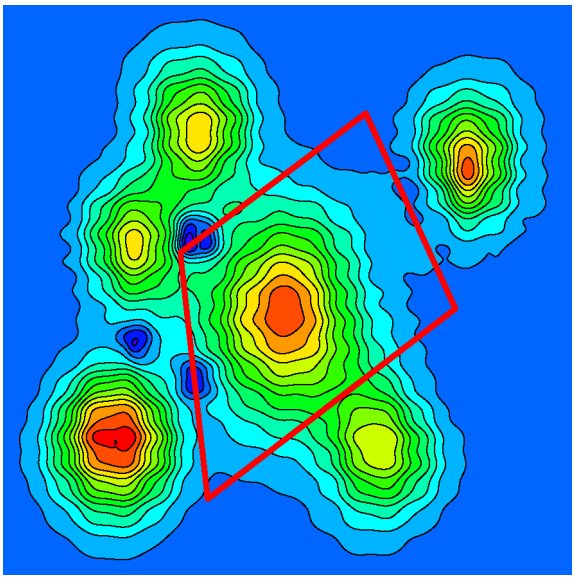

Fig. 3. A two-dimensional example of a potential energy surface with multiple possible product states and roughness that could arise from secondary degrees of freedom. The transition state dividing surface is represented by a collection of linear segments. In higher dimensions these would be hyperplanar segments. The free energy has been maximized with respect to the location and orientation of each of the segments.

4. Long time scale simulations

With a robust technique for finding variationally optimized dividing surfaces, the two step WKE procedure can be used as the basis for computer simulations of the long time scale evolution of a system. Given an initial state, a dividing surface is first constructed close to the region of maximum probability for the initial state, close enough that direct dynamics simulations can be used to estimate how often the trajectory takes the system to this surface. Then, the dividing surface is pushed out into regions of lower probability until

the maximum free energy dividing surface has been found. The relative free energy between the initial and final dividing surface can be used to estimate the probability that the system makes it to the optimized dividing surface and, thereby, the length of time one would need to wait until a large enough fluctuation in energy will bring the system there. This completes the first phase of the WKE procedure. Then, the system is placed at a point in the optimized dividing surface, according to the probability distribution within the dividing surface (obtained, for example, from a Monte Carlo simulation), and a dynamical trajectory started with an initial velocity drawn from a Maxwell distribution. Since the trajectory is started in a subspace corresponding to maximal free energy, it will most likely enter one of the possible product regions or go back to the initial state within a short amount of time. This represents the second stage in the WKE procedure which gives the dynamical corrections to the transition state theory approximation and reveals which product state is reached. This approach represents an extension of the Adaptive Kinetic Monte Carlo procedure which has previously been applied within harmonic transition state theory [4].

While the basic theory and even simple applications of the WKE procedure was already established in the 1960s [2], it is surprising how little work has been done to develop implementation procedures applicable to more complex systems. The methods for systematically optimizing hyperplanar dividing surfaces discussed here are a step in that direction.

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