

Reversible work based quantum transition state theory

Gregory K. Schenter

Molecular Science Research Center, Pacific Northwest Laboratory, Richland, Washington 99352

Gregory Mills and Hannes Jónsson

Department of Chemistry, BG-10, University of Washington, Seattle, Washington 98195

(Received 12 May 1994; accepted 3 August 1994)

A theoretical basis is presented for reversible work evaluation of transition rates within the framework of transition state theory. The method involves computing statistical averages of forces without having to evaluate transition state partition functions or densities, and therefore eliminates the need for a harmonic reference system. The method can be applied to systems of high dimensionality which is particularly important in calculations on quantum systems, where each quantum particle may be represented by several images in a Feynman path integral chain. The relationship between this method and the fixed centroid method of Gillan and centroid density theories is established. The various methods are compared on a model quantum system consisting of an Eckart barrier coupled to a harmonic oscillator.

I. INTRODUCTION

Gillan recently introduced a method for calculating the rate of transition in a quantum mechanical system based on a Feynman path integral (FPI) representation of the quantum particle.¹ In the FPI formalism, the quantum statistical mechanics of a particle is shown to be equivalent to the classical statistical mechanics of a chain of images of the particle connected by harmonic springs.² The distribution of the images in a FPI chain represents quantum delocalization of the particle. The high temperature or large mass classical limit is obtained naturally as the springs become stiffer and the chains contract to a point. The FPI formalism has proven to be very useful for calculating thermally averaged properties of quantum systems, even when multiple quantum degrees of freedom are included. In Gillan's method, a transition rate is estimated by calculating the reversible work of moving the centroid of the path integral chain from a reactant region up to the saddle point of the potential energy surface. A free energy barrier for the transition is obtained from this calculation.¹ In this sense, the method is a version of quantum mechanical transition state theory (TST). The method was originally justified by considering a one dimensional double-well coupled to a heat bath.^{1(a)} This is inherently a one-dimensional system. A generalization of a quantum particle in three-dimensional space and the technical details for calculating an effective free energy difference were later discussed.^{1(b),1(c)} The reversible work is obtained by evaluating the thermal average of the force acting on the quantum chain with the centroid held fixed. A line integral of the force is then evaluated over a path connecting a point in the reactant region to the saddle point.

Following Gillan's ideas, Voth, Chandler, and Miller (VCM),³ provided a quantum mechanical generalization of conventional classical TST by treating the FPI centroid coordinates as classical coordinates. Their theory gave an estimate for the pre-exponential factor in the rate expression that recovers the classical TST result in the classical limit. As formulated, the expressions for the rate constant no longer involved statistical averages of the force on the FPI images,

but rather the evaluation of partition functions and centroid densities. The method was applied to one- and two-dimensional test problems using Monte Carlo simulations with a harmonic reference system and the results were shown to be in good agreement with direct dynamical calculations.⁷ The multidimensional generalization of the method was discussed and relied on identifying a specific reaction coordinate for the centroid constraint. In this work and in work to follow, the role of a multidimensional dividing surface as a dynamical bottleneck was emphasized.^{3(b)}

In an effort to make a closer tie to classical variational TST, Messina, Schenter, and Garrett (MSG)⁴ provided a generalization of the VCM expression that allowed for arbitrary nonplanar and/or momentum dependent dividing surfaces. In this formulation an expression for the rate was introduced that was an explicit functional of a given dividing surface. The dividing surface was then allowed to rotate and move along the minimum energy path connecting reactants to the saddle point to find the lowest reactive flux through the dividing surface. In the classical limit, this is consistent with variational TST, where the dividing surface is placed in such a way as to minimize the calculated rate. The central approximation in classical transition state theory is the assumption that trajectories only cross the dividing surface once. Since recrossings are neglected, the TST estimate is always larger than the true rate, leading to a rigorous variational principle for the TST estimate. This theoretical justification for the variational principle does not apply in quantum mechanical systems. However, MSG found that optimization of the dividing surface led to a strict upper bound in the harmonic limit and gave much improved results for an anharmonic test problem.⁴ Garrett and Truhlar implemented classical variational TST calculations and quantized variational transition state theory with multidimensional semiclassical tunnelling corrections by generating a one-parameter sequence of generalized dividing surfaces and then minimizing the calculated rate constants with respect to this parameter.⁵ Although their methods employed different approximations than the current work, the idea of minimizing the rate along a path was similar.

Most recently, in evaluating the rate of H_2 dissociative adsorption on a Cu(110) surface, Mills and Jónsson⁶ proposed an extension of Gillan's method where the centroids were constrained to be on a multidimensional hypersurface instead of being at a point as in Gillan's method. The free energy barrier was obtained from the reversible work of gradually moving the system confined to a hyperplane from the reactant region towards products. This method is consistent with the transition state theories of VCM and MSG, but has an advantage over centroid density methods because only averages of forces need to be evaluated. This is particularly important in high dimensional systems where the Monte Carlo evaluation of partition functions and densities becomes ineffective. Furthermore, the method can be applied easily to systems where a good harmonic reference system does not exist (such as the double well problem). In the H_2 dissociative adsorption simulation, the two transition particles and eight of the surface atoms were treated quantum mechanically with up to 50 images in each FPI chain. In addition, the system included a couple of hundred classical atoms representing the solid.⁶

This article is organized as follows. The equations for the mean force and reversible work TST calculations are derived and compared with equivalent expressions for Gillan's fixed centroid method and the MSG centroid density expressions in Sec. II. We then present calculations on a model system described in Sec. III consisting of an Eckart barrier linearly coupled to a harmonic oscillator bath. Results calculated with the reversible work TST method are presented in Sec. IV and compared with calculations using Gillan's fixed centroid method and with the MSG centroid density method. The reversible work TST calculations have been carried out for two different paths with quite different characteristics but leading to very similar estimates for the rate. The results are shown to be in excellent agreement with the MSG centroid density method and in good agreement with an accurate estimate obtained from dynamical wave packet calculations, a calculation that is tractable for this low dimensional model system.⁷ We present our conclusions in Sec. V.

II. REVERSIBLE WORK TRANSITION STATE THEORY

In this section the rigorous relation between the centroid density TST expression and the reversible work evaluation of the rate constant will be established. We will begin by deriving an expression for the free energy barrier obtained by applying Gillan's fixed centroid method. We will then use the MSG expression for a dividing surface dependent rate constant to define a free energy associated with the system confined to a hypersurface. We then derive an expression for the generalized force on the system and show how the free energy barrier can be obtained by integration. With these expressions, the relation between Gillan's method, the MSG expression, and the present reversible work method for estimating the rate will become evident.

A. Fixed centroid free energy

In Gillan's method¹ the rate is obtained from a free energy difference between two point locations of the FPI cen-

teroid. The free energy F at a point Γ can be defined in terms of the centroid constrained imaginary time Feynman path integral as follows:

$$B e^{-\beta F(\Gamma)} = \int D\mathbf{r}(\tau) e^{-S/\hbar} \delta(\tilde{\mathbf{r}}_0 - \Gamma), \quad (1)$$

where B is an integration constant, $\beta = 1/k_B T$, T is the temperature of the system, and S is the Euclidean action,

$$S = \int_0^{\beta\hbar} d\tau \left\{ \frac{\mu}{2} \left[\frac{d\mathbf{r}(\tau)}{d\tau} \right]^2 + V[\mathbf{r}(\tau)] \right\}. \quad (2)$$

The centroid of the FPI chain, $\tilde{\mathbf{r}}_0$, is given by

$$\tilde{\mathbf{r}}_0 = \int_0^{\beta\hbar} \frac{d\tau}{\beta\hbar} \mathbf{r}(\tau) \quad (3)$$

and is constrained by the delta function in Eq. (1) to be at the point Γ . In the Feynman path integration, only closed paths $\mathbf{r}(\beta\hbar) = \mathbf{r}(0)$, with the centroid fixed at Γ , are included. Differentiating both sides of Eq. (1) with respect to Γ , one obtains an expression for the mean force on the centroid of the Feynman path integral chain. It is convenient here to Fourier expand the Feynman path and transform the path integration into an integration over the Fourier components.⁴ The zeroth order component is the centroid. The final result is

$$\nabla F(\Gamma) = \left\langle \int_0^{\beta\hbar} \frac{d\tau}{\beta\hbar} \nabla V[\mathbf{r}(\tau)] \right\rangle_{\Gamma}, \quad (4)$$

where the centroid constrained statistical average is defined as

$$\langle \dots \rangle_{\Gamma} = \frac{\int D\mathbf{r}(\tau) e^{-S/\hbar} \dots \delta(\tilde{\mathbf{r}}_0 - \Gamma)}{\int D\mathbf{r}(\tau) e^{-S/\hbar} \delta(\tilde{\mathbf{r}}_0 - \Gamma)}. \quad (5)$$

Line integration along a path connecting reactants (R) to the saddle point (sp) gives the reversible work and hence the change in the free energy associated with the two points on the path

$$F(\Gamma^{\text{sp}}) - F(\Gamma^R) = \int_R^{\text{sp}} d\Gamma \cdot \left\langle \int_0^{\beta\hbar} \frac{d\tau}{\beta\hbar} \nabla V[\mathbf{r}(\tau)] \right\rangle_{\Gamma}. \quad (6)$$

The free energy change is independent of the path chosen to connect the reactants to the saddle point. Therefore, any path can, in principle, be used to evaluate the free energy difference. In practice, it is best to choose a path which gives minimal cancellations in the numerical evaluation of the line integral.

B. Hypersurface free energy

Proceeding along similar lines as above, for convenience we start with the MSG expression for the rate constant in terms of an arbitrary $3N-1$ dimensional dividing surface in the coordinate space of the system defined here by the condition $Z(\mathbf{r})=0$. This equation becomes equivalent to a multi-dimensional version of VCM for the case of a planar dividing surface. The reactive flux is

$$Q_k^{Rk\text{QTST}}[Z] = \int \frac{D\mathbf{r}(\tau)}{\sqrt{2\pi\mu\beta}} e^{-S/\hbar} |\nabla Z(\tilde{\mathbf{r}}_0)| \delta[Z(\tilde{\mathbf{r}}_0)] \quad (7)$$

with Q^R being the reactant partition function and $k^{\text{QTST}}[Z]$ the centroid density quantum transition state theory estimate for the rate constant. In analogy to Eq. (1), we define the free energy, $F[Z]$, of the system confined to a hypersurface Z to be

$$A e^{-\beta F[Z]} = Q^R k^{\text{QTST}}[Z]. \quad (8)$$

The factor A is an arbitrary integration constant. We will obtain a TST estimate of the transition rate by evaluating the free energy difference, $F^\ddagger - F^R$, between a dividing surface Z^\ddagger separating reactants and products and a hypersurface Z^R of same dimensionality located in the reactant region. The transition rate is then given by

$$k^{\text{QTST}} = \frac{1}{\sqrt{2\pi\mu\beta}} \frac{Q^{Z^R}}{Q^R} e^{-\beta(F^\ddagger - F^R)}, \quad (9)$$

where Q^{Z^R} is the partition function for the system confined to the hypersurface Z^R . We will show below how the free energy barrier, $F^\ddagger - F^R$, can be evaluated from the average force acting on the system. The ratio of the partition functions Q^{Z^R}/Q^R can typically be evaluated easily, especially if a limit can be taken where the reactant coordinates decouple. Before proceeding to take variations of this expression with respect to the hypersurface in analogy to Eq. (4), we will restrict the analysis to hyperplane surfaces which intersect a reaction path $\Gamma(s) = \Gamma_s$ at a single point in coordinate space [see Fig. 1(a)]. We choose hyperplane surfaces here for convenience, but in general the optimal dividing surface is nonplanar¹¹ and in principle the present analysis can be extended to arbitrary surfaces. The parameter s will be referred to as the reaction coordinate. The hyperplane is given by the condition

$$Z(\mathbf{r}) = \mathbf{n}_s \cdot (\mathbf{r} - \Gamma_s) = 0, \quad (10)$$

where the normal to the hyperplane, \mathbf{n}_s , is a unit vector defined for all s .

With this choice for the s dependent hyperplanes, the expression for the hyperplane free energy, Eq. (8), becomes a one dimensional function of s ,

$$A e^{-\beta F(s)} = \int \frac{D\mathbf{r}(\tau)}{\sqrt{2\pi\mu\beta}} e^{-S/\hbar} \delta[\mathbf{n}_s \cdot (\tilde{\mathbf{r}}_0 - \Gamma_s)]. \quad (11)$$

C. Evaluation of the free energy barrier

In order to evaluate derivatives of F with respect to s , it is convenient to introduce a rotated set of local coordinates, \mathbf{z} , at each point along the reaction path. In terms of the local coordinates \mathbf{z} , the global coordinates \mathbf{r} can be obtained as

$$\mathbf{r} = \mathbf{U}_s \mathbf{z} + \Gamma_s, \quad (12)$$

where \mathbf{U}_s is an orthogonal rotation matrix with

$$\mathbf{U}_s \mathbf{U}_s^T = 1 \quad (13)$$

and

$$[\mathbf{U}_s]_{k1} = [\mathbf{n}_s]_k. \quad (14)$$

With this change of variables, the Feynman path integral expression becomes

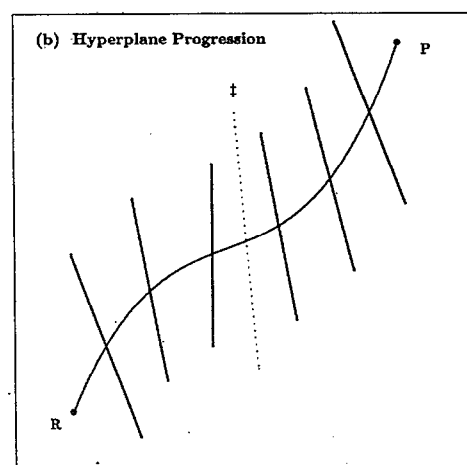
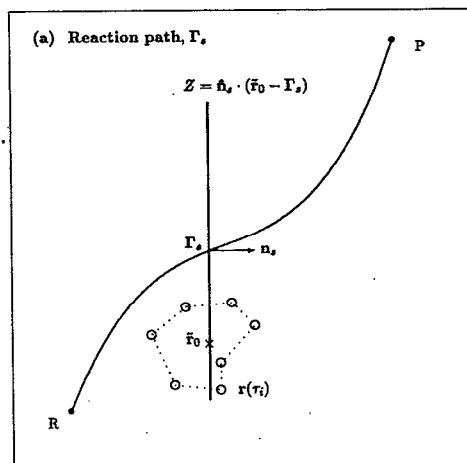


FIG. 1. (a) Reaction path Γ parametrized with reaction coordinate s . For each point along the path, a hyperplane intersecting the path at that point and having a normal \mathbf{n}_s is defined, $Z = \mathbf{n}_s \cdot (\mathbf{r} - \Gamma_s) = 0$. The force acting on the FPI images is evaluated and averaged over a statistical sample of configurations with the centroid of the FPI chain constrained to lie in the hyperplane. (b) The hyperplane is gradually moved from the reactant region towards products by varying the reaction coordinate, s . The activation free energy for the transition is obtained by calculating the reversible work involved in moving and rotating the hyperplane to an intermediate position chosen to be the dividing surface between reactant and product regions. The maximum free energy barrier is obtained where the force and torque on the hyperplane vanishes. This is equivalent to finding the optimal hyperplanar dividing surface in classical variational transition state theory.

$$A e^{-\beta F(s)} = \int \frac{D\mathbf{z}(\tau)}{\sqrt{2\pi\mu\beta}} e^{-S/\hbar} \delta[(\tilde{\mathbf{z}}_0)_1] \quad (15)$$

and all of the s dependence is contained in the Euclidean action

$$S = \int_0^{\beta\hbar} d\tau \left\{ \frac{\mu}{2} \left[\frac{d\mathbf{z}(\tau)}{d\tau} \right]^2 + V[\mathbf{U}_s \mathbf{z}(\tau) + \Gamma_s] \right\}. \quad (16)$$

Performing the differentiation of Eq. (11) with respect to s gives

$$F'(s) = \left\langle \int_0^{\beta\hbar} \frac{d\tau}{\beta\hbar} \nabla V[\mathbf{r}(\tau)] \cdot \left\{ \Gamma'_s + \mathbf{U}'_s \mathbf{U}'_s^T [\mathbf{r}(\tau) - \Gamma_s] \right\} \right\rangle_s, \quad (17)$$

where the primes denote differentiation with respect to s and the dividing surface statistical average is defined as

$$\langle \cdots \rangle_s = \frac{\int D\mathbf{r}(\tau) e^{-S/\hbar} \cdots \delta[\mathbf{n}_s \cdot (\tilde{\mathbf{r}}_0 - \Gamma_s)]}{\int D\mathbf{r}(\tau) e^{-S/\hbar} \delta[\mathbf{n}_s \cdot (\tilde{\mathbf{r}}_0 - \Gamma_s)]}. \quad (18)$$

By integrating Eq. (17), one obtains an expression for the reversible work involved in moving the system from the reactant region, R , to a dividing surface, \ddagger

$$F^\ddagger - F^R = \int_R^\ddagger ds \left\langle \int_0^{\beta\hbar} \frac{d\tau}{\beta\hbar} \nabla V[\mathbf{r}(\tau)] \cdot \left\{ \Gamma'_s + \mathbf{U}'_s \mathbf{U}'_s^T [\mathbf{r}(\tau) - \Gamma_s] \right\} \right\rangle_s. \quad (19)$$

This expression is similar in form to the fixed centroid expression, Eq. (6), but now there are two contributions to the free energy difference. The first term in the square bracket, Γ'_s corresponds to the work associated with translation of the hyperplane. The second term corresponds to work associated with the rotation of the hyperplane.

In three dimensions the rotational contribution can be rewritten to make a more direct connection with the work done against the torque acting on the hyperplane. The differential change in the free energy due to the rotation can be rewritten as

$$\delta F^{\text{rot}} = \left\langle \int_0^{\beta\hbar} \frac{d\tau}{\beta\hbar} \nabla V[\mathbf{r}(\tau)] \cdot \delta \mathbf{U} \mathbf{U}^T [\mathbf{r}(\tau) - \Gamma_s] \right\rangle_s. \quad (20)$$

We now consider a generalized rotation defined by the transformation

$$\mathbf{U} = e^{\sum_\alpha \mathbf{L}^\alpha \delta\theta^\alpha}, \quad (21)$$

where $L_{ij}^\alpha = -L_{ji}^\alpha$ are totally antisymmetric matrices of the dimension of \mathbf{r} and $\delta\theta^\alpha$ is an infinitesimal angle of rotation about direction α . For the case of a three dimensional system, we have $L_{ij}^\alpha = \epsilon_{\alpha ij}$, with ϵ_{ikj} being the totally antisymmetric tensor defining the cross-product. From Eq. (21), we have

$$\delta \mathbf{U} = \sum_\alpha \mathbf{L}^\alpha \delta\theta^\alpha \mathbf{U}. \quad (22)$$

Inserting this expression into Eq. (20) gives

$$\delta F^{\text{rot}} = \left\langle \int_0^{\beta\hbar} \frac{d\tau}{\beta\hbar} \sum_\alpha \nabla V[\mathbf{r}(\tau)] \cdot \mathbf{L}^\alpha \cdot [\mathbf{r}(\tau) - \Gamma_s] \delta\theta^\alpha \right\rangle_s. \quad (23)$$

For a three-dimensional system, this reduces to

$$\delta F^{\text{rot}} = - \left\langle \int_0^{\beta\hbar} \frac{d\tau}{\beta\hbar} [\mathbf{r}(\tau) - \Gamma_s] \times \mathbf{f}[\mathbf{r}(\tau)] \cdot \delta\boldsymbol{\theta} \right\rangle_s \quad (24)$$

an expression involving an averaged torque with $\mathbf{f}[\mathbf{r}(\tau)]$ representing the force on the bead at position $\mathbf{r}(\tau)$.

D. Summary of the reversible work TST calculation

The method for evaluating the free energy barrier and the transition rate, therefore, involves identifying some reaction path leading from the reactant to the product region and defining a series of hyperplanes intersecting the path. The force acting on the quantum chain confined to a hyperplane is evaluated and integrated according to Eq. (19) as the hyperplane is translated and rotated in such a way that a point of intersection between the hyperplane and the reaction path, Γ_s , gradually moves from reactants towards products [see Fig. 1(b)]. While many different paths can be used, it is important the path leads to a good dividing surface. A natural choice for the dividing surface is the position of the hyperplane giving maximum integrated free energy barrier. At each point along the path the hyperplane can be rotated to maximize the free energy, equivalent to zeroing the “torque” acting on the hyperplane. The optimal planar dividing surface, which gives a minimum rate, has zero force and zero torque acting on it. This search for the optimal hyperplanar dividing surface is consistent with a variational minimization of the quantum transition rate.⁹ In the classical limit, this corresponds to the optimal variational TST rate.¹⁰

III. CALCULATIONS ON A MODEL SYSTEM

As a model system, we consider the two dimensional Hamiltonian

$$H(q, p, x, p_x) = \frac{p^2}{2\mu} + \frac{p_x^2}{2\mu} + V_0 \operatorname{sech}^2\left(\frac{\alpha q}{2}\right) + \frac{1}{2} \mu \omega^2 (x - Cq)^2 \quad (25)$$

which consists of an Eckart barrier along a “solute” coordinate q with a single harmonic oscillator “bath,” x , linearly coupled through the coupling constant C to the solute reaction coordinate. This model system has been used in the past to make critical comparisons of approximate and accurate quantum mechanical calculations of the rate constants,⁷ and corresponds to a generalized Langevin equation description of the classical motion,⁸

$$\mu \ddot{q} = - \frac{dV(q)}{dq} - \int_0^t dt' \eta(t-t') \dot{q}(t') + F(t) \quad (26)$$

with μ the reduced mass, $\eta(t)$ the so-called friction kernel, and $F(t)$ a fluctuating force that is related to the friction kernel by the fluctuation-dissipation theorem.

It has been shown that a single oscillator bath recovers the same qualitative trends in reaction rates as a bath consisting of a continuum of harmonic oscillators. The values for the parameters α , V_0 , and μ are chosen to mimic a H+H₂ gas-phase reaction, and are $V_0=9.8$ kcal/mol, $\alpha=3.97$ Å⁻¹, and $\mu=0.672$ amu. The “bath” parameters are chosen to mimic the linear response of a friction kernel that has a Gaussian time dependence with the characteristic time scale $\sigma=86.6$ fs. We set $\omega=\pi/(4\sigma)=48$ cm⁻¹ and we vary the

strength of the coupling by considering the dimensionless integrated friction $f = \eta_0 / (\mu \omega_q)$, where $\omega_q = 1164 \text{ cm}^{-1}$ is the imaginary frequency for the unbound motion atop the Eckart barrier, and η_0 is the integrated viscosity. We use the expression⁷

$$C^2 = \frac{f \omega_q \sigma}{\omega \sigma} e^{-(\omega \sigma)^2 / 2} \quad (27)$$

to relate the coupling constant C to f , where we have taken advantage of the classical equivalence of the motion from the above Hamiltonian and the generalized Langevin equation with friction kernel $\eta(t) = \mu \omega^2 C^2 \cos(\omega t)$. The calculations were carried out for two different values of the friction, $f=10$ and $f=15$.

The contour plot of the potential energy surface is shown for the two cases in Fig. 2. The zero of the reaction coordinate s is taken to be the saddle point. There is significant distortion from a harmonic surface with these values of f causing considerable curvature in the minimum energy path along the surface. Because of the large deviation of this surface from a harmonic surface, it is difficult, both classically and quantum mechanically, to estimate the transition rate using harmonic system based TST with a planar dividing surface located at the saddle point.

IV. RESULTS AND DISCUSSION

We have used two different paths, Γ_s , to parametrize the progression of the hyperplane in the evaluation of the free energy barrier. We first present calculations using the minimum energy path (MEP) in configuration space. The MEP is such that for any direction \mathbf{p}_s perpendicular to the path, $\mathbf{p}_s \cdot \Gamma'_s = 0$, the potential energy is at a minimum, $\mathbf{p}_s \cdot \nabla V(\Gamma_s) = 0$. We then present a calculation where the path was chosen in such a way as to minimize the torque acting on the hyperplane. It turned out that this zero torque path (ZTP) nearly coincided with the collection of average centroid positions that were constrained to lie on the hypersurfaces defined by the MEP. Since the torque on the hyperplane was very small, the free energy was almost entirely composed of the translational component of the work and the rotational component was negligible. The net free energy barrier obtained from the two different calculations was very similar and therefore gave close estimates of the transition rate.

As a matter of convenience, we chose in both cases the hyperplanes in such a way that the normal to the hyperplane associated with the point Γ_s was parallel to the tangent of the reaction path

$$\mathbf{n}_s = \Gamma'_s / |\Gamma'_s|. \quad (28)$$

The calculations were carried out for $T=300 \text{ K}$ with 10 images included in the FPI representation of the quantum particle.

When the hyperplanes were constructed from the MEP the rotational contribution was very large. Figure 3 shows the generalized force acting on the system evaluated along the reaction path. The contributions, due to translation and rotation of the hyperplane, are shown separately in addition to

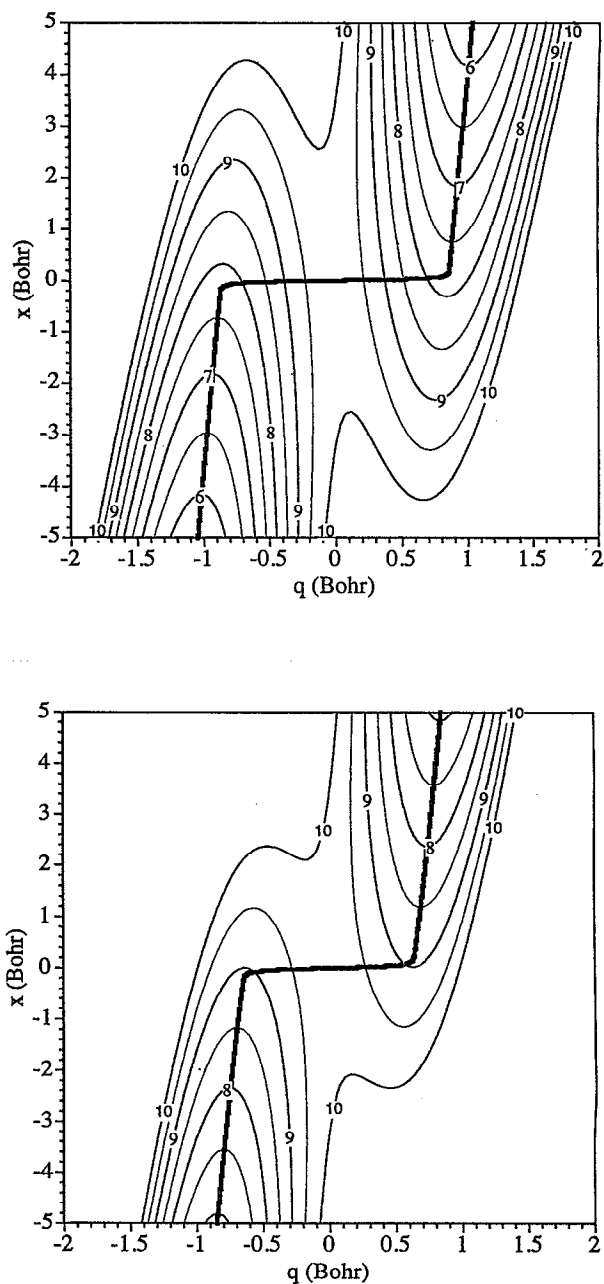


FIG. 2. Contour plot of the potential energy surface with q the solute coordinate and x the harmonic oscillator bath coordinate. Two different coupling strengths between the two coordinates are considered; (a) $f=10$, and (b) $f=15$. The thick line shows the minimum energy path.

the total mean force. In both the $f=10$ and $f=15$ cases the rotational contribution could be quite large where both the path curvature and the torque acting on the hyperplane were large. The translation dominated the contribution to the work near the saddle point and in the asymptotic regions and was positive throughout the path. The rotation contribution, which has a large negative component for the hyperplane rotating about the corner of the MEP, was responsible for lowering the free energy to yield a good estimate for the rate constant.

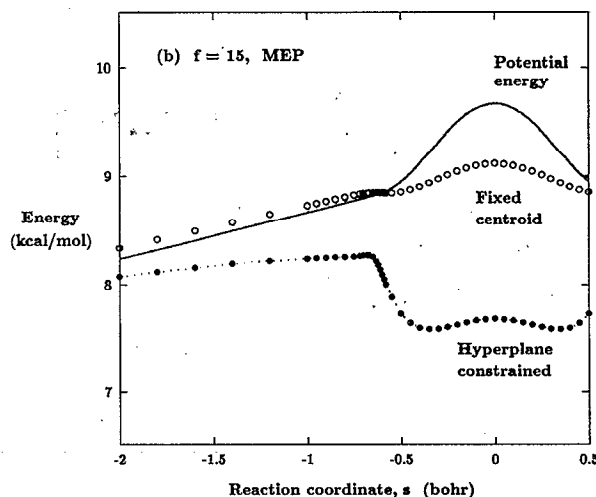
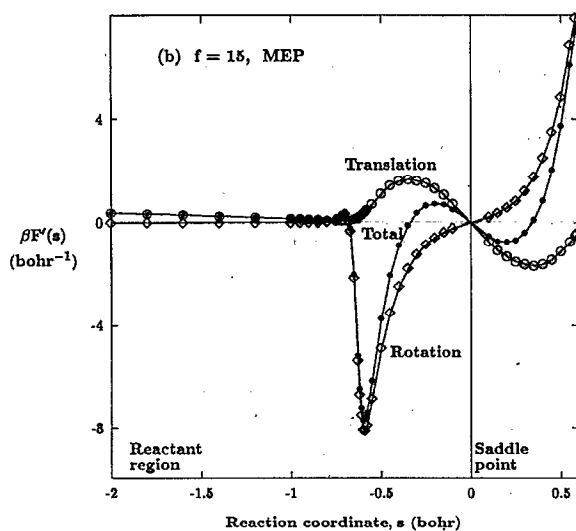
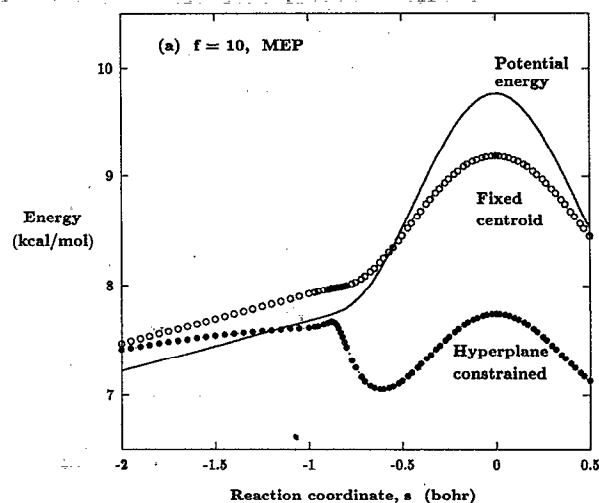
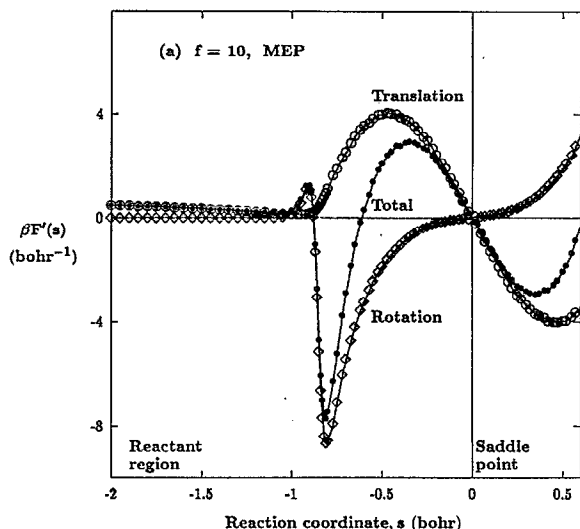


FIG. 3. The generalized force on the hyperplane along the minimum energy path [see Eq. (17)]. The system is confined to a hyperplane intersecting the path at s with the plane's normal tangent to the path. The contributions due to translation and rotation of the hyperplane are shown separately as well as the total force. The rotational contribution is large near $s = \pm 0.7$ bohr where both the path curvature and the torque acting on the hyperplane are large. The saddle point on the potential energy surface is at $s = 0$. (a) $f = 10$, and (b) $f = 15$.

Figure 4 shows the potential energy along the minimum energy path and the free energy change at $T = 300$ K obtained by evaluating the reversible work in moving the hyperplane [integration of Eq. (17) to give Eq. (19)]. For comparison, the free energy obtained from a fixed centroid calculation using Eq. (6) as given by Gillan is also shown. The effect of the large curvature of the reaction path in this system leads to an overestimate of the free energy barrier by the fixed centroid method of approximately 1 kcal/mol.

The estimate of the rate constant was obtained from the reversible work evaluation of the free energy barrier and Eq. (9) and is displayed in Fig. 5. For comparison, the rate ob-

FIG. 4. Potential energy along the minimum energy path and the change in the free energy evaluated from the reversible work in moving the hyperplane from reactant region towards products (filled circles). For comparison, the free energy obtained from a fixed centroid calculation is also shown (open circles). The fixed centroid method overestimates the free energy barrier by 1–2 kcal/mol. All three curves are arbitrarily set equal at $s = -50$ where the potential energy has dropped to ~ 0.1 kcal/mol. (a) $f = 10$, and (b) $f = 15$.

tained by MSG centroid density calculation using a harmonic reference is also shown. Excellent agreement was found between the two methods with differences being consistent with the numerical evaluation of averages. The transition rate has also been calculated for this system using wave packet propagation on the potential energy surface.⁷ We took this to be the best estimate of the rate and use it to give an indication of how well TST is working here. For both coupling constants, the TST calculation was found to give too large of an estimate of the transition rate; 85% too high when $f = 10$ but only 2% too high when $f = 15$. The Monte Carlo calculations of the MSG rate used 10^6 Monte Carlo moves for each point. The reversible work calculation used the same

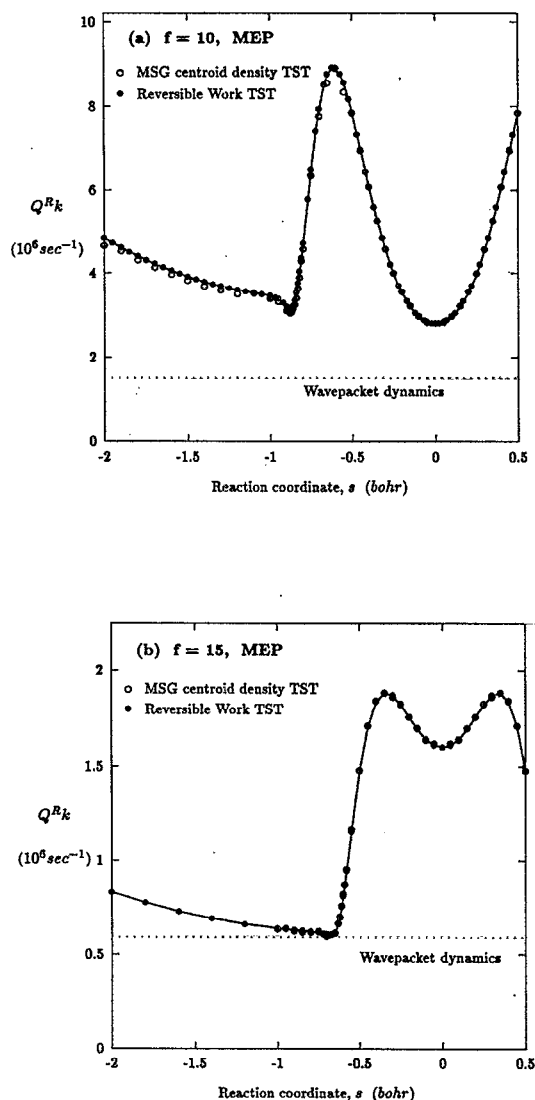


FIG. 5. The transition rate obtained from the reversible work evaluation of the activation free energy and Eq. (9) (solid circles). For each value of the reaction coordinate an activation free energy is obtained and the corresponding rate evaluated. The minimum rate corresponds to the maximum free energy barrier along the path. For comparison, the rate obtained from a calculation using the MSG centroid density theory and Monte Carlo sampling is also shown (open circles). The two methods give nearly identical results. Also shown is the transition rate obtained by dynamical wave packet calculations which can be taken as the best estimate of the true transition rate. The TST results are very close, but slightly overestimate the rate. (a) $f=10$, and (b) $f=15$.

number of moves with considerably less statistical uncertainty in the final results. Even in this two-dimensional test system it was computationally more efficient to evaluate the free energy using the current method instead of evaluating the ratio of the partition functions directly.

As an alternative to the MEP, we constructed a different path, the zero torque path (ZTP) resulting in negligible rotational contribution to the free energy barrier. Since the optimal planar dividing surface corresponded to zero torque, a starting point for the construction of the ZTP was to find an

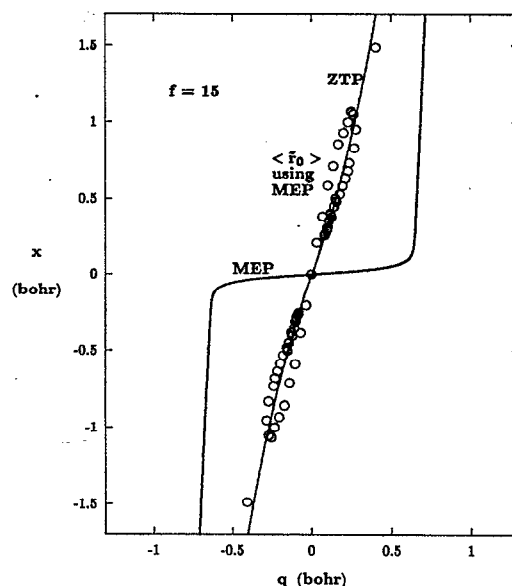


FIG. 6. Average FPI centroid position, $\langle \bar{r}_0 \rangle$, within hyperplanes constructed from the minimum energy path (MEP). Away from the saddle point, the average centroid position is shifted away from the MEP towards $q=0$ because the FPI chain is able to slide into both potential wells [see the contour plot of this potential surface in Fig. 2(b)]. This is a reflection of tunneling through the potential barrier. The zero torque path (ZTP) (shown with dotted line) was constructed to minimize the rotational contribution to the free energy barrier and nearly coincides with the average centroid position in the MEP calculation.

orientation of a hyperplane going through the saddle point with zero torque. The path was then continued in such a way as to asymptotically become parallel to the MEP in the reactant region. This was achieved by requiring the path to satisfy

$$\Gamma'_s = \Gamma'_R + (\Gamma'_0 - \Gamma'_R)e^{-\lambda s}, \quad (29)$$

where $\Gamma'_R = (1, C)/\sqrt{1+C^2}$ and the zero torque orientation was obtained at the saddle point for the $f=15$ case with $\Gamma'_0 = (0.316, 0.949)$ and $\lambda=0.5$. This path, the ZTP, is shown in Fig. 6 along with the MEP.

It turns out that the ZTP coincided roughly with the average centroid positions obtained in the previous calculation, when the centroids were constrained to lie on the hyperplanes constructed from the MEP. With the ZTP as reference, only the translational component of the work contributes to the free energy change. In Fig. 7 we compare the free energy along the MEP to that obtained along the ZTP. The shape of the two curves is quite different. The ZTP free energy is smooth and peaks at the saddle point, $s=0$, while the MEP free energy curve exhibits large variations and peaks at $s = \pm 0.7$ close to the region of large curvature in the MEP. However, the net free energy barrier is remarkably similar in the two cases giving close estimates for the transition rate.

V. SUMMARY

In the work reported here we have introduced a procedure for evaluating TST reaction rate constants following the

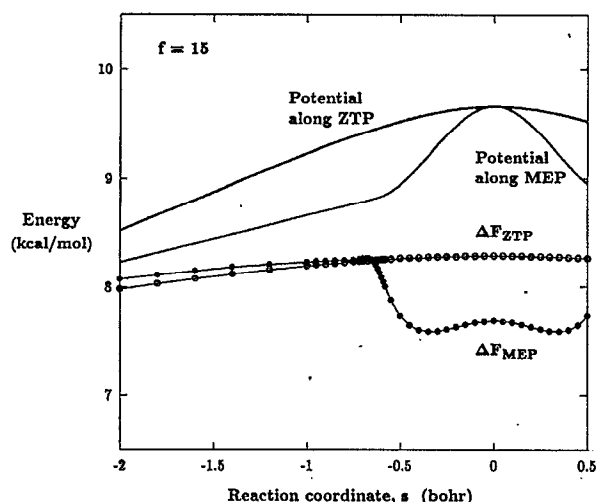


FIG. 7. Comparison of the hyperplane free energy calculated from the minimum energy path (solid circles) and the zero torque path (open circles). While the latter gives a much smoother variation of the free energy and has negligible rotational contribution, the net free energy barrier and therefore the transition rate obtained from the two calculations is nearly identical.

spirit of the original work of Gillan where free energy barriers were evaluated from a reversible work calculation. Starting with the MSG centroid density expression for the dividing surface dependent rate constant we define a free energy for the system confined in a $N-1$ dimensional hyperplane and recast the rate constant expression in terms of the free energy difference between a hyperplane dividing surface and a hyperplane in the reactant region. The method was applied here to a model system consisting of an Eckart barrier coupled to a harmonic oscillator and the results shown to be in good agreement with Monte Carlo simulations based on centroid density TST formulation. The method relies on identifying a path from reactants to products. This path was used to parametrize the gradual progression of the hyperplane from the reactant region to the optimal dividing surface. In this system the necessity of treating free energy contributions from both rotational and translational movement of

the dividing surface was exaggerated due to the large reaction path curvature along the MEP. With a different choice for the path, the ZTP, we were able to make the torque negligible and the free energy change was almost entirely due to the translational component. The resulting free energy barrier was nearly identical for the two different paths. For this low dimensional model system we were able to compare with results obtained by other methods. However, since the reversible work TST method only requires the evaluation of the statistical average of forces rather than partition functions, it can be readily applied to studies of high dimensional systems,⁶ and we expect it will become an important tool in the future.

ACKNOWLEDGMENTS

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Pacific Northwest Laboratory, that is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract No. DE-AC06-76RLO 1830 (G.S.), and under Grant No. DE-FG06-91ER14224 (G.M. and H.J.). G.M. is a Hertz foundation graduate fellow. We also would like to acknowledge useful discussions with Michael Messina, Huadong Gai, and Bruce C. Garrett.

- ¹(a) M. J. Gillan, *J. Phys. C* **20**, 3621 (1987); (b) *Phys. Rev. Lett.* **58**, 563 (1987); (c) *Philos. Mag. A* **58**, 257 (1988).
- ²R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
- ³(a) G. A. Voth, D. Chandler, and W. H. Miller, *J. Chem. Phys.* **91**, 7749 (1989); (b) G. A. Voth, *Chem. Phys. Lett.* **170**, 289 (1990); (c) *J. Phys. Chem.* **97**, 8365 (1993).
- ⁴M. Messina, G. K. Schenter, and B. C. Garrett, *J. Chem. Phys.* **98**, 8525 (1993).
- ⁵B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.* **83**, 1052, 3058(E) (1979); **87**, 4553(E) (1983).
- ⁶G. Mills and H. Jónsson, *Phys. Rev. Lett.* **72**, 1124 (1994).
- ⁷R. P. McRae, G. K. Schenter, B. C. Garrett, G. R. Haynes, G. A. Voth, and G. C. Schatz, *J. Chem. Phys.* **97**, 7392 (1992).
- ⁸R. J. Zwanzig, *J. Stat. Phys.* **9**, 215 (1973).
- ⁹M. Messina, G. K. Schenter, and B. C. Garrett, *J. Chem. Phys.* **99**, 8644 (1993).
- ¹⁰A. M. Berezhkovskii, E. Pollak, and V. Y. Zitserman, *J. Chem. Phys.* **97**, 2422 (1992).
- ¹¹E. Pollak and P. Pechukas, *J. Chem. Phys.* **69**, 1218 (1978); P. Pechukas, in *Dynamics of Molecular Collisions, Part B*, edited by W. H. Miller (Plenum, New York, 1976), p. 269; P. Pechukas, *Annu. Rev. Phys. Chem.* **32**, 159 (1981).