

The Quantum Instanton (QI) Model for Chemical Reaction Rates: The “Simplest” QI with One Dividing Surface[†]

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A new version of the quantum instanton (QI) approach to thermal rate constants of chemical reactions (Miller, W. H.; Zhao, Y.; Ceotto, M.; Yang, S. *J. Chem. Phys.* **2003**, 119, 1329) is presented, namely, the *simplest* QI (SQI) approximation with one dividing surface (DS), referred to here as SQI1. (The SQI approximation presented originally was applicable only with two DSs.) As with all versions of the QI approach, the rate is expressed wholly in terms of the (quantum) Boltzmann operator (which, for complex systems, can be evaluated by Monte Carlo path integral methods). Test calculations on some simple model problems show the SQI1 model to be slightly less accurate than the original version of the QI approach, but it is the easiest version to implement; it requires only a constrained free-energy calculation, location of the (transition-state) DS so as to maximize this free energy, and the curvature (second derivative) of the free energy at this maximum.

1. Introduction

A recent paper¹ has developed an approximate theoretical expression for the thermal rate constant of a chemical reaction that is expressed solely in terms of the quantum Boltzmann operator $e^{-\beta\hat{H}}$. Its derivation was motivated by the earlier² semiclassical (SC) “instanton”³ approximation for rate constants and is thus referred to as the *quantum* instanton (QI) approximation. Applications to some standard one- and two-dimensional model problems showed it to be capable of ± 10 –20% accuracy over a wide range of temperatures, from low temperatures deep in the tunneling regime to the high-temperature “over-barrier” limit. (More recent calculations⁴ have been carried out for the $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$ reaction in full Cartesian space.) The potential usefulness of this QI approach is that the quantum Boltzmann operator can be evaluated for quite complex molecular systems by Monte Carlo (or molecular dynamics) path integration methods.⁵ The QI model is a type of “quantum transition-state theory”, of which there are many varieties,^{6–14} its particular attraction is that it is not necessary to assume any reaction or tunneling path, all necessary information being contained in the Boltzmann operator.

The purpose of this paper is to develop one further aspect of the QI model that was not considered initially, namely, the variant of the model that was referred to as the *simplest* quantum instanton, or SQI approximation for the case that one uses a *single* dividing surface (DS). (The SQI given in the original work¹ is only meaningful when one uses two different DSs.) Since this is the simplest possible version of the QI idea, it is worthwhile to explore this version of the theory and see how it performs. Section 2 presents the theoretical development, section 3 presents the generalization to multidimensional systems, and section 4 shows the results of application to standard test problems. Though not quite as accurate as the original QI approximation¹ with two DSs, it is by far the easiest of all

versions of the QI approach to implement; as summarized by eq 2.16, it requires only a constrained free-energy calculation, location of the DS to maximize this free energy, and determination of the curvature (second derivative) of the free energy at this maximum.

2. Theoretical Development

We begin with the quantum instanton (QI) expression¹ for the thermal rate constant $k(T)$ for the case of a single DS, here for a one-dimensional potential barrier (the multidimensional generalization will be noted below)

$$k(T)Q_r(T) = \frac{\hbar(\pi)^{1/2}}{\Delta H(\beta)} \left(\frac{\hbar}{2m}\right)^2 \langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle \langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle \quad (2.1a)$$

where Q_r is the reactant partition function (per unit volume), $\Delta H(\beta)$ is an energy variance

$$\Delta H(\beta) = \left[\frac{\langle x_0 | e^{-\beta\hat{H}/2} \hat{H}^2 | x_0 \rangle}{\langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle} - \left(\frac{\langle x_0 | e^{-\beta\hat{H}/2} \hat{H} | x_0 \rangle}{\langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle} \right)^2 \right]^{1/2} \quad (2.1b)$$

and x_0 is the value of x for which

$$\frac{d}{dx} \langle x | e^{-\beta\hat{H}/2} | x \rangle = 0 \quad (2.1c)$$

The primes on the matrix elements in eq 2.1a denote differentiation with respect to the coordinate variable in the bra or ket. To develop the SQI approximation for this case of one DS, we proceed as before¹ and consider the SC limit of eq 2.1; i.e., we utilize the SC approximation for the matrix elements of the Boltzmann operator¹⁵

$$\langle x' | e^{-\beta\hat{H}/2} | x \rangle = \sum_k \left(\frac{-1}{2\pi\hbar} \frac{\partial^2 S_k}{\partial x' \partial x} \right)^{1/2} e^{-S_k(x', x; \hbar\beta/2)/\hbar} \quad (2.2)$$

where the sum in eq 2.2 is over all trajectories (in pure imaginary

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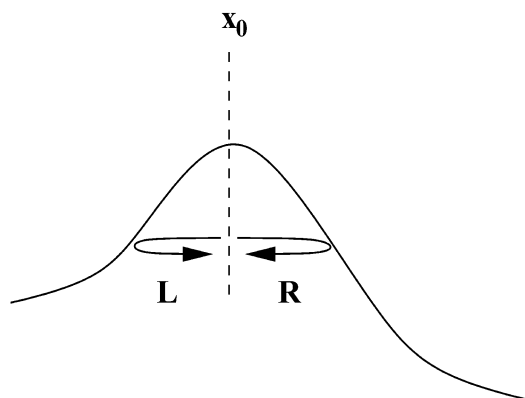


Figure 1. A sketch of a general one-dimensional potential barrier indicating the two (imaginary time) trajectories that contribute to the semiclassical approximation to the Boltzmann matrix element in eq 2.3.

time or real time on the upside-down potential surface) that go from x to x' in (imaginary) time $\hbar\beta/2$. (When using two DSs, there is only one such trajectory.) Figure 1 indicates that there will typically be *two* such trajectories in the present case, one that moves from x_0 to the left (L) and back to x_0 , and one that moves to the right (R) and back, so that

$$\langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle = \left(\frac{-1}{2\pi\hbar} \frac{\partial^2 S_L}{\partial x' \partial x} \right)^{1/2} e^{-S_L(x', x; \hbar\beta/2)/\hbar} + \left(\frac{-1}{2\pi\hbar} \frac{\partial^2 S_R}{\partial x' \partial x} \right)^{1/2} e^{-S_R(x', x; \hbar\beta/2)/\hbar} \quad (2.3)$$

with $x' = x = x_0$. Since

$$\frac{\partial S_k(x', x)}{\partial x'} = p_k', \quad \frac{\partial S_k(x', x)}{\partial x} = -p_k \quad (2.4)$$

where p_k (p_k') is the initial (final) momentum for trajectory $k = L$ or R , one sees that

$$\frac{d}{dx_0} \langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle = \left(\frac{-1}{2\pi\hbar} \frac{\partial^2 S_L}{\partial x' \partial x} \right)^{1/2} e^{-S_L/\hbar} \left(\frac{-p_L'}{\hbar} + \frac{p_L}{\hbar} \right) + \left(\frac{-1}{2\pi\hbar} \frac{\partial^2 S_R}{\partial x' \partial x} \right)^{1/2} e^{-S_R/\hbar} \left(\frac{-p_R'}{\hbar} + \frac{p_R}{\hbar} \right) \quad (2.5)$$

Thus if x_0 is chosen so that

$$S_L(x_0, x_0) = S_R(x_0, x_0) \quad (2.6)$$

then the RHS of eq 2.5 will be 0 (i.e., eq 2.1c will be satisfied) since (as seen in Figure 1) $p_L' = -p_L = -p_R' = p_R$. For a symmetric barrier, it is clear that x_0 is at the maximum of the potential $V(x)$, the conventional transition state.

Utilizing eqs 2.3–2.5, one thus has the following relations in the SC limit

$$\langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle = 2e^{-S/\hbar} \left(\frac{-1}{2\pi\hbar} \frac{\partial^2 S}{\partial x' \partial x} \right)^{1/2} \quad (2.7a)$$

$$\langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle' = 2e^{-S/\hbar} \left(\frac{-1}{2\pi\hbar} \frac{\partial^2 S}{\partial x' \partial x} \right)^{1/2} \left(\frac{p_0^2}{\hbar^2} - \frac{1}{\hbar} \frac{\partial^2 S}{\partial x' \partial x} \right) \quad (2.7b)$$

where $S = S_L(x_0, x_0) = S_R(x_0, x_0)$ and $p_0 = p_L' = -p_L = -p_R' = p_R$. For future reference we also note that

$$\langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle = \langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle' = 2e^{-S/\hbar} \left(\frac{-1}{2\pi\hbar} \frac{\partial^2 S}{\partial x' \partial x} \right)^{1/2} \left(\frac{p_0^2}{\hbar^2} - \frac{1}{\hbar} \frac{\partial^2 S}{\partial x' \partial x} \right) \quad (2.7c)$$

Using eqs 2.7a and 2.7b in eq 2.1a thus gives the SC limit of the QI rate constant as

$$k_{\text{SC-QI}} Q_r = \frac{\hbar(\pi)^{1/2}}{\Delta H} \left(\frac{\hbar}{2m} \right)^2 4e^{-2S/\hbar} \left(\frac{-1}{2\pi\hbar} \frac{\partial^2 S}{\partial x' \partial x} \right)^{1/2} \left(\frac{p_0^2}{\hbar^2} - \frac{1}{\hbar} \frac{\partial^2 S}{\partial x' \partial x} \right) \quad (2.8)$$

As before, we now equate this to the original SC instanton rate expression²

$$k_{\text{SC-I}} Q_r = \frac{\Delta H}{2\hbar(\pi)^{1/2}} e^{-2S/\hbar} \quad (2.9)$$

which implies that

$$\Delta H^2 = \left(\frac{\hbar}{m} \right)^2 \left[\left(\frac{\partial^2 S}{\partial x' \partial x} \right)^2 - \frac{p_0^2}{\hbar} \frac{\partial^2 S}{\partial x' \partial x} \right] \quad (2.10a)$$

solving this equation for $\partial^2 S/\partial x' \partial x$ gives

$$\frac{-\partial^2 S}{\partial x' \partial x} = \frac{1}{2} \left(\frac{-p_0^2}{\hbar} + \sqrt{\frac{+p_0^4}{\hbar^2} + \frac{2m\Delta H^2}{\hbar^2}} \right) \quad (2.10b)$$

Finally, substituting this result, eq 2.10b, back into eq 2.8 (and using eq 2.7a) gives the *simplest quantum instanton* for 1 DS (SQI1) as

$$k_{\text{SQI1}} Q_r = \frac{(\pi)^{1/2}}{2} \frac{\hbar}{2m} (\langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle)^2 (z + (1 + z^2)^{1/2}) \quad (2.11a)$$

where z is the dimensionless variable

$$z = \frac{1}{\Delta H} \frac{p_0^2}{2m} \quad (2.11b)$$

To complete the SQI1 model, one needs a way to determine the momentum p_0 , or more specifically, $p_0^2/2m$, the kinetic energy at the DS (i.e., at the transition state). A simple prescription for doing so is based on classical conservation of energy (for the imaginary time trajectory)

$$E(\beta) = -\frac{p_0^2}{2m} + V(x_0) \quad \text{or} \quad \frac{p_0^2}{2m} = V(x_0) - E(\beta) \quad (2.12a)$$

where $E(\beta)$ is given by

$$E(\beta) = \frac{\langle x_0 | e^{-\beta\hat{H}/2} \hat{H} | x_0 \rangle}{\langle x_0 | e^{-\beta\hat{H}/2} | x_0 \rangle} \quad (2.12b)$$

We have indeed used eq 2.12 in eq 2.11b, and the rate constants obtained are reasonably good. We do not consider this a satisfactory approach, however, because it does not generalize to the multidimensional case; eq 2.12 gives the *total* kinetic energy on the DS, while it is clear (e.g., by considering the separable limit) it should be only the kinetic energy in the reaction coordinate. A definition of $p_0^2/2m$ that does generalize

correctly is obtained by averaging eqs 2.7b and 2.7c, which gives

$$\frac{p_0^2}{2m} = \frac{\hbar^2}{4m} \left(\frac{\langle x_0 | e^{-\beta \hat{H}/2} | x_0 \rangle' + \langle x_0 | e^{-\beta \hat{H}/2} | x_0 \rangle''}{\langle x_0 | e^{-\beta \hat{H}/2} | x_0 \rangle} \right) + \frac{\hbar}{4m} \left(\frac{\partial^2 S}{\partial x' \partial x} + \frac{\partial^2 S}{\partial x'^2} \right) \quad (2.13)$$

In the high-temperature limit, $S(x', x) \propto (x' - x)^2$ so that the last term in eq 2.13 vanishes, and it is negligible compared to the first term in the low-temperature limit. To complete the SQII model we thus choose

$$\frac{p_0^2}{2m} = \frac{\hbar^2}{4m} \left(\frac{\langle x_0 | e^{-\beta \hat{H}/2} | x_0 \rangle' + \langle x_0 | e^{-\beta \hat{H}/2} | x_0 \rangle''}{\langle x_0 | e^{-\beta \hat{H}/2} | x_0 \rangle} \right) \quad (2.14)$$

Perhaps the most convenient aspect of eq 2.14 is that it can also be expressed as

$$\frac{p_0^2}{2m} = \frac{\hbar^2}{8m} \frac{d^2}{dx_0^2} \ln [\langle x_0 | e^{-\beta \hat{H}/2} | x_0 \rangle] \quad (2.15a)$$

where, as eq 2.1c implies, x_0 is determined by

$$\frac{d}{dx_0} \ln [\langle x_0 | e^{-\beta \hat{H}/2} | x_0 \rangle] = 0 \quad (2.15b)$$

i.e., one varies x_0 to find the value for which $\ln [\langle x_0 | e^{-\beta \hat{H}/2} | x_0 \rangle]$ is a minimum, and $p_0^2/2m$ of eq 2.15a is given in terms of the curvature at this minimum.

To summarize, one can also write the final result in thermodynamic language. Thus if the free energy $G(x_0)$ as a function of the reaction coordinate is defined by

$$\beta G(x_0) \equiv -\ln [\langle x_0 | e^{-\beta \hat{H}/2} | x_0 \rangle]^2 \quad (2.16a)$$

then x_0 is determined by the maximum of this free energy

$$G'(x_0) = 0 \quad (2.16b)$$

and the dimensionless variable z (of eq 2.11b) given in terms of its curvature at the maximum

$$z = \frac{-\hbar^2 \beta G''(x_0)}{16m \Delta H(\beta)} \quad (2.16c)$$

The SQII expression for the rate constant is then

$$k_{\text{SQII}} Q_{\text{r}} = \frac{(\pi)^{1/2}}{2} \frac{\hbar}{2m} e^{-\beta G(x_0)} (z + (1 + z^2)^{1/2}) \quad (2.16d)$$

3. Multidimensional Generalization

In light of the previous QI paper,¹ the multidimensional generalization of the SQII rate constant is straightforward. For simplicity, we consider the case that the coordinates of the system are (x, \mathbf{Q}) where x is the reaction coordinate. In terms of the thermodynamic language of eqs 2.16, the multidimensional expression for the free energy is

$$\beta G(x_0) = -\ln \left[\int d\mathbf{Q}_1 \int d\mathbf{Q}_2 \langle x_0 \mathbf{Q}_2 | e^{-\beta \hat{H}/2} | x_0 \mathbf{Q}_1 \rangle^2 \right] \quad (3.1)$$

and then eqs 2.16b–d pertain as written. The multidimensional energy variance ΔH is as given before

$$\Delta H(\beta)^2 = \frac{\int d\mathbf{Q}_1 \int d\mathbf{Q}_2 \langle x_0 \mathbf{Q}_2 | e^{-\beta \hat{H}/2} | x_0 \mathbf{Q}_1 \rangle \langle x_0 \mathbf{Q}_2 | e^{-\beta \hat{H}/2} | x_0 \mathbf{Q}_1 \rangle - \langle x_0 \mathbf{Q}_2 | e^{-\beta \hat{H}/2} | x_0 \mathbf{Q}_1 \rangle^2}{\int d\mathbf{Q}_1 \int d\mathbf{Q}_2 \langle x_0 \mathbf{Q}_2 | e^{-\beta \hat{H}/2} | x_0 \mathbf{Q}_1 \rangle^2} \quad (3.2)$$

The generalization of eqs 3.1 and 3.2 to the case of a more general form of the DS, e.g., specified by some function (the generalized reaction coordinate) $s(\mathbf{q}) = 0$, where $\mathbf{q} = (x, \mathbf{Q})$ denotes all the (Cartesian) coordinates of the system, has been given (and implemented) in ref 4.

4. Test Calculations

The first example we consider is the standard one-dimensional symmetric Eckart potential barrier

$$V(x) = V_0 \operatorname{sech}^2(ax) \quad (4.1)$$

with parameters $V_0 = 0.425$ eV, $a = 1.36$ au, and $m = 1060$ au, which correspond approximately to the H + H₂ reaction. For these elementary one-dimensional examples, it is simplest to evaluate the necessary matrix elements of the Boltzmann operator by quantum basis-set methods (we used a discrete variable representation),¹⁶ though the practical interest in the quantum instanton approach is that the Boltzmann operator can be evaluated for very complex systems by Monte Carlo path integral methods.⁵

Figure 2a first displays an Arrhenius plot of the rate constant given by the SQII model, i.e., eq 2.11 with 2.14 over the range $T = 100$ – 2000 K, along with the exact quantum rate, showing that on this scale the model gives excellent results. (For this symmetric case, the location of the transition state DS x_0 is always $x_0 = 0$.) To show the accuracy of the model more precisely, Figure 2b plots the ratio of the SQII rate to the exact quantum rate as a function of $1/T$; it is ~ 10 – 15% too small at the lowest and highest temperatures, with the greatest deviation (a factor of ~ 1.4) at intermediate temperature. By comparison of these results to the earlier QI model with one DS, the present SQII model is better at the lowest and highest temperature but not as accurate in the intermediate temperature regime.

The second example is the asymmetric version of the Eckart potential

$$V(x) = \frac{V_0(1 - \alpha)}{1 + e^{-2ax}} + \frac{V_0(1 + \alpha)^{1/2}}{4 \cosh^2(ax)} \quad (4.2)$$

with parameters $V_0 = 0.425$ eV, $a = 1.36$ au, $\alpha = 1.25$, and $m = 1060$ au; the barrier heights are 0.425 and 0.531 eV from the left and right sides of the barrier, respectively. As above, we first show in Figure 3a, an Arrhenius plot of the SQII rate constant, for the range $T = 150$ – 2000 K, again displaying very good agreement with the exact quantum rate over this large range of temperature. Here the location of the DS, x_0 , as determined by eq 2.1c or 2.15b, varies with temperature. Figure 3b shows the ratio of the SQII rate to the exact quantum value over this range of temperature. This plot is very similar to the symmetric case in Figure 2b except at the lowest temperatures (< 200 K) where the SQII rate becomes increasingly too large (off by a factor of ~ 1.4 at 150 K). Comparing these results to those given previously by the one DS version of the QI model,

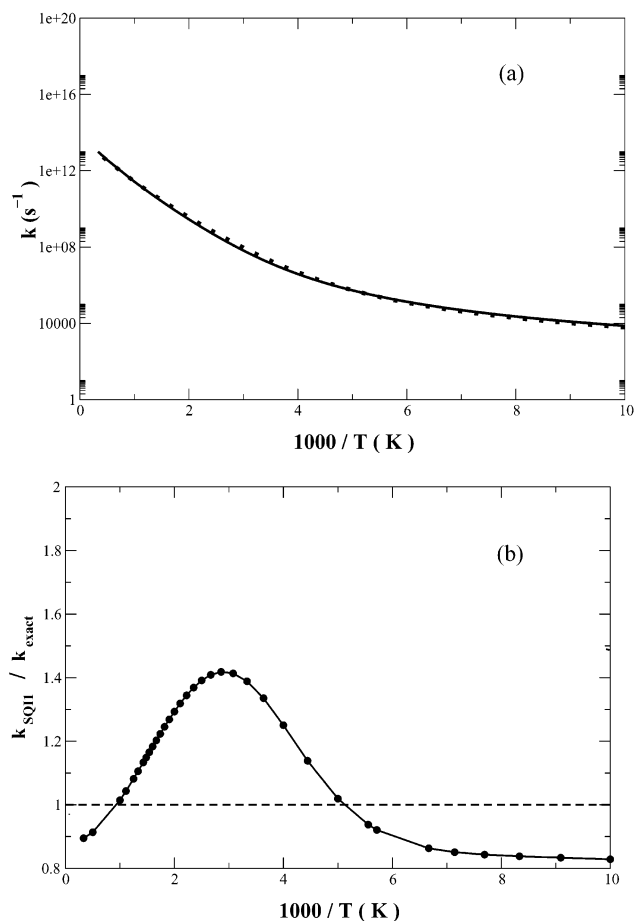


Figure 2. (a) Arrhenius plot of the rate constant given by the SQI1 model for the symmetric Eckart potential of eq 4.1. The solid curve is the exact result, and the dotted curve is the SQI1 result. (b) Ratio of the SQI1 rate constant to the exact quantum value for the symmetric Eckart potential.

the deviations of both from the correct quantum values are qualitatively similar, but those of the present SQI1 model are larger.

Finally, though it is beyond the scope of this paper, we note that the deviations of the SQI1 rates from the correct quantum values (Figures 2b and 3b) are similar if plotted as a function of the dimensionless variable z of eq 2.11b (with 2.14). The largest deviation, a factor of ~ 1.4 – 1.5 , occurs at $z \sim 1$. It is thus possible to introduce an empirical correction factor (i.e., a function of z) that significantly corrects this generic behavior of the SQI1 model. For example, if the factor $(\pi)^{1/2}/2 (z + (1 + z^2)^{1/2})$ in eq 2.11a and 2.16d is replaced by $5z/4 + ((z - 1)^2 + (1/4)^2)^{1/2}$, then the SQI1 rate agrees with the exact quantum value to within a few percent for all temperature in Figure 2 and down to ~ 250 K in Figure 3. It remains to be seen, of course, how universal this (or any) empirical correction factor may be.

5. Concluding Remarks

The analysis presented in section 2 shows that it is indeed possible to derive a version of the simplest quantum instanton model that utilizes a single DS, designated here SQI1. The rate expression is given by eq 2.11 with 2.14, or equivalently by eq 2.16 in thermodynamic language and its multidimensional generalization by eqs 3.1 and 3.2.

Though not as accurate for these test problems as the original QI model with two DSs, the SQI1 model is still of useful

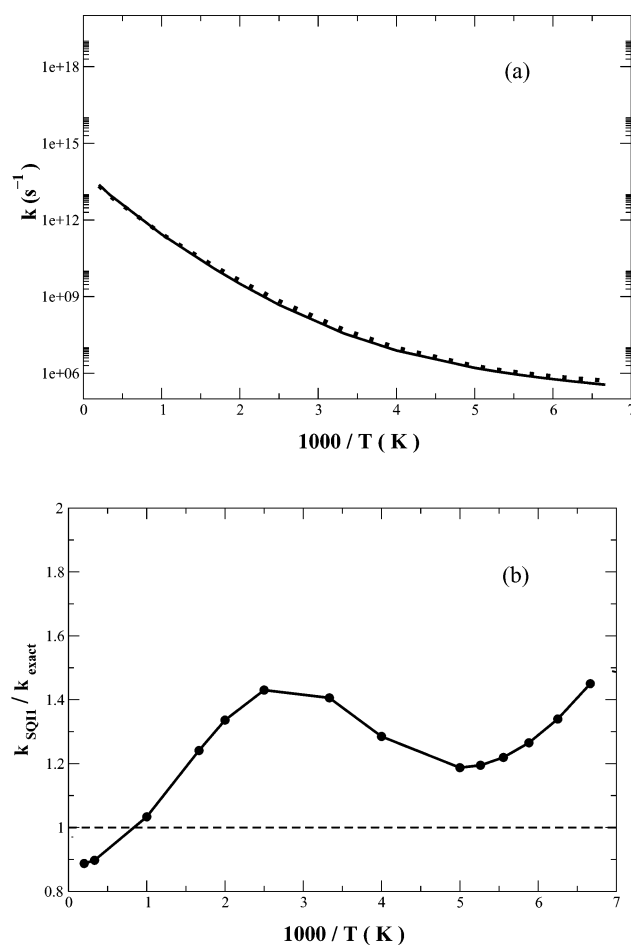


Figure 3. (a) Arrhenius plot of the rate constant given by the SQI1 model for the asymmetric Eckart potential of eq 4.2. The solid curve is the exact result, and the dotted curve is the SQI1 result. (b) Ratio of the SQI1 rate constant to the exact quantum value for the asymmetric Eckart potential.

accuracy (with empirical corrections being possible to make it even more accurate), and it is much easier to implement. For example, eqs 2.16 show that it is necessary only to carry out a rather standard constrained free-energy calculation, choose the transition state DS by (an again fairly standard) maximum free-energy criterion, and then the rate is given by this maximum free energy and a function of the dimensionless parameter z , which is expressed in terms of the curvature of the free energy at its maximum.

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