Test of the quantum instanton approximation for thermal rate constants for some collinear reactions

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Two variants of the recently developed quantum instanton (QI) model for calculating thermal rate constants of chemical reactions are applied to several collinear atom–diatom reactions with various skew angles. The results show that the original QI version of the model is consistently more accurate than the “simplest” quantum instanton version (both being applied here with one “dividing surface”) and thus to be preferred. Also, for these examples (as with other earlier applications) the QI results agree well with the correct quantum rates (to within ~20% or better) for all temperatures >200 K, except for situations where dynamical corrections to transition state theory (i.e., “re-crossing” dynamics) are evident. (Since re-crossing effects are substantially reduced in higher dimensionality, this is not a cause for serious concern.) A procedure is also described which facilitates use of the METROPOLIS algorithm for evaluating all quantities that appear in the QI rate expression by Monte Carlo path integral methods. © 2004 American Institute of Physics.

I. INTRODUCTION

The accurate calculation of thermal rate constants for chemical reactions remains one of the primary goals of theoretical chemistry. This is particularly so for reactions involving complex systems, e.g., in clusters (“nanomaterials”), on surfaces, in biomolecular systems, etc. The accuracy of the calculated rate constant obviously depends on the accuracy of the underlying potential energy surface, but with the continuing advances of electronic structure theory (“quantum chemistry”), the availability of sufficiently accurate potential surfaces is becoming a reality. It thus behooves one to put more effort into developing ways to carry out the dynamical calculation of the rate constant sufficiently accurately to be useful for application to these complex systems.

To this end we have recently developed a theory for calculating thermal rate constants of chemical reactions that we have referred to as the quantum instanton (QI) model or approximation, because of its relation to and motivation by an earlier semiclassical (SC) instanton2–3 approximation. Like the SC instanton model, the QI rate constant is expressed wholly in terms of the Boltzmann operator of the system, but by the quantum Boltzmann operator rather than its semiclassical approximation. Application of the QI approach to complex systems is feasible because Monte Carlo (or molecular dynamics) path integral methods for evaluating the Boltzmann operator are quite well developed.4 (In fact, for systems with many degrees of freedom it is probably easier to evaluate the quantum Boltzmann operator by Monte Carlo path integration, and thus obtain the QI rate, than it is to find the imaginary time periodic orbits necessary to evaluate the original SC instanton rate.) Recent work by Yamamoto and one of us (W.H.M.)5 has indeed described in detail the implementation of this path integral methodology for the QI rate constant, and Zhao et al.6 have carried out successful calculations using it for the H+CH4→H2+CH3 reaction. This latter calculation was carried out in the full (18-d) Cartesian coordinate space of all six atoms, thus including all anharmonic and rotational effects (and their couplings) without approximation.

The QI approximation is a kind of “quantum transition state theory” in that there is no account of “re-crossing” dynamics in the description. However this is rarely a problem in complex systems, for the effect of re-crossing on the rate typically diminishes dramatically with increasing dimensionality.7 There are, of course, a number of other “quantum transition state theories” that have been proposed8–18. The present QI approach is closest in spirit to the work of Andersen et al.,16 though the derivation and final rate expression are different. The primary advantage of the QI model over simpler transition state theories (e.g., those based on a minimum energy path and the reaction path Hamiltonian referenced to it4) is that one need not assume any specific reaction or tunneling path (and local harmonic approximation about it), for all information about the barrier crossing rate is contained in the (quantum) Boltzmann operator.

Previous applications1,5 of the QI approximation to several 1- and 2-d model problems have shown agreement with the correct quantum rate constants to within ~20% over a wide range of temperature, from the low temperature “deep” tunneling regime to high temperatures dominated by above-barrier dynamics. The purpose of this paper is to provide some additional applications to a variety of simple benchmark collinear atom+diatom reactions, A+BC→AB+C, to gain further confidence in the degree of accuracy one can
expect for the model. The specific applications treated are H+BrH (a light + heavy-light mass combination), H+H2 (an equal mass combination), and Cl+HCl (a heavy + light-heavy mass combination), along with some of their isotopic variants. All applications here use the “one dividing surface” version of the QI theory since it is simpler (and therefore more practical for complex systems) than the more general version that utilizes two dividing surfaces. (We have in fact carried out the calculations also using two dividing surfaces and find it to make no difference in the rates for temperatures $T > 200$ K, and only a few percent below that.)

II. SUMMARY OF THE QUANTUM INSTANTON MODEL

The derivation\(^1\) of the quantum instanton expression for the rate constant starts with the following formally exact expression:\(^{19}\)

$$k(T) = Q_r(T)^{-1} (2\pi\hbar)^{-1} \int \text{d}E e^{-\beta E} \times \frac{1}{2} \left( \frac{\hat{p}}{m} \delta(\hat{x} - x_0) + \delta(\hat{x} - x_0) \right)$$

and uses a steepest descent approximation to establish an approximate relation between the microcanonical density operator, $\delta(E - \hat{H})$, and the Boltzmann operator, $e^{-\beta \hat{H}/2}$. The integral over $E$ in Eq. (2.1) is also evaluated within the steepest descent approximation. $Q_r$ in Eq. (2.1) (and the following) is the reactant partition function (per unit of volume), $\beta$ is related to temperature in the usual way, $\beta = (k_B T)^{-1}$, and $\hat{F}$ is a flux operator, which has the form

$$\hat{F} = \frac{1}{2} \left( \frac{\hat{p}}{m} \delta(\hat{x} - x_0) + \delta(\hat{x} - x_0) \right)$$

for a Cartesian reaction coordinate $x$, where $x_0$ is the location of the “dividing surface.” The resulting QI rate expressions are given in the following.

A. QI1 approximation

For a molecular system characterized by a Hamiltonian of the form

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{\hat{Q}^2}{2m} + V(x, Q),$$

where $x$ is the reaction coordinate and $Q$ all other coordinates orthogonal to it, the 1-dividing surface (1 DS) version of the quantum instanton approximation (QI1) gives the rate constant as\(^1\)

$$k_{QI1}(T) = Q_r(T)^{-1} \frac{\hbar}{2m} \Delta H \left( \frac{\hbar}{2m} \right)^2 \int dQ_1 \int dQ_2$$

$$\times \langle x_0 Q_1 | e^{-\beta \hat{H}/2} | x_0 Q_2 \rangle \times \langle x_0 Q_2 | e^{-\beta \hat{H}/2} | x_0 Q_1 \rangle.$$

Here $\Delta H$ is a particular kind of energy variance,

$$\Delta H^2 = \int dQ_1 \int dQ_2 \langle x_0 Q_1 | \hat{H}^2 e^{-\beta \hat{H}/2} | x_0 Q_2 \rangle$$

$$\times \langle x_0 Q_2 | e^{-\beta \hat{H}/2} | x_0 Q_1 \rangle$$

$$- \langle x_0 Q_1 | \hat{H} e^{-\beta \hat{H}/2} | x_0 Q_2 \rangle \rangle$$

$$\int dQ_1 \int dQ_2 \langle x_0 Q_1 | e^{-\beta \hat{H}/2} | x_0 Q_2 \rangle^2,$$

and $x_0$, the value of the reaction coordinate that specifies the location of the dividing surface, is determined by the variational criterion

$$\frac{\partial}{\partial x_0} \int dQ_1 \int dQ_2 \langle x_0 Q_1 | e^{-\beta \hat{H}/2} | x_0 Q_2 \rangle^2 = 0.$$

In practice, $\Delta H$ of Eq. (2.2b) is modified as follows to correct the free particle (high temperature) rate (that would be $\sim 25\%$ too large otherwise):

$$\Delta H \rightarrow \Delta H + (\sqrt{\pi} - \sqrt{2})/\beta.$$

The primes on the matrix element in Eq. (2.2a) denote derivatives with respect to the reaction coordinate, i.e.,

$$\langle x_0 Q_1 | e^{-\beta \hat{H}/2} | x_0 Q_2 \rangle \prime$$

$$= \frac{\partial^2}{\partial x_1 \partial x_2} \langle x_1 Q_1 | e^{-\beta \hat{H}/2} | x_2 Q_2 \rangle |_{x_1 = x_2 = x_0}.$$

And finally, we note that one can write the QI rate expression in terms of a more general form of the dividing surface, but this simplified version is sufficient for applications in this paper.

B. SQI1 approximation

Venkataraman and Miller\(^2\) have derived a version of the “simplest” quantum instanton model with 1-dividing surface (SQI1); it is simpler to apply than the above-defined QI1 approximation, though somewhat less accurate. It requires only that one evaluate the quantity

$$A(x_0) = \int dQ_1 \int dQ_2 \langle x_0 Q_1 | e^{-\beta \hat{H}/2} | x_0 Q_2 \rangle^2$$

and then Eq. (2.3), which determines the value of $x_0$, reads

$$A'(x_0) = 0.$$  

The SQI1 rate constant is then given by

$$k_{SQI1}(T) = Q_r(T)^{-1} \frac{\hbar}{2m} A(x_0) F(z),$$

where $z$ is the dimensionless variable

$$z = \frac{\hbar}{16m \Delta H} \frac{d^2}{d x_0^2} \ln A(x_0),$$

$\Delta H$ is the same quantity as above [Eq. (2.2b)], and $F(z)$ is the function

$$F(z) = \sqrt{\frac{\pi}{2}} \left( z + \sqrt{z^2 + 1} \right).$$
Venkataraman et al. also noted that the SQI1 rate is more accurate if the function \( F(z) \) is Eq. (2.5e) is replaced by

\[
F_{\text{mod}} = \frac{5}{4} z + \sqrt{(z-1)^2 + (4/4)^2}.
\]  

The SQI1 rate expression can also be stated in thermodynamic language. The free energy \( G(x_0) \) is defined by

\[
\beta G(x) = -\ln A(x),
\]  

and Eq. (2.5b) for the location of the dividing surface is equivalent to the maximum free energy criterion

\[
G'(x_0) = 0.
\]  

The rate constant is then given by

\[
k_{\text{SQI1}} = Q_r(T)^{-1} \frac{h}{2m} e^{-\beta G(x_0)} F(z),
\]  

with the dimensionless variable \( z \) given by

\[
z = - \frac{h^2}{16 m} \frac{\beta G''(x_0)}{\Delta H}.
\]  

C. Log derivative implementation

In this paper all matrix elements of the Boltzmann operator were calculated by diagonalizing the Hamiltonian in a discrete variable representation (DVR) basis.\(^{31}\) For systems with many degrees of freedom, however, one will be using Monte Carlo path integral methods (MCPI), and in this case it is necessary that all the quantities to be calculated are normalized averages; cf. the discussion in Ref. 5. In the SQI1 rate expression, Eq. (2.5), for example, the quantities \( \Delta H \) and \( z \) have natural normalization factors, but the quantity \( A(x_0) \) does not. In Ref. 5 this was dealt with by using an umbrella sampling procedure that allowed use of the reactant partition function \( Q_r \) as the normalization factor for \( A(x_0) \). Here we show another strategy, one that avoids having to use the umbrella sampling procedure.

We thus denote the quantity in Eq. (2.5a) as \( A(x_0, \beta) \), emphasizing its dependence also on temperature. The value of \( x_0 \), determined by Eq. (2.5b),

\[
\frac{\partial A(x_0, \beta)}{\partial x_0} = 0,
\]  

is thus also temperature dependent, \( x_0(\beta) \), so that the temperature dependence of the quantity \( A \) is

\[
A(\beta) = A(x_0(\beta), \beta).
\]  

The logarithmic derivative of \( A(\beta) \) is thus given by

\[
E(\beta) = - \frac{A'(\beta)}{A(\beta)}
\]  

\[
= - \frac{1}{A(\beta)} \left[ \frac{\partial A(x_0, \beta)}{\partial x_0} x_0' + \frac{\partial A(x_0, \beta)}{\partial \beta} \right]
\]  

\[
= - \frac{1}{A(\beta)} \frac{\partial A(x_0, \beta)}{\partial \beta}
\]  

\[
= \int dQ_1 \int dQ_2 \exp \left[ \frac{\beta}{2} e^{-\beta H/2} |x_0 Q_1| \right] \times \left[ \langle x_0 Q_2 | e^{-\beta H/2} |x_0 Q_1| \rangle \right] \times \left[ \langle x_0 Q_2 | e^{-\beta H/2} |x_0 Q_1| \rangle \right] \times \left[ \langle x_0 Q_2 | e^{-\beta H/2} |x_0 Q_1| \rangle \right] \times \left[ \langle x_0 Q_2 | e^{-\beta H/2} |x_0 Q_1| \rangle \right].
\]  

\[
E(\beta) \text{ as defined by Eq. (2.9c) is thus a normalized average and amenable to calculation by the METROPOLIS Monte Carlo algorithm. The quantity } A(\beta) \text{ is then obtained by integration of Eq. (2.9a),}
\]  

\[
A(\beta) = A(\beta_0) \exp \left[ - \int_{\beta_0}^{\beta} d\beta' E(\beta') \right].
\]  

One thus obtains the quantity \( A(\beta) \) relative to its value at one reference temperature \( \beta_0 \), and the SQI1 rate constant at temperature \( T \) is then given by

\[
k_{\text{SQI1}}(T) = Q_r(T)^{-1} \frac{h}{2m} A(\beta) F(z).
\]  

The QI1 rate of Sec. II A can also be expressed in a way to take advantage of this log-derivative calculation of \( A(\beta) = A(x_0(\beta), \beta) \): multiplying and dividing Eq. (2.2a) by \( A(\beta) \) gives

\[
k_{\text{QI1}} = Q_r(T)^{-1} \frac{h}{2\pi} A(\beta) R(\beta)
\]  

where

\[
R(\beta) = \int dQ_1 \int dQ_2 \exp \left[ \frac{\beta}{2} e^{-\beta H/2} |x_0 Q_1| \right] \times \left[ \langle x_0 Q_2 | e^{-\beta H/2} |x_0 Q_1| \rangle \right] \times \left[ \langle x_0 Q_2 | e^{-\beta H/2} |x_0 Q_1| \rangle \right] \times \left[ \langle x_0 Q_2 | e^{-\beta H/2} |x_0 Q_1| \rangle \right] \times \left[ \langle x_0 Q_2 | e^{-\beta H/2} |x_0 Q_1| \rangle \right].
\]
The quantity $R(\beta)$ has a natural normalization factor and can thus be calculated by Metropolis Monte Carlo for any temperature $\beta$. $A(\beta)$ in Eq. (2.10a) is still given by Eq. (2.9d).

Finally, we note that the variational criterion for locating the dividing surface, i.e., Eq. (2.3) or (2.5b) or (2.6b), is effectively the same as choosing the dividing surface to minimize the rate constant itself, which is the standard variational procedure of classical transition state theory. The reason for this is that all the factors in Eq. (2.5c) (for the SQI1 rate) or Eq. (2.10a) (for the QI1 rate) other than $A(x_0)$ are very slowly varying functions of $x_0$; thus the value of $x_0$ that minimizes $A(x_0)$ is essentially indistinguishable from that which minimizes the rate constant.

III. RESULTS FOR SEVERAL COLLINER REACTIONS

For all the applications discussed in the following we have used standard transition state normal coordinates, i.e., the rectilinear coordinates obtained by diagonalizing the force constant matrix at the saddle point of the potential energy surface. The reaction coordinate $x$ is, as usual, the coordinate for the mode with an imaginary frequency, and $Q$ the coordinate corresponding to the real frequency. Other, more general choices for dividing surface are possible (cf. Refs. 5 and 6) but were not explored for these simple collinear examples. For the symmetric reactions the variational criterion, Eq. (2.3) [or equivalently, Eqs. (2.5b) or (2.6b)] always picks out the traditional transition state dividing surface $x_0=0$. This is not so, of course, for the asymmetric reactions. Figure 1, for example, shows the rate constant for the D+BrH reaction as a function of $x_0$, the location of the dividing surface, for temperatures $T=600$ and 150 K, showing the extent to which the minimum value varies with temperature.

Figure 2 shows the ratio of the QI1 rate constants to the correct quantum values as a function of $1000/T$ for several collinear $A+BC\rightarrow AB+C$ reactions: (a) HBrH and DBrH, (b) HHH and DHH, and (c) CIHCl and CIDCl, corresponding to mass combinations (a) light+light-light, (b) approximately equal masses, and (c) heavy+light-heavy. If the potential energy surfaces for these reactions are plotted using the usual mass-weighted coordinates, then case (a) has a
large skew angle (the angle between the entrance and exit valleys of the potential surface) of ~90°, case (b) to an intermediate skew angle of ~60°, and case (c) to a small skew angle of ~10°.

The results for cases (a) and (b), as seen in Figs. 2(a) and 2(b), show the QI1 rate constants to be in very good agreement (≤20%) with the correct quantum values for all temperatures between 200 and 1000 K. The slightly larger deviation at higher temperature for case (b), H + H₂ and D + H₂, is due to a breakdown of the transition state approximation (of no re-crossing dynamics) at these higher temperatures. This breakdown of transition state theory (TST) at high temperature (or energy) is well known, and it is also well known to be greatly diminished in higher dimension: e.g., re-crossing effects in the H + H₂ reaction can lead to a TST rate constant that is a factor of ~2 too large at the highest energies for the collinear version of the reaction, while it is only 10% too large at similar energy for the 3d version of the reaction.⁷

This breakdown of TST caused by re-crossing dynamics is even more evident in case (c), the heavy + light-heavy reactions Cl + HCl and Cl + DCl. Figure 3 presents an Arrhenius plot comparing the QI1 rate constant to the correct quantum values for these two reactions, showing how the recrossing effect increases with temperature and also is larger for Cl + HCl than for Cl + DCl because of the smaller skew angle in the H atom case. This phenomenon is very well known in collinear heavy + light-heavy reactions,²⁰ having been seen for example in quantum calculations of the flux-flux autocorrelation function.²⁰ Again, these re-crossing effects largely disappear for these reactions in 3d space and are largely absent in H-atom transfer reaction in condensed phase systems.²⁰

Figures 4 and 5 show the corresponding results for the SQI1 model and its modified version [i.e., using Eq. (2.5f) rather than Eq. (2.5e)], respectively. The comparisons are similar to those in Fig. 2, though the SQI1 rates are not as accurate as the QI1 values. (The modified SQI1 results of

**FIG. 4.** Same as Fig. 2, except for the SQI1 model (rather than the QI1).

**FIG. 5.** Same as Fig. 2, except for the modified SQI1 model [i.e., using Eq. (2.5f) in place of Eq. (2.5e)].

**FIG. 6.** A plot of the free energy defined by Eq. (2.6a) (for the reaction D + BrH), illustrating the well-defined maximum it shows (which determines the location of the dividing surface).
Fig. 5 are an improvement over the SQI1 results of Fig. 4, but still somewhat less accurate than the QI1 results in Fig. 2.) Figure 6 shows an example of the free energy $\beta G(x_0)$, defined in Eq. (2.6a), as a function of $x_0$, for the D+BrH reaction, clearly revealing the maximum, which determines the choice for $x_0$, and the negative curvature, which determines the dimensionless variable $z$ in Eq. (2.6d).

Finally, Fig. 7 shows results pertaining to the log-derivative procedure described in Sec. II C. Figure 7(a) shows $E(\beta)$ of Eq. (2.9a) as a function of $\beta$ ($\approx 1/T$) for the H+BrH reaction, illustrating that it is a very smooth function of $\beta$. For a complex system one would thus calculate $E(\beta)$ by Monte Carlo for a coarse grid of $\beta$ values and then obtain $A(\beta)$ for any $\beta$ relative to its value at one reference variable. The other quantities in the rate expressions are normalized quantities and thus amenable to calculation by Monte Carlo at any temperature. Figure 7(b) shows that the Q11 rate constants given by Eqs. (2.10) and (2.9d) for the H+BrH reaction are identical to those given by the original procedure in Sec. II A. Here the reference temperature $\beta_0$ was chosen to be the highest temperature (smallest $\beta$) in Fig. 7(b), and the rate at all lower temperatures was obtained relative to that at $\beta_0$. Similar results were obtained for the other reactions.

IV. CONCLUSIONS

The point of this paper has been to see how the quantum instanton (Q1) model (with one dividing surface, Q11) and its variant, the “simplest” quantum instanton (with one dividing surface, SQ11), perform for calculating thermal rate constants for a sequence of collinear atom–diatom reactions with various skew angles. The results we obtained confirm the earlier results for 1d examples that the QI1 rate constants are more accurate than the SQI1 values and thus that the QI1 version of the quantum instanton model is preferred.

The QI1 results are also seen to agree well (to $\sim 20\%$) with the correct quantum values over the whole temperature range considered, except for those situations where dynamical corrections to transition state theory (i.e., re-crossing dynamics) are evident. Such re-crossing effects are greatly diminished in higher dimensionality, however, and in most situations should not be relevant to reactions in complex systems.

Finally, we also showed how a log-derivative procedure can be used to facilitate use of the METROPOLIS Monte Carlo algorithm to compute all quantities appearing in the QI rate expression. This will be most useful when using Monte Carlo path integration to evaluate the QI rate for systems with many degrees of freedom.

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