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# Analytic continuation of real-time correlation functions to obtain thermal rate constants for chemical reaction

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## Abstract

It is shown how a particular correlation function, computed quantum mechanically or semiclassically as a function of real-time, can be analytically continued to obtain thermal rate constants (or other thermally averaged quantities) over a wide range of temperature. The correlation function is first evaluated at a reference temperature, and then analytically continued to obtain information at other desired temperatures. The method is applied to the calculation of the thermal rate constant for the $Cl + H_2 \rightarrow HCl + H$ ($J = 0$) reaction using the flux correlation function formalism, and it is seen to be capable of obtaining accurate rate constants over a broad temperature range. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

There has been a great deal of progress [1] in recent years in the development of rigorous quantum mechanical methods for calculating thermal rate constants of chemical reactions; cf. work in our group [2–4], that of Light et al. [5–7], that of Manthe et al. [8–10], and that of other [11]. These approaches are based on formally exact expressions [12–14] for the rate constant $k(T)$ either in terms of a flux time correlation function, e.g.,

$$k(T) = Q_r(T)^{-1} \int_0^\infty dt\, C_\beta^{ff}(t), \qquad (1a)$$

where

$$C_\beta^{ff}(t) = \mathrm{tr}\left[ e^{-\beta\hat{H}/2} \hat{F} e^{-\beta\hat{H}/2} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar} \right], \qquad (1b)$$

$\hat{H}$ and $\hat{F}$ being the Hamiltonian and flux operators, respectively, or in terms of the cumulative reaction probability $N(E)$,

$$k(T) = \frac{1}{2\pi\hbar Q_r(T)} \int_{-\infty}^\infty dE\, e^{-\beta E} N(E), \qquad (2)$$

where $Q_r(T)$ is the reactants partition function per unit volume and $\beta = (k_B T)^{-1}$. When using Eq. (1), one typically calculates $C_\beta^{ff}(t)$, and thus $k(T)$, for a single value of temperature $T$, while if one calculates $N(E)$ for a sufficiently wide range of energy $E$, then Eq. (2) can be used to obtain $k(T)$ for a range of values of $T$.

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In this Letter, we consider an alternate way of obtaining $k(T)$ over a wide temperature range – in this case solely from the time correlation function (and its analytic continuation). Section 2 presents the theoretical development and discusses how the resulting procedure relates to earlier work, Section 3 illustrates the approach by application to the Cl + H$_2$ → HCl + H reaction (in 3d for $J = 0$), and Section 4 concludes.

## 2. Theory

We consider the time integral of the flux correlation function of Eq. (1b) as a function of $\beta$,

$$R_\beta \equiv k(T) Q_r(T)$$

$$= \int_0^\infty dt \, tr\left[ e^{-\beta \hat{H}/2} \hat{F} e^{-\beta \hat{H}/2} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar} \right],$$

$$(3)$$

which we note can also be expressed [13] as the long time limit of the flux-side correlation function,

$$R_\beta = \lim_{t \to \infty} tr\left[ e^{-\beta \hat{H}/2} \hat{F} e^{-\beta \hat{H}/2} e^{i\hat{H}t/\hbar} \hat{h} e^{-i\hat{H}t/\hbar} \right],$$

$$(4)$$

where $\hat{h} = h(\mathbf{q})$ is the Heaviside function which is related to the flux operator $\hat{F} = \frac{i}{\hbar}[\hat{H}, \hat{h}]$. Taking $\beta$ to be complex,

$$\beta = \beta_0 - 2it'/\hbar, \qquad (5)$$

where $\beta_0$ $(= 1/k_B T_0)$ corresponds to a reference temperature and $t'$ is a real-time variable, the function $R_{\beta_0}(t')$ is defined as

$$R_{\beta_0}(t') \equiv R_{\beta_0 - 2it'/\hbar}, \qquad (6a)$$

and is given explicitly by

$$R_{\beta_0}(t') = \int_0^\infty dt \, tr\left[ e^{-\beta_0 \hat{H}/2} \hat{F} e^{-\beta_0 \hat{H}/2} \right.$$

$$\left. \times e^{i\hat{H}(t+t')/\hbar} \hat{F} e^{-i\hat{H}(t-t')/\hbar} \right], \qquad (6b)$$

The procedure, therefore, is to calculate $R_{\beta_0}(t')$ from Eq. (6b) for a range of (real) values of $t'$ and then use these to obtain $R_\beta$ (and thus $k(T)$) by (numerically) analytically continuing it to $t' = i\hbar \Delta \beta/2$, i.e.,

$$R_\beta = R_{\beta_0}(i\hbar \Delta \beta/2), \qquad (7)$$

where $\Delta \beta = \beta - \beta_0$. The calculation of $R_{\beta_0}(t')$ is carried out by the same very efficient procedure we have used earlier for calculating flux correlation functions [2–4]; here it involves a Lanczos calculation with the Boltzmann operator for the reference temperature, $\exp(-\beta_0 \hat{H}/2)$, and then real-time propagation (e.g., via the split-operator algorithm) to generate the time evolution operators $\exp[-i\hat{H}(t \pm t')/\hbar]$. The numerical analytic continuation is carried out by Schlessinger's point method [15] (a type of Padé Approximant [16]), and we find that a range of $t'$ of several $\hbar \Delta \beta$ is sufficient to obtain stable results. (We note that this approach was suggested earlier [1] by one of us for the case $\beta_0 \equiv 0$, but experience has shown that it works much better with a finite reference temperature.)

We now discuss several aspects of this result and procedure. First, recall that some years ago another type of analytic continuation was used for flux correlation functions and rate constants [13,17–19]. The goal then was to use Monte Carlo path integration methods to represent the exponential operators in evaluating Eq. (1b), and to avoid oscillatory integrands which cause trouble for such calculations one considered the *pure imaginary* time correlation function which involves only Boltzmann-like (i.e., real exponential) operators,

$$C(\tau) \equiv C_\beta^{ff}(-i\tau)$$

$$= tr\left[ e^{(-\beta/2 + \tau/\hbar)\hat{H}} \hat{F} e^{(-\beta/2 - \tau/\hbar)\hat{H}} \hat{F} \right]. \quad (8a)$$

The procedure was thus to calculate $C(\tau)$ for a range of real $\tau$ values and then use these to analytically continue (numerically) to imaginary $\tau = it$ to obtain the flux correlation function, i.e.,

$$C_\beta^{ff}(t) = C(it). \qquad (8b)$$

A major limitation of this procedure, however, is that the real values of $\tau$ for which Eq. (8a) can be evaluated are restricted to the interval

$$-\frac{\hbar \beta}{2} < \tau < \frac{\hbar \beta}{2}, \qquad (9)$$

meaning that it is not possible to generate numerical analytic continuation to real-times $t$ much longer than $\sim \hbar \beta/2$. This is sufficiently long to describe direct barrier crossing dynamics (including tunneling), but not long enough to describe non-transition

state theory dynamics, i.e., dynamical effects related to flux that recrosses the transition state region. The present approach, based on Eqs. (4) and (7), suffers no such limitation since one can carry out calculations for as wide a region of the real variable $t'$ as necessary in order to guarantee a stable numerical continuation to $t' = i\hbar\Delta\beta/2$.

The present analytic continuation procedure is in a sense, therefore, the *opposite* of the earlier one; there the goal was to have all the exponential operators appear as Boltzmann-like operators, so that Monte Carlo path integration would be well-behaved, while the present approach is to have most (*all* in the $\beta_0 \to 0$ limit) of the exponential operators as real-time propagators. This makes the present approach especially advantageous when using *semiclassical* approximations for the real-time dynamics; e.g., one can choose $\beta_0$ sufficiently small (i.e., the reference temperature $T_0$ sufficiently high) for the high temperature approximation to $\exp(-\beta\hat{H}/2)$ to be valid, and then the semiclassical initial value representation (SC-IVR) [20–32] can be used to approximate the real-time propagators $\exp[-i\hat{H}(t \pm t')/\hbar]$.

It is also clear that the analytic continuation procedure of Eqs. (4) and (7) can be applied to any thermal correlation function of the form

$$C_\beta(t) = \mathrm{tr}\left[e^{-\beta\hat{H}/2}\hat{A}\,e^{-\beta\hat{H}/2}\,e^{i\hat{H}t/\hbar}\hat{B}\,e^{-i\hat{H}t/\hbar}\right].$$
(10)

Thus with $\beta = \beta_0 - 2it'/\hbar$, one obtains

$$C_{\beta_0}(t,t') \equiv C_{\beta_0 - 2it'/\hbar}(t),$$
(11a)

which is given by

$$C_{\beta_0}(t,t') = \mathrm{tr}\left[e^{-\beta_0\hat{H}/2}\hat{A}\,e^{-\beta_0\hat{H}/2}\right.$$
$$\left. \times\,e^{i\hat{H}(t+t')/\hbar}\hat{B}\,e^{-i\hat{H}(t-t')/\hbar}\right],$$
(11b)

One evaluates Eq. (11b) for a range of real values of $t'$ and uses these to analytically continue to $t' = i\hbar\Delta\beta/2$, giving $C_\beta(t)$ as

$$C_\beta(t) = C_{\beta_0}(t,i\hbar\Delta\beta/2).$$
(12)

Finally, we note that in comparison with similar approaches by Light et al. [6]. and Manthe et al. [9]

our current method is not restricted to the quantum mechanical calculations that employ finite basis sets, as are necessary in previous work based on Fourier transforms involving certain wavefunctions [6,9]. Instead, it can be applied as long as the correlation function $C_{\beta_0}(t,t')$ in Eq. (11b) can be conveniently evaluated without referring to the specific (time-dependent) wavefunctions. It is thus applicable to a wider class of quantum and semiclassical calculations of time correlation functions. (We note that Matzkies and Manthe also recently proposed a method [9] based on the Fourier transform of $C_{\beta_0}^{ff}(t,t')$ in Eq. (6b), which can be viewed as another application of this correlation function.)

## 3. Flux correlation function calculations for the Cl + H$_2$ → HCl + H (J = 0) reaction

As a test example, the current analytic continuation methodology is applied to the quantum mechanical calculation of $k(T)$ for the Cl + H$_2$ → HCl + H reaction (in 3d for $J = 0$) over a wide range of temperature. The procedure is as described in the paragraph following Eq. (6) above, with a slightly different (but equivalent) expression for $R_{\beta_0}(t')$

$$R_{\beta_0}(t') = \int_0^{t_{\max}} dt\,\mathrm{tr}\left[\left(e^{-\beta_0\hat{H}/4}\hat{F}\,e^{-\beta_0\hat{H}/4}\right)\right.$$
$$\times\,e^{i\hat{H}(t+t')/\hbar}\left(e^{-\beta_0\hat{H}/4}\hat{F}\,e^{-\beta_0\hat{H}/4}\right)$$
$$\left. \times\,e^{-i\hat{H}(t-t')/\hbar}\right].$$
(13)

The Boltzmannized flux operator $e^{-\beta_0\hat{H}/4}\hat{F}\,e^{-\beta_0\hat{H}/4}$ is first diagonalized via a Lanczos procedure to give its eigenfunctions $\{\psi_i\}$ and eigenvalues $\{f_i\}$ [2–10], and the flux correlation function is obtained by propagating these eigenfunctions weighted by the appropriate eigenvalues [2–10]. Matrix elements of the time evolution operator $G_{ij}(t) = \langle\psi_i|e^{-i\hat{H}t}|\psi_j\rangle$, which are also needed in calculating a single rate constant [4], are obtained at each time step during the propagation. These $G_{ij}(t)$s are then used to generate all the $(t,t')$ pairs necessary in evaluating Eq. (13). In calculations presented below, 100 fs of real-time propagation was carried out in 500 time steps, so that
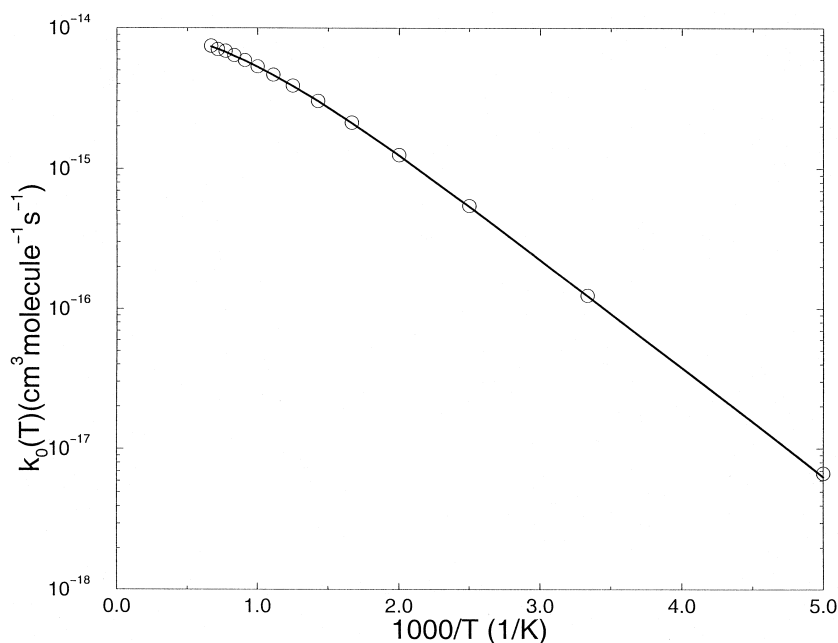
Fig. 1. Arrhenius plot of the thermal rate constant between 200 and 1500 K. The solid line is from the analytic continuation procedure with reference temperature $T_0 = 1500$ K, and the circles are from separate calculations (as in Ref. [3]) for each temperature.

$t'$ ranges from 0 to 50 fs. Finally, other specific details of the calculation (Hamiltonian, basis set, etc.) are the same as in the previous work [3].

Fig. 1 shows the comparison of $k(T)$ obtained via the current analytic continuation approach with a high reference temperature $T_0 = 1500$ K (solid line)
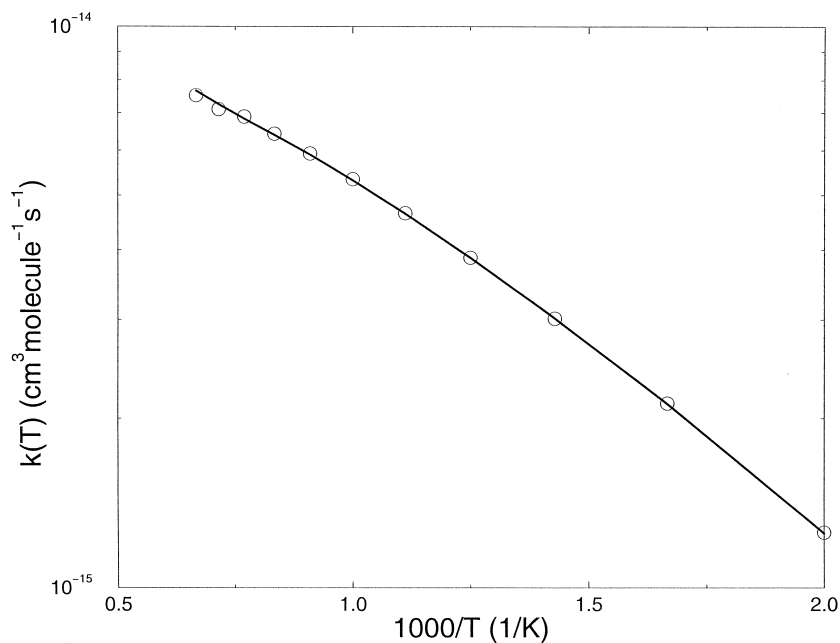


Fig. 2. Same as Fig. 1, except for the reference temperature $T_0 = 500$ K.

to the rate constants obtained previously [3] from separate calculations for each temperature (circles).
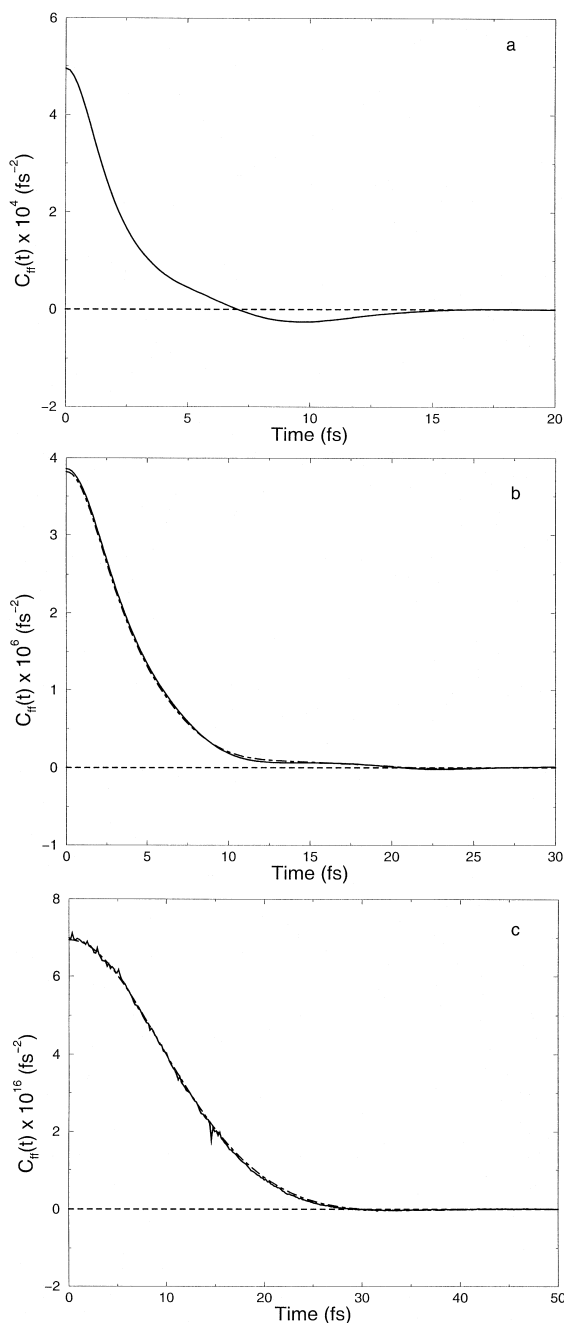


Fig. 3. Flux–flux autocorrelation function. (a) Result of the direct calculation (cf. Ref. [3]) for $T = 1500$ K. (b) Result of the present analytic continuation procedure with a reference temperature $T_0 = 1500$ K, for $T = 800$ K. (c) Same as (b) except for $T = 200$ K.

The agreement is excellent (to within a few percent) for a wide temperature range (200–1500 K). This is the way we envision one will usually employ the approach, i.e., with a high reference temperature (small $\beta_0$) and analytic continuation to a range of lower temperature. This is especially convenient because the high temperature approximation for the Boltzmann operator is so simple.

Analytic continuation is also possible (though not as reliable) for the opposite direction, i.e., from a low reference temperature $T_0$ continuing to higher temperatures. Fig. 2 shows the Arrehenius plot of $k(T)$ obtained from analytic continuation with $T_0 = 500$ K. Here again, they are in very good agreement with the previous results but for a somewhat smaller temperature range (500–1500 K). This, however, gives more flexibility for the analytic continuation method, since sometimes one may wish to perform a single reference calculation at a intermediate temperature $T_0$, and then continue to both lower and higher temperatures.

Finally, we note that one can also obtain an accurate representation of the flux correlation function $C_\beta^{\text{ff}}(t)$ itself via the analytic continuation procedure, i.e., Eqs. (11) and (12) with $\hat{A} = \hat{B} = \hat{F}$. Fig. 3 shows $C_\beta^{\text{ff}}(t)$ for three temperatures, obtained via analytic contiuation with $T_0 = 1500$ K. They are in excellent agreement with the previous calculations (dot dashed lines) [3]. The indication of recrossing effects (i.e., a negative lobe in $C_\beta^{\text{ff}}(t)$), which are visible at the high reference temperature (Fig. 3a), disappear for lower temperatures (Fig. 3b,c), exactly as the results obtained before [3]. For the lowest temperature, $T = 200$ K, there are very small oscillations in the analytically continued $C_\beta^{\text{ff}}(t)$ due to the finite precision of the computation. As seen from Fig. 3a,c, $C_\beta^{\text{ff}}(t)$ changes by about 12 orders of magnitude from 1500 to 200 K, so it is not surprising for a small amount of numerical noise to appear for the farthest extrapolation; this, of course, has essentially no effect on the *integral* of $C_\beta^{\text{ff}}(t)$ which gives the rate constant.

## 4. Concluding remarks

The analytic continuation approach presented in this Letter thus provides a simple and efficient way

of obtaining thermal rate constants (or other thermally averaged quantities) over a broad temperature range from one reference calculation. Although it is tested for the case of a rigorous quantum mechanical calculation, the approach is designed (and expected) to be more useful for a calculation employing the semiclassical initial value representation (SC-IVR) [20–32] where rigorous evaluation of the Boltzmann operator is difficult for low temperatures. The success in the present example suggests that it is promising to by-pass this difficulty by carrying out a SC-IVR calculation for a high reference temperature, and then extract information for a broad range of lower temperatures. Such applications are currently under investigation.

## Acknowledgements

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