Master’s Thesis

Semiquantal analysis of vibrational relaxation and adiabatic hydrogen atom transfer

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Abstract

The vibrational energy relaxation (VER) and adiabatic proton/hydrogen/hydride (H) atom transfer (HAT) in condensed phases are examined by the generalized Langevin equation (GLE) formalism with the semiquantal time-dependent Hartree (SQTDH) theory, which takes into account the zero-point effect and the dynamical modulation of the wavepacket width in the adiabatic transfer regime. The HAT rate formula is obtained by combining the SQTDH theory and the multidimensional transition state theory and dynamical solvent effects are considered by the GLE formalism for the adiabatic H transfer rate. The VER rates for the harmonic and Morse potentials calculated by the SQTDH theory agree better with those by the quantum master equation than the classical GLE, confirming the necessity of the dissipation of the wavepacket width’s energy. The analysis on DW1 and DW2 model potentials suggests that the SQTDH theory overestimates the overall transmission coefficient of the nonadiabatic H transfer rate especially in the weak-coupling (energy-diffusion-controlled) regime owing to the wrong estimate of the barrier frequency and height. The KIEs for these potentials show peaks between the energy- and spatial-diffusion-controlled regime, reminiscent of the previous study. (N. Sakumichi and K. Ando, J. Chem. Phys. 128, 164516 (2008).) The KIE with the the solvation and hydrogen bonding coordinate increases monotonously in the friction range in consideration.
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I INTRODUCTION

Vibrational energy relaxation (VER) and hydrogen/proton/hydride (H) atom transfer (HAT) reactions are central issues in chemistry and biochemistry. However, the (quantum) dynamical simulation of VER and HAT in condensed phases is challenging owing to nuclear quantum effects such as zero point energy (ZPE) and tunneling effects. Among others, quantum effects manifest themselves in determining the rates of VER and HAT in condensed phases. In general, several factors in condensed phases, e.g. the quantum effect of H, the supporting mode of heavy atoms, and the dynamical solvent effect, so complicate HAT that it will be useful to classify HAT in two regimes: the nonadiabatic\(^2\)–10 and adiabatic\(^11\)–17 regimes.

In the nonadiabatic HAT, the heavy atoms between which the H transfers are constrained with regard to both the distance and the valence directions, so that the barrier along the H displacement is high enough to hold at least a few H vibrational levels to exhibit resonance tunneling splittings. On the other hand, in the adiabatic HAT, the positions of the heavy atoms are more flexible, as are typically seen in intermolecular HATs. Consequently, they may approach each other close enough by thermal fluctuation to reduce the barrier along the H displacement in such ways that the picture of deep tunneling no longer applies, but the H wavepacket adiabatically follows the modulation of the potential coupled to the environment.\(^9\) While the nonadiabatic regime has been appropriately described by the perturbation theories based on the tight-binding picture,\(^18\) which are similar to the electron transfer...
theories in treating the environmental reorganization, theoretical description of the adiabatic regime is not so well established. In particular, the dynamical fluctuation of the wavepacket width, affected by the shape of the potential and the coupling to the environment, should be treated promptly beyond the tight-binding picture.

In addition, while there are few theories that consider dynamical solvent effects in the adiabatic HAT, the solvation coordinate has shown to play a pivotal role in the adiabatic proton transfers in aqueous solutions. Solvent fluctuation and reorganization then appear to bear significant clue both for understanding the mechanism and for determining the rate of the reaction. Actually, whereas the barrier height along the H coordinate for adiabatic HAT is approximately a few kcal/mol such that the H wave function is delocalized over the complex, the solvent reorganization energy may amount to some ten kcal/mol. Hence, it would be necessary to treat the H coordinate and hydrogen bonding coordinate (distance between the heavy atoms) quantum-mechanically, and includes the solvation coordinate.

The semiquantal time-dependent Hartree (SQTDH) theory, one of the semi-classical approaches, has been verified to offer much the same wavepacket as fully quantum mechanical calculations for some model potentials with one quantum degree of freedom, such as quartic double well and coupled Morse potentials. While this agreement is encouraging, the theory should be compared to exact quantum results for VER and HAT in condensed phases. Such a comparison would clarify the range of validity and limitations of the SQTDH theory for VER and HAT in
solutions and enzymes.

The purpose of this paper is to study VER and to develop a theory for the adiabatic HAT rate with considering the nuclear quantum effect. To this end, we combine the SQTDH theory\textsuperscript{25–29} and the multidimensional transition state theory (MTST).\textsuperscript{30,31} Employing the generalized Langevin equation (GLE) formalism, which is closely related to the Grote-Hynes (GH) theory,\textsuperscript{32,33} we examine the VER and obtain the semiquantal HAT rate expression. The numerically exact quantum rates are available for a HAT reaction represented by a double well system coupled to a harmonic bath,\textsuperscript{85} which has been extensively utilized for a variety of semiclassical methods as a benchmark.\textsuperscript{86–96} On the other hand, the numerically exact quantum rates for a VER reaction can be calculated via the quantum master equation (QME).\textsuperscript{71} Furthermore, we include the additional solvation coordinate to consider the dynamical solvation processes in the adiabatic HAT by the matrix partitioning method. The derived rate formula will be applied to examine the kinetic isotope effect (KIE) on the adiabatic HAT.

The VER rates for the harmonic and Morse potentials calculated by the SQTDH theory agree better with those by the quantum master equation than the classical GLE, confirming the necessity of the dissipation of the wavepacket width’s energy. The analysis on the DW1 and DW2 model potentials has suggested that the SQTDH theory overestimates the overall transmission coefficient of the nonadiabatic H transfer rate especially in the weak-coupling (energy-diffusion-controlled) regime, and the KIE on the adiabatic H transfer rate may exhibit a peak as a function of the coupling strength to the external degrees of freedom. The KIE with
the solvation and hydrogen bonding coordinate increases monotonously along the coupling strength considered.

The next section summarizes the SQTDH theory. The formulation for potential models to treat the hydrogen bonding and solvation coordinate, their semi-quantal treatments, the HAT rate formulas, simulation methods for GLE, and QME are described in Sec. III. The simulated vibrational relaxation rates and the transmission coefficients are studied and discussed in Sec. IV. The paper concludes in Sec. V.

II SQTDH THEORY

The SQTDH theory describes the wave function as a Hartree product of the squeezed coherent state Gaussian wavepackets characterized by the center and width parameters. The schematic picture of the wavepacket is illustrated in Fig. 1. The equation of motion for the parameters are determined from the time-
dependent variational principle.\textsuperscript{34–36} One of the marked feature is that the equations of motion for both the center and width parameters have the form of classical Hamiltonian equations of motion.\textsuperscript{37–39} This suggests us to extend the phase space to include the width coordinates and their conjugate momenta in addition to the center coordinates. The wave packet dynamics is thus viewed as classical motion on an effective potential in the extended phase space. In particular, the effect of dissipative bath can be taken into account straightforwardly and in a pictorial manner. Another computational advantage is that the optimal stationary state wave function is directly obtained from the minimum point on the extended potential.

For simplicity of notation, we set $\hbar = 1$ and assume that the coordinates $q_1, \cdots, q_f$ have been mass scaled. The trial wave function is defined with the time-dependent Hartree ansatz

$$\Psi(q_1, \cdots, q_f, t) = \prod_{\alpha=1}^{f} N_{\alpha} \exp\{A_{\alpha}(t)(q_{\alpha} - x_{\alpha}(t))^2 + ip_{\alpha}(t)(q_{\alpha} - x_{\alpha}(t))\}, \quad (1)$$

in which

$$A_{\alpha}(t) = \frac{-1 + 2i\rho_{\alpha}(t)\pi_{\alpha}(t)}{4\rho_{\alpha}(t)^2}. \quad (2)$$

$N_{\alpha} = (2\pi\rho_{\alpha}(t)^2)^{-1/4}$ is the normalization factor. The time-dependent parameters $x_{\alpha}(t)$ and $\rho_{\alpha}(t)$ describe the centers and widths of the wave packet. The parameters $p_{\alpha}(t)$ and $\pi_{\alpha}(t)$ are seen later to describe the conjugate momenta of $x_{\alpha}(t)$ and $\rho_{\alpha}(t)$, respectively.
The Lagrangian for the time-dependent variational theory is given by

\[
L = \left\langle \Psi, t \middle| i \frac{\partial}{\partial t} + \sum_{\alpha} \frac{\partial^2}{\partial^2 q_\alpha} - V(q_1, \cdots, q_f) \right\rangle \Psi, t \right\rangle.
\] (3)

in which \( V \) is the potential. The variational condition \( \delta \left( \int L dt / \delta X \right) = 0 \), where \( X \) represents all the parameters, yields the equations of motion,

\[
\dot{x}_\alpha = \frac{\partial H_{\text{ext}}}{\partial p_\alpha}, \quad \dot{p}_\alpha = -\frac{\partial H_{\text{ext}}}{\partial x_\alpha}, \quad \rho_\alpha = \frac{\partial H_{\text{ext}}}{\partial \pi_\alpha}, \quad \pi_\alpha = -\frac{\partial H_{\text{ext}}}{\partial \rho_\alpha},
\] (4)

in which the extended Hamiltonian is defined by

\[
H_{\text{ext}} = \sum_{\alpha=1}^{f} \left[ \frac{p_\alpha^2}{2} + \frac{\pi_\alpha^2}{2} + \frac{1}{8\rho_\alpha^2} \right] + \langle V \rangle.
\] (5)

These direct us to investigate the quantum dynamics in an extended phase space formed by \((x_\alpha, \rho_\alpha, p_\alpha, \pi_\alpha)\). The key quantity is the extended potential

\[
V_{\text{ext}} = \sum_{\alpha=1}^{f} \frac{\hbar^2}{8m_\alpha \rho_\alpha^2} + \langle V \rangle
\] (6)

defined in the configuration space \((x_\alpha, \rho_\alpha)\). Note that \( p_\alpha \) and \( \pi_\alpha \) vanish in \( \langle V \rangle \) as they appear only in the phase factor of \( \Psi \). Note also that and the atomic masses \( m \) have been retrieved in the first term of Eq. (6). This term serves to broaden the wave packet by forming a potential wall growing along \( \rho \to 0 \), with the stronger tendency when the mass is the lighter, and vanishes in the classical limit \( \hbar \to 0 \).

The calculation of \( \langle V \rangle \) is straightforward only in limited cases. The coupled
Morse potential described in the next section is an example where a compact analytical form is available. For general potentials, the Taylor expansion of $V$ around $\Delta q_\alpha \equiv q_\alpha - \langle q \rangle$ may be useful. Since $\langle q \rangle = x_\alpha$, $\Delta q_\alpha^2 \equiv \rho_\alpha^2$, $\Delta q_\alpha^4 \equiv 3\rho_\alpha^4$, and so on, we find

$$\langle V \rangle = V(x_1, \cdots, x_f) + \frac{1}{2} \sum_{\alpha=1}^{f} \frac{\partial^2 V}{\partial q^2_\alpha} \rho_\alpha^2 + \frac{1}{4} \sum_{\alpha < \beta} \frac{\partial^4 V}{\partial q^2_\alpha \partial q^2_\beta} \rho_\alpha \rho_\beta^2 + \frac{1}{8} \sum_{\alpha=1}^{f} \frac{\partial^4 V}{\partial q^4_\alpha} \rho_\alpha^4 + \cdots$$

(7)

We will assess the accuracy of the fourth-order expansion for the hydrogen bond model potentials. As the second derivative of the potential will be negative around the potential barrier region, divergence along may be caused if the expansion was truncated at the second order. Therefore, the fourth-order expansion would be the minimum requirement for double-well potentials. It is interesting to note that the fourth-order expansion is essentially equivalent to the QHD-2 theory$^{40}$ derived via an apparently different route from mixed quantum-classical Heisenberg equations of motion. In addition, the QHD theory has recently extended to the quantized cumulant dynamics theory$^{41}$ by considering the higher order contributions via the cumulant expansion.
III FORMULATION

A System-bath Hamiltonian

Before proceeding to the application of the SQTDH theory to the analysis of HATs, we construct a theory for an adiabatic HAT to include the additional solvent coordinate \( s \). To this end, we consider a harmonic bath model coupled to \( H \) coordinate. We employ a model of a linearly coupled system-bath Hamiltonian without a counterterm\(^1\)

\[
H = \frac{p^2}{2m} + V_0(r) + \sum_i \left( \frac{p_i^2}{2} + \frac{\omega_i^2}{2} x_i^2 + c_i x_i \right),
\]

where \( V_0 \) is the adiabatic double well potential for the system coordinate \( r \), which interacts with the mass-scaled bath coordinates \( x_i \) via the linear coupling constant \( c_i \). \( p_i \) denotes the mass-scaled bath momentum and \( \omega_i \) is the frequency for the \( i \)th mode.

Using the SQTDH theory, the standard prescription of the bath projection\(^42\) eliminates the bath coordinates \( x_i(t) \) to derive the semiquantal GLE (SQGLE) for \( r(t) \)

\[
m\ddot{r} = -V_0^{(1)}(r) - \frac{\partial}{\partial q} V_0(r,w) - m \int_0^t \zeta(t-\tau) \dot{r}(\tau) d\tau + R(t),
\]

\(^1\)Since the barrier height in the actual HAT in condensed phases changes with the system-bath coupling, the counterterms should be excluded in the Hamiltonian. Otherwise, the barrier height would be almost independent of the coupling. This can be seen in Fig. 17.
where

$$R(t) = \sum_i \left( c_i x_i(0) \cos \omega_i t + \frac{c_i p_i(0)}{\omega_i} \sin \omega_i t \right)$$

(10)

and

$$\zeta(t) = \frac{1}{m} \sum_i c_i^2 \frac{\omega_i^2}{\omega_i^2} \cos \omega_i t.$$

(11)

\[B\] Solvation coordinate

We define the solvation coordinate by the potential energy difference

$$s \equiv V_0(r_D) - V_0(r_A) + \sum_i c_i x_i (\delta r_D - \delta r_A) \equiv \Delta V_0 + \sum_i c_i x_i \Delta r$$

(12)

where D and A denote the donor and acceptor states and $\delta r = r - r_{eq}$ represents the displacement of the $H$ coordinate from its equilibrium value. In this definition, we assume that both $\Delta V_0$ and $\Delta r$ are independent of the system coordinate $q$ and hydrogen bonding coordinate $R$. Although this model cannot treat the nonadiabatic HAT because of the assumed adiabatic double well potential\(^2\), the resulting potential energy surface (PES) (Fig. 2) presents the essential feature that the distance between the well bottom points of the donor and acceptor increases as solvation proceeds.

The minimum energy point $x^\ddagger$ of the crossing seam $s = 0$ could be considered

\(^2\)The extension to the nonadiabatic HAT reaction is obvious as in Ref. 46, though Ref. 46 treats the charge transfer.
as the transition state of the reaction, which is given by

\[
x_i^\dagger = -\frac{c_i/\omega_i^2}{\sum_j c_j^2/\omega_j^2} \frac{\Delta V_0}{\Delta r} \equiv -\frac{c_i \Delta V_0 \Delta r}{\omega_i^2 \lambda}.
\] (13)

The energy difference coordinate like Eq. (12) has been used in many simulation studies, and shown to be a useful choice for a microscopic representation of the many-dimensional solvent motion. \(^{43-54}\) In particular, it is directly related to the nonadiabatic Golden Rule formula of the thermal rate constant. \(^{46,48,55,56}\) A mechanical significance of the coordinate has been shown by Kato et al. for gas-phase molecular reactions, \(^{57,58}\) and by Ando and Kato for a solution phase harmonic bath model. \(^{43}\) Here we show an alternative way based on a simpler idea, and derive a transformed Hamiltonian represented by the coordinate \(s\) and perpendicular bath modes.

With the use of Eqs. (12) and (13), we can see that the coordinate \(s\) is linear in \(x\) or the displacement vector \(\tilde{x} \equiv x - x^\dagger\), i.e.,

\[
s = \sum_i c_i x_i \Delta r + \Delta V_0 = \sum_i c_i \Delta r (x_i - x_i^\dagger),
\] (14)

which implies the significance of a unit vector \(\tilde{s}\) composed of the potential coupling coefficients \(c_i\),

\[
\tilde{s}_i = c_i \sqrt{\sum_j c_j^2}.
\] (15)

The energy difference coordinate \(s\) is now proportional to \(\tilde{s} \equiv \tilde{s} \cdot \tilde{x}\), a scalar pro-
jection of $\tilde{s}$ onto $\tilde{s}$, i.e.,

$$S \equiv \frac{s}{\Delta r} = \sqrt{\sum_i c_i^2 \tilde{s}_i}. \quad (16)$$

Hereafter, $S$, instead of $s$, will be used for the notational convenience. It is shown below [Eq. (18)] that the factor $(\sum_i c_i^2)^{1/2}$ is related to the effective mass of $s$. The vector $\tilde{s}$ is the same as the “reaction coordinate vector” defined by the steepest descent path passing through $x^\dagger$ in the mass-weighted Cartesian coordinate space.\textsuperscript{43,57,58} It is noted, however, that the coordinate $s$ is different from the so-called reaction path coordinate: a close connection is found only at $x^\dagger$.

To derive a Hamiltonian for $S$ and the normal bath coordinates perpendicular to it, it is convenient to employ a projection operator $\hat{P}$ with the element

$$\hat{P}_{ij} = c_i c_j / \sum_k c_k^2, \quad (17)$$

and the matrix partitioning technique with $\hat{Q} = I - \hat{P}$. Then, we obtain the transformed Hamiltonian

$$H = \frac{p_s^2}{2m} + V_0(r) + \frac{p_\tilde{s}_i^2}{2\mu} + \frac{\mu}{2} \bar{\omega}^2 S^2 + \left( \delta r - \frac{\Delta V_0}{\lambda} \right) S + \sum_j \left[ \frac{\tilde{p}_j^2}{2} + \frac{\bar{\omega}_{QQ,j}^2}{2} \tilde{y}_j^2 + \frac{\bar{\omega}_{PQ,j}^2}{2} \tilde{y}_j \right] \mu S + \frac{(\Delta V_0 \Delta r)^2}{\lambda}, \quad (18)$$

which is characterized by the frequency $\bar{\omega}^2 = \sum_i \bar{\omega}_i^2 \tilde{s}_i^2$ and the effective mass $\mu = (\sum_i c_i^2)^{-1}$. Frequencies of the bath modes $\bar{\omega}_{QQ,i}^2$ are obtained by diagonalizing the
matrix $\omega_{QQ}^2 \equiv \hat{Q} \omega^2 \hat{Q}$, whose elements are expressed as

$$\omega_{QQ,ij}^2 = \omega_1^2 \delta_{ij} + \left( \omega_1^2 - \omega_i^2 - \omega_j^2 \right) \tilde{s}_i \tilde{s}_j.$$ (19)

$\sum_j \omega_{QQ,j}^2 \tilde{y}_j \mu^{1/2} S$ represents bilinear coupling between $s$ and the bath modes $\tilde{y}_i$ with the coupling strength of $\omega_{QQ,i}^2$, which is obtained by unitary transforming the column vector $\omega_{QQ,i}^2 = (\omega_1^2 - \omega_i^2) \tilde{s}_i$ by using the eigenvectors of $\omega_{QQ}^2$ corresponding to the non-zero eigenvalues ($\omega_{QQ}^2$ has a zero eigenvalue corresponding to the direction of $\tilde{s}$).

The Hamiltonian of the form [Eq. (18)] has several advantages. Above all, the dynamics of the transferring $H$ is influenced by the bath only through the coupling with the one-dimensional coordinate $s$ in this representation. Thus, we can examine the reaction dynamics by averaging over the bath influences and focusing on the stochastic dynamics of $S$. A similar kind of transformation has been mentioned in a rather heuristic way by Garg et al.\cite{59} The classical PES for $q$ and $s$ is displayed in Fig. 2. We have used the parameters discussed in Section IV and altered $S$ to $s$ for clarification.

The SQTDH theory gives the extended Hamiltonian of Eq. (18)

$$H_{\text{ext}} = \frac{\rho_S^2}{2m} + V_{\text{ext}} + \frac{\rho_S^2}{2\mu} + \frac{\mu}{2} \omega^2 (S^2 + \rho_S^2) + \frac{\hbar^2}{8 \mu \rho_S^2} + \left( \delta r - \frac{\Delta V_0}{\lambda} \Delta r \right) S$$

$$+ \sum_j \left[ \frac{\tilde{p}_j^2}{2} + \omega_{Q,j}^2 \tilde{y}_j^2 \right] + \frac{\omega_{Q,j}^2 \tilde{y}_j \sqrt{\mu} S}{8 \rho_j^2} + \frac{\hbar^2}{8 \rho_j^2} + \frac{(\Delta V_0 \Delta r)^2}{\lambda}. \quad (20)$$

where $\rho_S$ and $\rho_j$ are the conjugate momenta of $S$ and $\tilde{y}_j$, respectively.

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FIG. 2. (a) Two-dimensional classical potential energy surface as a function of the H coordinate $q$ and solvation coordinate $s$. Contour spacing is 1 kcal/mol. (b) Schematic illustrations of the evolution of the HAT potential (the cross-section of (a)). R, $\hat{r}$, and P represents reactant, transition, and product state. The blue, black, and red lines in each panel corresponds to each other.

C Generalized Langevin equation (GLE)

Classical dynamics of the solvation coordinate is described by the generalized Langevin equation of the form\textsuperscript{33,43,60}

$$\ddot{s} = -\Omega^2 s - \mu^{-1} \bar{g} - \int_{0}^{t} \eta(t-\tau)\dot{s}(\tau) d\tau - \eta(t)s(0) + \mu^{-1/2} R(t), \quad (21)$$

where $\Omega = [\bar{\omega}^2 - \eta(0)]^{1/2}$ denotes the effective frequency for the harmonic free energy curves along $s$ and $\bar{g} \equiv q - \Delta V_0 \Delta q / \lambda$. The time-dependent friction kernel $\eta(t)$ is given by

$$\eta(t) = \sum_{j} (\tilde{\omega}_{PQ,j}^2)^2 \cos \tilde{\omega}_{QQ,j} t, \quad (22)$$

which is related to the random force

$$R(t) = -\sum_{j} \tilde{\omega}_{PQ,j}^2 \left( \tilde{y}_j(0) \cos \tilde{\omega}_{QQ,j} t + \frac{\dot{\tilde{y}}_j(0)}{\tilde{\omega}_{QQ,j}} \sin \tilde{\omega}_{QQ,j} t \right). \quad (23)$$
by the quantum fluctuation-dissipation theorem discussed in Sec.1. We assume the Drude spectral density of the bath modes given by

$$J_b = \frac{\pi}{2} \sum_{j} (\frac{\partial^2 \omega^2}{\partial \omega^2})_j^2 \delta(\omega - \omega_{QQ,j}) = \frac{\zeta \gamma^2 \omega}{\omega^2 + \gamma^2},$$

(24)

which is also useful for quantum-mechanical treatments as in Sec. F. The parameters $\gamma$ and $\zeta$ are related to the correlation time and strength of noise by the bath, respectively. Note that $J_b(\omega)$ represents the influence of the bath modes $\tilde{y}_i$ on the “solvent coordinate + transferring H” subsystem in the transformed Hamiltonian [Eq. (20)].

### 1 Quantum fluctuation-dissipation theorem

Since the center and width variables are decoupled from each other for the harmonic potential, the application of Eq. 9 with the classical fluctuation-dissipation theorem $\langle R(0)R(t) \rangle = m k_B T \zeta(t)$ yields the classical thermal average energy $k_B T$ rather than the quantum one $\hbar \omega/(e^{\beta \hbar \omega} - 1) + \hbar \omega/2$. To overcome this difficulty, we should, for the harmonic potential, employ the quantum bath autocorrelation function of the random force$^{62-64}$

$$\langle R(t)R(0) \rangle = \frac{\pi}{2} \int_0^\infty d\omega J(\omega) \frac{\hbar \omega}{2} \coth \frac{\beta \hbar \omega}{2} \cos \omega t.$$ 

(25)

On the other hand, for the general potential except a harmonic potential, with the minimal uncertainty explicitly built into the equations of motion (EOMs) in the SqTDH theory, the zero-point energy (ZPE) fluctuation should be excluded.
from the quantum noise, and the quantum fluctuation-dissipation theorem should be modified to read
\[
\langle R(t)R(0) \rangle = \frac{\pi}{2} \int_0^\infty d\omega J(\omega) \frac{\hbar \omega}{2} \left( \coth \frac{\beta \hbar \omega}{2} - 1 \right) \cos \omega t.
\] (26)

2 Random number generation

The Drude spectral density in Eq. (24) leads to the memory kernel
\[
\zeta(t) = \frac{2}{\pi m} \int_0^\infty d\omega J(\omega) \cos \omega t = \frac{2}{\pi m} \int_0^\infty d\omega \frac{\xi \gamma^2}{\omega^2 + \gamma^2} \cos \omega t = \frac{\zeta \gamma}{m} e^{-\gamma t}.
\] (27)

To generate the stochastic force \( R(t) \) consistent with the quantum fluctuation-dissipation relationship in Eq. (26), we will follow an approach developed by Rice.\(^{65-67} \) In this approach, the noise is assumed to be periodic in time with a period \( N\Delta t \) and expanded in a Fourier series such that
\[
R(t) = \sum_{k=1}^N (a_k \cos \omega_k t + b_k \sin \omega_k t),
\] (28)
where \( \omega_k = 2\pi k/N\Delta t \). The coefficients \( a_k \) and \( b_k \) are independent Gaussian variables with zero mean and variance, \( \langle a_k^2 \rangle = \langle b_k^2 \rangle = G(\omega_k)/N \), which are defined through the spectral density of the noise correlation function
\[
G(\omega) = 2 \int_{-\infty}^\infty dt \cos \omega t \langle R(t)R(0) \rangle.
\] (29)

The resulting autocorrelation function of the random force is displayed in Fig. 3.
FIG. 3. Normalized random force autocorrelation function calculated from Eq. (28) for the classical bath (CB; red), and quantum bath (QB) with and without zero-point energy (ZPE) (green and blue, respectively). $\omega_0$ in the normalization factor is the well frequency modeling O–H vibration and $m$ is the mass of H.

D Hydrogen bonding coordinate

We will include the hydrogen bonding coordinate $R$ in Eq. (20), assuming that this couples to the other bath than that couples to a H coordinate

$$V(r,R,S,Y_k,w,W,\rho_j,W_k) = V_{\text{ext}}(r,R,w,W) + \frac{M}{2} \zeta(0) R^2 + \frac{\mu}{2} \overline{\sigma}^2 (S^2 + \rho_S^2) + \frac{\hbar^2}{8 \mu \rho_S^2} + \left( \delta r - \frac{\Delta V_0}{\lambda} \Delta r \right) S + \sum_j \left[ \frac{\hbar^2}{\rho_j} \left( \hat{\rho}_j^2 + \rho_j^2 \right) + \frac{\hbar^2}{8 \rho_j^2} \right] + \sum_k \left[ \frac{M}{2} \Omega_k^2 (Y_k^2 + W_k^2) + C_k Y_k R + \frac{\hbar^2}{8 M_k W_k^2} \right]$$

(30)

where $W$ is the wavepacket width of $R$, which interacts with the mass-scaled bath coordinates $Y_k$ via the linear coupling constant $C_k$. $M_k$, $\Omega_k$, and $\rho_k$ respectively denote the mass, frequency, and the wavepacket width of the $k$th mode. Since the
bath modes to the H coordinate mainly arise from the change in dipole moments whereas those to the hydrogen bonding coordinate is predominantly due to the translational motion, this assumption seems reasonable. It should be noted that we include the counterterm $M\zeta(0)^2R^2/2$ to keep the barrier height along $R$ to be constant with the coupling strength $\zeta(0)$. The schematic picture of our model and classical PES for $s$ and $R$ are depicted in Fig. 4. Although we approximate the potential of $R$ as harmonic (quadratic), the inclusion of anharmonicity is indispensable and implementable by some orders of polynomials as in Ref. 68.

For a model of H transfers in condensed phase, we consider a double-well potential $V_0(r)$ with a symmetrically coupled mode $R$ and a collection of linearly coupled bath modes $Q_i$,

$$V(r,R,Q) = V_0(r) + \frac{M\omega^2}{2} \left(Q - \frac{D r^2}{M\omega^2}\right)^2 + \sum_i \frac{M_i\omega_i^2}{2} \left(Q_i - \frac{C_i Q}{M_i\omega_i^2}\right)^2,$$

(31)

$$V_0(r) = -\frac{a}{2}r^2 + \frac{b}{4}r^4.$$

(32)

This extends the well-studied “double-well plus harmonic bath” model by adding the mode $R$ representing the displacements of the heavy atoms between which the H transfers. Its importance has been noted in previous works, mostly in the context of the nonadiabatic H transfers. The linearly coupled modes $Q_i$ represent the environmental polarization, whose equilibrium configurations depend on the H transfer coordinate $r$. The coefficients $a$ and $b$ are related to the barrier height $E_b$ and the barrier frequency $\omega_b$ by $a = m\omega_b^2$ and $b = (m\omega_b^2)^2/4E_b$. The potential minima are at $r = \pm(a/b)^{1/2}$. at which the frequency is $\omega_0 = \sqrt{2}\omega_b$. The SQT
theory gives the extended potential of the system

\[ V_{\text{ext}}(r, R, Q_i, w, W, W_i) = \langle V \rangle(r, R, Q_i, w, W, W_i) + \frac{\hbar^2}{8mw^2} + \frac{\hbar^2}{8Mw^2} + \sum_i \frac{\hbar^2}{8M_iW_i^2}. \]  

(33)

in which

\[ \langle V \rangle(r, R, Q_i, w, W, W_i) = V(r, R, Q_i) + \frac{M}{2} \omega^2 W^2 + \sum_i \frac{M_i}{2} \omega_i^2 W_i^2 \]

\[ + \left( -\frac{3}{2} \frac{b \omega^2}{M \omega_i^2} r^2 + \frac{3D^2}{M \omega^2} \frac{m}{2} \zeta(0) \right) w^2 \]

\[ + \frac{3}{4} \left( b + \frac{2D^2}{M \omega^2} \right) w^4. \]  

(34)

Here, we have defined the friction kernel coupled to the hydrogen bonding coordinate

\[ \zeta(t) = \frac{1}{M} \sum_k \frac{C_k^2 \cos \Omega_k t}{M_k \Omega_k^2}. \]  

(35)
FIG. 4. (a) Classical potential energy surface for the hydrogen coordinate $r$ and hydrogen bonding coordinate $R$. Contour spacing is 1 kcal/mol. The parameters used are discussed in Sec. IV. B. (b) Schematic picture of our model. $R$ and $r$ represent the hydrogen bonding distance and hydrogen displacement, respectively. Each $R$ and $r$ is coupled to the separate harmonic bath, the coordinate of which are represented as $Q_i$ and $x_i$. (not shown) Note that $r$ and $R$ denote ‘displacements’ in the text for notational simplicity though $r$ and $R$ denote ‘distances’ and $\delta$ represents ‘displacement.’

E Semiquantant Grote-Hynes theory

To obtain the well and saddle points in the following, Eq. (30) should be minimized along $w_S$, $w_j$, $\tilde{y}_S$, $S$

$$V \geq V_{\text{ext}}(r,R,w,W) - \frac{1}{2\mu\Omega^2} \left( \delta r - \frac{\Delta V_0}{\lambda} \Delta r \right)^2 + \frac{\hbar\tilde{\omega}}{2} + \sum_j \frac{\hbar\tilde{\omega}_{QQ,j}}{2} + \sum_k \frac{\hbar\Omega_k}{2},$$

(36)

in which the equality holds when

$$w_S^4 = \frac{\hbar^2}{4\mu^2\tilde{\omega}^2}, \quad w_j^4 = \frac{\hbar^2}{4\tilde{\omega}_{QQ,j}^2}, \quad \tilde{y}_j = -\frac{\tilde{\omega}_{QQ,j}^2}{2\tilde{\omega}_{QQ,j}^2} \mu S^2, \quad S = -\frac{1}{\mu\Omega^2} \left( \delta r - \frac{\Delta V_0}{\lambda} \Delta r \right).$$

(37)
The analysis of the reactant well bottom and the saddle point of $V_{\text{ext}}$ in the framework of the MTST yields the reaction rate taking into account the quantum effects via the SQTDH model. We assume that the Hessian matrices should be derived from the function $V(r,R,w,W)$ obtained by minimizing along $S$, $\rho_S$, $\tilde{y}_j$, and $\rho_j$. An analogous “local adiabatic elimination” of the fluctuating coordinates has been examined to find excited states via the Einstein-Bohr-Sommerfeld-type ‘requantization’ of the wavepacket dynamics. The details on the well bottom and the saddle point and their Hessian matrices are described in the Appendix A.

Finally, given the eigenvalues of the Hessian matrices in terms of the mass-weighted coordinates at the reactant well bottom and the saddle point, \( \{ (\lambda_0^{(0)})^2, (\lambda_0^{(1)})^2, \ldots \} \) and \( \{ -\mu^2, (\lambda_0^{(1)})^2, \ldots \} \), the semiquantal reaction rate is derived as

\[
k_{\text{GH,sq}} = \frac{1}{2\pi} \prod_{i=0}^{\lambda_0^{(i)}} \lambda_0^{(i)} \exp(-\beta E_b) = \frac{\mu}{2\pi} \sqrt{\frac{\det K_0}{\det K_b}} \exp(-\beta E_b),
\]

where $E_b$ is the effective barrier height determined by minimizing the extended potential and $\mu$ is the reactive frequency, whose solution is given by solving the Grote-Hynes equation

\[
\mu^2 - \omega_{b,\text{eq}}^2 + \mu \zeta(\mu) = 0.
\]

Here, $\omega_{b,\text{eq}}$ is the (‘adiabatic’) barrier frequency at a saddle point, $\zeta$ is the Laplace
FIG. 5. Adiabatic double well potential. Shown are the curvatures $\lambda_{i,0}$ and $\lambda_{i,b}$ at the well bottom and saddle point and the barrier height $E_b$. The MTST theory estimates the reaction rate by $E_b$, $\lambda_{i,0}$, $\lambda_{i,b}$, the latter two of which are calculated by the normal mode analysis of the well bottom and saddle point.

The schematic illustration of the normal mode analysis of MTST is depicted in Fig. 5.
Quantum master equation (QME)

As a quantum dynamical equation of motion, we adopt the quantum master equation (QME) in a time-local (TL) form. The TL approach is also denoted as time-convolutionless formalism,\textsuperscript{70} partial time ordering prescription,\textsuperscript{71–74} or Tokuyama-Mori approach.\textsuperscript{75} It can be derived from a second-order cumulant expansion of the time-ordered exponential function and the influence functional formalism.\textsuperscript{76}

In the eigenstate representation of the system Hamiltonian $\hat{H}_S$, the equation of motion for the density operator $\hat{\rho}(t)$ can be written as

$$\frac{\partial \rho_{ab}(t)}{\partial t} = -\omega_{ab}\rho_{ab}(t) + \sum_{cd} R_{ab,cd}(t)\rho_{cd},$$  \hspace{1cm} (42)

where $\rho_{ab} = \langle a|\hat{\rho}|b\rangle$ and $\omega_{ab} = (E_a - E_b)/\hbar$. The tetradic relaxation matrix $R_{ab,cd}(t)$ is written as

$$R_{ab,cd}(t) \equiv \Gamma_{db,ac}(\omega_{ca};t) + \Gamma^{*}_{ca,bd}(\omega_{db};t)$$

$$- \delta_{bd}\sum_e \Gamma_{ae,ec}(\omega_{ce};t) - \delta_{ac}\sum_e \Gamma^{*}_{be,ed}(\omega_{de};t),$$  \hspace{1cm} (43)

in which

$$\Gamma_{ab,cd}(\omega_{dc};t) = \langle a|\hat{V}_S|b\rangle\langle c|\hat{V}_S|d\rangle\tilde{C}_B(\omega_{dc};t),$$  \hspace{1cm} (44)
\begin{equation}
\tilde{C}_B(\omega; t) = \frac{\hbar}{\pi} \int_{0}^{\infty} d\omega J(\omega) \left( \cos \omega t \coth \frac{\beta \hbar \omega}{2} - i \sin \omega t \right).
\end{equation}

With the Drude spectral density in Eq. (24), Eq. (45) is analytically evaluated as

\begin{equation}
\tilde{C}_B(\omega; t) = \frac{\zeta \gamma^2}{2 \omega_0} \left\{ \gamma \left( \cot \frac{\beta \hbar \gamma}{2} - i \right) \left( \gamma + i \omega \right) \frac{1 - e^{(i \omega - \gamma) t}}{\gamma^2 + \omega^2} \\
+ \frac{4}{\hbar \beta} \sum_{n=1}^{\infty} \frac{\nu_n}{\nu_n^2 - \gamma^2} \left( \nu_n + i \omega \right) \frac{1 - e^{(i \omega - \nu_n) t}}{\nu_n^2 + \omega^2} \right\}.
\end{equation}

IV RESULTS

A Vibrational energy relaxation (VER)

For numerous common processes in solution, e.g. photoisomerization and other barrier crossing phenomena, proton and electron transfer, and some photodissociation reactions, the relative rate for coupling energy into the reaction coordinate compared to that for energy transfer to the solvent and to other unreactive modes of the solute may dictate the rates, pathways, and efficiencies of the reactions. Therefore, a detailed microscopic understanding of solvent-induced vibrational relaxation processes is essential to support the framework of the SQTDH theory of reaction dynamics in solutions. To this end, the following 2 Secs. examine the VER for the harmonic and Morse potentials to model O–H stretching vibration, whose frequencies are determined from the curvature of the Lippincott-Schroeder
model potential,

1 Harmonic potential

First, we consider the vibrational relaxation of a harmonic potential $V_0(r) = m\omega^2 r^2/2$. The extended potential of the system is

$$V_{\text{ext}}(r,w) = \frac{m}{2} \omega^2 r^2 + \frac{m}{2} \omega^2 w^2 + \frac{\hbar^2}{8mw^2}. \quad (47)$$

Since $V_{\text{ext}}(r,w)$ is independent of $r$, the semiquantal dynamics is identical to the classical dynamics for the harmonic potential. This is consistent with the study by Bader and Berne\textsuperscript{84} which argued, using the perturbation theory, that the vibrational relaxation rate is identical between the classical and quantum calculations for the harmonic potential. The simulated energy relaxation for harmonic potential with GLE and QME are displayed in Fig. 6.

To compare GLE with QME, the classical harmonic energy is subtracted by
the equilibrium value and then normalized at \( t = 0 \). The GLE and QME simulation are performed by the velocity-Verlet\textsuperscript{65,67} with 10 000 trajectories and the Runge-Kutta integrator of fourth order with a time step of 0.1 fs, respectively. The excitation is performed by lengthening the O–H bond by the corresponding amount of \( \hbar \omega_0 \), where \( \omega_0 \) is the frequency at a bottom well, because the quantum bath contains the energy of \( \hbar \omega_0/2 \). The QME simulation is performed by setting the population of the excited (pure) state to be 1 at \( t = 0 \). The bath parameters are \( \tilde{\gamma} = \gamma/\omega_0 = 0.5 \) and \( \tilde{\zeta} = \zeta/m\omega_0 = 0.05 \), where \( m \) is the mass of H. The exponential fitting of Fig. 6 gives the (longitudinal relaxation time \( T_1 = 146 \) fs approximately for both GLE and QME. This result can also be obtained analytically by the ‘Landau-Teller formula’ \( T_1 = 1/\zeta'(\omega_0) \approx 146.8 \) fs, which is in excellent agreement with the numerical result. Here, \( \zeta'(\omega) \) is the real part of Fourier transform of Eq. (11). This formula holds rigorously for the hamonic potential and therefore this agreement supports our simulation. Moreover, the well-known Markov approximation of the present QME can also be utilized to confirm these results. This formula is given as \( T_1 = 1/C'_B(\omega_0) \approx 146.7 \) fs, in which \( C'_B(\omega) \) is the real part of Eq. (45). This is again in excellent agreement with the numerical result.

2 Morse potential

Second, we consider the Morse potential since the accuracy of the SQTDH theory to the anharmonic potential is nontrivial whereas that to the harmonic potential is excellent as we have seen. We define the Morse potential by \( V_0(r) = D[1 - \)
FIG. 7. Potential energy surface and lowest four energy levels of Morse potential. ($\tilde{\gamma} = 0.5, \tilde{\zeta} = 0.05$)

exp$(-a(r - r^0))^2$. The parameters $D$ and $r^0$ are the bond dissociation energy and the equilibrium bond length and $a$ is related to the potential well curvature. Fig. 7 depicts the PES of the Morse potential and its lowest four energy levels. The SQTDH theory yields the extended potential of the Morse potential

$$V_{\text{ext}}(r, w) = D[1 + e^{-a(r - r_0)} + 2a^2w^2 - 2e^{-a(r - r_0)} + a^2w^2/2].$$ (48)

In Fig. 8 (a), (b), and (c), we show the VER for the Morse potential by GLE, SQGLE, and QME, respectively. The relaxation rates are plotted in Fig 8 (d), which are obtained by the least square fitting by a single exponential. The energies in SQGLE are calculated via Eq. (48), and those in QME are evaluated by the expectation value of the system Hamiltonian. In obtaining $T_1$'s we have used the data up to 1 ps to eliminate the other relaxation discussed in the following and rescaled it to be 1 at $t = 0$ ps and 0 at $t = 1$ ps. The initial conditions for SQGLE are discussed in Appendix B. As seen in Fig 8 (d), SQGLE always gives
FIG. 8. Energy relaxation for Morse potential by GLE, SQGLE and QME. ($\tilde{\gamma} = 0.5$, $\tilde{\zeta} = 0.05$.)
FIG. 9. Energy relaxation for Morse potential by SQGLE for 20 ps. (\(\tilde{\varphi} = 0.1, \tilde{\zeta} = 0.5\).)

\(T_1\) between GLE and QME, and the accuracy worsens as excited to the higher levels. The fluctuation of energy at first can be explained by the non-Markovian effect and found in other studies.\(^67\) The distinction of this initial fluctuation, which has not been seen so strongly in the QME simulation, could be ascribed to the fact that in the QME simulation the excited state has been given by the pure state, while the Gaussian wavepacket assumes the coherent state. However, we expect that the VER rate may not differ appreciably.

Since we forbid the wavepacket widths from fluctuating and dissipating, however, the energy of widths remains constant in the simulation, which causes the unphysical slower relaxation. This can be seen in Fig. 9, which shows the much slower energy relaxation with a decay time of some ps. This slower relaxation, however, can be removed by attaching a bath to the width coordinate. Nonetheless, this attachment cannot be rationalized within the SQTDH theory and therefore the bath is definitely artificial. Recently, the QHD-2 theory has shown that the dissi-
pation term in the EOM of the width coordinate exists, yet necessity of the bath remains unclear.

Figs. 10 (a) through (d) depict the VER (rates) for the Morse potential by GLE, SQGLE, and QME. The relaxation rates are obtained by the least square fitting by a single exponential $\text{Const.} \times e^{-t/T_1}$, where $T_1$ is the relaxation time. After the system is equilibrated for $\approx 0.6$ ps, it is excited to the first excited state. Except the different bath parameters $\tilde{\gamma} = 0.1$ and $\tilde{\zeta} = 0.5$, and the dissipation of the wavapacket width’s energy, the simulation procedure is the same as in Figs. 8. These parameters, $\tilde{\gamma} = 0.1$ and $\tilde{\zeta} = 0.5$, strengthen the non-Markovian effect and therefore the initial fluctuation of energy becomes stronger compared with Figs.
B Hydrogen atom transfer rate

1 Quartic double well potential

Third, we consider the quartic double well potential, which is decoupled with the hydrogen bonding coordinate. We expect that this model will provide the HAT dynamics without the hydrogen bonding coordinate and show the applicability to the intermediate regime between the adiabatic and nonadiabatic regimes. We define the quartic double well potential by 

\[ V(r) = -ar^2/2 + br^4/4. \]

The coefficients \( a \) and \( b \) are related to the barrier height \( E_b \) and the barrier frequency \( \omega_b \) by \( a = m\omega_b^2 \) and \( b = (m\omega_b^2)^2/4E_b \). The potential minima are at \( q = \pm(a/b)^{1/2} \) at which the frequency is \( \omega_0 = \sqrt{2}\omega_b \). The parameters are determined for the low barrier case \((\hbar\omega_b/E_b = 0.8930)\) to give the same curvature at the well bottom as the Lippincott-Schroeder model potential.\(^{79,80}\) This PES, the barrier height of which is \( \approx 8 \) kcal/mol, is shown in Fig. 11 (a). The SQTDH theory gives the extended potential of the system

\[
V_{\text{ext}}(r,w,Q_i,w_i) = V(r,Q_i) + \frac{-a + 3br^2}{2}w^2 + \frac{3}{4}bw^4 + \frac{\hbar^2}{8mw^2} + \sum_i \left[ \frac{m_i}{2} \omega_i^2 w_i^2 + \frac{\hbar^2}{8m_i w_i^2} \right].
\]

yielding the PES shown in Fig. 11 (b). In actuality, this barrier is too high for the adiabatic HAT because the ZPE is \( \approx \hbar\omega_0/2 \approx 5 \) kcal/mol. However, this model
can afford the HAT dynamics in the intermediate regime, where the applicability of the SQTDDH theory is nontrivial.

The bath parameters are chosen so as to reproduce the correlation time\textsuperscript{43} and the reorganization energy of the transfer in water ($\approx 12$ kcal/mol)\textsuperscript{22–24}. The parameters in Eq. (24) for aqueous solution are $1/\gamma = 1/0.1\omega_0 \approx 90$ fs and $1/\zeta = 1/0.5\omega_0 \approx 18$ fs, where $\omega_0$ is the same curvature at the well bottom of the Lippincott-Schroeder model potential.\textsuperscript{82,83} $\tilde{\zeta}$ ($\tilde{\alpha} = \alpha/\omega_0$, where $\alpha = \zeta, \gamma$) is changed from 0.5 to 0.1.

The effective mass $\mu$ and frequency $\Omega$ are chosen as $2.1 \times 10^{-5}$ ps$^2$/eV $\Delta r^2$ and $417$ cm$^{-1}$ from Ref. 43, where the displacement between the donor and acceptor $\Delta r$ in Eq. (16) is taken as 0.6 Å. This effective mass $\mu$ is half as large as that in Ref. 43 because the value in Ref. 43 was too large for $\omega_b$ to be positive. While the parameters are taken from the simulation of $N,N$-dimethylaniline in water, we expect that this does not matter since $\mu$ and $\Omega$ would qualitatively be invariant.
FIG. 12. Semiquantal wavepacket trajectories for the quartic double well decoupled with a solvation coordinate. The wavepackets are normalized to unity at every time step.

and we have chosen the reorganization energy from the adiabatic proton transfer in aqueous solution.

The simulated semiquantal trajectories of wavepackets for Fig. 11 (b) are shown in Fig. 12. The system starts from one of the well bottoms in this simulation and we see that the wavepacket around $q \approx 0$ (i.e. when HAT occurs) spreads whereas that around $q \approx \pm 0.1 - 2\,\text{Å}$ (i.e. in bottom wells) contracts. This phenomena can also be observed in the other simulation, in which a solvation coordinate is coupled, and the trajectories of the wavepacket center and width, and a solvation coordinate in this simulation are depicted in Figs. 13 (a), and 13 (b), respectively.

2 Transmission coefficient

In the reactive flux approach, a reaction is described in terms of the reactive flux through a dividing surface that separates the reactants and products. The
FIG. 13. (a) Semiquantal wavepacket trajectories of a center $q$ and width $\rho$ for the quartic double well coupled with a solvation coordinate. The wavepacket center $q$ starts from $q = 0$. (b) Semiquantal wavepacket trajectories of a solvation coordinate $s$ for the quartic double well coupled with a solvation coordinate. The solvation coordinate $s$ starts from $s = 0$.

The overall rate can be expressed as

$$
k = \lim_{t \to \tau_p} \frac{\langle \dot{\xi}(0) \theta[\xi(t) - \xi^\dagger] \delta[\xi(0) - \xi^\dagger] \rangle}{\langle \theta[\xi^\dagger - \xi(0)] \rangle}
= \lim_{t \to \tau_p} \frac{\langle \dot{\xi}(0) \theta[\xi(t) - \xi^\dagger] \delta[\xi(0) - \xi^\dagger] \rangle}{\langle \theta[\xi^\dagger - \xi(0)] \rangle}
\times \frac{\langle \dot{\xi}(0) \theta[\dot{\xi}(t)] \delta[\xi(0) - \xi^\dagger] \rangle}{\langle \theta[\xi^\dagger - \xi(0)] \rangle}
= \kappa k_{TST}
$$

(50)

where $\kappa$ is the transmission coefficient and $k_{TST}$ is the transition state theory (TST) rate constant. Here $\xi$ is the reaction coordinate, which depends on the coordinates of the system. The dividing surface is defined as $\xi = \xi^\dagger$, and the reactant and product are defined to be in the regions $\xi < \xi^\dagger$ and $\xi > \xi^\dagger$, respectively. In Eq. (50), the term $\dot{\xi}$ is the time derivative of the reaction coordinate, $\delta(x)$ is the Dirac delta function, $\theta(x)$ is a Heaviside function, $\tau_p$ is the plateau time, and the angular brackets indicate an average over a thermodynamic ensemble.
The transition state theory rate constant $k_{\text{TST}}$ represents the equilibrium flux through the dividing surface and is defined as

$$k_{\text{TST}} = \frac{\langle \dot{\xi}(0) \theta[\dot{\xi}(t)] \delta[\xi(0) - \xi^{\ddagger}] \rangle}{\langle \theta[\xi^{\ddagger} - \xi(0)] \rangle}.$$  \hfill (51)

Transition state theory is based on the assumption that each trajectory passes through the dividing surface once and only once.\textsuperscript{101, 102} In general, trajectories can recross the dividing surface, and the transition state theory rate constant is an upper limit to the exact rate constant. The transmission coefficient accounts for the dynamical barrier recrossings\textsuperscript{103–107} and is defined as

$$\kappa = \lim_{t \to \tau_p} \frac{\langle \dot{\xi}(0) \theta[\dot{\xi}(t) - \xi^{\ddagger}] \delta[\xi(0) - \xi^{\ddagger}] \rangle}{\langle \dot{\xi}(0) \theta[\dot{\xi}(t)] \delta[\xi(0) - \xi^{\ddagger}] \rangle}.$$  \hfill (52)

According to this definition, the transmission coefficient is always between zero and unity (i.e., $0 \leq \kappa \leq 1$).

Topaler and Makri defined the transmission coefficient to be the ratio of the rate constant divided by the classical TST value\textsuperscript{85}

$$k_{\text{TST,cl}} = \frac{1}{\beta \hbar} \frac{Q^{\ddagger}}{Q_R} e^{-\beta E_b} = \frac{\omega_0}{2\pi} e^{-\beta E_b},$$  \hfill (53)

where $Q_R$ and $Q^{\ddagger}$ are the reactant and transition state partition functions, respectively. We denote this overall transmission coefficient as $\kappa'$ in this paper:

$$\kappa' = k/k_{\text{TST,cl}}$$  \hfill (54)
to distinguish it from the transmission coefficient defined in Eq. (52).

3 Dynamical GLE simulation

In the simulations that will follow, the transmission coefficient is calculated using the reactive flux method\textsuperscript{108,109}. The simulated transmission coefficients for the double well potential by GLE and SQGLE is depicted in Fig. 14 (a). The classical GLE gives $\kappa \approx 0.4$ whereas the semiquantal SQGLE gives almost zero because the SQTDH theory gives the minimum energy point in the saddle point. This drastic decrease in $\kappa$ can be explained by the recrossings of the hydrogen due to its quantum effect. Although $\kappa$ starts not from 0 as calculated by a quantum flux autocorrelation function but from 1 as calculated by a reactive flux method, we expect that the plateau values of $\kappa$ would end up approaching the quantum result as calculated in the mixed quantum-classical method.

Furthermore, the simulated transmission coefficients for the double well potential coupled with the solvation coordinate $s$ is depicted in Fig. 14 (b). The dividing surface is chosen as $q = 0$ (blue) and $s = 0$ (red). As in Fig. 14, classical (purple) and semiquantal (blue and red) results significantly deviate owing to the nuclear quantum effect. The real dividing surface is chosen to minimize $\kappa$ and therefore $q$ and $s$ can be reaction coordinates for this model and parameters because they are almost indistinguishable after the plateau time.
FIG. 14. (a) Transmission coefficients for the double well potential by GLE (red) and SQGLE (blue). (b) Transmission coefficients for the double well potential coupled with the solvation coordinate for 15 ps. Semiquantal results are plotted with the dividing surface $q = 0$ (blue) and $s = 0$ (red). Classical results are plotted with the dividing surface $q = 0$ (purple).

4 DW1 and DW2 models

To investigate how the nuclear quantum effect can be included by the SQTDH theory we calculate $\kappa$ for DW1 and DW2 models used by Topaler and Makri. Exact $\kappa$’s for the two models have been calculated by several methods, e.g. quasidiabatic propagator path integral (QUAPI) methodology, shown in Fig. 15. The first model (DW1) is characterized by a relatively high potential barrier and a large cutoff frequency, such that the memory effects introduced in the GLE are of short range. These conditions favor the validity of (multidimensional) transition-state-based theories in the large friction regime, as reactive trajectories tend to sample the parabolic region of the potential. Our numerical calculations presented later confirm this expectation. The second model (DW2) has a low barrier, while the cutoff frequency of the bath is smaller. In this case the barrier anharmonicity is more pronounced and memory effects are significant, causing substantial de-
FIG. 15. Quantum transmission coefficient as a function for damping strength for (a) DW1 (T=300K) (b) DW2 (T=200K). Numerical QUAPI results are shown by solid circles. The results of the Wolynes transmission factor (quantum Grote-Hynes theory) are shown by the dotted line. The solid and dashed lines correspond to the quantum turnover theories due to Hänggi, Pollak, and Grabert, and to Rips and Pollak, respectively. The triangles correspond to results obtained with the centroid method. The hollow circles correspond to parameters for which the flux correlation function did not read a well-defined plateau. (Reprinted from Ref. 84 without permission.)

viations from the results of transition state approaches. The barrier heights $E_b$, barrier frequencies $\omega_b$, well frequencies $\omega_0$, and bath cutoff frequencies $\omega_c$ are $2085 (1043)$, $500 (500)$, $707 (707)$, and $500 (100) \text{ cm}^{-1}$ for DW1 (DW2).

On the other hand, $\kappa$’s calculated by the SQTDD theory is depicted in Fig. 16. First of all, we show semiquantum barrier heights and relative TST rate in Figs. 16 (a) and (b). The classical barrier height is $E_b$ for both DW1 and DW2 models, independent of the coupling strength. In Fig. 16 (a), $E_b$’s are always below the classical values for all coupling strengths. For the DW2 model, the barrier frequency around $\zeta/m\omega_b < 0.5$ becomes negative and therefore we cannot
obtain results in this regime. In Fig. 16 (b), the relative TST rate defined by

$$\frac{k_{TST,sq}}{k_{TST,cl}} = \frac{\omega_{0,sq}}{\omega_{0,cl}} \exp[-\beta(E_{b,sq} - E_{b,cl})]$$

is depicted. Modified ones by the diagonalized semiquantal frequency, which is obtained by diagonalizing the Hessian matrix in the extended space of $r$ and $w$ and shown in Figs. 16 (c) and (e), are also depicted. Since the relative TST rate is larger than 1 due to the quantum effect ranging from a few to a hundred, we conclude that the SQTDH theory can include the nuclear quantum effect. However, this large TST rates are suppressed by smaller well frequencies and transmission coefficients. Classical barrier and well frequencies are constant ($\sqrt{2}$ and 1) and semiquantal ones increase with coupling strength. Moreover, the semiquantal well frequencies have to be diagonalized and we have to adapt the lower one, which is shown in Fig. 16 (c), (e) (yellow). Whereas classical transmission coefficients (red) decrease with increasing coupling strengths, semiquantal ones increase (black). In the high barrier model, DW1, the overall transmission coefficients have too large values especially in the energy-diffusion-controlled regime compared to the exact quantum result in Fig. 15. In the low barrier model, DW2, the overall transmission coefficients also have too large values, yet the deviation is not such large as in DW1 model. Hence, we can conclude that the SQTDH theory is cut out for the low barrier potential. Consequently, the diagonalization scheme in determining frequency, proposed by Shigeta, deems necessary for the SQTDH, QCD, and QHD simulation.
FIG. 16. (a) Barrier heights for DW1 and DW2 model. (b) Relative TST rate defined in the text for DW1 and DW2 model. Classical and semiquantal well, barrier frequencies and diagonalized semiquantal frequency are shown in (c) and (e) for DW1 and DW2 model. Classical, semiquantal, overall semiquantal, and diagonalized semiquantal $\kappa$’s are shown in (d) and (f) for DW1 and DW2 model. (g) Classical and semiquantal transmission coefficients ($\kappa$) and (h) Classical and semiquantal kinetic isotope effects (KIEs) for the two model potentials. The lines in the Figs. are guided to the eye.
Fig. (g) depicts classical and semiquantal transmission coefficients $\kappa$ for DW1 and DW2 models, representing the monotonous decrease in the classical $\kappa$ and the peak structure along $\zeta$ owing to small $\omega_{p,\text{eq}}$ in the energy-diffusion-controlled regime. The KIEs for DW1 and DW2 in Fig. 16 (g) represent peaks as a function of the coupling strength, which is reminiscent of our previous work. The KIE for DW1 (high barrier) is lower than that for DW1 (low barrier) since the non-Markovian effect manifest themselves ($\omega_c (\text{DW1}) > \omega_c (\text{DW2})$), which is justified by the fact that with the same $\omega_c$ KIE (DW1) > KIE (DW2) (not shown).

Note that the failure of the SQTDH theory can be ascribed to two reasons. First, the barrier height of DW1 and DW2 are so high that the HATs lies in the nonadiabatic regime. Since the theory assumes squeezed coherent states and cannot represent the splitting of the wavepacket, this difficulty might be lead to one of the limitations of the SQTDH theory. Second, the calculated semiquantal Grothe-Hynes theory cannot consider the dissipation of the wavepacket width’s energy. In the calculation, we have observed that the spreading of the wavepacket at a saddle point may cause the excessive decrease in the barrier height. We thus expect that the dynamical simulation of SQGLE would decrease the overall transmission coefficient $\kappa'$.

5 Rate evaluation with hydrogen bonding coordinate $R$ and solvation coordinate $S$

In this section, we evaluate the HAT rate with the hydrogen bonding coordinate $R$ and the solvation coordinate $S$ by Eqs. (38) – (41). To model O–H···O hydrogen
bonds,\textsuperscript{81,82} we take $\omega \approx 194 \text{ cm}^{-1}$ and $D/M\omega^2 = 0.25/\sqrt{\hbar/m_p\omega}$ to model the coupled Morse potential\textsuperscript{28}. The other parameters are the same in Sec. IV. B. 3. The optimal wave packet is obtained by minimizing the extended potential Eq. (36) in the extended coordinate space $(r,R,w,W)$ by \texttt{FindMinimum} function of Mathematica. $\omega_{b,eq}$'s in Figs. 17 (b) have been calculated by the curvature along $r$ on the semiquantum and classical PES, that is by differentiating Eq. (36) with respect to $r$.

In Fig. 17 (a) and (b), we show barrier heights and barrier and reactive frequencies for classical and semiquantum hydrogen and deuterium. As in Fig. 16 the barrier and reactive frequencies increase with coupling strengths, yet the curve is convex downward. Whereas the semiquantum frequencies in Fig. 16 approach the classical values in the strong coupling limit, those in Fig. 17 (b) seem to remain different because the additional coordinates $R$ and $S$ are included. Fig. 17 (c) and (d) show the semiquantum Grote-Hynes reaction rate for classical and semiquantum hydrogen and deuterium and the KIE for (c). The ordinate in Fig. 17 (c) is plotted in a logarithm scale. $k_{\text{GH},\text{sq}}$ diminishes drastically with increasing the coupling strength $\zeta$, which may be attributed to that we have not included a counterterm in Eq. (8) because classical and semiquantum results represent the same tendency. For $\zeta/m\omega_0 = 0.5$, det $K$ becomes negative and therefore we cannot obtain $k_{\text{GH},\text{sq}}$. Note that KIE increase with the coupling strength $\zeta$. This is consistent with the general fact that KIE increases with increasing the barrier height.

To investigate only the effect of friction on $k_{\text{GH},\text{sq}}$ and KIE we add a countterm in Eq. (8). The simulation results are depicted in Figs. (e) – (h), correspond-
FIG. 17. (a) Barrier heights for classical and semiquantum hydrogen and deuterium. (b) Barrier and reactive frequencies for classical and semiquantum hydrogen and deuterium. (c) Semiquantum Grote-Hynes reaction rate for classical and semiquantum hydrogen. (d) The kinetic isotope effect (KIE) for (c). (e) – (h) correspond to (a) – (d) with a counterterm. The lines in the Figs. are guided to the eye.
ing to (a) – (d). The parameter $\Omega$ is chosen as approximately $753\text{cm}^{-1}$ and the other ones are the same as in (a) – (d). The distinction between with and without a counterterm is that the values does not vary widely. Despite this, KIE increase with $\zeta$, albeit a small variation.

Although we have not yet observed this phenomenon in a similar experimental situation, the increase of KIE with macroscopic pressure actually exists in the experiment of enzymatic hydrogen-tunneling reactions.\textsuperscript{110} This KIE increase with pressure in the above-mentioned experiment, however, arises from conformational reasons of molecules, which is distinct from solvent reorganization. Nevertheless, we hope that the KIE increase as system couples to dynamical solvent reorganization will be observed in the experiment.

V CONCLUDING REMARKS

In this work, the VER rates for the harmonic and Morse potentials calculated by the SQTDH theory agree better with those by the quantum master equation than the classical GLE, confirming the necessity of the dissipation of the wavepacket width’s energy. A theory for the adiabatic HAT rate has been developed by combining the SQTDH theory and the MTST, taking into account the zero-point effects and the dynamical solvent effect. The analysis on the DW1 and DW2 model potentials has suggested that the SQTDH theory overestimates the overall transmission coefficient of the nonadiabatic H transfer rate especially in the weak-coupling (energy-diffusion-controlled) regime, and the KIE on the adiabatic H
transfer rate may exhibit a maximum as a function of the coupling strength to the external degrees of freedom. The HAT rate with the dynamical solvent effect increases monotonously in the friction range considered. Although we have not yet seen experimental evidence or signature, this might be observed with controlled external pressure\textsuperscript{111} and viscosity.\textsuperscript{112,113} A more detailed analysis for its origin and the conditions in which to enhance or suppress the peak would be needed to offer further clues for experimental examinations.

It is also desired to extend the approach toward more realistic and complex systems than the model of Eq. (7), which would be possible in various ways. One of the most straightforward would be to generalize from the quartic double well to more generic forms of the potential. In this regard, encouraging results have been obtained on the structural correlations and the geometric isotope effects of the hydrogen bond structure. Although we have tried the coupled Morse model potential, since this potential is cut out for the molecule in the gas phase the dynamical simulation quickly leads to the dissociation of the hydrogen bond. Another direction in which to proceed would be to combine the SQTDH theory with the reaction path/surface Hamiltonian approaches,\textsuperscript{11,12,16,17} because their application to the adiabatic regime seems rather scarce. Moreover, in cases where the choice of the reaction coordinate is not as obvious, e.g., in the collective multiple proton transfers in protic liquids, it will become necessary to properly account for the correlations among different degrees of freedom. While the thawed Gaussian wavepacket approach, which is closely related to the present model, will appropriately handle this aspect, analogous treatment in the present framework will
require additional considerations and approximations in order to maintain the extended Hamiltonian form. Works along this issue with applications are currently under way and will be reported elsewhere. We envisage that the present model study would serve as a basic reference for these extensive applications.

Additionally, to prove the applicability of Eqs. (38) – (41) the present model, the exact evaluation of shall be given. Some of the candidates are the path integral Monte Carlo (PIMC)\textsuperscript{114,115} and the quantum master equation. We envisage that the present model can be extended to the double proton transfer by considering a system with several baths and their interactions.\textsuperscript{116} Combining with the electronic structure calculations is another direction to progress, in which, for example, the non-Born-Oppenheimer electron-hydrogen coupling and transfers\textsuperscript{18,117–119} seem to represent interesting and important open questions.

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A NORMAL MODE ANALYSIS OF MTST

Converting to the mass-weighted coordinates, \((r, w) \equiv \sqrt{m}(r, w), (R, w) \equiv \sqrt{\mu}(R, w), (S, w_S) \equiv \sqrt{\mu}(S, w_S), \) and \((Y_k, W_k) \equiv \sqrt{M_k}(Y_k, W_k)\)

\[
V = V_{ext}(r, R, w, W) + \frac{\zeta(0)}{2} R^2 + \frac{\bar{\omega}^2}{2} (S^2 + w^2_S) + \frac{\hbar^2}{8 w_S^2} + \left( r - \frac{\Delta V_0}{\lambda} \right) \frac{S}{\sqrt{\mu \mu}} + \sum_j \left[ \frac{\bar{\omega}_{QQ, j}^2}{2} (\bar{y}_j^2 + w_j^2) + \bar{\omega}_{PQ, j} \bar{y}_j S + \frac{\hbar^2}{8 w_j^2} \right] + \sum_k \left[ \frac{\Omega_k^2}{2} (Y_k^2 + W_k^2) + \frac{C_k Y_k R}{\sqrt{M_k M}} + \frac{\hbar^2}{8 W_k^2} \right]
\] (56)
The Hessian matrix at the reactant well is

$$K_{\text{well}} \equiv \begin{bmatrix}
\partial^2_S & \partial_S \partial_r & \partial_S \partial_{y_1} & \ldots & \partial_S \partial_Q & \partial_S \partial_{y_1} & \ldots \\
\partial_r \partial_S & \partial^2_r & \partial_r \partial_{y_1} & \ldots & \partial_r \partial_Q & \partial_r \partial_{y_1} & \ldots \\
\partial_{y_1} \partial_S & \partial_{y_1} \partial_r & \partial^2_{y_1} & \ldots & \partial_{y_1} \partial_Q & \partial_{y_1} \partial_{y_1} & \ldots \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ldots \\
\partial_Q \partial_S & \partial_Q \partial_r & \partial_Q \partial_{y_1} & \ldots & \partial_Q^2 & \partial_Q \partial_{y_1} & \ldots \\
\partial_{y_1} \partial_S & \partial_{y_1} \partial_r & \partial_{y_1} \partial_{y_1} & \ldots & \partial_{y_1} \partial_Q & \partial_{y_1}^2 & \ldots \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ldots 
\end{bmatrix} V$$

$$= \begin{bmatrix}
\bar{\omega}^2 & \partial_r \partial_S V & \omega_{PQ,1}^2 & \ldots & 0 & 0 & \ldots \\
\partial_r \partial_S V & \partial^2_r V & 0 & \ldots & \partial_Q \partial_r V & 0 & \ldots \\
\omega_{PQ,1}^2 & 0 & \omega_{QQ,1}^2 & \ldots & 0 & 0 & \ldots \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ldots \\
0 & \partial_Q \partial_r V & 0 & \ldots & \partial_Q^2 V & \tilde{C}_1/\sqrt{MM_1} & \ldots \\
0 & 0 & 0 & \ldots & \tilde{C}_1/\sqrt{MM_1} & \Omega_1^2 & \ldots \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ldots 
\end{bmatrix} \text{ (57)}.$$
The determinant is
\[
\det K = \prod_{i=1}^{\tilde{\omega}} \omega_{Q,i}^2 \prod_{j=1}^{\Omega} \Omega_{j}^2 \left[ (\partial^2_{Q} V - \sum_{j=1}^{C_j} \frac{C_j}{MM_{j} \Omega_{j}^2}) \left\{ \partial^2_{V} (\omega^2 - \sum_{i=1}^{\tilde{\omega}} \omega_{PQ,i}^2) \right\} - (\partial_{R} \partial_{S} V)^2 \right] - \left( \omega^2 - \sum_{i=1}^{\tilde{\omega}} \omega_{PQ,i}^2 \right) (\partial_{R} \partial_{V} V)^2 \right) \]
\[
= \prod_{i=1}^{\tilde{\omega}} \omega_{Q,i}^2 \prod_{j=1}^{\Omega} \Omega_{j}^2 \left[ (\partial^2_{Q} V - \zeta(0)) (\Omega^2 \partial^2_{V} V - (\partial_{R} \partial_{S} V)^2) - \Omega^2 (\partial_{R} \partial_{V} V)^2 \right].
\]

(58)

B INITIAL CONDITIONS FOR MORSE POTENTIAL

We take the initial condition for the 1st excited state to be
\[
V = D[1 - e^{-ax_{ini}}]^2 = \hbar \omega - \frac{9\hbar^2 \omega^2}{16D}.
\]

(59)

The initial conditions for widths can be given tentatively by minimizing the extended potential
\[
\frac{\partial V_{ext}}{\partial \rho} = -2a^2 D \rho (2e^{2a^2 \rho^2 - 2as} - e^{a^2 \rho^2/2 - as}) - \frac{\hbar^2}{4m \rho^3} = 0.
\]

(60)

Those for the 2nd and 3rd excited states are determined accordingly.
References


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