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ABSTRACT

We applied the semiclassical initial value representation (SC-IVR) method with the classical electron analog to deal with electronically nonadiabatic reactive barriers and calculated the thermal reaction rate constant. The symmetric form of the flux-flux correlation function is used, and the matrix element of the Boltzmannized flux operator is derived using imaginary-time path integral techniques. This combined use of non-adiabatic SC-IVR and non-adiabatic path-integral sampling (NA-IVR&PI) is beyond the treatment of mean-field, and we analyze its performance in comparison with some existing mean-field methods for different scenarios of potential energy surface. We found a systematically better performance. One exception is the deep tunneling regime, where the mean-field ring-polymer instanton is superior. In the golden rule limit, where all these mean-field methods break down, the significant advantage of NA-IVR&PI is shown by using the electronic states for description of the dividing surface.

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I. INTRODUCTION

The thermal rate constant is one of the most important quantities in chemical reaction theory. Many methods are developed aiming to give it a quantitatively accurate description. Among these methods, the most rigorous one is to solve the problem in a fully quantum mechanical manner, such as the quantum reactive scattering approaches and the discrete variable representation methods.^{1–3} However, for realistic complex systems, it is known that the computational cost of them grows exponentially with the nuclear degrees of freedom (DOFs). To cope with this problem, one can resort to the classical treatment, e.g., using molecular dynamics.^{4,5} However, the quantum nature of the nuclei will be also of crucial importance at relatively low temperatures, where the barrier height is no longer small compared to thermal kinetic energy and tunneling has a non-negligible contribution to the reaction rate. ^{6,7} In these cases, the classical methods are bound to fail.

This situation can become even more complicated when the electronic DOFs are further involved.^{8,9} In these cases, the quantum dynamics include not only quantum tunneling of the nuclei but also electronic transitions.^{10–12} When the Born–Oppenheimer approximation breaks down, the significant difference between adiabatic and non-adiabatic dynamics forces us also to handle the non-adiabatic effects correctly.^{9,10,13} Therefore, it is fair to say that an aspect that makes the problem of accurately simulating chemical reaction rates so challenging is the mixed quantum nature of the



electrons and nuclei, which means that the imaginary-time statistics and the real-time dynamics plus non-adiabatic effects need to be considered in the same framework.

Apart from the fully quantum methods and the classical ones, many methods developed in recent years can partially address all these three aspects. These include methods based on the transition state theory, the instanton method, and the ring-polymer molecular dynamics (RPMD).^{13–18} These different families of methods have their own advantages and shortcomings. Many variants of them are also proposed to settle their problems. These variants include ring-polymer surface hopping (RPSH), isomorphic RPMD, and golden-rule instanton.^{19–22} A weakness in common is their rigorous definition in describing real-time quantum dynamics. The lack of real-time coherence in these methods makes them unreliable especially in the case of high temperature and strong non-adiabatic effects where the reaction probability can be lowered mainly by real-time non-adiabatic dynamics.²³

A better defined theoretical method in describing quantum dynamics is the so-called semiclassical initial value representation (SC-IVR). It is based on the semiclassical approximation of the quantum propagator, which is made applicable by transformation of variables from root-searching form into initial value representation.^{24–26} The quantum propagation is described by classical trajectory dynamics on the nuclear potential energy surface (PES). By keeping additional information of the action and the phase space volumes, it is capable of describing the quantum nature of nuclei and has good potential on quantum dynamics. The method has been successfully put into use in the calculation of vibrational spectrum, where it has been greatly developed in the past few decades with many improvements proposed to enhance its numerical behavior and extend its usefulness.^{27–35}

Besides spectral calculation, it can also be applied to solve many other problems involving the quantum propagator.^{36–38} The determination of rate constant is apparently one of them. Using the formally exact expression of rate constant in terms of flux–side correlation function,³⁹ it can be straightforwardly transformed into a double phase space integral. With the aid of an efficient and accurate method for evaluating matrix elements involving the Boltz-mann operator, the integral can be carried out to obtain very precise results for different scenarios of the reaction barrier. There are also many other extensions proposed to address the thermal operators, including the linearized approximation,⁴⁰ the classical path approximation,^{37,41} and the forward–backward propagation method,³⁷ largely for adiabatic systems.

The SC-IVR method may also be applied to study nonadiabatic dynamics.⁴² By bosonizing electron levels, the classical electron analog gives a way to transform electronic DOFs to classical ones.^{43,44} This creates the possibility to deal with the electronic and nuclear DOFs on the same footing. After the transformation, the electron states are treated as coupled oscillators with parameters linked to the nuclear coordinates. The Hamiltonian of the system is then expressed in terms of additional virtual coordinates and momenta, and the equation of motion can be solved by classical dynamics. In so doing, the dynamics of the non-adiabatic system can be handled within the same framework of SC-IVR for nuclear motions. At the moment, it is fair to say that many attempts exist for extending the SC-IVR to non-adiabatic systems.^{40,42-45} The simultaneous consideration of the contribution of electronic DOFs to the nuclear thermal average and the real-time non-adiabatic dynamics within the SC-IVR framework, however, is rarely studied. In this paper, we explore this possibility and combine the methods of treating non-adiabatic dynamics and Boltzmannized operators.

This paper is organized as follows: in Sec. II, we introduce the basic ideas and explain the details of theories in the different aspects of our method. In Sec. III, we present the results. In Sec. IV, a brief summary and conclusions are given.

II. THEORY AND METHODS

A. The correlation functions and rate constant

The thermal rate constant of a chemical reaction can be expressed in terms of the correlation function³⁹ by

$$k(T) = \frac{1}{Q_{\rm r}(T)} \lim_{t \to \infty} C_{\rm fs}(t), \tag{1}$$

where $Q_{\rm r}(T)$ is the reactant partition function and $C_{\rm fs}(t)$ is the flux-side correlation function, defined as

$$C_{\rm fs}(t) = {\rm Tr}\Big[\hat{F}(\beta)e^{i\hat{H}t/\hbar}\hat{h}e^{-i\hat{H}t/\hbar}\Big].$$
(2)

The notation $\hat{F}(\beta)$ stands for the Boltzmannized flux operator,

$$\hat{F}(\beta) = e^{-\beta \hat{H}/2} \hat{F} e^{-\beta \hat{H}/2}.$$
(3)

The side operator $\hat{h} = h(\hat{s})$ is a projection operator, which takes value of identity at the asymptotic product region and is zero at the asymptotic reactant region. It is usually chosen to be a Heaviside function of the reactive coordinate. The flux operator is the time derivative of \hat{h} , which equals

$$\hat{F} = \frac{i}{\hbar} \Big[\hat{H}, \hat{h} \Big], \tag{4}$$

where \hat{H} is the Hamiltonian of the system.

By taking the time derivative of the flux–side correlation, one obtains the flux–flux correlation function,

$$\frac{dC_{\rm fs}(t)}{dt} = {\rm Tr}\Big[\hat{F}(\beta)e^{i\hat{H}t/\hbar}\hat{F}e^{-i\hat{H}t/\hbar}\Big] \equiv C_{\rm ff}(t).$$
(5)

By rearranging the commutative exponential terms, one can write it in a symmetric form,

$$C_{\rm ff}(t) = \mathrm{Tr}\bigg[\hat{F}\bigg(\frac{\beta}{2}\bigg)e^{i\hat{H}t/\hbar}\hat{F}\bigg(\frac{\beta}{2}\bigg)e^{-i\hat{H}t/\hbar}\bigg],\tag{6}$$

which is numerically more efficient.³⁸

B. Semiclassical initial value representation

The SC-IVR propagator can be expressed as a phase-space integral, $^{\rm 26}$

$$e^{-i\hat{H}t} = \int d\mathbf{q}_0 \int d\mathbf{p}_0 \left[\left| \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right| / (2\pi i\hbar)^D \right]^{1/2} e^{iS_t(\mathbf{q}_t, \mathbf{q}_0)/\hbar} |\mathbf{q}_t\rangle \langle \mathbf{q}_0 |, \quad (7)$$

which originates from the semiclassical approximation of the quantum propagator⁴⁶ and is made computationally useful by transforming variables to the initial phase space.²⁵ Here and after, *D* refers to the total DOFs of the system.

A useful different formulation of the propagator is the coherent state representation developed by Herman and Kluk, ^{25,26}

$$e^{-i\hat{H}t/\hbar} = \frac{1}{(2\pi\hbar)^{D}} \int d\mathbf{p}_{0} \int d\mathbf{q}_{0} C_{t}(\mathbf{p}_{0}, \mathbf{q}_{0})$$
$$\times e^{iS_{t}(\mathbf{p}_{0}, \mathbf{q}_{0})/\hbar} |\mathbf{p}_{t}, \mathbf{q}_{t}\rangle \langle \mathbf{p}_{0}, \mathbf{q}_{0}|.$$
(8)

Here \mathbf{q}_t , \mathbf{p}_t is the coordinate and momentum at time *t*, with the phase-space trajectory starting from \mathbf{q}_0 , \mathbf{p}_0 and dominated by classical dynamics. S_t is the action along this trajectory,

$$S_t(\mathbf{p}_0, \mathbf{q}_0) = \int_0^t dt' \mathbf{p}_{t'} \dot{\mathbf{q}}_{t'} - H(\mathbf{p}_{t'}, \mathbf{q}_{t'}).$$
(9)

 C_t is the Herman–Kluk pre-exponential factor,

$$C_t(\mathbf{p}_0, \mathbf{q}_0) = \sqrt{\frac{1}{2^D} \left| \frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_0} + \Gamma^{-1} \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0} \Gamma - i\hbar \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \Gamma + \frac{i}{\hbar} \Gamma^{-1} \frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_0} \right|}, \quad (10)$$

with all partial derivatives defined under classical trajectory dynamics and Γ being the width matrix of coherent states in Eq. (8), which are minimum-uncertainty wave packets,

$$\langle \mathbf{x} | \mathbf{p}, \mathbf{q} \rangle = \left(\frac{\det \Gamma}{\pi^{D}} \right)^{1/4} e^{-\frac{1}{2} (\mathbf{x} - \mathbf{q})^{\mathrm{T}} \Gamma(\mathbf{x} - \mathbf{q}) + \frac{i}{\hbar} \mathbf{p}^{\mathrm{T}}(\mathbf{x} - \mathbf{q})}.$$
 (11)

Its value is arbitrary but usually chosen with respect to the characteristic frequency of the system. Both formulations of the semiclassical propagator give quantum exact results for potentials no more than quadratic, including free particles and harmonic oscillators, and also have good accuracy in many other situations.

The integrand in Eq. (8) is completely determined by the initial position and momentum of the nuclei and the potential energy surface they move on. Thus, one can substitute the expression for the quantum propagator and obtain the SC-IVR formula of the observables of interest. Since we are dealing with multiple propagators in one expression, for simplicity and conciseness, we will use the notations $\mathbf{z} \equiv (\mathbf{p}, \mathbf{q})$, $\hat{F}_{\beta} \equiv \hat{F}(\beta)$, and

$$e^{-i\hat{H}t/\hbar} = \int d\mathbf{z}_0 |\mathbf{z}_t\rangle \nleftrightarrow \langle \mathbf{z}_0 |, \qquad (12)$$

where the constant factor is absorbed in $d\mathbf{z}_0$ and the symbol \nleftrightarrow is an abbreviation for the factor $C_t(\mathbf{z}_0)e^{iS_t(\mathbf{z}_0)/\hbar}$ in the integrand. We will then use \rightsquigarrow for its complex conjugate. Their values must be evaluated according to the classical trajectory implied by the initial or final state that they point to.

Substituting Eq. (12) into Eq. (6), one gets the flux-flux correlation function under the SC-IVR as

$$C_{\rm ff}(t) = \operatorname{Tr} \int d\mathbf{z}_0 \int d\mathbf{z}_0' \hat{F}_{\beta/2} |\mathbf{z}_0'\rangle \rightsquigarrow \langle \mathbf{z}_t' | \hat{F}_{\beta/2} | \mathbf{z}_t \rangle \rightsquigarrow \langle \mathbf{z}_0 |$$
$$= \int d\mathbf{z}_0 \int d\mathbf{z}_0' \langle \mathbf{z}_0 | \hat{F}_{\beta/2} | \mathbf{z}_0' \rangle \rightsquigarrow \langle \mathbf{z}_t' | \hat{F}_{\beta/2} | \mathbf{z}_t \rangle \rightsquigarrow.$$
(13)

The above double integral in phase space can be evaluated by Monte Carlo sampling of trajectory pairs. Furthermore, if one chooses the weighting function as

$$W(\mathbf{z}_0, \mathbf{z}_0') \propto \left| \left\langle \mathbf{z}_0 | \hat{F}_{\beta/2} | \mathbf{z}_0' \right\rangle \right|^2, \tag{14}$$

then the Monte Carlo average can be rewritten as³⁸

$$C_{\rm ff}(t) = C_{\rm ff}(0) \left\{ \frac{\nleftrightarrow \left(\mathbf{z}'_t | \hat{F}_{\beta/2} | \mathbf{z}_t \right) \bigstar}{\left\langle \mathbf{z}'_0 | \hat{F}_{\beta/2} | \mathbf{z}_0 \right\rangle} \right\}_W.$$
(15)

The same kind of matrix element in the numerator and denominator results from the symmetric form of the flux–flux correlation [Eq. (6)] and is friendlier for implementation. The averaged function is always equal to 1 at t = 0 and very smooth at short times, implying good numerical stability. This will, in some sense, justify the choice of this correlation function formula.

Now, the last thing to be resolved before the Monte Carlo sampling can be done is the evaluation of coherent state matrix elements of the Boltzmannized operator $\hat{F}_{\beta/2}$.

C. Electronically non-adiabatic dynamics

In order to describe dynamics with multiple electronic states, we use the classical electron analog to transform to classical dynamics.^{43,44} The Hamiltonian of an electronically non-adiabatic system is of the form

$$H = \frac{\mathbf{p}^2}{2m} + \begin{bmatrix} V_{11}(\mathbf{x}) & V_{12}(\mathbf{x}) \\ V_{21}(\mathbf{x}) & V_{22}(\mathbf{x}) \end{bmatrix},$$
(16)

where \mathbf{p}, \mathbf{x} refers to nuclear DOFs. When those of the electrons are used in later discussions, we will denote them with a subscript "e." Here, we only consider the simplest case of two diabatic electronic basis, but it is straightforward to extend the formalism to any number of diabatic states.

By making linear transformation from the electronic Hilbert space to the Fock space of two bosonic modes,

$$|0\rangle_{\text{elec}} \rightarrow |1_1 0_2\rangle, |1\rangle_{\text{elec}} \rightarrow |0_1 1_2\rangle, \tag{17}$$

the electronic Hamiltonian can be rewritten as

$$\hat{H}_{e} = \sum_{ij \in \{1,2\}^2} \hat{a}_i^{\dagger} V_{ij}(\mathbf{x}) \hat{a}_j.$$
(18)

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The original system is mapped into the subspace with particle number $n_1 + n_2 = 1$. Transforming the ladder operators to electronic coordinate and momentum by

$$\hat{x}_{i,e} = \frac{1}{\sqrt{2}} (\hat{a}_i^{\dagger} + \hat{a}_i), \qquad \hat{p}_{i,e} = \frac{i}{\sqrt{2}} (\hat{a}_i^{\dagger} - \hat{a}_i),$$
(19)

one finally gets the Hamiltonian in terms of classical position and momentum of the electrons. In a two-level non-adiabatic system, the corresponding Hamiltonian reads

$$H = \frac{\mathbf{p}^2}{2m} + \sum_{i=1}^2 \frac{V_{ii}(\mathbf{x})}{2} \left(x_{i,e}^2 + p_{i,e}^2 - 1 \right) \\ + \frac{V_{12}(\mathbf{x}) + V_{21}(\mathbf{x})}{2} \left(x_{1,e} x_{2,e} + p_{1,e} p_{2,e} \right).$$
(20)

To apply SC-IVR to this non-adiabatic system, the Hamiltonian in Eq. (20) must be used to derive the dynamics. The phase space is now composed of both nuclear and electronic DOFs. The propagator is in the same form as Eq. (12), i.e.,

$$e^{-i\hat{H}t/\hbar} = \int d\mathbf{z}_0 \int d\mathbf{w}_0 |\mathbf{z}_t \mathbf{w}_t\rangle \, \boldsymbol{\swarrow} \, \langle \mathbf{z}_0 \mathbf{w}_0 |.$$
(21)

As stated, z and w refer to the nuclear and electronic variables, respectively. The width parameters of the electronic DOFs are set to 1, which is inherent from the form of the transformation.

D. Non-adiabatic extension of path-integral based methods

When dealing with things related to quantum thermal average, path-integral methods and polymers are almost inevitable in computations. The mainstream methods, including quantum transition state theory (QTST), instanton method, and RPMD, all involve a ring polymer connected with harmonic spring potential whose total energy corresponds to the action of closed trajectories in imaginary time.^{16,23} In order to extend them to non-adiabatic systems, one natural way, in principle, is to introduce the electronic states in the imaginary-time action and then taking partial trace to obtain the effective potential for nuclear degrees of freedom.

In this way, the ring-polymer potential for a single-state system,

$$V_n(\mathbf{x}) = \sum_{k=1}^n \left[\frac{1}{2} m \omega_n^2 (x_j - x_{j+1})^2 + V(x_j) \right],$$
 (22)

will be replaced by its non-adiabatic analog,^{13,47}

$$V_n(\mathbf{x}) = \sum_{k=1}^n \frac{1}{2} m \omega_n^2 (x_j - x_{j+1})^2 - \frac{1}{\beta_n} \ln \operatorname{Tr} \prod_{k=1}^n e^{-\beta_n \hat{V}(x_k)}, \quad (23)$$

which reproduces the nuclear probability density for the polymer. The QTST and instanton methods extended in this way will be used for comparison in this paper to which we refer as mean-field QTST (MF-QTST) and mean-field ring-polymer instanton (MF-RPI). By MF, we mean the fact that the partial trace on electronic DOFs is used for the sampling of the nuclear partition functions. With MF-QTST (MF-RPI), one simply performs a QTST simulation (RPI minimization) using the effective potential in Eq. (23).

E. Path integral method for the Boltzmannized operator

To address the matrix elements in Eq. (15), we use the imaginary-time path integral technique with Monte Carlo sampling. It has been proven to work well on adiabatic reactive systems.³⁸ By taking imaginary-time slices, one can approximate the Boltzmann operator as

$$e^{-\beta \hat{H}/2} = \left(e^{-\Delta\beta \hat{H}}\right)^{P/2} \simeq \left(e^{-\Delta\beta \hat{T}/2} e^{-\Delta\beta \hat{V}} e^{-\Delta\beta \hat{T}/2}\right)^{P/2}, \qquad (24)$$

where $\Delta\beta = \beta/P$. Then, by inserting identity operators, one gets a path-integral form,

$$F_{fi} \equiv \langle \mathbf{z}_{f} | F(\beta) | \mathbf{z}_{i} \rangle$$

$$= \int d\mathbf{x}_{1} d\mathbf{x}_{2} \cdots d\mathbf{x}_{P} \langle \mathbf{z}_{f} | e^{-\Delta\beta\hat{T}/2} | \mathbf{x}_{P} \rangle$$

$$\times \langle \mathbf{x}_{P} | e^{-\Delta\beta\hat{T}} | \mathbf{x}_{P-1} \rangle \cdots \langle \mathbf{x}_{P/2+2} | e^{-\Delta\beta\hat{T}} | \mathbf{x}_{P/2+1} \rangle$$

$$\times \langle \mathbf{x}_{P/2+1} | e^{-\Delta\beta\hat{T}/2} \hat{F} e^{-\Delta\beta\hat{T}/2} | \mathbf{x}_{P/2} \rangle$$

$$\times \langle \mathbf{x}_{P/2} | e^{-\Delta\beta\hat{T}} | \mathbf{x}_{P/2-1} \rangle \cdots \langle \mathbf{x}_{2} | e^{-\Delta\beta\hat{T}} | \mathbf{x}_{1} \rangle$$

$$\times \langle \mathbf{x}_{1} | e^{-\Delta\beta\hat{T}/2} | \mathbf{z}_{i} \rangle e^{-\Delta\beta\sum_{k=1}^{P} V(\mathbf{x}_{k})}. \quad (25)$$

Here, the subscript *i* and *f* stand for the initial and final states of the nuclei, respectively. To simplify the notation, we consider a one-dimensional case in which *x* is the reaction coordinate. Assuming that the side projection operator can be interpreted as a dividing surface $\hat{h} = \Theta(\hat{x})$, the terms in the equation above all have analytical expressions, and

$$F_{fi} = D_{fi} \int dx_1 dx_2 \cdots dx_P (x_{P/2+1} - x_{P/2}) \\ \times \exp\left\{-\frac{\Gamma_{\beta}\Gamma}{2(\Gamma_{\beta} + \Gamma)} \Big[(x_f - x_P)^2 + (x_1 - x_i)^2 \Big] \\ - \frac{\Gamma_{\beta}}{4} \sum_{k=2}^{P} (x_k - x_{k-1})^2 - \frac{\Gamma_{\beta}}{4} (x_{P/2+1} + x_{P/2})^2 \\ + \frac{i}{\hbar} \frac{\Gamma_{\beta}}{(\Gamma_{\beta} + \Gamma)} \Big[p_f (x_f - x_P) + p_i (x_1 - x_i) \Big] - \frac{\beta}{P} \sum_{k=1}^{P} V(x_k) \Big\},$$
(26)

where $\Gamma_{\beta} = 2\Delta\beta^{-1} = 2P/\beta$. D_{fi} is relevant to the initial and final states, and independent of the bead positions inserted. Equation (26) can be reformulated to an expectation value under multi-dimensional Gaussian distribution,

$$F_{fi} = D_{fi} \prod_{j} \sqrt{2\pi} \sigma_{j} \left(\left(x_{P/2+1} - x_{P/2} \right) \exp \left\{ -\frac{\beta}{P} \sum_{k=1}^{P} V(x_{k}) \right\} \right) \\ \times \exp \left\{ \frac{i}{\hbar} \frac{\Gamma_{\beta}}{(\Gamma_{\beta} + \Gamma)} \left[p_{f} \left(x_{f} - x_{P} \right) + p_{i} (x_{1} - x_{i}) \right] \right\} \right)_{w}, \\ w = \exp \left\{ -\frac{\Gamma_{\beta} \Gamma}{2 \left(\Gamma_{\beta} + \Gamma \right)} \left[\left(x_{f} - x_{P} \right)^{2} + \left(x_{1} - x_{i} \right)^{2} \right] \right. \\ \left. - \frac{\Gamma_{\beta}}{4} \sum_{k=2}^{P} \left(x_{k} - x_{k-1} \right)^{2} - \frac{\Gamma_{\beta}}{4} \left(x_{P/2+1} + x_{P/2} \right)^{2} \right\},$$
(27)

and, thus, can be calculated by Monte Carlo sampling.³⁸

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Now, we extend this Boltzmannization to non-adiabatic systems. To the best of our knowledge, it has not been studied. The formulation is nearly unchanged, except for the potential term due to the fact that the potential operators in this case are not scalar or commutable anymore. Adding electronic basis to the inserted identity resolution during derivation of Eq. (25), one obtains the correct form of the term,

$$\mathcal{P} \exp\left\{-\frac{\beta}{P} \sum_{k=1}^{P} \hat{V}(x_k)\right\} = \prod_{k=P}^{1} e^{-\beta \hat{V}(x_k)/P},$$
(28)

where \mathcal{P} is the path-ordering operator, whose meaning is self-explained by the formula. This is exactly the same modification as introduced in Sec. II D, except that in this case, we are dealing with a linear polymer and the two ends are replaced by coherent state wave packets. The final path-integral form is

$$\mathbf{z}_{f} \mathbf{w}_{f} |\hat{F}(\beta)| \mathbf{z}_{i} \mathbf{w}_{i} \rangle$$

$$= \int d\mathbf{x}_{1} d\mathbf{x}_{2} \cdots d\mathbf{x}_{P} \langle \mathbf{z}_{f} | e^{-\Delta\beta \hat{T}/2} | \mathbf{x}_{P} \rangle$$

$$\times \langle \mathbf{x}_{P} | e^{-\Delta\beta \hat{T}} | \mathbf{x}_{P-1} \rangle \cdots \langle \mathbf{x}_{P/2+2} | e^{-\Delta\beta \hat{T}} | \mathbf{x}_{P/2+1} \rangle$$

$$\times \langle \mathbf{x}_{P/2+1} | e^{-\Delta\beta \hat{T}/2} \hat{F} e^{-\Delta\beta \hat{T}/2} | \mathbf{x}_{P/2} \rangle$$

$$\times \langle \mathbf{x}_{P/2} | e^{-\Delta\beta \hat{T}} | \mathbf{x}_{P/2-1} \rangle \cdots \langle \mathbf{x}_{2} | e^{-\Delta\beta \hat{T}} | \mathbf{x}_{1} \rangle$$

$$\times \langle \mathbf{x}_{1} | e^{-\Delta\beta \hat{T}/2} | \mathbf{z}_{i} \rangle \langle \mathbf{w}_{f} | \hat{P} \prod_{k=P}^{1} e^{-\beta \hat{V}(\mathbf{x}_{k})/P} \hat{P} | \mathbf{w}_{i} \rangle, \quad (29)$$

where

(

$$\hat{P} = \int d\mathbf{x} |\mathbf{x}, 0_1 \mathbf{1}_0\rangle \langle \mathbf{x}, 0_1 \mathbf{1}_0 | + |\mathbf{x}, \mathbf{1}_0 \mathbf{0}_1\rangle \langle \mathbf{x}, \mathbf{1}_0 \mathbf{0}_1 |.$$
(30)

It is the projection operator of the single excitation subspace. This projection is essential. Otherwise, the electronic part of coherent

state will contain components from the ground vibrational state or higher excited states that are spurious due to the bosonic mapping. This is especially important when one wants to treat the mapped electronic coordinates with path-integral.⁴⁸

Despite the dividing surface formulation described above, sometimes, it is also appropriate to define projection operators based on electronic states. Let us assume that the second electronic state is the product state. The side operator in this case is

$$\hat{h} = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}.$$
 (31)

In addition, the flux operator is still defined by Eq. (4),

$$\hat{F} = \frac{i}{\hbar} \left[\hat{H}, \hat{h} \right] = \frac{i}{\hbar} \begin{bmatrix} 0 & V_{12}(\mathbf{x}) \\ -V_{12}(\mathbf{x}) & 0 \end{bmatrix},$$
(32)

which contains no derivatives with respect to coordinate. The term in the middle involving the flux operator is now a Gaussian integral,

$$\left\langle \mathbf{x}_{P/2+1} | e^{-\Delta \beta \tilde{T}/2} \hat{F} e^{-\Delta \beta \tilde{T}/2} | \mathbf{x}_{P/2} \right\rangle$$

$$\propto \int d\mathbf{x} \hat{F} \exp\left\{-\frac{\Gamma_{\beta}}{4} \left(\mathbf{x} - \frac{\mathbf{x}_{P/2+1} + \mathbf{x}_{P/2}}{2}\right)^{2}\right\}$$

$$= -\frac{\sigma_{y}}{\hbar} \int d\mathbf{x} V_{12}(\mathbf{x}) \exp\left\{-\frac{\Gamma_{\beta}}{4} \left(\mathbf{x} - \frac{\mathbf{x}_{P/2+1} + \mathbf{x}_{P/2}}{2}\right)^{2}\right\}. \quad (33)$$

It can be evaluated by very low-order approximations when the width of the Gaussian is small enough, which is usually the case with a properly chosen bead number *P*. Following the previous steps in this section, one can derive the path-integral form with this flux operator,

$$\left\langle \mathbf{z}_{f} \mathbf{w}_{f} | \hat{F}(\beta) | \mathbf{z}_{i} \mathbf{w}_{i} \right\rangle = \int d\mathbf{x}_{1} d\mathbf{x}_{2} \cdots d\mathbf{x}_{P} \left\langle \mathbf{z}_{f} | e^{-\Delta\beta \hat{T}/2} | \mathbf{x}_{P} \right\rangle \times \left\langle \mathbf{x}_{P} | e^{-\Delta\beta \hat{T}} | \mathbf{x}_{P-1} \right\rangle \cdots \left\langle \mathbf{x}_{P/2+2} | e^{-\Delta\beta \hat{T}} | \mathbf{x}_{P/2+1} \right\rangle$$

$$\times \left\langle \mathbf{w}_{f} | \hat{P} \prod_{k=P}^{P/2+1} e^{-\beta \hat{\nabla} (\mathbf{x}_{k})/P} \left\langle \mathbf{x}_{P/2+1} | e^{-\Delta\beta \hat{T}/2} \hat{F} e^{-\Delta\beta \hat{T}/2} | \mathbf{x}_{P/2} \right\rangle \prod_{k=P/2}^{1} e^{-\beta \hat{\nabla} (\mathbf{x}_{k})/P} \hat{P} | \mathbf{w}_{i} \right\rangle$$

$$\times \left\langle \mathbf{x}_{P/2} | e^{-\Delta\beta \hat{T}} | \mathbf{x}_{P/2-1} \right\rangle \cdots \left\langle \mathbf{x}_{2} | e^{-\Delta\beta \hat{T}} | \mathbf{x}_{1} \right\rangle \times \left\langle \mathbf{x}_{1} | e^{-\Delta\beta \hat{T}/2} | \mathbf{z}_{i} \right\rangle.$$

$$(34)$$

In both formulations, the matrix element will be localized around the dividing surface or potential crossings, which makes the weighting function in Eq. (14) an appropriate and efficient one.

The zero-time correlation function $C_{\rm ff}(0)$ can be formulated in the same manner, with two flux operators and twice the number of slices. It only needs to be determined once before initial condition sampling and, thus, can be calculated to a very good precision.

III. RESULTS AND DISCUSSIONS

A. Exponential crossing model

The diabatic Hamiltonian for this simple and precise avoided crossing model is

$$\hat{H} = \frac{\hat{p}^2}{2m} + \begin{bmatrix} Ae^{Bx} & \Delta \\ \Delta & Ae^{-Bx} \end{bmatrix},$$
(35)

where x and p refer to nuclear coordinate and momentum and Δ is the coupling matrix element. The fixed parameters are m = 2000, A = 0.02, and B = 2, all in atomic unit so that $\hbar = 1$. A schematic plot of the potential is shown in Fig. 1. The adiabatic energy surface exhibits a gap of 2Δ at x = 0 while the diabatic energies cross here. As can be seen from the step-like curve of the diabatic angle, the derivative coupling is maximized around the gap. In the asymptotic reactant and product region, the electron can only live on the corresponding diabatic (and also adiabatic) basis since the energy of the other is too large. This indicates that the reaction must be accompanied by electron transition and, thus, can be strongly influenced by the coupling strength. For $\Delta \rightarrow 0$, the coupling can be regarded as perturbation and the reaction rate constant is predicted to be $\sim \Delta^2$ according to the Fermi golden rule.

The dividing surface is chosen such that $h = \Theta(x)$. Pairs of initial conditions are generated by the Metropolis algorithm with the weighting function in Eq. (14). They are then propagated for long enough time for the flux-flux correlation function to converge to zero. The trapezoidal rule is applied on equally spaced time grids for numerical integration to get the flux-side correlation function. The number of beads is chosen to be P = 4 at 1000 K and is adjusted to be inversely proportional to temperature. To accelerate Monte Carlo sampling of matrix elements of the Boltzmannized operator,



FIG. 1. Schematic plot of diabatic potential surface, adiabatic energies, and diabatic angle of the avoided crossing model with $\Delta = 0.004$. The adiabatic angle with respect to reactant electronic states is scaled and plotted in green dots. V_{11} and V_{22} are defined in Eq. (35).



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FIG. 2. Arrhenius plots of the avoided crossing model. The sharp turns on instanton results indicate the breakdown point (the crossover temperature).

the random numbers are drawn from a Sobol quasi-random number generator, and the sample size is set to 2^{14} . About 10^6 trajectories are propagated for each data point to reach a statistical error less than 2%. The Arrhenius plots are shown in Fig. 2. It is based on the flux-flux and flux-side correlation functions, of which some are plotted in Fig. 3. One can see that these functions are well-converged from their imaginary parts whose expected values are zero. In Fig. 2, quantum exact values, MF-QTST results, and MF-RPI results are taken into comparison.

For $\Delta = 4 \times 10^{-3}$ (upper panel), our NA-IVR&PI results are very accurate at high temperatures, while at low temperatures, there is an error of about 20% in the rate constant. This is due to the systematic error of the semiclassical approximation on the description of deep barrier tunneling. However, it still works better than 2



FIG. 3. The calculated correlation functions of the avoided crossing model. The parameters are T = 1000 K and $\Delta = 4 \times 10^{-3}$ for the upper panel and T = 500 K and $\Delta = 4 \times 10^{-4}$ for the lower panel. All correlation functions are normalized by dividing by the initial flux-flux correlation $C_{\rm ff}(0)$.

the MF-QTST method, which is only approximately accurate at both high and low temperature regions. The instanton methods work well at very low temperatures, but they break down due to instanton collapse above certain temperature and are no longer available at this region.

For $\Delta = 4 \times 10^{-4}$ (lower panel), the low-temperature region shows the same trend as mentioned above, but the high-temperature region is different because it is reaching the golden rule limit where $\Delta/kT \rightarrow 0$. The system in this limit shows a strong non-adiabatic effect and recrossing behavior, and all tested methods tend to break down here. The reason for the breakdown of the NA-IVR&PI method can be intuitively understood from the lower panel of Fig. 3. The flux-side correlation function in this case is not monotonic and converges to a small value with respect to its maximum. The absolute error of the flux-flux correlation is small at all time, but the sign canceling makes it accumulated and results in a relatively large error after integration.

In order to overcome the difficulty, we make use of the flexibility of choice discussed in Sec. II E and use the projection operators based on electronic states as specified by Eq. (32). The rate constant is independent of this choice and shall keep the same value, while the shape of the correlation functions will change accordingly. In the weak coupling limit, the zero-time flux-flux correlation tends to zero at the order of Δ^2 so that we can expect a good numerical behavior of the normalized flux-side correlation. The correlation functions obtained under different projection operators are plotted in Fig. 4, and the result from the new one is marked in Fig. 2 as NA-IVR&PI-e. While the dividing surface formulation totally breaks down, the choice based on electronic states yields very wellbehaved and accurate results. In this way, we have circumvented the problem while keeping the main body of the theoretical framework. By reasonably choosing the projection operator, it is now possible to handle almost all parameter ranges within this NA-IVR&PI framework.



FIG. 4. Flux–side correlation functions calculated under T = 1000 K and Δ = 4 \times 10⁻⁴. The upper panel is based on the dividing surface, while the lower panel is based on the electronic state.

IV. CONCLUSION

In this paper, we implemented the non-adiabatic semiclassical initial value representation with path-integral sampling (NA-IVR&PI) and investigated the correlation functions and the reaction rate constant of the exponential avoided crossing model. With the aid of electronic state-based dividing surface, the method is capable of handling the extreme case of the golden rule limit. The results are accurate enough compared to other existing methods, and it works well in almost all scenarios with different parameters, showing very good generality.

These outcomes are promising and show the potential of the NA-IVR&PI method. In the future, it might be a powerful tool for the investigation of chemical reactions.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jiaxi Zeng: Conceptualization (equal); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Writing – original draft (lead); Writing – review & editing (equal). Xin-Zheng Li: Conceptualization (equal); Funding acquisition (lead); Resources (lead); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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