Nonadiabatic instanton rate theory beyond the golden-rule limit

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Fermi’s golden rule describes the leading-order behaviour of the reaction rate as a function of the diabatic coupling. Its asymptotic ($\hbar \to 0$) limit is the semiclassical golden-rule instanton rate theory, which rigorously approximates nuclear quantum effects, lends itself to efficient numerical computation and gives physical insight into reaction mechanisms. However the golden rule by itself becomes insufficient as the strength of the diabatic coupling increases, so higher-order terms must be additionally considered. In this work we give a first-principles derivation of the next-order term beyond the golden rule, represented as a sum of three components. Two of them lead to new instanton pathways that extend the golden-rule case and, among other factors, account for effects of recrossing on the full rate. The remaining component derives from the equilibrium partition function and accounts for changes in potential energy around the reactant and product wells due to diabatic coupling. The new semiclassical theory demands little computational effort beyond a golden-rule instanton calculation. It makes it possible to rigorously assess the accuracy of the golden-rule approximation and sets the stage for future work on general semiclassical nonadiabatic rate theories.

I. INTRODUCTION

Semiclassical instanton rate theory\textsuperscript{1–8} is becoming a well-established method for describing chemical reactions on a single Born–Oppenheimer potential energy surface (PES).\textsuperscript{9–17} The theory accounts for nuclear quantum effects such as tunnelling in an approximate but rigorous manner and scales favourably with system size. Hence it can be readily applied to full-dimensional \textit{ab initio} simulations of chemical transformations. The favourable scaling arises because (in the simplest case) the instanton rate derives from a single classical trajectory. This not only simplifies the calculation compared to the full quantum treatment, but also offers direct mechanistic insight, as this trajectory defines the dominant tunnelling pathway, which can easily be visualised.

However, a description in terms of a single Born–Oppenheimer PES is only valid for systems with strong diabatic coupling, $\Delta$. Away from this limit the Born–Oppenheimer approximation breaks down, and the chemical process is said to be nonadiabatic. For weak diabatic coupling, nonadiabaticity can be effectively described with perturbation theory, taking the uncoupled diabatic Hamiltonian\textsuperscript{18} as the reference. In the case of reaction rates, the leading-order perturbation term (second order in $\Delta$) is the well-known Fermi’s golden rule (GR).\textsuperscript{19,20} This can be formally expressed in terms of path integrals, whose evaluation by steepest descent leads to semiclassical golden-rule instanton rate theory.\textsuperscript{21–25} Like its Born–Oppenheimer counterpart, this semiclassical theory rigorously approximates the quantum rate using information from (typically) a single classical trajectory and hence enjoys the same computational advantages. The theory has been extended\textsuperscript{25,26} into the Marcus inverted regime\textsuperscript{27,28}—a considerable methodological challenge for most path-integral methods—and has been used for \textit{ab initio} calculations of spin-crossover rates for thio-phosgene, showing unprecedented accuracy when compared with experiment.\textsuperscript{29}

That said, Fermi’s golden rule is only accurate if the next term in the perturbation expansion of the full nonadiabatic rate is small by comparison. In other words, the GR expression should only be used if the diabatic coupling is sufficiently weak. This assumption is often true for electron-transfer\textsuperscript{18,28,30–33} and spin-crossovers\textsuperscript{34,35} reactions, although its validity is by no means guaranteed. One expects to also find systems with intermediate values of the diabatic coupling, lying in a “grey area” where neither Born–Oppenheimer nor golden-rule rate theory are valid.\textsuperscript{36–41} This intermediate regime has always been of great interest, and the search for a corresponding practical nonadiabatic rate theory is ongoing.\textsuperscript{42}

Considerable progress\textsuperscript{43–48} has been made for dissipative systems that can be mapped onto a spin–boson model,\textsuperscript{49} which is typically used to represent electron transfer in solution.\textsuperscript{50} Our goal, however, is to develop a full-dimensional theory of molecular reactions, for which instanton methods are particularly well suited. In contrast to studies of electron transfer in solution, here we do not focus on solvent effects or chemical processes dominated by diffusive motion along the reaction coordinate. Instead the key requirement for our theory is that it be applicable to multidimensional anharmonic potentials, such as those found in \textit{ab initio} simulations of gas-phase reactions.

Early work that paved the way for such developments includes Landau–Zener (LZ) theory,\textsuperscript{51,52} which gives the correct classical (high-temperature) rate constant for a one-dimensional linear system in the GR limit\textsuperscript{33,53,54} and which has been used in uniform rate expressions for reduced models of electron transfer.\textsuperscript{44,45,50} Zhu–Nakamura theory\textsuperscript{55–58} is a generalisation of LZ that accounts for nuclear quantum effects and hence yields an approximation to the reaction rate, applicable at any temperature or...
strength of diabatic coupling. Both theories are, however, limited to one-dimensional systems, and are only strictly rigorous for linear potentials.\textsuperscript{54,58} Their other limitation is conceptual, as neither provides the same mechanistic insight as semiclassical instantons, since no stationary-action pathways are computed.

An alternative approach was proposed in a recent publication by Lawrence et al.,\textsuperscript{59} who introduce an interpolation formula connecting the golden-rule and the adiabatic (Born–Oppenheimer) limits. The formula is inspired by the Zusman equation, originally derived for the rate of electron transfer in the classical, high-friction limit.\textsuperscript{43,48,60} In contrast to the Zusman equation, the interpolation formula can account for nuclear tunnelling and zero-point energy effects, as it inherits "quantumness" from its inputs of a golden-rule and an adiabatic rate theory (originally Wolynes theory\textsuperscript{61} and ring-polymer molecular dynamics (RPMD),\textsuperscript{62–64} but could equally be the closely related instanton rate theories\textsuperscript{4,21}). Unlike Landau–Zener and Zun–Nakamura theories, the interpolation formula is obtained following a more heuristic approach, wherein lie both its strength and its weakness. On the one hand, the method is readily applicable to multidimensional systems. On the other hand, because it is not derived from a rigorous nonadiabatic rate theory, there is no systematic way of improving it. It is also not obvious that the interpolation formula should be effective in cases where golden-rule and adiabatic reaction mechanisms are qualitatively different. An extreme example of this is provided by the Marcus inverted regime, for which the adiabatic rate is undefined.\textsuperscript{59} In light of this we think that approaches such as the interpolation formula can be complemented by a first-principles rate theory tackling the intermediate nonadiabatic regime.

A general nonadiabatic instanton solution for arbitrary diabatic coupling strengths has been proposed by Voth and co-workers.\textsuperscript{65–68} It is based on the assumption that the reaction rate is related to the imaginary part of the barrier partition function. This approach, known as the Im $F$ premise,\textsuperscript{69–73} has been validated for both adiabatic\textsuperscript{6,8,74} and golden-rule instantons\textsuperscript{21,66} by demonstrating that the Im $F$ expressions recover the semiclassical limits of the corresponding quantum rate theories based on the flux-correlation formalism.\textsuperscript{75} The same has not yet been accomplished in the general nonadiabatic case, implying that the definitions of (imaginary) barrier partition functions used by Voth and co-workers are not rigorously justified. The first formulation to be suggested\textsuperscript{65,66} was later determined to be incomplete, as it fails to recover adiabatic rates.\textsuperscript{67} It was superseded by the approach in Ref. 67, later given the name “mean-field ring-polymer instanton”\textsuperscript{76} Although this has the correct behaviour in the adiabatic limit, like all mean-field path-integral methods, it fails to recover the classical golden-rule limit without \textit{ad hoc} corrections.\textsuperscript{68} Furthermore, like with the interpolation formula, it is not obvious how it can be generalised to describe the Marcus inverted regime.

In light of this, the search is still out for a rigorous nonadiabatic instanton theory. This would be of interest not only as a numerical method for predicting rates, but also as a key to understanding the interplay of nuclear tunnelling and electronic nonadiabaticity in chemical reactions. Moreover, instanton theories are a powerful tool for the design and/or theoretical justification of path-integral sampling and dynamics approaches that go beyond steepest-descent integration. Such a connection to semiclassical instantons has been made both in the adiabatic and weak-coupling limits for RPMD,\textsuperscript{6,62–64} quantum transition-state theory,\textsuperscript{4,77,78} quantum instanton\textsuperscript{79–81} and golden-rule quantum transition-state theory (GR-QTST).\textsuperscript{82,83} Approaches proposed for intermediate coupling strengths\textsuperscript{68,84–94} currently lack this rigorous connection,\textsuperscript{82,83,95,96} and their future development may be inspired and aided by a first-principles semiclassical theory.

In this paper we develop a semiclassical instanton theory for the second term in the perturbation expansion of the exact nonadiabatic reaction rate. The term appears in the series immediately after the golden-rule expression and is fourth order in the diabatic coupling $\Delta$. In Sec. II we formally define the rate, develop a perturbation series in the diabatic representation and give a brief summary of how the semiclassical limit of the leading-order term (the GR instanton) can be derived. In Sec. III we derive the quantum-mechanical fourth-order term, casting it as a sum of three components that are individually amenable to approximation by steepest descent. Applying the approximation in Sec. IV we arrive at a semiclassical formula for the new term, whose numerical accuracy is tested on a one-dimensional predissociation model and a multidimensional spin–boson system in Sec. V. Our results and outlook on future work are summarised in Sec. VI.

Because the fourth-order rate comprises three components, and the asymptotic behaviour of each has to be analysed individually, the amount of mathematical manipulation in Secs. III and IV is considerable. The salient point is that the semiclassical instanton expressions in this work derive from a rigorous flux-correlation formulation of the quantum rate. For reference, the final results are given by Eqs. (68)–(71), Eqs. (82)–(88) and Eqs. (90)–(93), which define the three components of the fourth-order rate constant. Despite the lengthy derivations, these expressions are all easily evaluated and require little computational effort beyond a golden-rule instanton calculation.

II. THEORETICAL BACKGROUND

We consider a system that comprises two diabatic states,\textsuperscript{50} $|0\rangle$ and $|1\rangle$, with corresponding nuclear Hamil-
tonian operators

\[ \hat{H}_n = \sum_{j=1}^{f} \frac{\hat{p}_j^2}{2m} + V_n(\hat{x}), \tag{1} \]

where \( n \in \{0,1\} \). Here \( f \) is the number of nuclear coordinates, which have been mass-weighted so that each has the same mass \( m \), and \( V_n \) are the diabatic potential energy surfaces (PESs). We assume that the system is in the Marcus normal regime, implying that the diabatic PESs intersect along a seam for which \( \nabla V_0 \cdot \nabla V_1 < 0 \). The states interact via the diabatic electronic coupling operator, \( \Delta = \Delta(\hat{x}) \), which is assumed to vary slowly with respect to \( x \). The total Hamiltonian expressed in the diabatic basis is then

\[ \hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} = \left( \begin{array}{cc} \hat{H}_0 & 0 \\ 0 & \hat{H}_1 \end{array} \right) + \lambda \left( \begin{array}{cc} 0 & \Delta \\ \Delta & 0 \end{array} \right), \tag{2} \]

where \( \lambda \) is a dimensionless parameter used to track the order of the perturbative terms. At the end of the derivation we set \( \lambda = 1 \). Identifying \( |0\rangle \) and \( |1\rangle \) as the reactant and product states respectively, we introduce the operator \( \hat{h} = |1\rangle \langle 1| \) that projects onto the product state. Its time derivative is the flux operator,

\[ \hat{F} = \frac{1}{i\hbar}[\hat{h}, \hat{H}] = \lambda \left( \begin{array}{cc} 0 & -\Delta \\ \Delta & 0 \end{array} \right). \tag{3} \]

In what follows we give the formally exact expression for the thermal rate constant associated with the transition from \( |0\rangle \) to \( |1\rangle \) and outline the derivation of its \( \lambda \to 0 \) limit (i.e., Fermi’s golden rule) and the corresponding semiclassical approximation.

A. The flux-correlation and Green’s function formalisms

Following Ref. 97, we define the reactant and product partition functions

\[ Z_r = \text{Tr} \left[ e^{-\beta \hat{H}} (1 - \hat{h}) \right], \quad Z_p = \text{Tr} \left[ e^{-\beta \hat{H}} \hat{h} \right], \tag{4} \]

and the initial reactant population

\[ \chi_r = \frac{1}{Z_r} \text{Tr} \left[ \hat{\rho}_r (1 - \hat{h}) \right], \tag{5} \]

where \( \beta = 1/k_B T \) and \( Z_r = \text{Tr} [\hat{\rho}_r] \). Here \( \hat{\rho}_r \) is the symmetric thermal density operator\textsuperscript{75,98}

\[ \hat{\rho}_r = e^{-\beta \hat{H}/2} (1 - \hat{h}) e^{-\beta \hat{H}/2}, \tag{6} \]

which models the system at thermal equilibrium in the reactant well. Depending on the system, the initial reactant population may be exactly equal, or very close to, one. In our theory the deviation of \( \chi_r \) from unity cannot always be neglected, and so we use Eq. (2.21) of Ref. 97 to define the rate \( k(\beta) \) as

\[ k(\beta) = \frac{\tilde{k}(\beta)}{Z_r} = \frac{1}{Z_r} \int_0^{t_{pl}} C_{FF}(t) \, dt, \tag{7a} \]

\[ C_{FF}(t) = \frac{1}{i\hbar} \text{Tr} \left\{ [\hat{H}, \hat{\rho}_r] e^{i\hat{H}t/\hbar} \tilde{F} e^{-i\hat{H}t/\hbar} \right\}, \tag{7b} \]

\[ \tilde{Z}_r = Z_r \left( \chi_r - [1 - \chi_r] Z_r/Z_p \right), \tag{7c} \]

where \( C_{FF}(t) \) is the flux-correlation function and \( \tilde{k}(\beta) \) is a “reduced” thermal rate introduced for notational convenience. The expression assumes a separation of time scales, such that the flux-correlation function decays to zero for \( t_{pl} < t < t_{rxn} \). Here \( t_{pl} \) is some “plateau time” that is significantly shorter than the reaction time scale \( t_{rxn} \).\textsuperscript{75,100} In this work we consider the limit of small diabatic coupling, for which \( t_{rxn} \to \infty \), enabling us to also take the limit \( t_{pl} \to \infty \).

In cases when \( \chi_r = 1 \) (e.g., bimolecular scattering reactions), this rate expression reduces to the well-known form\textsuperscript{75,100} with \( Z_r \) in place of \( \tilde{Z}_r \). However, if \( \chi_r \neq 1 \) (e.g., in the condensed phase), there exist other reasonable choices for \( \hat{\rho}_r \), not necessarily leading to equivalent rate constants (see Appendix of Ref. 97). In all of the systems and regimes considered here (see Sec. V) this effect is essentially negligible, as can be explained with the help of the asymptotic analysis presented in this work.\textsuperscript{101} The same analysis shows that significant differences between alternatives can in principle emerge in extremely asymmetric and/or low-temperature systems. Cases where this effect becomes noticeable may arise for one of the following reasons. Firstly, the assumption of separation of time scales may break down, so that the more general expression in Eq. (2.13) of Ref. 97 must be used to define the rate.\textsuperscript{59} Secondly, the ambiguity may be due to how we determine if a chemical species is a reactant or a product (i.e., the definition of the projection operator \( \hat{h} \)).\textsuperscript{99} Lastly, the phenomenological rate constant may depend on the initial state of the system.\textsuperscript{97} The last two possibilities indicate that a “unique” thermal rate constant can occasionally be an ill-defined quantity, even within exact quantum theory and experiment. However, in many cases (such as those we consider in this paper) the rate constant is well behaved and essentially independent of these choices.

With the terms in Eq. (2) treated as a reference Hamiltonian, \( \hat{H}^{(0)} \), and a perturbation, \( \hat{H}^{(1)} \), we can expand the rate constant \( k(\beta) \) as a power series in \( \lambda \), namely

\[ k(\beta) = \sum_{\nu=1}^{\infty} \lambda^{2\nu} k_{2\nu}(\beta). \tag{8} \]

Note that in the above expression, coefficients of odd powers of \( \lambda \) are identically zero. The leading (second-order) term is obtained by noting that \( \tilde{Z}_r \sim Z_{r,0} = \text{Tr} [e^{-\beta \hat{H}_0}] \) and \( e^{-\hat{H}z/\hbar} \sim \hat{K}_0(z) |0\rangle \langle 0| + \hat{K}_1(z) |1\rangle \langle 1| \) as
\[ \lambda \to 0, \text{ where we define the propagator } K_n(z) = e^{-\hat{H}_n z / \hbar} \]

and complex time \( z = \tau + i t \). Here \( \text{Re}(z) \equiv \tau \) corresponds to imaginary time, and \( \text{Im}(z) \equiv t \) corresponds to real time. To second order, the flux correlation is \( C_{FF}(t) \sim \lambda^2 [c_2(z) + c_2(\beta \hbar - z)] \), with

\[ c_2(z) = \text{Tr} \left[ \hat{K}_0(\beta \hbar - z) \hat{K}_1(z) \right]. \tag{9} \]

Substituting this into Eq. (7a) with \( t_{pl} \to \infty \) yields upon simplification\(^8,18,60,102\)

\[ k_2(\beta) = \frac{1}{Z_{r,0}} \int_{-\infty}^{\infty} c_2(z) \, dt, \tag{10} \]

which follows because \( \text{Re}[c_2(z)] \) is even in \( t \), allowing us to first replace the original integral with \( \frac{1}{2} \int_{-\infty}^{\infty} dt \). Then, since \( c_2(z) \) is an analytic function, we can use Cauchy’s integral theorem\(^3\) to show that the integrals over \( c_2(z) \) and \( c_2(\beta \hbar - z) \) are equal, resulting in Eq. (10). This also shows that \( k_2 \) does not depend on \( \tau \), since both \( Z_{r,0} \) and the integral are \( \tau \)-independent. An important consequence of this is that \( \tau \) can be freely chosen in a way that simplifies the evaluation of the integral, as discussed later.

Equation (10) is precisely the GR limit mentioned previously. To go beyond it to the next-order contribution, \( k_4(\beta) \), one could proceed via the flux-correlation formalism, expanding the propagator in a time-dependent perturbation series. Doing so results in a \( k_2 \) expressed in terms of components that have similar magnitudes but opposite signs. Apart from the numerical difficulties associated with evaluating such an expression accurately, it is not obvious how it can be effectively approximated using integration by steepest descent. We will show that a better starting point is afforded by the Green’s function formalism\(^21,50,106\). Central to this is the Green’s function operator, which is the Laplace transform of the full propagator,

\[ \hat{G}(E) = \lim_{\eta \to 0^+} -\frac{1}{\hbar} \int_0^\infty e^{-i\hat{H} t / \hbar} e^{i(E+\imath \eta) t / \hbar} \, dt \]

\[ = \lim_{\eta \to 0^+} \frac{1}{E + i \eta - \hat{H}}. \tag{11} \]

Its imaginary part can be more simply written as the Fourier transform of the propagator, and is thus related to the density of states,

\[ \text{Im} \hat{G}(E) = -\frac{1}{2\hbar} \int_{-\infty}^{\infty} e^{-i\hat{H} t / \hbar} e^{iE t / \hbar} \, dt \]

\[ = -\pi \delta(E - \hat{H}). \tag{12} \]

This can be used to calculate the cumulative reaction probability at energy \( E \),\(^75,106\)

\[ P(E) = 2\hbar^2 \text{Tr} \left[ \text{Im} \hat{G}(E) \hat{F} \text{Im} \hat{G}(E) \hat{F} \right], \tag{13} \]

which in turn is related to the thermal rate constant in Eq. (7a) with \( t_{pl} \to \infty \) via

\[ \tilde{k}(\beta) = \int_0^\infty C_{FF}(t) \, dt = \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} e^{-\beta E} P(E) \, dE. \tag{14} \]

One advantage of this formalism is that the perturbation series for the Green’s function operator, readily obtained from the Dyson equation,\(^50\) has a particularly simple form,

\[ \hat{G} = \sum_{\nu=0}^{\infty} \lambda^\nu \left[ \hat{G}^{(0)} \hat{H}^{(1)} \right]^\nu \hat{G}^{(0)}, \tag{15} \]

where \( \hat{G}^{(0)} = \hat{G}_0 |0\rangle \langle 0 | + \hat{G}_1 |1\rangle \langle 1 | \) is the Green’s function operator for the unperturbed problem, with \( \hat{G}_n \) given by Eq. (11) with Hamiltonian \( \hat{H}_n \). Substituting this into Eqs. (13) and (14) leads to a perturbation series for \( \tilde{k} \) that is analogous to Eq. (8). The crucial difference is that this formalism leads to expressions for rate constants that are naturally separated into terms amenable to semiclassical approximation.

To illustrate how the two alternative formalisms connect, let us re-derive Eq. (10) starting from the perturbation series

\[ P(E) = \sum_{\nu=1}^{\infty} \lambda^{2\nu} P_{2\nu}(E) \tag{16} \]

and considering its \( \nu = 1 \) term,

\[ P_2(E) = 4 \text{Tr} \left[ \text{Im} \hat{G}_0(E) \hat{\Delta} \text{Im} \hat{G}_1(E) \hat{\Delta} \right]. \tag{17} \]

Taking the Boltzmann average and using the relation in Eq. (12) gives the first term in the perturbation series for \( \tilde{k} \),

\[ \tilde{k}_2(\beta) = \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} e^{-\beta E} P_2(E) \, dE \]

\[ = \frac{-\beta}{2\pi \hbar} \int_{-\infty}^{\infty} du_1 \int_{-\infty}^{\infty} du_2 \frac{e^{-\beta E(iu_1+iu_2)/\hbar}}{\text{Tr} \left[ \hat{K}_0(iu_2) \hat{\Delta} \hat{K}_1(iu_1) \hat{\Delta} \right]}. \tag{18} \]

The integral over energy can be simplified by the variable transformation \( i = u_1 + u_2 \), \( t = (u_2 - u_1)/2 \), and the integration contour for the new variable \( i \) can be shifted along the imaginary-time axis, \( t \to t - i \beta \hbar \), so that the energy integral becomes

\[ \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} e^{iEt/\hbar} \, dE = \delta(t). \tag{19} \]

Integrating over \( t \) leaves

\[ \tilde{k}_2 = \int_{-\infty}^{\infty} \text{Tr} \left[ \hat{K}_0(\beta \hbar - i t) \hat{\Delta} \hat{K}_1(\beta \hbar + i t) \hat{\Delta} \right] \, dt. \tag{20} \]

At this point we recognise that the remaining integration variable can also be shifted along the imaginary-time axis, and use \( k_2 = k_2/Z_{r,0} \) to recover Eq. (10). This approach is generalised in Sec. III to derive the next term in the series, \( k_4 \).
B. Semiclassical approximation

We now summarise previous derivations of the semiclassical approximation to $k_2(\beta)$.\textsuperscript{8,25} Calculating the quantum correlation function is only computationally feasible for low-dimensional or particularly simple model systems. Applications to realistic chemical reactions call for approximations to Eq. (10) that make the calculation computationally tractable. The approach that we use is to expand the trace in terms of position eigenstates and replace the exact quantum propagator with its semiclassical counterpart,\textsuperscript{107–109}

$$\langle x_i | \hat{K}_n (\tau_n) | x_i \rangle \sim K_n^\infty (x_i, x_i, \tau_n) = \sum_{\text{traj.}} \frac{C_n}{(2\pi \hbar)^{1/2}} e^{-S_n/\hbar},$$

where ‘$\sim$’ denotes an asymptotic relationship\textsuperscript{110} and the sum is over all classical trajectories that travel from $x_i$ to $x_f$ in imaginary time $\tau_n$ (typically only one of which dominates). $S_n \equiv S_n(x_i, x_i, \tau_n)$ is the corresponding stationary Euclidean action,

$$S_n[x(\cdot)] = \int_0^{\tau_n} \left[ \frac{m}{2} \left| \frac{dx}{du} \right|^2 + V_n(x(u)) \right] du,$$  

and

$$C_n = \left| \frac{\partial^2 S_n}{\partial x_i \partial x_i} \right|.$$  

Hence we can write

$$\tilde{k}_2 \sim \int \int \int_0^\infty dx' dx'' dt \left[ \frac{C_0 C_1}{(2\pi \hbar)^{1/2}} \frac{\Delta(x') \Delta(x'')}{\hbar^2} e^{-S_2/\hbar},$$

where $S_2(x', x'', \tau) = S_0(x', x'', \beta \hbar - \tau) + S_1(x', x', \tau)$. The semiclassical approximation to the exact propagator in Eq. (21) is obtained by steepest-descent integration of its path-integral representation.\textsuperscript{111} The same technique can be applied to approximate the remaining integrals in Eq. (24). For a one-dimensional example this typically reads

$$\int_a^b \frac{g(x) e^{-\phi(x)/\hbar}}{dx} dx = \frac{g(x) e^{-\phi(x)/\hbar}}{dx} \int_{-\infty}^\infty \exp \left[ -\frac{d^2 \phi(x - \bar{x})^2}{2 \hbar} \right] dx$$

as $\hbar \to 0$, where the double derivative $d^2 \phi / dx^2 > 0$ is evaluated at the point $\bar{x}$ where $\phi(x)$ reaches its minimum value on the interval $(a, b)$, with the corresponding first derivative satisfying $d\phi / dx = 0$. In effect, the steepest-descent approximation consists in replacing the exponentiated function with its Taylor series expansion about $\bar{x}$, truncated at the second-order term. All remaining factors are replaced with the leading-order terms in their series expansions about the same point, and the integration bounds are extended to $\pm \infty$. The resulting Gaussian integral can then be evaluated analytically. The relative error associated with this approximation becomes vanishingly small as $\hbar \to 0$, provided certain conditions are satisfied. In particular, we can ignore higher-order terms in the Taylor series expansion of $\phi(x)$ as long as $d^2 \phi / dx^2$ is not itself vanishingly small. Similarly, we can extend the integration range to span the entire real line provided the stationary point $\bar{x}$ does not lie infinitesimally close to either of the bounds. Finally, we can replace $g(x)$ with its value at the stationary point, provided $g(x)$ does not vary rapidly in its vicinity. Later in the paper we encounter cases where some of these conditions are not satisfied, at which point the procedure is modified accordingly.

For completeness we note that all of the above also applies to functions with multiple minima within the integration domain, provided these are well separated from each other. If this condition is satisfied, one may sum over the contributions from all such minima, as in Eq. (21), which ultimately leads to a sum over contributions from competing reaction mechanisms. However, no general steepest-descent prescription is available for when this condition is not satisfied, such as is typically encountered when calculating reaction rates in liquid systems, to which the instanton approach is not directly applicable.\textsuperscript{8} Tackling such systems would require the use of path-integral sampling methods. From here on we assume that our system is well behaved such that the relevant minima are isolated from each other, and focus on one minimum at a time.

The asymptotic limit of Eq. (24) can then be obtained by generalising Eq. (25) to multiple dimensions. The stationary point $(x', x''; \tau)$ satisfies\textsuperscript{8,21,25}

$$\frac{\partial S_2}{\partial x'} = p_0 - p_1 = 0$$

$$\frac{\partial S_2}{\partial x''} = p_1' - p''_0 = 0$$

$$\frac{\partial S_2}{\partial \tau} = E_1 - E_0 = 0,$$

where $E_n$ are the energies of a classical trajectory comprised of two parts $(n \in \{0, 1\})$. The first part corresponds to travelling on $V_0$ from $x'$ to $x'$ over an imaginary time $\beta \hbar - \tau$, with initial and final momenta $p_0'$ and $p_0'$. The second part corresponds to travelling on $V_1$ from $x'$ to $x'$ over an imaginary time $\tau$. The conditions in Eq. (26) follow directly from the definition of $S_2$ and the relations

$$\frac{\partial S_2}{\partial x_i} = -p_i, \quad \frac{\partial S_2}{\partial x_i} = p_i, \quad \frac{\partial S_2}{\partial \tau} = E_n.$$  

The path that makes the combined $S_2$ action stationary is therefore a periodic classical trajectory in imaginary time with period $\beta \hbar$, comprised of a reactant and
a product segment. Conservation of energy and momentum imposed by Eq. (26) implies that at the hopping points $x', x''$, where the two segments join, the trajectory is continuous. Together with time-reversal symmetry this typically imposes $x' = x'' = x^1$, where $x^1$ is a point on the seam along which the reactant and product potential energies are equal. This stationary path is known as the golden-rule instanton.

In the Marcus normal regime, which we assume throughout this work, the value of $\tau$ that extremises the action (which we will call $\tau_\text{g}$) is in the range $0 < \tau_\text{g} < \beta \hbar$. The instanton is a first-order saddle point of the action and can be found by discretising the trajectory (i.e., representing it as a ring polymer) and performing multidimensional optimisation of the resulting extended classical system. This is closely related to the analogous procedure for adiabatic instantons, except now one must optimise the action in $\tau$ as well as $x'$ and $x''$. At the end of the optimisation one calculates the action $S_2$ and its Hessian

$$\Sigma_2 = \begin{pmatrix}
\frac{\partial^2 S_2}{\partial x'^2} & \frac{\partial^2 S_2}{\partial x'^2 \partial x''} & \frac{\partial^2 S_2}{\partial x''^2} \\
\frac{\partial^2 S_2}{\partial x'^2 \partial \tau} & \frac{\partial^2 S_2}{\partial x'^2} & \frac{\partial^2 S_2}{\partial x'^2 \partial \tau} \\
\frac{\partial^2 S_2}{\partial x''^2 \partial \tau} & \frac{\partial^2 S_2}{\partial x''^2} & \frac{\partial^2 S_2}{\partial x''^2 \partial \tau}
\end{pmatrix}$$

(28)

at the stationary point $(x'^1, x''^1, \tau_\text{g})$. The multidimensional generalisation of Eq. (25), along with the Cauchy–Riemann equations relating the partial derivatives with respect to $\tau$ and $t$, gives

$$\tilde{k}_2 \sim \tilde{k}^{sc}_2 = \sqrt{2\pi \hbar} \frac{\lambda^2}{h^2} \sqrt{-\Sigma_2} \, e^{-S_2/\hbar}.$$  

(29)

To complete the derivation, the semiclassical approximation to the reactant partition function $Z_{r,0}$ is evaluated following the same approach. This time the trajectory that makes the action stationary is collapsed at the bottom of the reactant well, and in the absence of translational or rotational degrees of freedom the expression reduces to

$$Z_{r,0} \sim Z^{sc}_{r,0} = e^{-\beta \epsilon_r} \prod_{j=1}^f \frac{1}{2} \cosh \left( \frac{3\hbar \omega_{t,j}}{2} \right),$$

(30)

where $\epsilon_r$ is the energy at the minimum of the reactant well, and $\omega_{t,j}$ is the frequency of its $j$-th vibrational normal mode. If present, translational and rotational modes can also be accounted for. Combining Eqs. (29) and (30) gives the final result, $k_2 \sim k^{sc}_2 = k^{sc}_2/|Z^{sc}_{r,0}|$.

By representing the instanton trajectory as a ring polymer, the formula can be readily applied to realistic molecular potentials, for which the analytic form of the stationary action is not known. In this representation finding the stationary action is equivalent to a multidimensional optimisation problem, which can be solved efficiently with well-established numerical techniques.

Semiclassical instanton theory is however not limited to the golden-rule term. In other work, we have already shown how to generalise the approach to tackle the breakdown of GR in multistate systems reacting via the superexchange mechanism. Specifically, a three-state system that reacts via this mechanism has a rate constant with a leading fourth-order dependence on $\Delta$. We have shown how instanton theory can be applied to such systems, enabling semiclassical calculations of bridge-mediated electron-transfer rates. In what follows, we develop another kind of fourth-order rate theory, one that describes contributions to the nonadiabatic rate beyond leading order. The underlying instantons (see Sec. IV) share some similarities with those presented in Ref. 25, but at the same time exhibit a set of new features that stem from nuclear tunnelling and nonadiabaticity combining to influence the reaction mechanism.

### III. EXACT FOURTH-ORDER RATE EXPRESSION

Substituting Eq. (15) into Eq. (13) shows that the fourth-order contribution to the cumulative reaction probability is

$$P_4(E) = -P_{4A}(E) + P_{4B}(E),$$

(31)

where

$$P_{4A}(E) = 8 \text{Tr} \left[ \text{Im} \hat{G}_0 \Delta \text{Im} \hat{G}_1 \Delta \text{Im} \hat{G}_0 \Delta \text{Im} \hat{G}_1 \Delta \right],$$

(32a)

$$P_{4B}(E) = 8 \text{Tr} \left[ \text{Im} \hat{G}_0 \Delta \text{Re} \hat{G}_1 \Delta \text{Re} \hat{G}_0 \Delta \text{Im} \hat{G}_1 \Delta \right].$$

(32b)

Both terms are comprised of four $\hat{G}_n$ factors, alternating between the reactant ($n = 0$) and product ($n = 1$) diabats. This corresponds to a total of four state changes in a single trace, as opposed to the two changes in the golden-rule expression [Eq. (17)]. One could directly approximate the terms in Eq. (32) with semiclassical methods, arriving at expressions that have simple physical interpretations in terms of instanton trajectories. As discussed in Ref. 21, in the forbidden regime the dominant contribution to $\langle \psi | \text{Re} \hat{G}_n | \psi \rangle$ comes from a trajectory that goes directly from $\psi_0$ to $\psi_f$. On the other hand, the dominant contribution to $\langle \psi_f | \text{Im} \hat{G}_n | \psi_0 \rangle$ comes from a trajectory that reaches a turning point where $V_n(x) = E$. This feature is known as a “bounce”. The GR probability in Eq. (17) corresponds therefore to an instanton trajectory that bounces a total of two times: once off the reactant and once off the product diabat, as shown schematically in Fig. 1(c). The $P_{4A}$ term corresponds to an instanton with four bounces, as in Fig. 1(b), and the $P_{4B}$ term to an instanton with two bounces and two consecutive direct segments on alternating diabats, as in Fig. 4.

Despite the ease of physical interpretation, the semiclassical Green’s function is not as well behaved as the imaginary-time propagator. For this reason we convert the microcanonical reaction probabilities into
thermal rate constants, expressed in terms of imaginary-time propagators. Throughout the derivation it is assumed that we can take the limit $t_{pl} \to \infty$, just as in the case of the GR rate constant. The derivation then amounts to finding the $O(\lambda^4)$ term $k_4 = k_{4A} - k_{4A}$ in the expansion of $\tilde{k}(\beta)$ [Eq. (14)] and the $O(\lambda^2)$ term $\tilde{Z}_{r,2}$ of $\tilde{Z}_r$ [Eq. (7c)]. Together these give the total fourth-order rate constant

$$k_4 = k_2 \left( -\frac{\tilde{k}_{4A}}{k_2} + \frac{\tilde{k}_{4B}}{k_2} - \frac{\tilde{Z}_{r,2}}{\tilde{Z}_{r,0}} \right).$$

Continuing in the same fashion one can obtain analogous expressions for $k_6$, $k_8$, etc., which we intend to pursue in future work.

### A. A-type term

Following a similar approach to Sec. II A, we use the Fourier transform representation of the imaginary Green’s function operator to yield

$$\tilde{k}_{4A} = \frac{1}{2\hbar^4} \int_{-\infty}^{\infty} \frac{dE}{2\pi \hbar} \int d^4 u \ e^{-E(\beta h i \Sigma u_i)/\hbar} \times \text{Tr} \left[ \hat{K}_0(iu_4) \Delta \hat{K}_1(iu_3) \Delta \hat{K}_0(iu_2) \Delta \hat{K}_1(iu_1) \Delta \right],$$

where $\int d^4 u \equiv \int_{-\infty}^{\infty} du_1 \cdots \int_{-\infty}^{\infty} du_4$. Applying the variable transformation

$$\begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix} = \begin{bmatrix} 0 & 0 & -1 & \frac{1}{2} \\ \frac{1}{2} & -1 & 0 & -\frac{1}{2} \\ 0 & 0 & 1 & \frac{1}{2} \\ \frac{1}{2} & 1 & 0 & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} \bar{t} \\ t_0 \\ t_1 \\ t \end{bmatrix},$$

allows us to integrate over $E$ and $\bar{t}$ in the same fashion as before. The remaining integration variables are shifted into the complex plane, so that $t_0 \to z_0$, $t_1 \to z_1$ and $t \to z$, where $z_n \equiv \tau_n + it_n$. This leads to the final expression

$$\tilde{k}_{4B} = \frac{1}{2} \int_0^{\infty} dt_0 \int_0^{\infty} dt_1 \int_0^{\infty} dt \ c_{4A}(z_0, z_1, z),$$

$$c_{4A}(z_0, z_1, z) = \text{Tr} \left[ \hat{K}_0 \left( \frac{z_0}{2} + z_0 \right) \hat{K}_1 \left( \frac{z_0}{2} + z_1 \right) \hat{A} \right] \times \hat{K}_0 \left( \frac{z_p}{2} - z_0 \right) \hat{K}_1 \left( \frac{z_p}{2} - z_1 \right) \hat{A},$$

where we introduce the notation $z_r \equiv \beta h - z$ and $z_p \equiv z$. The expression defines the quantum $\tilde{k}_{4A}$ and will be given a semiclassical treatment in Sec. IV A.

### B. B-type term

We rewrite the second component of the fourth-order reaction probability as

$$P_{4B} = P_{4A} + 8 \text{Re} \left\{ \text{Tr} \left[ \hat{G}_0 \Delta \hat{G}_1 \Delta \hat{G}_0 \Delta \hat{G}_1 \Delta \right] \right\},$$

and recast the Green’s function operators as integral transforms according to Eqs. (11) and (12), to yield

$$\tilde{k}_{4B} = \tilde{k}_{4A} + 2 \text{Re} \left\{ \int_{-\infty}^{\infty} dE \int_{-\infty}^{\infty} dt \ c_{4B} \right\},$$

where the integration ranges are now

$$\int d^4 u \equiv \int_{-\infty}^{\infty} du_1 \int_{-\infty}^{\infty} du_2 \int_{-\infty}^{\infty} du_3 \int_{-\infty}^{\infty} du_4.$$

Under the variable transformation

$$\begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix} = \begin{bmatrix} 0 & 0 & -1 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & -1 & 0 & -1 \end{bmatrix} \begin{bmatrix} \bar{t} \\ t_0 \\ t_1 \\ t \end{bmatrix},$$

the expression simplifies and can be integrated over $E$ and $\bar{t}$ as before, so that

$$\tilde{k}_{4B} = \tilde{k}_{4A} + 2 \text{Re} \left\{ \int_{0}^{i\infty} dz_0 \int_{0}^{i\infty} dz_1 \int_{-\infty}^{\infty} dt \ c_{4B}(z_0, z_1, z) \right\},$$

$$c_{4B}(z_0, z_1, z) = \text{Tr} \left[ \hat{K}_0 \left( z_0 - z_0 \right) \hat{K}_1 \left( z_1 \right) \hat{A} \right] \times \hat{K}_0 \left( z_p - z_0 \right) \hat{K}_1 \left( z_p - z_1 \right) \hat{A},$$

The integration contours for $z_n$ can be deformed to simplify evaluation. Introducing

$$L_{4B}(z_0, z_1) = \int_{-\infty}^{\infty} c_{4B}(z_0, z_1, z) \, dz,$$

we apply Cauchy’s integral theorem\(^{103}\) iteratively to get

$$\int_{0}^{i\infty} \int_{0}^{i\infty} L_{4B}(z_0, z_1) \, dz_0 \, dz_1 = \left[ \int_{0}^{i\infty} \int_{0}^{i\infty} \int_{0}^{i\infty} \int_{0}^{i\infty} \int_{0}^{i\infty} L_{4B}(z_0, z_1) \, dz_0 \, dz_1 \right]$$

where $\sigma_n^* \equiv \sigma_n^* + i\infty$. For further reference we label the integration domains on the right-hand side of Eq. (43) as $A_{rr}$, $A_{rt}$, $A_{tr}$ and $A_{tt}$. A suitable choice of $\tau_n^*$ simplifies the numerical evaluation of the integral by minimising the oscillations in $L_{4B}(z_0, z_1)$. The final result of
this section is the formally exact definition of the quantum \( \hat{k}_{4B} \), which will be given a semiclassical treatment in Sec. IV B.

At this point it is worth re-emphasising that we have pursued this particular route to \( \hat{k}_4 \) because the \( \hat{k}_{4A} \) and \( \hat{k}_{4B} \) terms can be well approximated by semiclassical techniques. Both terms are expressed as integrals over three-time correlation functions which quickly decay to zero along appropriately chosen contours (see Sec. IV). Taking the route via time-dependent perturbation theory\(^{105}\) similarly results in a sum of integrals over three-time correlation functions. Although the corresponding value of \( k_4 \) is identical to that obtained from the Green’s function approach, the individual correlation functions are not straightforwardly related to \( c_{4A} \) and \( c_{4B} \). The various transforms leading to the latter mean that the \( \text{Im} z \equiv t \) in these expressions does not refer to the same physical quantity as in \( C_{FF}(t) \). Even among \( c_{4A} \) and \( c_{4B} \) the symbol \( t \) assumes different meanings, which follows from the different transformations in Eqs. (35) and (40).

Crucially, as far as we can tell, the functions that emerge from time-dependent perturbation theory cannot be made to decay quickly with time, regardless of how the integration contours are deformed. For this reason they are not readily amenable to steepest-descent integration, which is why we employ the Green’s function approach.

C. Partition function

To derive the \( O(\lambda^2) \) term in the perturbation expansion of \( \bar{Z}_r \), we use\(^{118}\)

\[
Z_r = \sum_{\nu=0}^{\infty} \lambda^{2\nu} Z_{r,2\nu},
\]

(44a)

\[
Z_{r,2\nu} = \frac{1}{\hbar^{2\nu}} \int_0^{\beta \hbar} du_2 \int_0^{u_2} du_{2\nu-1} \cdots \int_0^{u_2} du_1 \Tr \left[ e^{-\beta H_0} \prod_{\mu=0}^{\nu-1} \tilde{K}_0(r_{\nu-\mu}) \Delta \tilde{K}_1(s_{\nu-\mu}) \Delta \right],
\]

(44b)

where \( s_{\mu} \equiv u_{2\mu} - u_{2\mu-1}, r_{\mu} \equiv u_{2\mu+1} - u_{2\mu} \) and \( u_{2\nu+1} \equiv u_1 \). Explicitly, the first two terms are

\[
Z_{r,0} = \Tr \left[ e^{-\beta H_0} \right],
\]

(45a)

\[
Z_{r,2} = \int_0^{\beta \hbar} [\beta \hbar - u] c_2(u) du.
\]

(45b)

The integrand in Eq. (45b) contains a factor that is precisely the golden-rule correlation function in Eq. (10), except it is now integrated over imaginary time instead of \( t \). Analogous results for \( Z_{p,2\nu} \) can be obtained by exchanging the diabatic state labels \( 0 \leftrightarrow 1 \), e.g., \( Z_{p,0} = \Tr \left[ e^{-\beta H_1} \right] \). We can write a similar perturbation series for the initial reactant population,

\[
\chi_r = \sum_{\nu=0}^{\infty} \lambda^{2\nu} \chi_{r,2\nu}
\]

(46)

where \( \chi_{r,0} = 1 \) and

\[
\chi_{r,2} = \frac{1}{Z_{r,0}} \left\{ \int_0^{\beta \hbar} [\beta \hbar - 2u] c_2(u) du - Z_{r,2} \right\}.
\]

(47)

It follows that

\[
\bar{Z}_{r,2} = Z_{r,2} + Z_{r,0} \chi_{r,2} \left( 1 + \frac{Z_{r,0}}{Z_{p,0}} \right),
\]

(48)

which, together with our previous expressions for \( \hat{k}_{4A} \) and \( \hat{k}_{4B} \), gives the overall \( k_4 \) rate. This can then be added to \( k_2 \), producing a revised weak-coupling approximation to the full (non-perturbative) rate. However one may rightly question whether a partial sum makes the best use of the post-GR terms, since perturbation series often have poor convergence properties and may even diverge. We now discuss how this issue can be circumvented.

D. Padé summation

An introductory account of series acceleration can be found in Chapter 8 of the textbook by Bender and Orszag.\(^{110}\) Here we only summarise some key points. Slowly convergent and divergent series are common features of asymptotic analysis that typically arise when the quantity being described is not an analytic function of the perturbation. There nonetheless exist several techniques that can yield high-accuracy approximations to the true values of such functions given a limited number of terms. These approaches work by assuming a representation of the target function that, unlike a Taylor series, can describe non-analytic features such as poles. One widely used approach of this type is Padé summation, which represents the target function as a ratio of two polynomials. The ratio is known as a Padé approximant and is characterised by the degrees of the denominator and numerator polynomials, \( M \) and \( N \).

The advantages of Padé summation can be seen by taking as an example the geometric series \( 1 + x + x^2 + x^3 + \ldots \), which diverges for \( |x| \geq 1 \). However its formal sum \( (1 + x)^{-1} \) is defined everywhere except at \( x = -1 \), and any Padé approximant with denominator degree \( M \geq 1 \) will exactly recover the formal result. This particular example of a divergent series may seem oversimplified, but it does appear in physical contexts, e.g., in adiabatic microcanonical instanton theory.\(^1\)

Another example can be drawn from the perturbation expansion of the nonadiabatic cumulative reaction probability, Eq. (16). At present we do not have a useful resummation formula for the entire series, however one can be derived for the subset of terms that only involve
imaginary parts of reactant and product Green’s function operators (“all-bounce terms”), such as \(P_2\) in Eq. (17) and \(P_{4A}\) in Eq. (32a). Denoting the sum over that subset with \(P_A\), it can be shown that

\[
P_A(E) = \sum_{s=1}^{\infty} 4s \left( -\frac{P_2(E)}{4} \right)^s = \frac{P_2(E)}{1 + \frac{1}{4} P_2(E)}, \tag{49}
\]

which converges for \(|P_2(E)| < 4\). In this case the exact result is recovered by any Padé approximant with \(M \geq 2\) and \(N \geq 1\). Even the approximant derived from just the first two terms in the series, \(P_2(E)/(1 + \frac{1}{2} P_2(E))\), offers a substantial improvement over partial summation.

Of course these examples are series for which all of the terms are known and can be summed without recourse to series acceleration. Here the effectiveness of Padé summation is easy to prove since the resummed series is in each case precisely a ratio of polynomials. However in cases when Padé summation becomes practically useful one only knows the first few terms of a series, as is the case for the thermal rate constant (even within the all-bounce subset). To quote from Bender and Orszag, “Padé approximants often work quite well, even beyond their proven range of applicability.” In the spirit of this quotation, we do not attempt to prove that Padé summation of the perturbation series for the thermal rate converges to the exact result, and use it as a heuristic means of extending the range of coupling strengths at which our new theory gives reasonable predictions. As with Eq. (49), we only Padé the all-bounce terms (\(k_2\) and \(k_{4A}\)), since they appear in the series with alternating signs. This ensures that the resulting Padé approximant does not have any artificial singularities for physically relevant values of the diabatic coupling. The remaining contribution, \(\tilde{k}_{4B}/\tilde{Z}_{r,0} - k_2\tilde{Z}_{r,2}/\tilde{Z}_{r,0}\), is usually positive, and we find it is best to add it to the \(k_{4A}\) Padé approximant in the usual manner,

\[
[k_{2+4}]_{\text{Padé}} = k_2 \left( 1 + \tilde{k}_{4A}/k_2 \right)^{-1} \left( 1 + \frac{\tilde{k}_{4B}}{k_2} - \frac{\tilde{Z}_{r,2}}{\tilde{Z}_{r,0}} \right). \tag{50}
\]

The choice of terms included in the Padé approximant is not unique, and we do not undertake to explore all the possibilities at this stage. A rigorous justification of the current approach (or indeed an alternative) can only emerge once the theory of further high-order terms (\(k_6, k_8, \text{etc.}\)) is developed. For the present we note that: (i) Eqs. (33) and (50) by construction agree at small \(\Delta\) up to fourth order; (ii) Eq. (50) makes remarkably accurate numerical predictions at intermediate \(\Delta\) for multidimensional spin–boson models in Sec. VB (see Fig. 10); and (iii) our Padé-summed term is analogous to the non-diabatic rates derived in Refs. 46 and 47 for a reduced model of electron transfer in solution using complementary techniques.

The total rate defined either as in Eq. (50) or as a partial sum satisfies detailed balance for the forward and backward reactions to fourth order in the diabatic coupling. This also holds when the constituent terms are replaced by their semiclassical approximations, which we derive next.

IV. FOURTH-ORDER INSTANTON RATE THEORY

Having split \(k_4\) into three different terms, we now derive a semiclassical approximation for each of them in turn. Derivations for \(k_{4A}^{\text{sc}}\) and \(k_{4B}^{\text{sc}}\) follow the same pattern. First, we consider their high-temperature limits, which happen to be identical to the quantum rate constants for a system of two one-dimensional linear diabatic potentials, \(V_n(x) = V^\dagger + \kappa_n x\). Then we generalise this result to arbitrary temperatures and potentials. The remaining term, which describes changes in the reactant partition function, is obtained directly, without special consideration of the high-temperature regime. To keep the derivations as simple as possible we assume here that there are no translational or rotational normal modes. If such zero-frequency modes are present, they can be accounted for as described in Refs. 8 and 25.

A. Semiclassical A-type contribution

In order to derive the semiclassical instanton formulation of \(k_{4A}^{\text{sc}}\), we insert a set of four position-state resolutions of the identity into Eq. (36b) and replace each instance of \(\langle x_i | \tilde{K}_n | x_j \rangle\) with the corresponding semiclassical propagator [Eq. (21)]. This gives rise to the combined action

\[
S_{4A} = S_0(x_1, x_4, \frac{\kappa_0}{2} + z_0) + S_1(x_4, x_3, \frac{\kappa_1}{2} + z_1) + S_0(x_3, x_2, \frac{\kappa_2}{2} - z_0) + S_1(x_2, x_1, \frac{\kappa_3}{2} - z_1). \tag{51}
\]

We then look for the path that makes the action stationary. As discussed in Sec. III, we expect this to be a four-bounce trajectory comprised of two identical loops, as depicted in Fig. 1(b).

a. High-temperature limit. As \(\beta \to 0\), the action in Eq. (51) becomes stationary for trajectories in the immediate vicinity of the minimum-energy crossing point (MECP) between the diabats. For the sake of convenience, we position it at the origin of our coordinate system. The compactness of the high-temperature instanton allows us to approximate the diabatic PESs as

\[
V_n(x) \sim V^\dagger + \kappa_n q + \frac{1}{2} Q^\dagger H_0 Q. \tag{52}
\]

The gradients \(g_n = \nabla V_n(0)\) of the two diabatic surfaces are antiparallel at the MECP, and we use \(\kappa_n\) to denote their signed norms, \(\kappa_n = \|g_n\|\), \(\kappa_1 = -\|g_1\|\). We call the Cartesian coordinate aligned with the gradients \(q\), and the \(f - 1\) orthogonal coordinates \(Q\). Each appears in the expansion to its lowest order. The results in this section can equally be derived using a more general expansion.
keeping all second-order terms, but such a derivation is more laborious and has the same $\beta \to 0$ limit. In this limit, the terms appearing in the semiclassical propagator are

$$
C_n(x''', x', z) \sim \left(\frac{m}{2\pi \hbar z} \right)^{f/2},
$$

(53a)

$$
S_n(x''', x', z) \sim S_n^{\text{lin}}(q'', q', z) + S_n^{\text{vib}}(Q'', Q', z),
$$

(53b)

$$
S_n^{\text{lin}}(q'', q', z) = V^+ z + \frac{mn_2^2}{2z} + \frac{z\kappa_0q_+ - \frac{k_2^2 + k_3^2}{24m}}{\hbar},
$$

(53c)

$$
S_n^{\text{vib}}(Q'', Q', z) = \frac{m||Q''||^2}{2z} + \frac{z}{2}Q_+^\dagger H_n Q_+.
$$

(53d)

Here $q_- = q'' - q'$ and $q_+ = (q' + q'')/2$, with analogous definitions for $Q_\pm$. The stationary trajectory follows a path along $q$, with no lateral displacement ($i.e., Q = 0$). Since the combined action is quadratic in the positions, integration over these variables can be performed analytically to yield $c_{4A}(\tau_0, z_1, z)$. Choosing the real parts of its arguments such that $\tau = \beta m\kappa_0$, and $\tau_0 = \tau_1 = 0$ makes the three-time correlation function proportional to $\delta(t)$. By analogy with $L_{4B}$ in Eq. (42), we then define

$$
L_{4A}(t_0, t_1) = \int_{t_0}^{t_1} c_{4A}(t_0, t_1, \tau + it) dt
$$

(54a)

$$
\sim \frac{\Delta^4}{\hbar^3} \sqrt{\frac{2\pi m}{\beta(\kappa_0 - \kappa_1)^2}} Z_1 e^{-\beta V_1} \exp \left[ \frac{\beta^2 \hbar^2 \kappa_0^2 \kappa_1^2}{96m(\kappa_0 - \kappa_1)^2} \right] \times \exp \left[ -\frac{d_0 t_0^2 + d_1 t_1^2 + d_0 t_1^2}{2\hbar} \right]
$$

(54b)

as $\beta \to 0$. Here $\Delta$ is evaluated at the MECP, and we define a transition-state partition function

$$
Z_1 = \left[ \frac{\beta^2 \hbar^2 \kappa_0^2 \kappa_1^2}{m} \right]^{-1/2} \text{with} \quad \tilde{H} = \frac{\kappa_0 H_1 - \kappa_1 H_0}{\kappa_0 - \kappa_1},
$$

(55)

as well as the coefficients

$$
d_n = \frac{\beta \hbar \kappa_0^2}{4m}, \quad d_0 = \frac{1}{\beta \hbar} \frac{\kappa_0 - \kappa_1}{m}.
$$

(56)

In general, the asymptotic relation in Eq. (54b) only holds at high temperatures and short times $t_0$ and $t_1$. However, for one-dimensional linear diabats, $V_n(x) = V^+ + \kappa_0 x$, Eq. (54b) is not an approximation and is precisely equal to the quantum $L_{4A}(t_0, t_1)$. It is therefore meaningful to make a digression into the low-temperature regime ($\beta \to \infty$). In this limit, the coefficient $d_{01}$ of the quartic term in Eq. (54b) becomes vanishingly small, and so the marginalised correlation function $L_{4A}(t_0, t_1)$ becomes well approximated by a Gaussian, as seen in Fig. 2(a). Neglecting the quartic term and integrating over $t_n$ yields the low-temperature limit of $\tilde{k}_{4A}$ for a linear system,

$$
\tilde{k}_{4A}^{\text{lin}} = \sqrt{\frac{2\pi m}{\beta(\kappa_0 - \kappa_1)^2}} \frac{4\pi m \Delta^4 e^{-\beta V_1}}{\beta h^4 |\kappa_0\kappa_1|} \exp \left( \frac{\tilde{\beta}^3}{48} \right),
$$

(57)

to be compared with the golden-rule rate

$$
\tilde{k}_2^{\text{lin}} = \sqrt{\frac{2\pi m}{\beta(\kappa_0 - \kappa_1)^2}} \frac{\Delta^2 e^{-\beta V_1}}{h^2} \exp \left( \frac{\tilde{\beta}^3}{12} \right),
$$

(58)

where

$$
\tilde{\beta} = \beta \left[ \frac{d_0 d_1}{\hbar d_{01}} \right]^{1/3} = \beta \left[ \frac{\hbar^2 \kappa_0^2 \kappa_1^2}{2m(\kappa_0 - \kappa_1)^2} \right]^{1/3}.
$$

(59)

The similarity between Eqs. (57) and (58) arises because at low temperatures steepest-descent integration of $c_{4A}$ is a straightforward generalisation of the procedure for the golden-rule correlation function $c_2$. One can therefore expect to see some similarities between the physical interpretations of these two expressions.

In the golden-rule case, the value of the rate constant $\tilde{k}_2$ is determined by the behaviour of $c_2(\tau + it)$ in the small-$t$ limit. Resolved in terms of position eigenstates, the function at $t = 0$ reads

$$
c_2(\tau) = \int_{-\infty}^{\infty} dx_i dx_f \left\| \langle x_i | \hat{K}_1(\tau) \hat{K}_0(\tau) | x_f \rangle \right\|^2,
$$

(60)

which is dominated by $x_i$ and $x_f$ near the GR instanton turning points [see Fig. 1(c)]. Reading the integrand from right to left, the dominant contribution corresponds to the probability of the system starting near the reactant turning point, evolving in imaginary time for $\tau_r/2 = (\beta\hbar - \tau)/2$, “switching” from $V_0$ to $V_1$, propagating for $\tau_p/2 = \tau/2$, and finally arriving at the product turning point. Imaginary-time evolution indicates
that the transition proceeds via a tunnelling mechanism, with the dominant tunnelling pathway following the half-instanton from \( x_1 \) to \( x_2 \). The dynamics before and after tunnelling is not explicitly included in the half-instanton but may be deduced from the locations of the turning points and the corresponding momenta (which are zero). Given these boundary conditions we conclude that the thermally activated system initially moves up \( V_0 \) with just enough energy to reach \( x_4 \), at which point it tunnels to \( x_0 \) and continues moving down \( V_1 \). This is precisely the kind of qualitative picture we were looking for in order to describe the processes underlying \( k_2 \), and it was possible to deduce from just the GR half-instanton.

\[
\begin{array}{ll}
\text{low temperature} & \text{high temperature} \\
\begin{array}{ll}
t_1 & t_1 \\
t_0 & t_0 \\
\end{array} & \\
\begin{array}{ll}
t_0 & t_1 \\
\end{array} & \\
\begin{array}{ll}
t_0 & t_1 \\
\end{array} & \\
\end{array}
\]

\begin{align}
\text{energy} & \\
\text{position} & \\
\text{energy} & \\
\text{position} & \\
\end{align}

FIG. 2. (a) Marginalised \( L_{4A}(t_0, t_1) \) correlation function for a system of linear diabats with \( \kappa_0 = 4, \kappa_1 = -3, m = 1, \hbar = 1 \) and \( \beta = 5 \). (b) The same for \( \beta = 0.1 \). In both cases the darkest blue corresponds to the maximum value, white corresponds to zero, and \(-2 \leq t_0, t_1 \leq 2\). At low temperature the function is approximately Gaussian and dominated by \( t_0 = t_1 = 0 \), whereas at high temperature the function becomes star-shaped, developing rays along the \( t_0 \) and \( t_1 \) axes. In the top panels, one point of importance is picked out with a yellow circle and defines the parameters of the instanton shown in the lower panels. (c) Shows the low-temperature half-instanton trajectory associated with \( t_0 = t_1 = 0 \), and (d) shows the high-temperature half-instanton for a point on the ray along \( t_1 \). Blue colour is used for the half-instanton segments that reside on \( V_0 \) and orange is used for \( V_1 \). The dashed black lines depict system dynamics on \( V_0 \) before and after the scattering events associated with the half-instantons.

A similar analysis can be conducted for \( \tilde{k}_{4A} \), whose value at low temperatures is determined by \( c_{4A}(z_0, z_1, z) \) around \( z_0 = z_1 = 0, z = \tau \) [see Fig. 2(a)]. Expanding \( c_{4A} \) in terms of position eigenstates yields

\[
c_{4A}(0, 0, \tau) = \int_{-\infty}^{\infty} dx_0 dx_1 \left| \langle x_0 | \tilde{K}_0 (\beta) \tilde{K}_1 (\beta) \hat{K}_0 (\beta) \hat{K}_1 (\beta) | x_1 \rangle \right|^2,
\]

where the dominant contributions to the integral come from \( x_1 \) and \( x_0 \) both in the vicinity of the reactant turning point. The integrand is once again in the form of a probability density and describes a double scattering event in which the system tunnels from the reactant state into the product state, then back to reactant. This scattering process is associated with the half-instanton derived from the double-loop trajectory in Fig. 1(b), and is shown schematically with solid lines in Fig. 2(c). The real-time dynamics immediately before and after the tunnelling event are indicated on the same figure with dashed lines.

It is now clear why \( \tilde{k}_{4A} \) decreases the full nonadiabatic rate (recall that it appears in Eq. (33) with a minus sign). The golden-rule expression implicitly assumes that after every reactant-to-product transition the system remains in the product state. In reality there is a non-zero probability that the system recrosses back to reactant, which the golden rule entirely neglects, thus overestimating the full rate constant. The \( \tilde{k}_{4A} \) term accounts for such recrossing events to leading order in \( \Delta \), correcting the overestimate. According to our analysis, this correction is expected to be small at low temperatures, since the underlying tunnelling mechanism is relatively inefficient compared to the direct (reactive) transition. For the linear case this can be deduced from the exponents of Eqs. (57) and (58), and we will see later that the same applies to other potentials.

When considering the high-temperature (\( \beta \rightarrow 0 \)) limit, our approach has to be modified, since we can no longer neglect the quartic term in Eq. (54b). The change comes about because the coefficient \( d_{01} \) is proportional to \( \beta^{-1} \), whereas the quadratic coefficients \( d_n \) are linear in \( \beta \) [Eq. (56)]. This highlights a curious feature of the \( c_{4A} \) correlation function: unlike its GR counterpart, it cannot be uniformly approximated as Gaussian in its arguments. Steepest-descent integration over \( t \) can always be done in the usual manner, giving us \( L_{4A}^R(t_0, t_1) \), but the remaining two variables show some unexpected behaviour. At low temperatures, \( L_{4A}^R \) has an (approximately) Gaussian shape that broadens with increasing temperature. Eventually the broadening becomes noticeably anisotropic and largely confined to the \( t_0 \) and \( t_1 \) axes. Along all other directions the function shrinks rapidly, so that in the \( \beta \rightarrow 0 \) limit it assumes the distinctly non-Gaussian four-pointed star shape in Fig. 2(b). Hence we must modify the steepest-descent procedure outlined in Sec. II B and take the fourth-order term into account. This results in the asymptotic relation

\[
\tilde{k}_{4A}(\beta) \sim \frac{\Delta^4}{\hbar^4} \frac{\pi \kappa_1}{2 \beta (\kappa_0 - \kappa_1)^2} \beta^3 e^{-\beta y_1} \exp \left( \frac{2 \pi \hbar}{\beta y_0} \right) K_0 \left( \frac{\beta y_0}{3} \right)
\]

as \( \beta \rightarrow 0 \), where \( K_0(y) \equiv e^{y}K_0(y) \) and \( K_0 \) is a modified Bessel function of the second kind.\textsuperscript{120} For one-dimensional linear diabats this relation is exact and hence
valid at all temperatures. From the small-argument asymptotic behaviour of $K_0$ it follows that $\tilde{k}_{4A}$ tends to

$$\tilde{k}_{4A}^a(\beta) = \frac{\pi m \Delta^4 Z^4 e^{-\beta V_1}}{K^3(\kappa_0 - \kappa_1)^4} \left\{ \ln \left( \frac{64}{\beta^3} \right) - \gamma \right\}$$  \hspace{1cm} (63)

as $\beta \to 0$, where $\gamma = 0.577 \ldots$ is the Euler–Mascheroni constant. It is absolutely necessary to include the quartic $d_0$ term to arrive at this result.

To understand the change in the asymptotics of $\tilde{k}_{4A}$, we refer to Fig. 2(b), which shows that $c_{4A}(z_0, z_1, z)$ still has a stationary point at $z_0 = z_1 = 0$ and $z = \tau$. The corresponding instanton has the same shape as in the low-temperature regime, but is now contracted almost to a point at the transition state, implying that nuclear tunnelling does not play a major role. From the same figure we see that significant contributions to $\tilde{k}_{4A}$ also come from combinations of arguments where one of $z_0$ or $z_1$ assumes a non-zero imaginary value. Without loss of generality we focus on $z_0 = 0$ and $z_1 = i\tau_1$ (the alternative simply interchanges the roles of $V_0$ and $V_1$). At this point the $c_{4A}$ correlation function can be written as

$$c_{4A}(0, i\tau_1, \tau) = \int_{-\infty}^{\infty} dx_1 dx_2 \left\langle \langle x_1 | \hat{K}_0(\tau_1) \hat{K}_1(\tau_1 + i\tau_1) \hat{K}_0(\tau_1) | x_2 \rangle \right\rangle^2.$$  \hspace{1cm} (64)

closely resembling Eq. (61). As before, the integrand describes the probability of an unreactive back-and-forth transition, although now there is hardly any imaginary-time propagation, since both $\tau_1$ and $\tau_p$ tend to 0 in the high-temperature limit. The matrix element in Eq. (64) now corresponds to a system starting in the reactant state and almost immediately getting scattered into the product state. The product then follows a real-time trajectory of duration $t_1$, at the end of which it is scattered back into the reactant state. The corresponding half-instanton follows a path in the complex plane whose imaginary component becomes vanishingly small as $\beta \to 0$. The real part of the path is shown with solid lines in Fig. 2(d). On this occasion, the momenta at the end-points of the half-instanton are non-zero, from which it follows that before and after the scattering event the system follows the trajectories indicated with dashed lines.

The change in the asymptotics of $\tilde{k}_{4A}$ is therefore a consequence of a change in mechanism: at low temperature the recrossing proceeds largely via tunnelling, whereas at high temperature such transitions are mostly due to high-energy “over-the-barrier” trajectories that overshoot the hopping point at first and are only scattered on their way back. We note that these trajectories (emerging naturally from our theory) are precisely what motivates the Holstein transmission coefficient,\textsuperscript{54,121} based on Landau–Zener theory,\textsuperscript{51,52} which was previously used to construct uniform nonadiabatic rate expressions.\textsuperscript{33,44,45} It should then come as no surprise that at high temperatures, rates based on the Holstein transmission coefficient are consistent with our Eq. (63), as shown in Appendix F. What our new theory brings to the table is an accurate description of transitions at energies close to the MECP, whereas LZ only applies in the high-energy limit. As a result, the Holstein expression can only establish the dependence in Eq. (63) up to an additive constant. Furthermore, this expression only accounts for over-the-barrier transitions, hence it cannot be used to describe low-temperature reaction rates, which are dominated by tunnelling under the barrier. Our new approach can do so rigorously, even for multidimensional nonlinear potentials, as shown below.

b. General case. The high-temperature regime requires additional care because we need to account for the $O(t_0^4 t_1^2)$ term in Eq. (54b) in order to obtain the correct semiclassical limit. This can be done with relative ease for a classical action in its short-time asymptotic form [Eq. (53)]. However deriving the term without relying on the short-time/linear approximation is not straightforward, since the derivation calls for high-order derivatives of the action not normally available from standard instanton calculations. At the same time, our previous discussion indicates that such high-order terms are negligible at low temperatures, implying that the standard steepest-descent prescription can be safely followed in this regime. We therefore aim to derive a semiclassical approximation to Eq. (54a) correct to second order in $t_0$ and $t_1$, expressing all the relevant coefficients in terms of second derivatives of the classical action [Eq. (22)]. The quartic term will be based on an analytically tractable model, yielding a $d_0$ coefficient that has the correct high-temperature limit. It will not necessarily be accurate at low temperatures, but this should not be an issue provided the coefficient vanishes sufficiently quickly as $\beta \to \infty$, since in that regime $\tilde{k}_{4A}$ is leading order independent of $d_{01}$.

To begin, we locate the set of arguments $\mathbf{x} = (x_1, x_2, x_3, x_4)$ and $\tau = (\tau_0, \tau_1, \tau)$ that make the combined action in Eq. (51) stationary. Generally this action will not be known in closed form, however it can be calculated efficiently using numerical algorithms.\textsuperscript{8,22,25} At the stationary point, the derivatives of the action satisfy

$$\frac{\partial S_{4A}}{\partial \mathbf{x}} = 0, \quad \frac{\partial S_{4A}}{\partial \tau} = 0.$$  \hspace{1cm} (65)

The trajectory that makes $S_{4A}$ stationary at temperature $\beta$ is related to the trajectory that makes $S_2$ stationary at temperature $\beta/2$, as shown in Fig. 1. All the information required to calculate $\tilde{k}_{4A}^b$ can therefore be extracted from a GR instanton at twice the temperature (that is $\beta/2$). For the remainder of this section all quantities pertaining to the GR instanton, namely the hopping point $x^1$, the imaginary time $\tau_1$, the stationary action $S_2$ and its Hessian $\Sigma$ are quantities calculated at this higher temperature.

Explicitly, the conditions in Eq. (65) are satisfied by $x_{1,4} = x^1$, $\tau_0 = \tau_1 = 0$ and $\tau = \tau_0$. It follows that the stationary action $S_{4A} = 2S_2$. To relate the derivatives of the two actions, let us denote $S_0 = S_0(x', x', \frac{\partial}{\partial x} - \tau_0)$
and $S_1 \equiv S_1(x', x', \tau_g)$. We then define

$$
\Theta = \frac{\partial^2 S_0}{\partial \mathbf{x}' \partial \mathbf{x}'} + \frac{\partial^2 S_1}{\partial \mathbf{x}' \partial \mathbf{x}''}, \quad \Theta_n = \frac{\partial^2 S_n}{\partial \mathbf{x}' \partial \mathbf{x}''},
$$

$$
\omega_n = \frac{\partial^2 S_n}{\partial \mathbf{x}'' \partial \tau_g}, \quad \zeta_n = \frac{\partial^2 S_n}{\partial \tau_g^2},
$$

where $\Theta, \Theta_n$ are symmetric $f \times f$ matrices, $\omega_n$ are $f$-dimensional column vectors, $\zeta_n$ are scalars, and the derivatives are all evaluated at the GR stationary point. Thus all of the above quantities are directly available from a GR instanton calculation and can be evaluated numerically within the ring-polymer formulation as described in Ref. 22.

Given this information one can derive the general steepest-descent approximation to Eq. (54a) by following the procedure in Appendix A. Defining

$$
\Theta_\pm = \Theta \pm (\Theta_0 - \Theta_1),
$$

we find that the coefficients $d_n$ in Eq. (54b) are given by

$$
d_0 = 4\omega_1[\Theta_+^{-1}w_0 - 2\zeta_0],
$$

$$
d_1 = 4\omega_1[\Theta_+^{-1}w_1 - 2\zeta_1].
$$

An analogous expression for $d_{01}$ would require high-order derivatives of $S_2$ that are not readily available from standard GR instanton calculations. We can circumvent this by noting that, based on Eq. (56) and on general physical considerations, the ratio $\eta d_{01}/d_{01}$ tends to zero as $\beta \to \infty$. In this limit the factor arising from integrating over $t_0$ and $t_1$ behaves as

$$
\sqrt{\frac{2\pi h}{d_{01}}} \sim \frac{2\pi h}{\sqrt{d_{01}}} \left(1 - \frac{h d_{01}}{2 d_{01}}\right),
$$

i.e., to leading order it is independent of $d_{01}$. Therefore any reasonable approximation to $d_{01}$ should lead to a good estimate of $\tilde{k}_{4A}^{\infty}$, provided the expression satisfies $\eta d_{01}/d_{01} < 1$ as $\beta \to \infty$ and tends to Eq. (56) in the high-temperature limit. We suggest the following expression, which is exact for a one-dimensional spin–boson model [Eq. (98) with $f = 1$]:

$$
d_{01} = \max \left\{0, \frac{\omega}{2m} \left[\left(\kappa_0 - \kappa_1\right)^2 \text{csch} \left(\frac{\beta h_0}{4}\right) \right]^{\frac{1}{2}} \right\}.
$$

Here $\kappa_n$ are the signed norms of $\nabla V_n$ at the MECP and $\omega > 0$ is a parameter ensuring that $d_{01}$ vanishes sufficiently quickly as $\beta \to \infty$. A suitable value can be obtained from the curvature along the direction of steepest descent at the MECP, $\omega^2 = m^{-1} \nabla^2 V_n(x')$, calculated for whichever diabatic PES yields the larger value. Unlike Eq. (56), this expression for $d_{01}$ can become negative at sufficiently low temperatures, tending to zero from below as $\beta \to \infty$. In such cases the most straightforward course of action is to set $d_{01} = 0$, which is equivalent to neglecting contributions from the quartic term. More sophisticated approximations to $d_{01}$ could be constructed, but any modification is expected to only have a significant effect at temperatures where $\tilde{k}_{4A}^{\infty}$ is subdominant to the other components, namely $\tilde{k}_{4B}^{\infty}$, as will be shown later.

Combining Eqs. (68), (70) and (A.6), we arrive at the final expression for the rate constant,

$$
\tilde{k}_{4A}^{\infty} = \left[\tilde{k}_{2}^{\infty}(\beta)\right]^2 \sqrt{\frac{-\Sigma}{2d_{01}|\Theta_x|\Theta_0}} \tilde{K}_0 \left(\frac{dd_1}{4d_{01}}\right),
$$

where $\tilde{k}_{2}^{\infty}$ is defined in Eq. (29). The expression is a uniform approximation that is expected to be valid at any temperature. Additionally, the $\omega \to 0$ limit of Eq. (70) is precisely equal to Eq. (56), and so our current prescription for $d_{01}$ exactly recovers the quantum $\tilde{k}_{4A}^{\infty}$ for two-state systems of one-dimensional linear diabats.

B. Semiclassical B-type contribution

The considerations in Sec. III B allow us to write

$$
\tilde{k}_{4B} \sim \tilde{k}_{4B}^{\infty} + 2 \text{Re} \left\{ \int_{\cal A_{r+}} \int_{\cal A_{r+}} \int_{\cal A_{r+}} \int_{\cal A_{r+}} L_{4B}^{\infty}(z_0, z_1) \text{d}z_0 \text{d}z_1 \right\},
$$

where $L_{4B}^{\infty}$ is obtained by substituting semiclassical propagators into Eq. (42) and integrating over positions and time $t$ by steepest descent. As before, we identify the combined action,

$$
S_{4B} = S_0(x_1, x_4, z_0 - z_0) + S_1(x_1, x_3, z_1) + S_0(x_3, x_2, z_0) + S_1(x_2, x_1, z_0 - z_1),
$$

which we expect to be minimised by a two-bounce (single-loop) trajectory like the one shown in Fig. 4. To prove this we need to determine the optimal integration domains (i.e., the optimal $\tau_n^*\beta$) which is most easily done in the high-temperature limit, as we now show.

a. High-temperature limit. Once again, we expand the diabatic PESs in a Taylor series about the MECP and consider the corresponding propagators defined by Eq. (53). Integration over position and time $t$ gives

$$
L_{4B}^{\infty}(z_0, z_1) \sim \frac{\Delta^4}{h^4} \sqrt{\frac{2\pi m}{\beta(\kappa_0 - \kappa_1)^2}} Z^2 e^{-\beta V^2 + \beta^2/12} \times \exp \left\{ -\frac{1}{h} \left[ \frac{\left(\kappa_0 - \kappa_1\right)^2}{2m h} z_0^2 z_1 - \frac{\beta h k_0 k_1}{2m} z_0 z_1 - \frac{\left(\kappa_0 - \kappa_1\right)}{2m} \left(\kappa_0 z_0^2 z_1 - \kappa_1 z_1^2 z_0\right) \right] \right\},
$$

"
where all the terms are defined as in Sec. IV A. From here it can be shown that the remaining integrals over \( z_n \) in Eq. (72) can be performed most easily by setting
\[
\tau_0^* = \frac{\hbar}{2} \frac{\kappa_1}{\kappa_1 - \kappa_0}, \quad \tau_1^* = \frac{\hbar}{2} \frac{\kappa_0}{\kappa_0 - \kappa_1}.
\] (75)

This choice removes any oscillations in the integrand and allows for further simplifications, which will be discussed shortly. Note that these values of \( \tau_n^* \) are related to the stationary imaginary time of a golden-rule instanton at temperature \( \beta \) in a linear system or the high-temperature limit, namely \( \tau_0^* = \tau_0 / 2 \) and \( \tau_1^* = (\beta \hbar - \tau_0) / 2 \). Under this definition, contributions from \( \mathcal{A}_s \) and \( \mathcal{A}_t \) are purely imaginary and are therefore discarded. Furthermore, the contribution from \( \mathcal{A}_d \) cancels exactly with \( \kappa_{4A} \) in Eq. (72), meaning that the semiclassical rate is
\[
\tilde{k}_{4B} \sim 2 \int_0^{\tau_0^*} \int_0^{\tau_1^*} L^\alpha_{4B}(\tau_0, \tau_1) d\tau_0 d\tau_1
\] (76)
as \( \beta \to 0 \). We observe that similarly to \( \tilde{k}_{4A} \), the \( \tilde{k}_{4B} \) rate cannot be approximated with a Gaussian integral. Also like with \( \tilde{k}_{4A} \), the high-temperature asymptotic relation given for \( k_{4B} \) by Eqs. (74)–(76) is exact across all temperatures for the linear system. Hence we may use the results of this section to inspire the derivation in the general case.

In Fig. 3(a) we plot \( L_{4B} \) at different temperatures for \((\tau_0, \tau_1) \in \mathcal{A}_{TT} \). As \( \beta \to 0 \), the function becomes flat across the entire domain of integration; as \( \beta \to \infty \), the function becomes dominated by the edges for which \( \tau_0 \) or \( \tau_1 \) is 0. In Fig. 3(b) we show the instanton trajectories that correspond to different points inside the domain of integration. As anticipated at the beginning of Sec. III, trajectories that dominate the integral at low temperatures have two consecutive segments that bounce once, and two consecutive segments that travel directly between the endpoints. Overall, these follow the path of a golden-rule instanton, with either a short reactant segment along a product trajectory or vice versa. As we move to trajectories for which neither \( \tau_n \) is small, the segments become elongated and the entire instanton more localised around the barrier region. In the most extreme case (top right trajectory), we arrive at the four-bounce instanton that corresponds to the \( \tilde{k}_{4A} \) term in Sec. IV A. For large \( \beta \) these trajectories have considerably larger action and do not contribute much to the integral in Eq. (76). Hence we expect that the general semiclassical expression for \( \tilde{k}_{4B} \) will be dominated by trajectories for which at least one of the direct segments is vanishingly short (\( \tau_0 \to 0 \) or \( \tau_1 \to 0 \)). All such trajectories reduce exactly to a standard (two-bounce) GR instanton corresponding to temperature \( \beta \).

b. General case In order to derive a general expression for \( \tilde{k}_{4B} \) we need to express the coefficients in
\[
L^\alpha_{4B}(\tau_0, \tau_1) \sim L^\alpha_{4B}(\tau_0, 0) \exp \left\{ -\frac{1}{\hbar} \left[ \alpha_1 \tau_1 - \frac{\gamma_1 \tau_1^2}{2} \right] \right\}
\] (77)

(valid as \( \tau_1 \to 0 \)) in terms of derivatives of the GR action. From Eqs. (41) and (42) it follows that
\[
L^\alpha_{4B}(\tau_0, 0) = \tilde{k}_{4B}^\alpha(\beta) \frac{\Delta[x(\tau_0)]^2}{\hbar^2},
\] (78)
where \( \Delta[x(\tau_0)] \) is the diabatic coupling along the reactant segment of a GR instanton after travelling for an imaginary time \( \tau_0 \) away from the hopping point. Deriving expressions for \( \alpha_1 \) and \( \gamma_1 \) (both functions of \( \tau_0 \)) is somewhat laborious, but the underlying approach is similar to the one used in Sec. IV A to derive \( d_\alpha \). Treatment \( \tau_0 \) as a parameter, we consider a series expansion of \( S_{4B} \) in the remaining six variables and integrate over \((t, x_1, x_2, x_3, x_4)\) by steepest descent. The resulting effective action is in the form of the bracketed expression in Eq. (77), and so yields the desired coefficients. To begin, we transform to a more convenient set of coordinates,
\[
\begin{align*}
x' &\equiv x_1, \\
x'' &\equiv x_2, \\
x &\equiv (x_3 + x_4)/2, \\
x_- &\equiv x_4 - x_3,
\end{align*}
\] (79)
as indicated in Fig. 4. We then define
\begin{align}
S_0' &\equiv S_0(x', \ x, \ \beta \hbar - \tau - \tau_0), \\
S_0'' &\equiv S_0(x, \ x', \ \tau_0), \\
S_1 &\equiv S_1(x', \ x', \ \tau),
\end{align}
and introduce the notation \( \nu \equiv (x' \times x'') \). Treating \( \tau_0 \) as a parameter, we expand \( S_{4B} \) to second order about \( \tau_1 = 0, \ x_x = 0, \) and a \( \nu \) such that
\[
\frac{\partial}{\partial \nu} (S_0' + S_0'' + S_1) = 0.
\]

We shall focus on the first of the two terms; the result for the second term follows upon exchanging the labels \( 0 \leftrightarrow 1 \). The outer integral over \( \tau_0 \) is not amenable to steepest-descent integration but can readily be evaluated numerically using information directly available from standard ring-polymer instanton optimisation. The inner integral is of the form
\[
\int_0^{\tau_0} \int_0^{\tau_1} e^{-\frac{1}{\hbar} \left[ \frac{1}{2} \alpha_1 (\tau_0 - \tau_1) + \gamma_1 \tau_1^2 \right]} \, d\tau_1,
\]
where \( \alpha_1 \) and \( \gamma_1 \) are defined in Eq. (82). The standard procedure (see Chapter 6.4 of Ref. 110) for calculating this integral by steepest descent is to replace the integrand with
\[
\exp \left[ -\frac{\alpha_1 \tau_1}{\hbar} + \frac{\gamma_1 \tau_1^2}{2 \hbar} \right] \sim e^{-\alpha_1 \tau_1 / \hbar} \left[ 1 + \frac{\gamma_1 \tau_1^2}{2 \hbar} \right],
\]
and integrate the resulting expression analytically. This yields
\[
\mathcal{J}^{sc}(\tau_0) = \frac{h}{\alpha_1} \left[ 1 - e^{-\phi_1} \right] + \frac{h^2 \gamma_1}{\alpha_1} \left[ 1 - e^{-\phi_1} \left( \frac{\hbar^2}{16} + \phi_1 + 1 \right) \right],
\]
with \( \phi_1 = \frac{\alpha_1 \tau_1}{\hbar} \). The outer integral over \( \tau_0 \) is formed from the rows and columns corresponding to \( \tau_0 \). The same considerations apply to the asymptotic form of \( L_{4B}^{sc}(\tau_0, \tau_1) \) as \( \tau_0 \to 0 \), and expressions for \( \alpha_0 \) and \( \gamma_0 \) can be obtained by swapping the indices 0 \( \leftrightarrow 1 \) in the preceding derivation.

It remains to evaluate the double integral in Eq. (76) over the rectangular domain \( \mathbb{A}_{\tau_0, \tau_1} \) defined by \( \tau_1^* = \frac{1}{2} \tau_0(\beta), \ \tau_0^* = \frac{1}{2} (\beta \hbar - \tau_0(\beta)) \). To do this, we split the domain along the diagonal connecting the bottom left and top right corners of the rectangles in Fig. 3(a).

\[
\int_0^{\tau_0^*} d\tau_0 \int_0^{\tau_1^*} d\tau_1 = \int_0^{\tau_0} d\tau_0 \int_0^{\tau_1} d\tau_1 + \int_0^{\tau_0^*} d\tau_0 \int_0^{\tau_1} d\tau_1 + \int_0^{\tau_0^*} d\tau_0 \int_0^{\tau_1^*} d\tau_1.
\]
Second, we should stress that the rectangular domains in Fig. 3, which we have adopted throughout the derivation, are only strictly optimal in the high-temperature limit (unless the system is linear, in which case the domains are optimal at any temperature). It is also only in those limits that integrals over $\mathcal{A}_\tau$ and $\mathcal{A}_t$, are purely imaginary, and therefore do not contribute, and only here that the integral over $\mathcal{A}_t$ cancels exactly with $k_{\text{TA}}$. Nevertheless, any significant deviations are expected to occur at low temperatures, for which the integral is entirely dominated by regions of small $\tau_0$ or $\tau_1$. Deformation of the optimal $\mathcal{A}_\tau$ from the rectangular shape would only become prominent in parts of the $(\tau_0, \tau_1)$ plane that contribute little to the overall integral. Furthermore, we expect terms derived from integration over optimal $\mathcal{A}_\tau$, $\mathcal{A}_t$, and $\mathcal{A}_t$, as well as the rate constant $k_{\text{TA}}$, to become subdominant to $k_{\text{TA}}$ in the low-temperature limit. Therefore any real part acquired by the first two terms, or any imperfect cancellation between the latter are expected to be negligible, and thus Eq. (88) remains the correct asymptotic limit of the $k_{\text{TB}}$ rate constant.

Finally, we come to the question of physical interpretation. Mirroring the discussion in Sec. IV A, we consider $c_{4B}(z_0, z_1, z)$ at a point that makes a significant contribution to $k_{\text{TB}}$, expressing the function in the position basis. In what follows we consider the contribution that corresponds to the instanton in Fig. 4, for which $z_0 = \tau_0 \in (0, \frac{\beta}{2})$, $z_1 \rightarrow 0$ and $z = \tau$. This can be written as

$$c_{4B}(\tau_0, 0, \tau) = \int_{-\infty}^{\infty} dx_1 dx_2 \langle x_1 | \hat{K}_0 (\frac{\tau_0}{\beta}) \hat{\Delta} \hat{K}_1 (\frac{\tau_0}{\beta}) | x_2 \rangle \times$$

$$\langle x_1 | \hat{K}_1 (\frac{\tau_0}{\beta}) \hat{\Delta} \hat{K}_0 (\tau_0) \hat{\Delta} \hat{K}_1 (0) \hat{\Delta} \hat{K}_0 (\frac{\tau_0}{\beta} - \tau_0) | x_2 \rangle. \tag{89}$$

Unlike in Eqs. (61) and (64), here the integrand is not the square of a single matrix element and hence cannot be directly identified with the probability of a scattering event. Instead, the integrand takes the form of a quantum interference term. The first of the two interfering alternatives is described by the matrix element on the first line of Eq. (89) and corresponds to a golden-rule transition, as follows from comparing to Eq. (60). The second alternative, corresponding to the second line of Eq. (89), is a new type of scattering process that involves an excitation into a virtual state.

The half-instanton trajectory corresponding to this process is shown in Fig. 5 and is identical to the GR case, except for the infinitesimally short excitation process is shown in Fig. 5 and is identical to the τ along the half-instanton. As secondly, the excitation does not conserve the energy in Fig. 3, which we have adopted throughout the derivation. The half-instanton segments residing on $V_0$ are shown in blue and those on $V_1$ are shown in orange. The wavy line indicates an excitation into a “virtual” state, which is infinitesimally short and not energy-conserving. The dashed black lines depict the system dynamics before and after the scattering event associated with the half-instanton.

It seems reasonable that this type of scattering process should describe how the upper diabatic state influences the probability of tunnelling from reactant to product. Casting the system in the adiabatic representation, it becomes evident that the shape of the lower Born–Oppenheimer PES depends on $\Delta$ and both of the diabats $V_n$ all along the tunnelling pathway (not just at the hopping point). $k_{\text{TB}}$ takes this into account and serves to increase the overall rate. This is consistent with the notion that a larger $\Delta$ will tend to lower the (adiabatic) activation energy barrier, increasing the probability of tunnelling and hence speeding up the reaction.

C. Semiclassical partition-function correction

It is often the case that the diabatic coupling $\Delta(x)$ becomes negligible as $x$ approaches the minimum of $V_0$. The term considered in this section is then itself negligible and can be omitted altogether. If the coupling remains considerable around the reactant/product minimum, it can be accounted for as follows. We begin by rewriting Eq. (48) as

$$Z_{r,2} = \int_0^{\beta \hbar} [\beta \hbar - 2u] c_2(u) \, du \tag{90}$$

$$- \left[ \int_0^{\beta \hbar} u \, c_2(u) \, du + \int_0^{\beta \hbar} u \, c_2(\beta \hbar - u) \, du \right] \frac{Z_{r,0}}{Z_{p,0}}.$$

For imaginary times $u \in [0, \beta \hbar]$, the only stationary point of $c_2(u)$ is a minimum at $u = \tau_0(\beta)$, which corresponds to the GR instanton. In the absence of maxima, the asymptotic expansion of Eq. (90) is determined by how $c_2(u)$ behaves near the edges of the integration domains, namely $u = 0$ and $u = \beta \hbar$. These correspond to instantons collapsed at the bottom of the reactant and the product well respectively.
In principle we should also consider the integrand around \( u = \beta \hbar / 2 \), but the corresponding contribution is small and can usually be neglected. It only becomes important if the system is in the near-activationless regime or the activation energy is appreciable but the system is asymmetric and the temperature is extremely low. In both these cases the value of \( c_2(\beta \hbar / 2) \) can become comparable to (or exceeds) one of \( c_2(0) \) or \( c_2(\beta \hbar) \). Otherwise in such cases, our approximation holds because the instanton trajectory associated with \( c_2(\beta \hbar / 2) \) is localised near the barrier region. It will thus resemble a GR instanton and give rise to a relatively large stationary action, making its contribution negligible compared to those from the reactant and product wells. This is shown in Fig. 6, where on panel (a) we plot a representative \( c_2(u) \), normalised by \( Z_{r,0} \). Panel (b) shows the logarithm of \( c_2(u) \)—in this case simply the stationary action at a given \( u \), multiplied by \(-1/\hbar\).

Hence to obtain an asymptotic approximation to Eq. (90) we require the asymptotic form of \( c_2(u) \) as \( u \to 0 \),

\[
c_2(u) \sim Z^{-1}_{r,0} \frac{\Delta^2}{\hbar^2} e^{-\frac{1}{2}(\alpha_{s} u - \frac{1}{4} \gamma_{n} u^2)} \sim Z^{-1}_{r,0} \frac{\Delta^2}{\hbar^2} e^{-\alpha_{s} u / \hbar} \left(1 + \frac{2 u^2}{\hbar^2}\right),
\]

where \( \Delta_r \equiv \Delta(x_r) \), and \( x_r \) is the minimum of \( V_0 \). The coefficients \( \alpha_r \) and \( \gamma_r \) are derived analogously to the \( \alpha_n \) and \( \gamma_n \) in Sec. IV B,

\[
\alpha_r = V_1(x_r) - V_0(x_r), \quad \gamma_r = \sum_{j=1}^{f} g_{p,j}^2 \coth\left(\frac{\beta \omega_{r,j}}{2}\right),
\]

and \( Z_{r,0}^{-1} \) is defined in Eq. (30). As before, \( \omega_{r,j} \) is the frequency of the \( j \)-th reactant normal mode, and \( g_{p,j} \) is the derivative of the product diabat at \( x_r \) with respect to that mode. An analogous expansion can be obtained for \( c_2(\beta \hbar - u) \) as \( u \to 0 \) by exchanging the subscripts \( r \leftrightarrow p \) and potentials \( V_0 \leftrightarrow V_1 \) in Eqs. (91) and (92). These expressions are plotted as dotted lines in Fig. 6, alongside the quantum \( c_2(u) \), which they seen to approximate accurately, at least in regions that contribute significantly to the integrals over \( u \).

Following standard procedure, we substitute the asymptotic expansion of \( c_2(u) \) on the second line of Eq. (91) into the original integrals, which yields

\[
\frac{1}{Z_{r,0}} \int_{0}^{\beta \hbar / 2} c_2(u) \, du \sim \frac{\Delta^2}{\alpha_r^2} \left[ \beta - \frac{2 \theta_r}{\alpha_r} \right] + \frac{\Delta^2}{\alpha_r^2} \left[ - \frac{6 \theta_r}{\alpha_r^2} + \frac{\beta(3 - 2 \theta_r)}{\alpha_r} + \frac{\beta^2 e^{-\beta \alpha_r / 2}}{4} \right]
\]

\[
+ \frac{1}{Z_{s,0}} \int_{0}^{\beta \hbar / 2} u \, c_2(u) \, du \sim \frac{\Delta^2}{\alpha_s} \left[ \theta_s - \frac{\beta e^{-\beta \alpha_s / 2}}{2} \right] + \frac{\Delta^2}{\alpha_s} \left[ - \frac{3 \beta}{2 \alpha_s^2} + \frac{3 \beta^2}{8 \alpha_s} + \frac{3 \beta^3}{16} e^{-\beta \alpha_s / 2} \right]
\]

where \( \theta_s = 1 - e^{-\beta \alpha_s / 2} \), the subscript ‘s’ is either ‘r’ or ‘p’, \( u_r \equiv u \) and \( u_p \equiv \beta \hbar - u \). Substituting Eq. (93) into Eq. (90) then gives the semiclassical approximation to \( Z_{r,2} \) that applies when both \( V_0 \) and \( V_1 \) have stable minima. When \( V_1 \) is unbound, only the first integral in Eq. (90) needs to be calculated, as in this case \( Z_{r,0}/Z_{p,0} \) evaluates to zero, and so the second line of Eq. (90) makes no contribution.

The correction discussed here predominantly accounts for changes in the potential energy at the bottom of the reactant well. In the adiabatic representation, an increase in \( \Delta \) lowers the energy of the well, thus increasing the activation energy barrier. The term in Eq. (90) serves therefore to decrease the overall reaction rate [see Eq. (33)]—an effect that we correctly predict to be negligible if \( \Delta(x) \) decays to zero in the vicinity of the PES minima.

**V. APPLICATION TO MODEL SYSTEMS**

Equation (71) for the \( \tilde{k}_{4A} \) component of the rate constant is identical to the quantum result for one-dimensional linear systems. Equation (88) for \( \tilde{k}_{4B} \) is a highly accurate approximation of the quantum result for the same type of system, reproducing it to within
The black circles are the quantum results. The semiclassical approximations to $\tilde{k}_{A4}$ on the leftmost panel are calculated according to Eq. (88), in combination with either Eq. (87) (red line) or Eq. (C.1) (blue line). On the central panel, the semiclassical $\tilde{k}_{A3}$ are calculated according to Eq. (88), in combination with either Eq. (87) (red line) or Eq. (C.1) (blue line). On the rightmost panel, the semiclassical approximation to $\tilde{Z}_{e,2}/Z_{e,0}$, in red, is calculated as described in Sec. IV C. Each panel includes an inset showing the relative error in the red semiclassical estimate. The dash-dotted line on the middle inset indicates the point at which the reference quantum result is changed as described in the main text.

2.8% or better. It remains to see how accurate these expressions are for nonlinear or anharmonic potentials and in multiple dimensions. To ensure high numerical accuracy of our tests, in this section we consider systems for which the stationary action can either be found using a one-dimensional root-finding algorithm (Sec. V A) or is known analytically (Sec. V B). Since the semiclassical expressions being tested are based on the golden-rule instanton, we anticipate no particular difficulties in extending the approach to more general potentials. We have discussed in other work how to calculate the GR instanton in such cases using the ring-polymer formalism,\textsuperscript{8,22,25,29} and our fourth-order components can be obtained from the output of these calculations during post-processing.

A. Predissociation model

In this example we show that the new theory performs well in anharmonic potentials, using as our test case the predissociation model considered in Refs. 26, 123, and 124,

\begin{align}
V_0(x) &= \frac{1}{2}m\omega^2 x^2 \\
V_1(x) &= D_e e^{-2\alpha(x-\zeta)} - \epsilon,
\end{align}

(94a)

(94b)

where $m = 1$, $\hbar = 1$, $\omega = 1$, $D_e = 2$, $\alpha = 0.2$, $\zeta = 5$, $\epsilon = 2$. The quantum results were calculated by expanding Eqs. (36), (41), and the first line of (90), in terms of the eigenstates of $\hat{H}_{0,1}$ and performing the time integrals analytically. Where applicable, the infinite integration limits for $t$ and $t_1$ were replaced with $t_{\max} = 10$, and with $\pi/\omega$ for $t_0$. Energies up to $E_{\max} = 75$ were included in the calculation and only those eigenfunctions of $\hat{H}_1$ were considered that had a node at $x_{\max} = 35$, which is equivalent to truncating the space at that point. $E_{\max}$, $t_{\max}$ and $x_{\max}$ are all convergence parameters that were confirmed to be sufficiently large for the range of temperatures considered in this section.

All semiclassical results were derived from the stationary action, which is directly available\textsuperscript{104} for the harmonic reactant potential in Eq. (94a), and can be related to the abbreviated action for the repulsive Morse potential in Eq. (94b), as discussed in Appendix D.

We have taken the diabatic coupling to be constant, $\Delta(x) = \Delta$, and calculated the quantum and semiclassical GR thermal rates along with their fourth-order corrections. The three components of the latter are plotted in Fig. 7 across a set of temperatures ranging from the classical to the deep-tunnelling regime. For the $\tilde{k}_{A4}$ contribution plotted on the leftmost panel, we show semiclassical results calculated according to Eq. (71) using two different approximations for $d_{01}$: the red curve uses the expression in Eq. (70), whereas the blue curve sets $d_{01} = 0$. The latter was included to show why it is important to account for the $t_{01}^{(4)}$ term in Eq. (54b), as failing to do so causes the semiclassical estimate to diverge from the correct result in the high-temperature limit. In this example neglecting the quartic term leads to an overestimation of the $\tilde{k}_{A4}$ component by a factor of 3 at the highest temperature considered in our quantum calculations ($\beta = 0.5$).

Including the $d_{01}$ term results in a value that is within a few per cent from the quantum expression down to $\beta = 12$. At lower temperatures, the magnitude of the relative error increases to approximately 20%, which is

FIG. 7. The three components of the $k_4$ thermal rate, calculated for the potentials in Eq. (94) at constant diabatic coupling $\Delta$. The expressions being tested are based on the golden-rule instanton, we anticipate no particular difficulties in extending the approach to more general potentials. We have discussed in other work how to calculate the GR instanton in such cases using the ring-polymer formalism.\textsuperscript{8,22,25,29} and our fourth-order components can be obtained from the output of these calculations during post-processing.

A. Predissociation model

In this example we show that the new theory performs well in anharmonic potentials, using as our test case the predissociation model considered in Refs. 26, 123, and 124,
comparable to the \( \approx 25\% \) error developed by the GR instanton rate in the \( \beta \to \infty \) limit [Fig. 8(a)]. Further down, the relative error appears to decrease—an artefact that can be traced down to our quantum results. Their calculation involves truncating the integration bounds for \( t_0 \) at \( \pm \tau/\omega \) because of recurrences in the \( c_{4A} \) correlation function. At sufficiently low temperatures, this function no longer decays to zero by the cut-off points, and so the quantum \( \tilde{k}_{4A} \) becomes ill-defined.

The \( \tilde{k}_{4B} \) contribution, plotted on the middle panel of Fig. 7 is also approximated using two different semiclassical expressions: the red curve follows the general prescription in Eqs. (87) and (88), and the blue curve replaces Eq. (87) with Eq. (C.1), which would recover the quantum result if the system were linear. Quantum results are calculated according to Eq. (41), with the integration contours for \( z_n \) deformed as in Eq. (43). We use the \( \tau_g \) from the GR instanton to deﬁne the deformed contours and to set the real part of \( z \) in Eq. (42). Ideally, instead of using a ﬁxed \( \text{Re}(z) \) for all \( z_n \), one would choose an optimal value for each combination \( (z_0, z_1) \). This would minimise the oscillations of the integrand in Eq. (42) and reduce the error due to truncating the integration range to \( (-t_{\text{max}}, t_{\text{max}}) \). However we found this computationally demanding and used a ﬁxed \( \text{Re}(z) = \tau_g \) instead. We can verify that this is a reasonable approximation by comparing the output of Eq. (41) to the value obtained from only the \( A_{\tau} \) term. The two are expected to be close across the entire temperature range, and indeed for \( \beta \geq 2 \) the values are within \( 10\% \) of each other.

For smaller \( \beta \) the magnitudes of \( \tilde{k}_{4A} \) and \( A_{\tau} \) are large enough that accurately calculating Eq. (41) poses numerical difﬁculties. For this reason the \( \tilde{k}_{4B} \) plotted at the three highest temperatures includes only the contribution from \( A_{\tau} \). This change is the cause of the small discontinuity in the relative error shown on the inset.

As anticipated, the two semiclassical approximations are very close at high temperatures (small \( \beta \)), but only Eq. (88) is well-behaved for large \( \beta \). Eq. (C.1) predicts a rate constant that rapidly diverges from the quantum result as \( \beta \to \infty \). In the same regime, the “good” approximation develops a constant relative error of around 25\%. This is not an error in the fourth-order expression per se, but is rather a consequence of \( k_{4B}^{sc} \) being proportional to \( k_{4A}^{sc} \), which itself overestimates the GR rate in the \( \beta \to \infty \) limit, as shown in Fig. 8(a). The same observation applies to the partition-function component plotted on the rightmost panel of Fig. 7. Like \( \tilde{k}_{4B} \), it is proportional to the semiclassical golden-rule rate constant and hence develops a (nearly) constant relative error in the low-temperature regime, inherited from \( k_{4C}^{sc} \). Otherwise, the quantum and semiclassical results for this component are in good agreement.

One of the key applications of a fourth-order rate theory is estimating the error introduced by approximating the full thermal rate with just the second-order (golden-rule) term. Specifically, we are interested in the relative error, whose estimate in the small-\( \Delta \) limit is \( k_4/k_2 \), provided \( k_4 \neq 0 \). The latter is important to bear in mind, since \( k_4 \) contains both positive and negative components. Their relative magnitudes are temperature-dependent, such that \( -k_{4A}/k_2 < 0 \) dominates as \( \beta \to 0 \) and \( (\tilde{k}_{4B}/k_2 - \tilde{Z}_{\tau} / \tilde{Z}_{\tau,0}) > 0 \) dominates as \( \beta \to \infty \). Hence there will be a temperature at which these expressions cancel exactly. At that point, strictly speaking, one has to consider the next term in the series, \( k_5 \), in order to estimate the error.

With this in mind, we plot the golden-rule rate constant \( k_2 \) and the ratio \( k_4/k_2 \) in panels (a) and (b) of Fig. 8 respectively, alongside the corresponding semiclassical approximations. As mentioned previously, \( k_{4C}^{sc} \) develops a constant relative error in the low-temperature regime, where the rate plateaus. However, because the terms that dominate \( k_{4C}^{sc} \) at such temperatures are themselves proportional to \( k_{4C}^{sc} \), the ratio \( k_{4C}^{sc}/k_{4C}^{sc} \) beneﬁts from near-complete error cancellation and is a remarkably accurate approximation to the quantum result across the entire temperature range. Like the quantum result, it (approximately) plateaus at low temperatures, when only the reactant vibrational ground state contributes to the process. The semiclassical expression deviates from quantum by no more than 5\% of its maximum absolute value, with the largest deviations found at \( \beta \leq 2.5 \). The errors at
these high temperatures are likely overestimated because of numerical artefacts in the corresponding quantum calculations, but even the apparent level of accuracy is more than sufficient to gauge the validity of the GR approximation. Under favourable circumstances these results should even enable us to correct the GR approximation, which we explore further in Sec. V B.

B. Spin–boson model

Here our attention turns to the multidimensional spin–boson model. As mentioned in the introduction, this type of model potential is not our main target. Even so, it provides a good test system as the corresponding stationary action is known exactly and can be evaluated with relative ease (see Appendix E). Furthermore, because the action is known exactly and can be evaluated with relative ease (see Appendix E). Furthermore, because the model has been extensively studied in the past, benchmark non-perturbative quantum rates are available for a broad parameter range.50

The diabatic PESs for the spin–boson model in “reaction coordinate” form are given by

$$V_n(q, Q) = \frac{1}{2} \Omega^2 \left( q \pm \sqrt{\frac{\Lambda}{2 \Omega^2}} \right)^2 + V_{sb}(q, Q) - \epsilon_n \tag{95a}$$

$$V_{sb}(q, Q) = \sum_{j=1}^{f-1} \frac{1}{2} \omega_j^2 \left( Q_j - \frac{c_j q}{\omega_j} \right)^2, \tag{95b}$$

where \( \omega \) are the bath modes, \( q \) is the reaction coordinate and \( \Lambda \) is the Marcus reorganisation energy. The plus and minus signs are taken for \( n = 0 \) and \( 1 \) respectively, and \( \epsilon_1 - \epsilon_0 = \epsilon \). The coupling coefficients \( c_j \) and normal-mode frequencies \( \omega_j \) are all encoded in the spectral density

$$J(\omega) = \frac{\pi}{2} \sum_{j=1}^{f} \frac{c_j^2}{\omega_j} \delta(\omega - \omega_j). \tag{96}$$

The diabatic coupling, \( \Delta \), is taken to be a constant. Following Ref. 59, we go to the continuum limit (\( f \to \infty \)) and consider a purely Ohmic spectral density

$$J(\omega) = \gamma \omega, \tag{97}$$

where \( \gamma \) is the friction coefficient along the reaction coordinate. We then re-express the diabatic potentials in the conventional spin–boson form,

$$V_n(x) = \sum_{j=1}^{f} \frac{1}{2} \omega_j^2 \left( x_j \pm \frac{e_j \gamma}{\omega_j} \right)^2 - \epsilon_n, \tag{98}$$

where the new coordinates \( x \) are related to \( (q, Q) \) by an orthogonal transformation, and \( \omega_j, e_j \) derive from the Brownian oscillator spectral density,60,118

$$J(\omega) = \frac{\Lambda}{2} \frac{\gamma \Omega^2 \omega}{\omega^2 - \Omega^2 + \gamma^2 \omega^2}. \tag{99}$$

The two-state system in Eq. (98) has been studied extensively, and some of the previously derived analytical results are used by us below.

For harmonic potentials, the semiclassical propagator is exact, the corresponding action \( S_n \) quadratic in the end-points, and the prefactor \( C_n \) independent of positions. Therefore, semiclassical three-time correlation functions for the spin–boson model (obtained following the prescriptions in this paper) are identical to their quantum counterparts. As shown, for example, by Weiss,118 these are generally of the form \( e^{-\phi_{n}(x; a_{0}, z_{f})}/h \). It follows that the time derivatives of \( \phi_{n} \) agree exactly with the coefficients \( d_{n} \) in Eq. (68), and \( a_{n}, \gamma_{n} \) in Eq. (82). The same considerations apply to the single-time correlation function from which the GR rate constant and the partition-function correction are derived. In Appendix E we give the general form of \( \phi_{n}(z) \), where \( \nu = 1, 2, \ldots, \) and \( z \) is a set of \( 2\nu - 1 \) complex time variables. These are used to calculate the quantum \( k_{2} \) and \( k_{4} \) rate constants, and it is also from these that we derive all of the coefficients required for the steepest-descent approximation. The only exception is \( d_{01} \), whose rigorous calculation would in general require high-order derivatives of the action that are not available from standard GR instantaneous calculations. For simplicity, we use the approximate expression for \( d_{01} \) in Eq. (70) with \( \omega = \Omega \), even though in this case the exact value can in principle be obtained.

In Table I we list the second- and fourth-order rate constants for a set of underdamped symmetric (\( \epsilon = 0 \)) and asymmetric (\( \epsilon = 15 \)) spin–boson models, with \( \beta = 1, \ h = 1, \ \Lambda = 60, \) and \( \gamma = \Omega \) ranging from 0.5 to 6. With temperature, reorganisation energy and bias kept constant within each set of systems, rates predicted by classical theories such as Marcus28,30,50 or Zusman43,48,60 are all of the same order of magnitude within a given set. Hence any major variation seen in practice is due to contributions from quantum tunnelling, which becomes more important with increasing \( \Omega \).

All quantum results are calculated by numerical integration of the corresponding correlation functions, and \( k_{3B} \) only includes the contribution from the imaginary-time integral over \( A_{\tau \tau} \). As expected, \( k_{3B}^{\infty} \) is in close agreement with the quantum GR rate for the entire parameter range. Semiclassical approximations of the fourth-order rate components are also accurate across the board, lying within about 10% of quantum.

Notwithstanding the accuracy of its individual components, at \( \Omega = 2 \) the semiclassical approximation to the total \( k_{4} \) rate constant [Eq. (33)] deviates quite significantly from the quantum result. This should come as no surprise, since the three components contribute to the total fourth-order rate constant with different signs. One expects therefore to encounter a combination of parameters for which these contributions cancel exactly. Unless there is some fortuitous cancellation of errors, semiclassical predictions around that point are necessarily expected to show a large relative error. However the key point is that the absolute error remains small. What the semi-
classical theory predicts correctly is that here the fourth-order dependence of the total rate on $\Delta$ is weak, and that the GR expression remains accurate up to greater diabatic coupling strengths than would normally be expected. For additional information one could consider the next term in the perturbation series, $k_6$, which we do not pursue in this work. With this proviso, the semiclassical results in Table I are of sufficient accuracy to establish whether a system is in the GR regime and to estimate the sign and magnitude of the error introduced by making the GR approximation.

It was mentioned in the introduction that the methods developed in this paper are not generally aimed at reactions in solution and do not attempt to describe rate processes involving diffusive motion along the reaction coordinate. Hence it was reasonable to base the preceding discussion on an underdamped spin–boson model ($\gamma = \Omega$). Even so, it is instructive to also analyse the predictions for a strongly overdamped system, which may shed light on the limitations of the method and give insight into the underlying physics. In Table II we list the results for a symmetric spin–boson model at a range of temperatures, with $\Omega = 2$, $\gamma = 32\Omega$, and the remaining parameters kept the same as in Table I. At $\beta = 1$, $k_2^{sc}$, $k_4^{sc}$ and $Z_{12}^{sc}$ are all in excellent agreement with their quantum counterparts, whereas $k_4^{4A}$ underestimates the corresponding quantum value by about an order of magnitude, completely compromising the total rate, $k_4$. The same pattern (not shown) is found at other values of $\epsilon$ and $\Omega$ listed in Table I. This suggests that the assumptions underlying our derivation of $k_4^{4A}$ do not hold in the high-temperature, high-friction regime. We can narrow the issue down to the behaviour of $L_{4A}(t_0, t_1)$, previously defined in Eq. (54a). In Fig. 9 we compare this function to its semiclassical approximation

$$L_{4A}^{sc}(t_0, t_1) = \frac{\Delta^4}{10^4} \left( \frac{\partial^2 \phi_{4A}}{\partial t^2} \right)^{-1/2} e^{-\phi_{4A}/\hbar} \times \exp \left( -\frac{d_0 t_0^2 + d_1 t_1^2 + d_0 t_0^2 t_1^2}{2\hbar} \right),$$

with $\phi_{4A}$ defined as in Eq. (E.4a), and both it and its derivative evaluated at the stationary point.

| $\beta$ | 1 | 2 | 4 |
|---|---|---|---|
| $k_2$ | $7.895 \times 10^{-8}$ | $4.929 \times 10^{-14}$ | $2.781 \times 10^{-26}$ |
| $k_2^{sc}$ | $7.893 \times 10^{-8}$ | $4.928 \times 10^{-14}$ | $2.781 \times 10^{-26}$ |
| $\frac{k_4^{4A}}{k_2}$ | 2.309 | 1.701 | 0.789 |
| $\frac{k_4^{sc}}{k_2}$ | 0.399 | 0.557 | 0.762 |
| $\frac{k_4}{k_2}$ | 0.121 | 0.443 | 1.289 |
| $\frac{k_6}{k_2}$ | 0.123 | 0.469 | 1.424 |
| $\frac{Z_{12}^{sc}}{Z_{12}}$ | 0.016 | 0.033 | 0.066 |
| $\frac{Z_{12}}{Z_{12}^{sc}}$ | 0.016 | 0.033 | 0.066 |
| $\frac{k_4^{4A}}{k_2}$ | $-2.204$ | $-1.291$ | 0.433 |
| $\frac{k_4^{sc}}{k_2}$ | $-0.292$ | $-0.121$ | 0.595 |

TABLE I. Thermal rate constants for the underdamped spin–boson system in Eq. (98), calculated for $\beta = 1$, $\hbar = 1$, $\Lambda = 60$, and $\gamma = \Omega$. The quantum results were calculated by numerical quadrature of the corresponding correlation functions. All results are divided by $\Delta^2$.

| $\epsilon$ | 0 | 2 | 4 | 6 | 0 | 2 | 4 | 6 |
|---|---|---|---|---|---|---|---|---|
| $k_2$ | $7.56 \times 10^{-8}$ | $1.80 \times 10^{-7}$ | $1.00 \times 10^{-6}$ | $5.25 \times 10^{-6}$ | $5.30 \times 10^{-5}$ | $1.12 \times 10^{-4}$ | $4.59 \times 10^{-4}$ | $1.57 \times 10^{-3}$ |
| $k_2^{sc}$ | $7.56 \times 10^{-8}$ | $1.80 \times 10^{-7}$ | $9.91 \times 10^{-7}$ | $5.12 \times 10^{-6}$ | $5.30 \times 10^{-5}$ | $1.12 \times 10^{-4}$ | $4.56 \times 10^{-4}$ | $1.56 \times 10^{-3}$ |
| $\frac{k_4^{4A}}{k_2}$ | 0.947 | 0.0744 | 0.0122 | 0.0042 | 0.992 | 0.0866 | 0.0181 | 0.0088 |
| $\frac{k_4^{sc}}{k_2}$ | 0.859 | 0.0679 | 0.0115 | 0.0042 | 0.891 | 0.0778 | 0.0164 | 0.0079 |
| $\frac{k_6^{4A}}{k_2}$ | 0.122 | 0.0942 | 0.0637 | 0.0485 | 0.114 | 0.0900 | 0.0626 | 0.0487 |
| $\frac{k_6^{sc}}{k_2}$ | 0.122 | 0.0956 | 0.0649 | 0.0492 | 0.115 | 0.0914 | 0.0639 | 0.0494 |
| $\frac{Z_{12}^{sc}}{Z_{12}}$ | 0.0161 | 0.00162 | 0.00164 | 0.00168 | 0.0225 | 0.00229 | 0.00239 | 0.00255 |
| $\frac{Z_{12}}{Z_{12}^{sc}}$ | 0.0160 | 0.00161 | 0.00164 | 0.00167 | 0.0222 | 0.00225 | 0.00231 | 0.00239 |
| $\frac{k_4^{4A}}{k_2}$ | $-0.8417$ | 0.0036 | 0.0350 | 0.0274 | $-0.9000$ | $-0.0194$ | 0.0206 | 0.0143 |
| $\frac{k_4^{sc}}{k_2}$ | $-0.7527$ | 0.0117 | 0.0370 | 0.0284 | $-0.7986$ | $-0.0088$ | 0.0244 | 0.0177 |
The comparison allows us to identify two distinct factors that cause the accuracy of the semiclassical approximation to deteriorate. Firstly, from the plots of $L_{4A}(s,s)$ in Fig. 9(c–d) we see that the approximation in Eq. (70) significantly overestimates the true value of $d_{01}$ at high friction. In principle this can be fixed by basing the approximation on a more sophisticated analytically soluble model. Alternatively one could evaluate $d_{01}$ numerically, which requires implementing the necessary high-order action derivatives in addition to those calculated during GR instanton optimisation. If necessary, we may pursue one or both of these strategies in future work.

Nevertheless a refined estimate of $d_{01}$ would still not bring the semiclassical $\tilde{k}_{4A}$ into alignment with the quantum results due to a second feature, illustrated in Fig. 9(e–f). There we plot $L_{4A}(0,s)$, whose semiclassical approximation is proportional to $\exp(-d_1 s^2/2\hbar)$ and contains no contributions from the quartic $d_{01}$ term. It is apparent that the quantum and semiclassical values agree at short times (indicating that $d_1$ is calculated correctly), but whereas the semiclassical function is shaped like a Gaussian, at long times the quantum expression behaves like a decaying exponential. The emergence of this “fat” exponential tail is almost certainly due to the motion along the reaction coordinate becoming diffusive. This implies that the system spends more time in the barrier region and is more likely to undergo an unreactive transition of the kind described in Sec. IV A, resulting in a larger $\tilde{k}_{4A}$ and a diminished overall rate constant.

That the semiclassical approximation fails to capture the long-time behaviour of $L_{4A}(t_0,t_1)$, and hence the true magnitude of $\tilde{k}_{4A}$, is not a problem of the instanton method per se, but rather a breakdown of steepest-descent in time that affects all transition-state theories (TST). To avoid this, one has to define a more suitable dividing surface/projection operator $\tilde{h}$, leading to an altogether different set of instantons. Thankfully we need not implement so radical a change, since the primary target of our semiclassical rate theory is gas-phase reactions in the deep-tunnelling regime, where instanton theories are typically most useful. In this regime, the reaction rate is unlikely to have significant contributions from diffusive over-the-barrier motion, even if it happens to be a feature at higher temperatures. Instead the rate is dominated by nuclear tunnelling contributions, which are captured accurately by our theory, as shown by the low-temperature results in Table II. As $\beta$ increases, the $\tilde{k}_{4A}$ term decreases relative to the other fourth-order contributions and becomes better approximated by the semiclassical expression. At the lowest temperature considered ($\beta = 4$), the overall agreement between the semiclassical and the quantum rates is comparable to that in Table I, even though the system is heavily overdamped. We expect that a similar level of accuracy will be seen for more chemically realistic potentials.

Our results so far imply that Eq. (33) evaluated semiclassically provides a reliable indicator of whether a reaction is in the golden-rule limit (as long as the rate is not dominated by diffusive motion through the barrier region). The GR rate, $k_g$, should be a reliable approximation to the full (non-perturbative) rate only if $|k_g/k_2| \ll 1$. When this condition is not satisfied, we may attempt to correct the GR approximation using the Padé-summed expression, as discussed in Sec. III D.

In Fig. 10 we compare the semiclassical results to the exact (non-perturbative) rate constants from Ref. 59. Plotted alongside is the same Padé expression calculated using the quantum GR and fourth-order rates from Table I. The semiclassical results overlap their quantum counterparts almost exactly. Hence deviations between our theory and the full nonadiabatic rate that emerge at large $\Delta$ are due to the truncation of the perturbation series, and not the result of making a semiclassical approximation. Also included are the plain GR rate $k_{2g}$, the partial sum $k_{2g} + k_{4g}$, and the output of the Zusman equation. The latter is accurate at high temperature and weak coupling, and is a classical reference that illustrates the magnitude of nuclear quantum effects.

In all cases the corrected semiclassical expression (be it the sum or Padé) is to within graphical accuracy coinci-
all temperatures.

Our goal was to derive a correction to GR in the weak-coupling limit, and consequently we have not incorporated any information from the strong-coupling (adiabatic) limit into our theory. Because of this, our approach cannot rival the global accuracy of the interpolation formula by Lawrence and co-workers at large $\Delta$.\textsuperscript{59} It does, however, go a long way towards fixing the rate at intermediate coupling. Furthermore, the new theory predicts the correct high-temperature dependence of $k_4$ [Eq. (63)] for reactions whose rate is not solvent controlled (i.e., away from the high-friction regime). As mentioned in Sec. IV A, Appendix F shows that classical rates based on the Landau–Zener transmission probability\textsuperscript{51,52} are consistent with our theory in the high-temperature limit. In contrast, the Zusman equation, and hence the interpolation formula, are not—a discrepancy due to Zusman’s underlying assumption of strong solvent friction.\textsuperscript{43,48,60} Our approach thus offers insight into nonadiabatic rate processes at temperatures and frictions that could not be accurately described by pre-existing (semi)classical theories.

VI. DISCUSSION

In this paper we have derived the second term, $k_4$, in the perturbation series expansion of the nonadiabatic rate constant $k$ in powers of the diabatic coupling $\Delta$ (the first term being the golden-rule rate constant $k_2$). Our expression consists of three components, each of which is well approximated by semiclassical instanton methods. The first component, $\tilde{k}_{4A}^{sc}$, corresponds to a four-bounce instanton path. It dominates $k_4$ at high temperatures, decreasing the overall rate, and accounts for recrossing transitions between the two diabats, which can either take place via tunnelling or during the passage of the system through the barrier region. The second component, $\tilde{k}_{4B}^{sc}$, corresponds to a two-bounce instanton path. It dominates $k_4$ at low temperatures and accounts for the enhanced tunnelling probability at stronger diabatic coupling, increasing the overall rate. The final component, $\tilde{Z}_{1,2}$, derives from the minima of the reactant and product wells. Along with $\tilde{k}_{4B}^{sc}$, it dominates at low temperature, but decreases the rate instead. This term largely accounts for changes in the potential energy around the reactant minimum.

Like the semiclassical golden-rule rate, the $\tilde{k}_{4A}^{sc}$ and $\tilde{k}_{4B}^{sc}$ components are identical to their corresponding quantum rate constants for systems comprised of two linear diabats (at least if $\tilde{k}_{4B}^{sc}$ is defined as in Appendix C). As far as we are aware, this is the first time that these expressions are reported in the literature, and hence the first time that the high-temperature asymptotics of $k_4$ are rigorously derived for a system of one-dimensional diabatic potentials. By extension, we expect that the high-temperature rates for multidimensional systems with low to moderate friction along the reaction

![FIG. 10. Exact (non-perturbative) rates calculated with HEOM\textsuperscript{39} (black circles), compared against three semiclassical approximations: golden-rule $k_2$ on its own (GR), the sum $k_2^{sc} + k_4^{sc}$ (SC sum), and the Padé approximation in Eq. (50) (SC Padé). Also shown are Eq. (50) evaluated with quantum rate constants (QM) and rates calculated using the Zusman equation [Eq. (70) in Ref. 59]. The semiclassical approximation is almost exactly on top of the analogous Padé-summed quantum result. Top-row panels (a–b) correspond to symmetric systems, $\epsilon = 0$, and bottom-row panels (c–d) to asymmetric systems, $\epsilon = 15\beta^{-1}$. Plots on the left are for the high-temperature regime ($\beta\hbar\Omega = 0.5$), and plots on the right are for low temperature ($\beta\hbar\Omega = 4$). In all cases $h = 1$, $\Omega = \gamma$ and $\beta\Lambda = 60$.]

\[\text{log}_{10}(k/\hbar) \quad \text{log}_{10}((\beta\Lambda)^{-1})\]

\[\text{Symmetric} \quad \text{Asymmetric}\]

\[\text{SC sum} \quad \text{QM} \quad \text{HEOM} \quad \text{SC Padé} \quad \text{GR} \quad \text{Zusman}\]
coordinate are more accurately described by our theory than by, e.g., the Zusan equation\textsuperscript{43,48,60} or uniform rate expressions\textsuperscript{44,45,50} derived from the Holstein nonadiabatic transmission coefficient\textsuperscript{121} (based in turn on Landau–Zener theory).\textsuperscript{51,52} It should, however, be noted that the latter is consistent with our new theory, as discussed in Appendix F, although the assumptions underlying the Holstein expression mean it can only give the asymptotic form of \( k_{4} (\beta \rightarrow 0) \) up to a temperature-independent constant. Our theory goes beyond LZ and Holstein expressions: not only does it fully establish the high-temperature asymptotics of \( k_{4} \), it also captures the mechanistic transition from over-the-barrier to tunnelling processes, and can therefore be applied at low temperatures.

Calculations of \( k_{4} \) in a one-dimensional predissociation model have shown that our semiclassical expressions readily generalise to anharmonic systems, with the model in Sec. V A displaying deviations from the quantum ratio \( k_{4A} / k_{2} \) that are no greater than 5\% of its maximum absolute value. Analogous calculations for a spin–boson model have shown that the semiclassical rates are also accurate in multidimensional systems. Problems only arise when both the temperature and friction are high, at which point the motion of the nuclei through the barrier region becomes diffusive\textsuperscript{60} and recrossing events quite likely. In line with our physical interpretation, this affects the \( k_{4A}^{SC} \) term, causing it to considerably underestimate the value of its quantum counterpart. One could attempt to fix the problem either by redefining the product projection operator (which would lead to a different semiclassical theory) or by employing our knowledge of the real-time dependence of the quantum \( c_{4A} \) time correlation function for the spin–boson model. Neither is pursued in this work, as our intended domain of application is low-temperature reactions in the gas phase, which are not likely to be rate-limited by diffusion along the reaction coordinate. Nevertheless, in future work it could be interesting to study the spin–boson \( c_{4A} \) correlation function more closely, as such investigations could lead to a generalisation of the Zusan formula\textsuperscript{43,48,60} that would rigorously account for nuclear quantum effects.

For spin–boson models at moderate friction our theory captures the behaviour of the full non-perturbative rate for a wider range of diabatic coupling strengths than the GR rate on its own, and correctly predicts the sign and magnitude of the error introduced by making the golden-rule approximation. Under favourable conditions, one can use the fourth-order terms to obtain significantly improved estimates of the full nonadiabatic rate. Crucially, few additional calculations are necessary to evaluate the new expression. Its \( k_{4A} \) component derives from a GR instanton at \( \beta/2 \), i.e., at twice the temperature of the simulation. Since instanton optimisation typically involves starting at high temperature and cooling the system down,\textsuperscript{3,5,8} it is easy to arrange for \( \beta/2 \) to be visited along the way. All the quantities needed to evaluate \( k_{4A}^{SC} \) are in that case directly available from the output of the optimisation.

The \( k_{4B} \) component derives from a GR instanton at the simulation temperature, \( \beta \). In addition to the output of the GR optimisation, the calculation of \( k_{4B} \) requires the potential energy and gradient of the upper diabatic state (\( V_{1} \) on the reactant side and \( V_{0} \) on the product side), as well as the diabatic coupling \( \Delta \) along the instanton trajectory. However no instanton re-optimisation is required, and the additional quantities need only be evaluated on a relatively sparse grid. The computational overhead thus remains marginal compared to the initial GR optimisation.

The final (partition-function) component, rather than deriving from a delocalised instanton structure, comes from just two points—the minima of the reactant and product diabats. Consequently this term should also add little to the overall computation time. Moreover, this term is expected to often be insignificant in practice, as it is proportional to the square of the diabatic coupling at the reactant/product minimum, which may be negligible.

On the whole, lengthy derivation notwithstanding, one can obtain \( k_{4C} ^{SC} \) in a simple post-processing step to a GR instanton optimisation, involving only a few additional electronic-structure calculations. It has all the makings of a practical method that, like GR instanton theory, can be applied to \textit{ab initio} simulations of real molecules.\textsuperscript{29} Our theoretical approach should also help address the long-standing issue of tackling the Marcus inverted regime beyond the golden-rule limit. Although here we have initially assumed that the two-state system under consideration is in the normal regime, the analytical formulae we have derived for linear diabats are in fact general.\textsuperscript{126} This suggests that \( k_{4C} ^{SC} \) can be reformulated to encompass the inverted regime for arbitrary potentials, much like has been done for golden-rule instantons.\textsuperscript{25,26} We intend to pursue a similar generalisation of our fourth-order semiclassical rates in future work.

Furthermore, the derivations in this paper suggest how one might obtain further high-order terms: \( k_{5} ^{SC} \), \( k_{6} ^{SC} \), and so on. Based on the Green’s function formalism we expect \( k_{6} ^{SC} \) to comprise contributions from three instantons. The first two are likely simple generalisations of the terms encountered so far: a six-bounce 6A term and a two-bounce 6C term, now with two points sampling the upper diabat. The remaining 6B term is expected to combine these elements, resulting in a four-bounce path with a single point sampling the upper diabat. In addition to that, \( k_{6} ^{SC} \) is expected to contain contributions derived from the minima of the diabatic PESs, likely to be insignificant in practice due to the small magnitude of the diabatic coupling at these points. We see no reason why the methods presented in this paper cannot be applied to the derivation of all these components.

Of course it is likely that, beyond a certain point, there is little merit to calculating increasingly high-order terms. Since all of them are associated with golden-rule, rather than adiabatic, instantons, this may not be
the most accurate or efficient way of describing nonadiabatic rates close to the Born–Oppenheimer limit. An alternative would be to apply the ideas developed in this paper to deriving a correction to the adiabatic rate constant, and to then connect the two limits using a suitable interpolation formula (e.g., a two-point Padé approximation), not unlike Ref. 59. Apart from encompassing the full range of coupling strengths, this approach would offer new mechanistic insight into nonadiabatic reactions, rigorously derived from the instantons that underlie the correction terms.

Looking beyond semiclassical instantons, our theory may inspire the search for fourth-order analogues to abatic reactions, rigorously derived from the instantons approach would offer new mechanistic insight into nonadiabatic extensions of RPMD.

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Appendix A: Asymptotic expansion of L_{4\alpha}

Given the quantities in Eq. (66), the Hessian of \( S_{4\alpha} \) [Eq. (51)] at its stationary point can be written as the symmetric matrix

\[
\Sigma_{4\alpha} = \frac{\partial^2 S_{4\alpha}}{\partial \mathbf{v} \partial \mathbf{v}^\top} = \begin{bmatrix}
2\zeta_0 & 0 & 2\zeta_1 \\
0 & \zeta & 0 \\
-w_0 & -w_1 & \bar{w} \Theta \\
w_0 & w_1 & \tilde{\Theta} \\
-w_0 & w_1 & \bar{w} \Theta_0 \Theta \\
\end{bmatrix}, \quad (A.1)
\]

where \( \mathbf{v} \) is a vector formed by concatenating \( \mathbf{\tau} \) and \( \mathbf{x} \), \( \bar{w} = \frac{1}{2}(w_0 + w_1) \) and \( \bar{\zeta} = \frac{1}{2}(\zeta_0 + \zeta_1) \). To integrate Eq. (54a) by steepest descent we rewrite the Hessian as

\[
\Sigma_{4\alpha} \equiv \begin{bmatrix}
M_{11} & M_{12} \\
M_{21} & M_{22}
\end{bmatrix}
\]

where \( \Theta_0 \) and \( \Theta_\pm \) are defined in Eqs. (28) and (67) respectively. Using the same transformation it can be shown that

\[
\begin{aligned}
\mathbf{S}_{4\alpha}^\text{eff} &= S_2 + \frac{1}{2} \begin{pmatrix}
\zeta_0 \\
\zeta_1
\end{pmatrix} \Theta \begin{pmatrix}
\zeta_0 \\
\zeta_1
\end{pmatrix} \quad (\zeta \to 0), \quad (A.4)
\end{aligned}
\]

where \( S_2 \) is evaluated at the stationary point. The second term, multiplied by \(-1/\hbar\), corresponds to the quadratic part of the argument of the exponential on the second line of Eq. (54b). Subsequent calculations are simplified by the orthogonal transformation given by

\[
U = \begin{bmatrix}
1 & 0^\top & 0^\top & 0^\top & 0^\top \\
0 & 1 & 1 & 1 & 1 \\
0 & 1 & 1 & 1 & 1 \\
0 & 1 & 1 & 1 & 1 \\
0 & 1 & 1 & 1 & 1
\end{bmatrix} \quad (A.5)
\]

(here \( 1 \equiv 1_f \)), which can be used to show that

\[
|M_{22}| = |U^\top M_{22} U| = \frac{1}{2} |\Sigma_2| \Theta_\pm \Theta_\pm, \quad (A.6)
\]

with \( \Sigma_2 \) and \( \Theta_\pm \) defined in Eqs. (28) and (67) respectively. Using the same transformation it can be shown that

\[
\begin{aligned}
\mathbf{A} &= \mathbf{M}_{11} - \mathbf{M}_{12} \mathbf{U}^\top \mathbf{M}_{22} \mathbf{U}^{-1} \mathbf{U}^\top \mathbf{M}_{21} = -\begin{pmatrix}
d_0 & 0 \\
0 & d_1
\end{pmatrix},
\end{aligned}
\]

where we identify the diagonal elements with the coefficients \( d_n \), whose explicit form in terms of GR action derivatives is given in Eq. (68).

Appendix B: Asymptotic expansion of L_{4\beta}

Here we derive the expressions in Eq. (82). To this end, it is convenient to perform steepest-descent integration of \( S_{4\beta} \) in stages, treating the difference coordinate \( \mathbf{x}_- \) first, followed by all the remaining variables. We begin by expressing Eq. (73) in terms of the new position variables in Eq. (79) and use the short-time form of the action for the segment of length \( \tau_1 \). The remaining terms are Taylor expanded to second order about \( \tau_1 = 0 \) and \( \mathbf{x}_- = 0 \),

\[
u^\top \Sigma_{4\alpha} \nu = \left( \tau_0 \right)^\top \mathbf{A} \left( \tau_0 \right) + y^\top \mathbf{M}_{22} y \quad (A.3)
\]

allowing one to integrate over \( y \) to get a prefactor \( \sqrt{-(2\pi\hbar)^{4J/J+1}/|\mathbf{M}_{22}|} \) and an effective action

\[
\mathbf{S}_{4\alpha}^\text{eff} = 2S_2 + \frac{1}{2} \begin{pmatrix}
\zeta_0 \\
\zeta_1
\end{pmatrix} \Theta \begin{pmatrix}
\zeta_0 \\
\zeta_1
\end{pmatrix} \quad (\zeta \to 0), \quad (A.4)
\]

where \( S_2 \) is evaluated at the stationary point. The second term, multiplied by \(-1/\hbar\), corresponds to the quadratic part of the argument of the exponential on the second line of Eq. (54b). Subsequent calculations are simplified by the orthogonal transformation given by

\[
U = \begin{bmatrix}
1 & 0^\top & 0^\top & 0^\top & 0^\top \\
0 & 1 & 1 & 1 & 1 \\
0 & 1 & 1 & 1 & 1 \\
0 & 1 & 1 & 1 & 1 \\
0 & 1 & 1 & 1 & 1
\end{bmatrix} \quad (A.5)
\]

(here \( 1 \equiv 1_f \)), which can be used to show that

\[
|M_{22}| = |U^\top M_{22} U| = \frac{1}{2} |\Sigma_2| \Theta_\pm \Theta_\pm, \quad (A.6)
\]

with \( \Sigma_2 \) and \( \Theta_\pm \) defined in Eqs. (28) and (67) respectively. Using the same transformation it can be shown that

\[
\begin{aligned}
\mathbf{A} &= \mathbf{M}_{11} - \mathbf{M}_{12} \mathbf{U}^\top \mathbf{M}_{22} \mathbf{U}^{-1} \mathbf{U}^\top \mathbf{M}_{21} = -\begin{pmatrix}
d_0 & 0 \\
0 & d_1
\end{pmatrix},
\end{aligned}
\]

where we identify the diagonal elements with the coefficients \( d_n \), whose explicit form in terms of GR action derivatives is given in Eq. (68).
yielding
\[
S_{4B} \sim S_0' + S_0'' + S_1 + \frac{m||x_-||^2}{2\tau_1} + \tau_1 V_1(x)
\]
\[
+ \left( \frac{\partial S_0'}{\partial x} - \frac{\partial S_0''}{\partial x} \right) \cdot \left( \frac{x_-}{2} \right) - \frac{\partial S_1}{\partial \tau_1} \tag{B.1}
\]
\[
+ \frac{1}{2} \left( \frac{x_-}{2} \right) \cdot \left[ \frac{\partial^2 (S_0' + S_0'')}{\partial x \partial x} \right] \cdot \left( \frac{x_-}{2} \right) + \frac{1}{2} \frac{\partial^2 S_1}{\partial \tau^2} \tau_1^2,
\]
with \(S_0', S_0'', \) and \(S_1\) defined in Eq. (80). Substituting this expansion for \(S_{4B}\), we evaluate the integral
\[
\int_{-\infty}^{\infty} e^{-S_{4B}/\hbar} \, dx_\perp \sim A e^{-S_{4B}/\hbar}, \tag{B.2}
\]
where
\[
S_{4B}^\text{eff} \sim S_0' + S_0'' + S_1
\]
\[
+ \tau_1 \left\{ V_1(x) - \frac{||p||^2}{2m} + \frac{\partial S_1}{\partial \tau} \right\} \tag{B.3}
\]
\[
+ \frac{1}{2} \tau_1^2 \left\{ \bar{p} \cdot \left[ \frac{\partial^2 (S_0' + S_0'')}{\partial x \partial x} \right] \cdot \bar{p} + \frac{\partial^2 S_1}{\partial \tau^2} \right\}
\]
and we define
\[
\bar{p} = \frac{1}{2} \frac{\partial (S_0' - S_0'')}{\partial x}. \tag{B.4}
\]
The symbol \(A\) denotes a prefactor whose derivation can be skipped here, since it can be deduced by simpler means and has already been given in Eq. (78).

The new, effective action is now expanded to second order in the fluctuations \(\delta v\) about the point \(v\) that satisfies Eq. (81). At this point \(x, x'\), and \(\tau\) assume the values that minimise the GR instanton action; \(x\) is the coordinate along the GR instanton after travelling for imaginary time \(\tau_0\) on the reactant diabat, away from \(x'\). A few simplifications can now be made. Equation (27) relates the derivative of the stationary action to the energy of the corresponding classical imaginary-time trajectory, which we write as
\[
-\frac{\partial S_0'}{\partial \tau_0} = -\frac{1}{2m} \left\| \frac{\partial S_0'}{\partial x} \right\|^2 + V_0(x) \tag{B.5a}
\]
\[
\frac{\partial S_0''}{\partial \tau_0} = -\frac{1}{2m} \left\| \frac{\partial S_0''}{\partial x} \right\|^2 + V_0(x). \tag{B.5b}
\]
Differentiating the difference of these two equations with respect to either \(x\) or \(\tau_0\) and using the fact that at the stationary \(v\)
\[
\bar{p} = \frac{\partial S_0'}{\partial x} = -\frac{\partial S_0'}{\partial x}, \tag{B.6}
\]
we can show that
\[
\frac{\bar{p}}{2m} \cdot \frac{\partial^2 (S_0' + S_0'')}{\partial x \partial x} \cdot \frac{\bar{p}}{2m} = \frac{1}{4} \frac{\partial^2 (S_0' + S_0'')}{\partial \tau_0^2}. \tag{B.7}
\]
Furthermore, considering the factor multiplying \(\tau_1\) in Eq. (B.3) together with Eqs. (B.5a) and (B.6), we can write
\[
-\frac{||p||^2}{2m} - \frac{\partial S_1}{\partial \tau} = V_1(x) - V_0(x) - \frac{\partial S_0'}{\partial \tau_0} - \frac{\partial S_1}{\partial \tau} \tag{B.8}
\]
\[
= V_1(x) - V_0(x),
\]
where the last equality follows from the relation
\[
\frac{\partial S_0'}{\partial \tau_0} = \frac{\partial S_0'}{\partial \tau} = -\frac{\partial S_1}{\partial \tau} \tag{B.9}
\]
at the stationary \(v\). Last, to calculate the \(O(\tau_1 \delta v)\) coefficient, we need the derivative of the same factor with respect to \(v\). In particular, consider
\[
\frac{1}{2} \frac{\partial}{\partial v} \left\| \frac{\partial^2 (S_0' - S_0'')}{\partial v \partial x} \right\|^2 = \frac{1}{2m} \left\| \frac{\partial^2 (S_0' - S_0'')}{\partial v \partial x} \right\|^2 \tag{B.10}
\]
According to Eq. (B.6) this can be rewritten as
\[
\frac{1}{2} \left\{ \frac{\partial^2 S_0'}{\partial v \partial x} \cdot \left[ \frac{\partial S_0''}{m} \frac{\partial^2 S_0''}{\partial v \partial x} \right] + \frac{\partial^2 S_0'}{\partial v \partial x} \cdot \frac{1}{m} \frac{\partial S_0''}{\partial v} \right\} = \frac{1}{2} \frac{\partial}{\partial v} \left\{ \frac{1}{2m} \left\| \frac{\partial S_0''}{\partial v} \right\|^2 + \frac{1}{2m} \left\| \frac{\partial S_0'}{\partial v} \right\|^2 \right\}. \tag{B.11}
\]
From Eq. (B.5) it then follows that
\[
\frac{1}{2m} \frac{\partial}{\partial v} = \frac{\partial V_0(x)}{\partial v} - \frac{1}{2} \frac{\partial^2 (S_0' - S_0'')}{\partial v \partial \tau_0}. \tag{B.12}
\]
Combining all these results we have the following terms in the Taylor series expansion of \(S_{4B}^\text{eff}\):
\[
O(1) : S_0' + S_0'' + S_1 \equiv S_2(\beta), \tag{B.13a}
\]
\[
O(\tau_1) : \tau_1 [V_1(x) - V_0(x)], \tag{B.13b}
\]
\[
O(\tau_1^2) : \frac{1}{2} \tau_1^2 \left[ \frac{1}{4} \frac{\partial^2 (S_0' + S_0'')}{\partial \tau_0^2} + \frac{\partial^2 S_1}{\partial \tau^2} \right], \tag{B.13c}
\]
\[
O(\delta v \delta v) : \frac{1}{2} \delta v \cdot \Phi_0 \cdot \delta v, \tag{B.13d}
\]
\[
O(\tau_1 \delta v) : \tau_1 \delta v \cdot a, \tag{B.13e}
\]
where \(\Phi_0\) is defined in Eq. (83), \(\Phi_0\mid_{\tau=1}\) refers to its column of derivatives with respect to \(\tau\), and
\[
a = \frac{\partial [V_1(x) - V_0(x)]}{\partial v} + \frac{1}{2} \frac{\partial^2 (S_0' + S_0'')}{\partial v \partial \tau_0} - [\Phi_0]_{\tau=1}. \tag{B.14}
\]
The exponential of this truncated Taylor series can now be integrated over \(\tau\) to get another effective action, now depending on \(\tau_0\) only. This has the same \(O(1)\) and \(O(\tau_1)\) terms as in Eq. (B.13), and a quadratic term
\[
\frac{1}{2} \tau_1^2 \left[ \frac{1}{4} \frac{\partial^2 (S_0' + S_0'')}{\partial \tau_0^2} + \frac{\partial^2 S_1}{\partial \tau^2} - a \cdot \Phi_0^{-1} \cdot a \right]. \tag{B.15}
\]
The latter can be simplified by noting that
\[
\Phi_0^{-1} \cdot [\Phi_0]_{\tau=1} = (1, 0, \ldots, 0)^\top \tag{B.16}
\]
and
\[
\frac{d^2(S'_0 + S''_0)}{d\tau_0^2} = \frac{\partial^2(S'_0 + S''_0)}{\partial \tau_0 \partial v} \cdot \Phi^{-1} \cdot \frac{\partial^2(S'_0 + S''_0)}{\partial v \partial \tau_0} = \frac{d^2(S'_0 + S''_0 + S_1)}{d\tau_0^2} = 0. \tag{B.17}
\]

The final relation follows because $S'_0 + S''_0 + S_1$ is equal to the GR instanton stationary action regardless of the value of $\tau_0$. Therefore a full derivative of this expression with respect to $\tau_0$ necessarily evaluates to zero. After this simplification, the bracketed terms in Eqs. (B.13b) and (B.15) can be identified with $\alpha_1$ and $-\gamma_1$ respectively, leading to the final result in Eq. (82).

Appendix C: Exact $k_{AB}$ for linear diabats

For a general potential, evaluating Eq. (85) exactly is not mathematically justified since the integrand is an asymptotic approximation to the quantum $L_{AB}$ that is only valid for $\gamma_1 \to 0$. Linear diabats are a notable exception, since in this case the quantum $L_{AB}$ is precisely of the form in Eq. (77). Hence for these systems it is meaningful to evaluate the expression in Eq. (85) as is, yielding
\[
j_0^{lin}(\tau_0) = \sqrt{\frac{2h}{\gamma_1}} \left[ \text{daw}(\lambda_1) - \exp \left( \frac{\phi_1^2}{4\lambda_1^2} - \phi_1 \right) \text{daw} \left( \lambda_1 - \frac{\phi_1}{2\lambda_1} \right) \right], \tag{C.1}
\]
where $\phi_1 = \frac{2\lambda_1}{\hbar} \gamma_1^* \tau_0$, $\lambda_1 = \alpha_1 / \sqrt{2\gamma_1 \epsilon_1}$, and
\[
\text{daw}(x) \equiv e^{-x^2} \int_0^x e^{t^2} dt \tag{C.2}
\]
is the Dawson function. Substituting this and the analogous $j_1^{lin}$ into Eq. (88) instead of $j_n^{sc}$ defines the quantum $k_{AB}$ for linear diabats with constant coupling $\Delta$. Alternatively we can evaluate Eq. (76) directly, without splitting the $A_\tau$ domain along the diagonal. Both approaches lead to the same expression,
\[
k_{AB}^{lin}(\beta) = \tilde{k}_2^{lin}(\beta) \Delta^{\frac{1}{2}} \sqrt{\frac{8\pi m}{\hbar |\kappa_0 - \kappa_1|}} \int_0^{\frac{\tau^*}{2}} \text{daw} \left( \frac{\tilde{\beta}^2 \sin \theta}{4} \right) d\theta, \tag{C.3}
\]
with $\tilde{k}_2^{lin}$ and $\tilde{\beta}$ defined in Eqs. (58) and (59).

It can be shown that the rate calculated using the approximate $j_n^{sc}$ tends to the quantum result for a system of linear diabats both as $\beta \to 0$ and $\beta \to \infty$. Furthermore, for any combination of parameters the semiclassical rate, $k_{AB}^{sc}$, is never in error by more than 2.8%, with the largest deviation seen at $\tilde{\beta} \approx 3.5$ (in all instances the approximation is a lower bound).

Appendix D: Stationary action for the scattering Morse potential

The abbreviated action is defined as
\[
W(x'', x', E) = \int_{x'}^{x''} p(x, E) \cdot dx, \tag{D.1}
\]
where $p$ is the imaginary-time momentum whose magnitude is $p(x, E) = \sqrt{2m |V(x) - E|}$. For the scattering Morse potential in Eq. (94b), this integral can be evaluated analytically. One must distinguish two types of trajectories: those going directly from $x'$ to $x''$, with action
\[
W_4(x'', x', E) = \left| \frac{p' - p''}{\alpha} - \frac{\mu}{\alpha} \tan^{-1} \left( \frac{\mu p' - \mu p''}{\mu^2 + p'p''} \right) \right|, \tag{D.2}
\]
and those passing through a turning point, with
\[
W_3(x'', x', E) = \left| \frac{p' + p''}{|\alpha|} - \frac{\mu}{|\alpha|} \tan^{-1} \left( \frac{\mu p' + \mu p''}{\mu^2 + p'p''} \right) \right|. \tag{D.3}
\]
Here $p' \equiv p(x', E)$, $p'' \equiv p(x'', E)$, $\mu = \sqrt{2m(E - \epsilon)}$ and $\tan^{-1}(y/x)$ refers to the principal value of the argument of $x + iy$. The abbreviated action satisfies
\[
S(x'', x', \tau) = W(x'', x', E) + E\tau, \tag{D.4}
\]
where for a given $\tau$ the energy is such that
\[
\frac{\partial W}{\partial E} = -\tau. \tag{D.5}
\]
The first-order derivatives of $S$ are given by
\[
\frac{\partial S}{\partial x'} = \frac{\partial W}{\partial x'}, \quad \frac{\partial S}{\partial x''} = \frac{\partial W}{\partial x''}, \quad \frac{\partial S}{\partial \tau} = E, \tag{D.6}
\]
and the second-order derivatives are
\[
\frac{\partial^2 S}{\partial x'^2} = -\left( \frac{\partial^2 W}{\partial E^2} \right)^{-1}, \tag{D.7a}
\]
and
\[
\frac{\partial^2 S}{\partial x''\partial \tau} = -\frac{\partial^2 W}{\partial x''\partial E} \left( \frac{\partial^2 W}{\partial E^2} \right)^{-1}, \tag{D.7b}
\]
\[
\frac{\partial^2 S}{\partial x'^2\partial x''} = -\frac{\partial^2 W}{\partial x'^2\partial E} - \frac{\partial^2 W}{\partial x''\partial E} \left( \frac{\partial^2 W}{\partial E^2} \right)^{-1} \frac{\partial^2 W}{\partial E\partial x''}, \tag{D.7c}
\]
along with all possible variations with $x'$ and $x''$ variously interchanged. This gives all the information necessary to calculate $k_{A\tau}^{sc}$, $k_{2A}^{sc}$ and $k_{AB}^{sc}$. The only other, minor modification is the change of integration variable in Eq. (88) from imaginary time to position,
\[
\int_0^{\tau^*} j_n(\tau_n) d\tau_n \to \int_{x_<}^{x_>} \frac{m j_n(\tau_n(x, E))}{\sqrt{2m |V_n(x) - E|}} dx, \tag{D.8}
\]
where $x_<$ and $x_>$ are respectively the leftmost and the rightmost of $x_1$ (hopping point) and $x_{\beta}$ (turning point), and
\[
\tau_n(x, E) = -\frac{\partial W(x, x_<, E)}{\partial E}. \tag{D.9}
\]
The integral over position gives the same result as the integral over imaginary time, but is the simpler alternative to implement for a one-dimensional system.
Appendix E: Quantum correlation functions for the spin–boson model

In Eq. (44) we give the perturbation series expansion of Tr[|e^{−βH}00]| for the Hamiltonian in Eq. (2). The terms in this series are nested imaginary-time integrals, whose integrands are precisely the multi-time correlation functions that define the rate constants \( k_{2\nu} \) in the perturbation expansion of the total rate. Weiss, in Chapter 19.1 of Ref. 118, gives the analytic form of these correlation functions for the spin–boson model described in Sec. V B, namely

\[
\frac{\phi_{2\nu}(u_{1,..,2\nu})}{Z_{\tau,0}} = \frac{\lambda^{2\nu}}{\hbar^{2\nu}} e^{-\phi_{2\nu}(u_{1,..,2\nu})/\hbar} \quad (E.1a)
\]

\[
\phi_{2\nu} = -\epsilon \sum_{j=1}^{\nu} s_j + \sum_{j=2}^{2\nu} \sum_{i=1}^{j-1} (-1)^{i+j} Q(u_j - u_i), \quad (E.1b)
\]

where

\[
Q(u) = \int_{0}^{\infty} \frac{4J(\omega)}{\pi \omega^2} \left[ \frac{1 - \cosh(\omega u)}{\tan \left( \frac{\beta \omega}{2} \right)} + \sinh(\omega u) \right] d\omega, \quad (E.2)
\]

and \( s_j = u_{2j} - u_{2j-1} \). Obtaining the correlation function that corresponds to a particular component of the \( k_{2\nu} \) rate constants amounts to finding the appropriate variable transformation from \( u_{1,..,2\nu} \) to \( \{z, z_0,..,z_{2\nu-2}\} \). Note that because the exponent in Eq. (E.1) depends only on the differences of \( u_j \), one of the original variables can be eliminated prior to the transformation. For \( \nu = 1 \) this procedure yields the familiar expression used to define the GR rate,\(^{26,33,124}\)

\[
\phi_2 = Q(z) - \epsilon z. \quad (E.3)
\]

For \( \nu = 2 \) we get

\[
\phi_{4A} = Q\left( \frac{\beta h - z}{2} + z_0 \right) + Q\left( \frac{z}{2} + z_1 \right) + Q\left( \frac{\beta h - z}{2} - z_0 \right) + Q\left( \frac{z}{2} - z_1 \right) - Q\left( \frac{\beta h - z_0 - z_1}{2} \right) - Q\left( \frac{\beta h - z_0 + z_1}{2} \right) - \epsilon z, \quad (E.4a)
\]

\[
\phi_{4B} = Q\left( \frac{\beta h - z - z_0}{2} \right) + Q\left( z_1 \right) + Q\left( z_0 \right) + Q\left( z - z_1 \right) - Q\left( z + z_0 - z_1 \right) - Q\left( z_0 + z_1 \right) - \epsilon z. \quad (E.4b)
\]

Continuing in the same fashion, one can generate further multi-time correlation functions, although the expressions quickly become cumbersome, as \( \phi_{2\nu} + \epsilon z \) contains a total of \( \nu(2\nu - 1) \) terms.

Appendix F: Nonadiabatic rates in the high-temperature limit

As \( \beta \rightarrow 0 \), the \( O(\Delta^4) \) correction to the GR rate becomes dominated by the \( k_{4A} \) contribution, whose high-temperature form is given in Eq. (63). Combining this with the high-temperature limit of the GR rate,

\[
k_{2}^{ht}(\beta) = \sqrt{\frac{2\pi m}{\beta h^2}} \frac{\Delta^2}{h[\kappa_0 - \kappa_1]} Z_{\tau,0} e^{-\beta V\hat{1}}, \quad (F.1)
\]

gives

\[
k(\beta) \sim \frac{Z_{\tau}^{1} e^{-\beta V\hat{1}}}{Z_{\tau,0}} \left[ \sqrt{\frac{2\pi m}{\beta h^2}} \frac{\Delta^2}{h[\kappa_0 - \kappa_1]} - \right. \left. \frac{\pi m \Delta^4}{h^3 (\kappa_0 - \kappa_1)^2} \left\{ \ln \left[ \frac{128 m (\kappa_0 - \kappa_1)^2}{\beta^3 h^2 \kappa_0 \kappa_1} \right] - \gamma \right\} \right].
\]

We know that this expansion is correct for a linear model, and we have confirmed that it gives accurate rates in non-linear and multidimensional systems, except at high friction, where the steepest-descent approximation to the integral over \( e_{4A}(t_0, t_1, z) \) breaks down. We especially want to emphasise this, since the logarithmic dependence on \( \beta \) at \( O(\Delta^4) \) seems unusual when compared, for example, to the Zusman equation

\[
k_{\text{Zus}} = \frac{k_{2}^{ht} k_{\text{ad},0}}{k_{2}^{ht} + k_{\text{ad},0}}, \quad (F.3)
\]

which gives the classical limit of the spin–boson rate at small \( \Delta \) and large friction. Here \( k_{\text{ad},0} \) is the classical rate on the lower (cusped) adiabatic surface in the limit as \( \Delta \rightarrow 0 \),

\[
k_{\text{ad},\Delta} = \frac{1}{2\pi \beta h} \frac{Z_{\tau,0}}{Z_{\tau,0}} \exp \left[ 2\beta \Delta \sqrt{\frac{\kappa_0 \kappa_1}{\kappa_0 - \kappa_1}} \right], \quad (F.4)
\]

and hence

\[
k_{\text{Zus}}(\beta) \sim k_{2}^{ht}(\beta) - \frac{Z_{\tau}^{1} e^{-\beta V\hat{1}}}{Z_{\tau,0}} \frac{4\pi^2 m \Delta^4}{h^3 (\kappa_0 - \kappa_1)^2}, \quad (F.5)
\]

which is clearly different from Eq. (F.2). Ultimately this should not come as a surprise, since \( k_{\text{Zus}} \) is derived assuming high friction,\(^{43,60}\) and is therefore valid in a different limit to our semiclassical rate theory.

The interpolation formula of Ref. 59 also fails to recover Eq. (F.2) as \( \beta \rightarrow 0 \). The key change here compared to Eq. (F.3) is that the \( k_{\text{ad},0} \) in the denominator is replaced with \( k_{\text{ad},\Delta} \). This results in a modification to the \( O(\Delta^3) \) term in Eq. (F.5) that is of order \( \beta \) and therefore negligible in this limit. Additionally, the interpolation formula introduces an unphysical term of order \( \Delta^3 \), although this is proportional to \( \beta^2 k_{\text{ad}}^4 \) and hence also negligible in this limit. In short, the Zusman equation and the interpolation formula agree with each other to leading order in \( \beta \Delta \) but predict the wrong high-temperature behaviour for the one-dimensional linear system.
The temperature dependence of our semiclassical rate constants can also be compared to that of thermal rates derived from the cumulative reaction probability

\[ P_H(v) = \frac{2P_{LZ}(v)}{1 + P_{LZ}(v)}, \quad (F.6) \]
given in the form suggested by Holstein.\(^{121}\) Here \( v \) is the velocity of the system along the reaction coordinate in the vicinity of the hopping point, and

\[ P_{LZ}(v) = 1 - \exp \left( -\frac{2\pi \Delta^2}{\hbar v|\kappa_0 - \kappa_1|} \right), \quad (F.7) \]
is the Landau-Zener transmission coefficient.\(^{31,52}\) The latter approximates the probability of transmission between two linear diabatic states during a single passage through the hopping point, and is valid at all coupling strengths \( \Delta \), but only for sufficiently large \( v \). \( P_H(v) \) has been proposed as the starting point for uniform approximations to classical nonadiabatic rates, via

\[ k_{Z,0} = \frac{e^{-\beta V}}{2\pi \hbar} \int_0^\infty mvP_H(v)e^{-\beta mv^2/2} dv \quad (F.8) \]
or similar expressions,\(^{33,35,44,50,53}\) where for simplicity we have taken the system to be one-dimensional. Equation (F.8) is in part motivated by the observation that replacing \( P_H(v) \) with its \( \Delta \to 0 \) limit correctly recovers the classical GR rate. However the next term in the weak-coupling expansion of \( P_H(v) \), which should give the \( \mathcal{O}(\Delta^2) \) behaviour, causes the integral to diverge. This happens because \( P_{LZ}(v) \) is only valid at high velocities. At \( \mathcal{O}(\Delta^2) \), the (spurious) contribution from low velocities as \( \beta \to 0 \) is small enough that Eq. (F.8) can be integrated all the way from 0. At \( \mathcal{O}(\Delta^4) \) this is no longer the case, and a non-zero bound has to be introduced. Hence the correct \( \mathcal{O}(\Delta^4) \) behaviour cannot be obtained using \( P_H(v) \) on its own—for this we would also require the transmission coefficient at low velocities, which is not available in closed form.\(^{54}\) Nevertheless, Eq. (F.8) gives us qualitative insight. First, we rewrite it as

\[ k = k_{Z,0}^2 - \frac{e^{-\beta V}}{Z_{r,0}} \frac{3\pi m \Delta^4}{h^3 (\kappa_0 - \kappa_1)^2} \int_{w_0}^\infty \frac{e^{-w}}{w} dw + \mathcal{O}(\Delta^6) \]
\[ \approx k_{Z,0}^2 - \frac{e^{-\beta V}}{Z_{r,0}} \frac{\pi \Delta^4}{h^3 (\kappa_0 - \kappa_1)^2} \left\{ \ln \left( \frac{1}{w_0^6} \right) - 3\gamma \right\}, \quad (F.9) \]
where \( w = \beta mv^2/2 \) and we have introduced a lower bound \( 0 < w_0 \ll 1 \). Next we note that the exact transmission coefficient for any linear system can be expressed in terms of just two parameters.\(^{28}\) One can then use dimensional arguments to show that \( w_0 \) has to be proportional to the reduced temperature \( \beta \) that we defined previously in Eq. (59). It is no coincidence that the same parameter also appears in the quantum \( k_2 \), \( k_{4A} \) and \( k_{4B} \) for the linear system [Eqs. (58), (62) and (C.3)].

Landau-Zener theory cannot give us the proportionality constant in \( w_0 = \beta/\alpha \), as this requires knowing the small-\( v \) behaviour of \( P(v) \), which falls outside the range of validity of Eq. (F.7). For the same reason, this approach fails to account for transitions at energies below \( w_0/\beta + V \). However the latter are expected to be small for \( \beta \to 0 \), and indeed Eq. (F.9) reproduces the leading behaviour of \( k_4 \) in this limit, correctly predicting the \( \ln(1/\beta^4) \) term inside the curly brackets. The asymptotic behaviour of \( k_4 \) is therefore determined up to an additive constant, and setting \( \alpha = 4 e^{2\gamma/3} \) happens to recover Eq. (F.2) exactly, bringing LZ into agreement with our theory. This suggests that expressions like Eqs. (F.6) and (F.8), when combined with our analysis, can inform future work on rigorous uniform nonadiabatic rate theories, valid across the entire spectrum of diabatic coupling strengths.

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