

Closed-Form Expressions of Quantum Electron Transfer Rate Based on the Stationary-Phase Approximation[†]

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Closed-form rate expressions are derived on the basis of the stationary-phase approximation for the Fermi golden rule expression of the quantum electron-transfer (ET) rate. First, on the basis of approximate solutions of the stationary-phase points near $\Delta G = 0$, $-\lambda$, and λ , where ΔG is the reaction free energy and λ is the reorganization energy, three closed-form rate expressions are derived, which are respectively valid near each value of ΔG . Numerical tests for a model Ohmic spectral density with an exponential cutoff demonstrate good performance of the derived expressions in the respective regions of their validity. In particular, the expression near $\Delta G = -\lambda$, which differs from the semiclassical approximation only by a prefactor quadratic in ΔG , works substantially better than the latter. Then, a unified formula is suggested, which interpolates the three approximate expressions and serves as a good approximation in all three regions. We have also demonstrated that the interpolation formula can serve as a good quantitative means for understanding the temperature dependence of the quantum ET rate.

1. Introduction

Quantum electron transfer (ET), the process where the transferring electron is coupled to quantum mechanical nuclear degrees of freedom, is a subject that has long captured the interest of many researchers in various contexts.^{1–3} In general, the nuclear quantum degrees of freedom have significant effects on the rate of ET for molecular systems with high-frequency vibrational modes and in condensed-phase quantum environments. In the former case, explicit consideration of a few quantum modes is possible, and well-established rate expressions are available at least at the level of the Fermi golden rule.^{1–3} However, in the latter case, for example, for glassy media⁴ or biological systems^{4–6} at cryogenic temperatures, the distribution of quantum modes is more complex, and there is no closed-form rate expression as widely accepted and tested as that in the former case.

For ET reactions in condensed media, it is often necessary to understand the temperature dependence of the rate, so as to achieve a complete clarification of the reaction mechanism.^{4,6–10} However, the variation in temperature may be accompanied by a change in the structural and dynamical properties of the medium, obscuring clear theoretical understanding of the temperature dependence of the experimental rate.^{4,7,8} In fact, for glassy material^{9,11–15} and many biological systems,^{2,6,16,17} the dynamical and spatial heterogeneity of the medium can cause complex temperature dependences, a subject that requires careful theoretical analysis in itself.^{18–25} In this context, a closed-form expression for the ET rate with minimal restriction on the characteristics of the medium is important because it can help to distinguish the temperature dependence solely due to the change of the ET mechanism (assuming temperature-indepen-

dent spectral density) from that due to the temperature dependence of the spectral density, which can occur if the nature of the “effective” medium coupled to the ET changes with temperature. Since it is frequently the case that nuclear quantum effects become significant within the range of the temperature being studied, a quantum expression generalizing the classical Marcus expression^{26–28} becomes necessary in this type of study.

At present, there are two well-known closed-form quantum rate expressions that are applicable to a general spectral density of the bath. One is the semiclassical approximation,^{29,30} and the other is the stationary-phase rate expression for the thermoneutral case.^{31,32} While the latter is more accurate, it cannot be applied to the case with nonzero reaction free energy. On the other hand, the semiclassical approximation might seem appropriate for arbitrary values of reaction free energy. The semiclassical approximation was first introduced in the field of spectral line-shape theory^{33,34} and has been useful for rough quantitative analysis of quantum effects in spectral line shapes,³⁵ photoinduced ET,³⁶ and excitation energy transfer.^{37,38} However, when it comes to its use for ET reactions in the deep normal or inverted regimes, which correspond to exponentially small tails in the case of a spectral line, the semiclassical approximation can cause large relative errors,^{39,40} sometimes exceeding those from the classical approximation.^{39,41} Thus it is not in fact appropriate for arbitrary values of reaction free energy.

Although less well-known, some attempts^{31,42,43} have been made to derive closed-form rate expressions based on the stationary-phase approximation beyond the thermoneutral case. van Duyne and Fischer³¹ derived a rate expression⁶⁰ that is Gaussian with respect to the reaction free energy (ΔG) and valid for small ΔG magnitudes compared to the reorganization energy. Later, Lang et al.⁴² rederived this expression in their extensive mathematical analysis of the Fermi golden rule expression of the quantum ET rate. Tang⁴³ considered a different situation where the bath consists of well-separated classical and quantum

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modes, and derived a new type of Gaussian form expression under the assumption that the classical modes dominate the reorganization energy. The assumptions behind these expressions are less restrictive than the thermoneutral condition. However, all of these still fall short of being general rate expressions applicable to an arbitrary value of reaction free energy.

The evidence so far shows that the stationary-phase approximation provides a reasonable approximation for the Fermi golden rule rate for general values of ΔG . Therefore, if a closed-form rate expression can be derived at the level of the stationary-phase approximation without any restriction on the value of ΔG , it can serve as a more reliable means than the semiclassical approximation and can be quite useful for understanding the quantum ET processes in various condensed media. It is the purpose of this paper to examine this issue thoroughly and to explore the possibility of deriving such an expression. We tackle this problem by first generalizing the known approaches^{31,42,43} to other limiting values of ΔG and then devising an interpolation formula. In this procedure, we make careful analysis of the derived expressions and provide numerical tests. Section II is a preliminary step toward this goal, defining important terms and addressing issues regarding the semiclassical approximation in detail. Section III is the main section of the present paper, and provides extensive discussion about closed-form rate expressions derived from the stationary-phase approximation, important numerical tests, and a new interpolation formula useful for practical applications. Section IV concludes the paper with a summary and discussion about the implications of the present work.

II. Fermi Golden Rule and Semiclassical Approximation

The starting rate expression for many of ET reactions in the nonadiabatic limit, according to the Fermi golden rule, can be expressed as

$$k = \frac{\Delta^2}{\hbar^2} \int_{-\infty}^{\infty} dt e^{-it\Delta G/\hbar - (\mathcal{K}(0) - \mathcal{K}(t))} \quad (1)$$

where Δ is the electronic coupling between the electron donor and the acceptor, ΔG is the reaction free energy, and $\mathcal{K}(t)$ is the bath correlation function given by

$$\mathcal{K}(t) \equiv \int_0^{\infty} d\omega J(\omega) \left(\coth\left(\frac{\hbar\omega}{2k_B T}\right) \cos(\omega t) - i \sin(\omega t) \right) \quad (2)$$

where $J(\omega)$ is the spectral density of the bath (all other degrees of freedom coupled to the ET system). Equation 1 can be derived in a number of ways, for example, by assuming a spin-boson-type Hamiltonian,^{44–49} or by invoking a linear response approximation starting from a non-Hamiltonian model with a linearly coupled dielectric medium.⁵⁰ Equation 1 can represent a broad range of ET processes by an appropriate choice of the spectral density. For example, the rate expression by Jortner⁵¹ corresponds to the case where $J(\omega)$ consists of discrete molecular vibrational modes (inner sphere) well separated from the continuous spectrum of classical bath modes (outer sphere). For general condensed-phase quantum environments, where $J(\omega)$ exhibits more complex patterns, derivation of a reliable closed-form rate expression based on eq 1 is a yet unsettled theoretical issue.

Given the spectral density $J(\omega)$, the reorganization energy λ playing the central role in the classical ET theory^{2,3,26–28} can be expressed as

$$\lambda = \int_0^{\infty} d\omega J(\omega) \hbar\omega \quad (3)$$

In the high temperature limit where all the bath modes can be treated classically, the only information (about the bath) needed for the calculation of the ET rate is this reorganization energy unless the effects of nonlinear coupling^{52–56} become important. However, in the regime where the quantum effects of the bath are important, additional terms characterizing the bath spectral density are needed, even for the case of linear coupling. Here we introduce three such terms as follows:

$$\lambda_{q,c} \equiv \frac{\hbar}{2k_B T} \int_0^{\infty} d\omega J(\omega) \coth\left(\frac{\hbar\omega}{2k_B T}\right) \omega^2 \quad (4)$$

$$\lambda_{q,s} \equiv \frac{\hbar^2}{2k_B T} \int_0^{\infty} d\omega J(\omega) \frac{\omega^2}{\sinh(\hbar\omega/2k_B T)} \quad (5)$$

$$\lambda_{q,t} \equiv 4k_B T \int_0^{\infty} d\omega J(\omega) \tanh\left(\frac{\hbar\omega}{4k_B T}\right) \quad (6)$$

These all approach the reorganization energy λ in the high-temperature limit,⁶¹ and we call these quantum “reorganization” energies.⁶² It turns out that information on each of these three quantities is needed for reasonable description of the quantum effects at arbitrary values of ΔG .

In the limit where all the nuclear degrees of freedom become classical, it is well known that eq 1 reduces to the following Marcus expression:^{26,27}

$$k_M = \frac{\Delta^2 \left(\frac{\pi \hbar^2}{k_B T \lambda} \right)^{1/2}}{\hbar^2} \exp \left\{ -\frac{(\Delta G + \lambda)^2}{4k_B T \lambda} \right\} \quad (7)$$

The semiclassical approximation²⁹ is often used as a convenient means to derive the above expression from eq 1. Expanding the exponent in eq 1 around $t = 0$ up to the second order of t , one finds that

$$\mathcal{K}(0) - \mathcal{K}(t) \approx \frac{k_B T}{\hbar^2} \lambda_{q,c} t^2 + \frac{i}{\hbar} \lambda t \quad (8)$$

where $\lambda_{q,c}$ is defined by eq 4. Inserting eq 8 into eq 1 and then performing a Gaussian integration, we obtain the following semiclassical approximation for the rate:

$$k_{sc} = \frac{\Delta^2 \left(\frac{\pi \hbar^2}{k_B T \lambda_{q,c}} \right)^{1/2}}{\hbar^2} \exp \left\{ -\frac{(\Delta G + \lambda)^2}{4k_B T \lambda_{q,c}} \right\} \quad (9)$$

In the high-temperature limit, $\lambda_{q,c} \rightarrow \lambda$, and the above expression reduces to k_M .

As has been shown above, the semiclassical approximation, eq 9, is derived under the assumption that the stationary-phase point of the exponent in eq 1 is $t = 0$. It should be noted that this assumption is valid only for $\Delta G + \lambda = 0$ unless the temperature is high enough to approach the classical limit. That is, while it is perfectly valid to use the semiclassical approximation as an intermediate step for deriving the classical Marcus expression, it will not serve as a reliable quantitative means for describing the quantum ET rate at arbitrary values of ΔG . Indeed, some researchers^{39,57} have reported situations in which its performance is not satisfactory. To examine this issue in more detail, here we employ eq 9 for a model Ohmic spectral density with an exponential cutoff given below:

$$J_o(\omega) = \frac{1}{\omega} e^{-\omega/\omega_c} \quad (10)$$

For this spectral density, the reorganization energy λ is equal

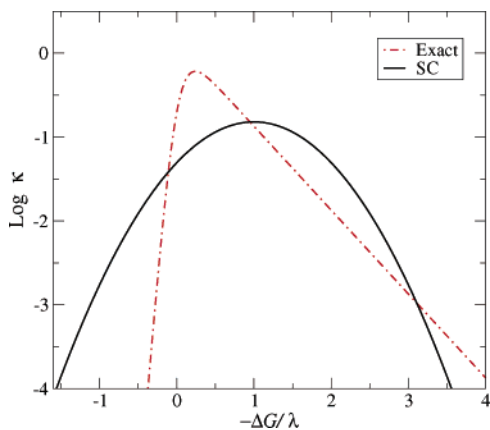


Figure 1. Logarithm (natural) of a dimensionless scaled rate κ versus $-\Delta G/\lambda$. κ is calculated by multiplying k or k_{sc} by $\hbar\sqrt{k_B T\lambda}/(\sqrt{\pi}\Delta^2)$. The units are such that $\hbar = \omega_c = k_B = 1$, and the temperature $T = 1/10$. “Exact” represents eq 1, evaluated exactly through fast Fourier transform, and “SC” represents the semiclassical approximation, eq 9.

to $\hbar\omega_c$. A useful closed-form expression³⁵ for $\lambda_{q,c}$ is used. Figure 1 compares the rate calculated from the semiclassical approximation with the exact numerical calculation of eq 1. Units are such that $\hbar = \omega_c = k_B = 1$, where the reorganization energy λ for the spectral density of eq 10 becomes unity. A low-temperature value of $T = 1/10$ was chosen. Figure 1 shows that the deviation of the semiclassical approximation from the exact evaluation of eq 1 is significant, except at $\Delta G = -\lambda$ and two other coincidental points. The semiclassical approximation does not reproduce the asymmetry of the curve between the normal ($-\Delta G \leq \lambda$) and the inverted ($-\Delta G > \lambda$) regions, an essential feature for the quantum bath. The slope of the logarithm of the semiclassical approximation with respect to ΔG differs from that of the exact numerical data, even at $\Delta G = -\lambda$. This discrepancy indicates that the accuracy of semiclassical approximation is not sufficient for a quantitative description of the temperature dependence of the quantum ET rate, even near the barrierless region.

The issue regarding the semiclassical approximation as addressed above underscores why a better approximation based on the stationary-phase approximation is desired. In the next section, we first analyze the stationary-phase approximation in detail near three values of reaction free energy— $\Delta G = 0$, $-\lambda$, and λ —so as to derive three approximate but closed-form rate expressions valid near the respective ΔG values. The expression near $\Delta G = 0$ reduces to the known expression^{31,39} for ΔG exactly equal to zero, but with an additional approximation for the preexponential factor, in the case of a small departure from $\Delta G = 0$. Expressions for the cases $\Delta G \sim \pm\lambda$ also have interesting properties. In particular, the expression near $\Delta G = -\lambda$, which modifies the semiclassical approximation by a simple preexponential factor, improves the accuracy substantially. On the basis of the three expressions, we then derive an interpolation formula. Numerical tests of these expressions are performed for the spectral density of eq 10, which demonstrate the validity of the first three approximations and the interpolation formula.

III. Stationary-Phase Approximation

Let us denote the stationary-phase point of the integrand of eq 1 as t_s . Then, from the condition that the time derivative of the exponent of the integrand is zero, one can obtain the following implicit equation:

$$\int_0^\infty d\omega \frac{J(\omega)\omega}{\sinh(\omega\tau_{th})} \sinh(\omega(\tau_{th} - it_s)) = -\frac{\Delta G}{\hbar} \quad (11)$$

where τ_{th} represents the thermal time scale and is defined by

$$\tau_{th} \equiv \frac{\hbar}{2k_B T} \quad (12)$$

Assuming that there is an imaginary solution for t_s and that the steepest descent path across the solution is parallel to the real axis, the stationary-phase integration of eq 1 near t_s leads to the following rate expression:

$$k_{sp} = \frac{\Delta^2}{\hbar^2} \left(\int_0^\infty d\omega \frac{J(\omega)\omega^2}{2\pi \sinh(\omega\tau_{th})} \cosh(\omega\tau_s) \right)^{-1/2} \times \exp \left\{ \frac{\Delta G}{\hbar} (\tau_s - \tau_{th}) - \int_0^\infty d\omega J(\omega) \frac{\cosh(\omega\tau_{th}) - \cosh(\omega\tau_s)}{\sinh(\omega\tau_{th})} \right\} \quad (13)$$

where we have introduced a new variable,

$$\tau_s = -it_s + \tau_{th} \quad (14)$$

which satisfies the following equation:

$$\int_0^\infty d\omega \frac{J(\omega)\omega}{\sinh(\omega\tau_s)} \sinh(\omega\tau_s) = -\frac{\Delta G}{\hbar} \quad (15)$$

For general ΔG and $J(\omega)$, there is no known analytic solution of the above equation. However, at three values of ΔG (0, λ , and $-\lambda$), eq 15 has simple solutions valid for a general spectral density. On the basis of these solutions, we derive closed-form approximations for eq 13 that are valid near the three respective values of ΔG .

A. Approximation for Equation 13 near $\Delta G = 0$. When $\Delta G = 0$, $\tau_s = 0$ becomes the solution of eq 15. As long as ΔG remains small, one can make the approximation $\sinh(\omega\tau_s) \approx \omega\tau_s$ and insert it into eq 15, which leads to the following approximate solution for the stationary-phase point:

$$\tau_s \approx -\tau_{th} \frac{\Delta G}{\lambda_{q,s}} \quad (16)$$

where $\lambda_{q,s}$ is defined by eq 5 and τ_{th} is given by eq 12. This solution is accurate through the second order of ΔG . Inserting eq 16 into eq 13 and then retaining terms up to the second order of ΔG , we find an approximation for k_{sp} near $\Delta G = 0$, which is denoted as $k_{sp,1}$:

$$k_{sp,1} = \frac{\Delta^2}{\hbar^2} \left(\frac{\pi\hbar^2}{(1 + Q_1)k_B T \lambda_{q,s}} \right)^{1/2} \times \exp \left\{ -\frac{(\Delta G + \lambda_{q,s})^2}{4k_B T \lambda_{q,s}} + \frac{\lambda_{q,s} - \lambda_{q,t}}{4k_B T} \right\} \quad (17)$$

where $\lambda_{q,s}$ and $\lambda_{q,t}$ are defined by eqs 5 and 6, and

$$Q_1 \equiv \frac{\Delta G^2}{2(2k_B T \lambda_{q,s})^3} \int_0^\infty d\omega \frac{J(\omega)(\hbar\omega)^4}{\sinh(\omega\tau_{th})} \quad (18)$$

The above rate expression, eq 17, except for the additional term Q_1 in the preexponential factor, is the same as the expression derived by van Duijne and Fischer³¹ and later rederived by Lang et al.⁴² As has been stated in the Introduction,

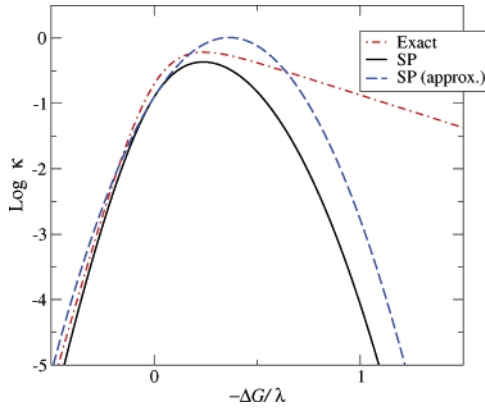


Figure 2. Logarithm (natural) of a dimensionless scaled rate κ versus $-\Delta G/\lambda$. κ is calculated by multiplying k or its approximations by $\hbar\sqrt{k_B T\lambda}/(\sqrt{\pi}\Delta^2)$. The units are such that $\hbar = \omega_c = k_B = 1$, and the temperature $T = 1/10$. “Exact” represents eq 1, evaluated through fast Fourier transform; “SP” represents the stationary-phase approximation, eq 17; and “SP(approx.)” represents eq 17 with the approximation of $Q_1 = 0$.

this expression is less restrictive than the thermoneutral condition and seems complementary to the semiclassical approximation. However, to our knowledge, eq 17, even with the assumption of $Q_1 = 0$, has not been tested numerically nor applied to an actual system, unlike the well-known rate expression for the thermoneutral case.^{49,57} The rate expression derived by Tang⁴³ has not been numerically tested either. It employs basically the same type of linearization approximation for the stationary-phase point and approaches the same limit, eq 17, when $\Delta G = 0$. However, its derivation is based on an additional physical assumption. That is, Tang’s rate expression for nonzero ΔG is valid only when there is clear separation between the classical and quantum bath modes, and the former dominates the reorganization energy. Although many physical systems can meet such assumptions, it seems inappropriate for low-temperature glassy or protein media, which do not always have clear separation between the classical and quantum baths. Thus we do not consider Tang’s rate expression⁴³ further in the present paper.

Equation 17 is valid as long as the next (cubic) term in the expansion of $\sinh(\omega\tau_s)$ makes a much smaller contribution than that of the leading linear term. One can show that this condition is equivalent to the following inequality:

$$Q_1 \ll 3 \quad (19)$$

For nonzero ΔG and a given spectral density, this condition sets the lower bound for the temperature, below which eq 17 is not applicable.

In Figure 2, we test eq 17 against the exact numerical results of eq 1. The spectral density and the choice of parameters are the same as those in Figure 1. Also shown is eq 17 with $Q_1 = 0$, the rate expression derived in refs 31 and 42. The comparison of the two approximations (with and without Q_1) shows that the inclusion of Q_1 extends the region where eq 17 works well. The results shown in the figure demonstrate that eq 17 is complementary to the semiclassical approximation. The performance of eq 17 is reasonably good in the region of $|\Delta G/\lambda| \leq 1/4$ at the particular temperature chosen ($T = 1/10$). However, according to the condition of eq 19, this region is expected to shrink as the temperature goes down.

It is interesting to examine how and under what conditions eq 17 approaches k_M (eq 7). Before providing the analysis, let us first introduce the third moment of the spectral density defined as

$$M_3 \equiv \int_0^\infty d\omega J(\omega)(\hbar\omega)^3 \quad (20)$$

Then, expanding all the terms defined by eqs 5, 6, and 18 with respect to $1/(k_B T)$, we find that

$$\lambda_{q,s} \approx \lambda - \frac{M_3}{24(k_B T)^2} \quad (21)$$

$$\lambda_{q,s} - \lambda_{q,t} \approx -\frac{M_3}{48(k_B T)^2} \quad (22)$$

$$Q_1 \approx \frac{\Delta G^2 M_3}{8(k_B T)^2 \lambda^3} \quad (23)$$

In the high-temperature limit satisfying the following conditions,

$$\frac{M_3}{(k_B T)^2} \ll \lambda, k_B T \quad (24)$$

$\lambda_{q,s} \approx \lambda$ and $\lambda_{q,s} - \lambda_{q,t} \approx 0$. As long as ΔG is at most comparable to λ in magnitude, which is naturally satisfied by the smallness of $\Delta G/\lambda_{q,s}$ as assumed in this subsection, the condition of eq 24 also implies that $Q_1 \approx 0$. These constitute the conditions for eq 17 to approach the classical limit k_M . It is important to note that eq 19, the necessary condition for eq 17, is automatically satisfied under the above high-temperature conditions. Thus, the above analysis serves as another derivation of the classical Marcus expression from the Fermi golden rule expression.

B. Approximation for Equation 13 near $\Delta G = -\lambda$. When $\Delta G + \lambda = 0$, $\tau_s = \tau_{th}$ becomes a solution of eq 15. As long as $\Delta G + \lambda$ remains small, we can expand τ_s around τ_{th} up to the second order of $\tau_s - \tau_{th}$ as follows:

$$\sinh(\omega\tau_s) \approx \sinh(\omega\tau_{th}) + \cosh(\omega\tau_{th})\omega(\tau_s - \tau_{th}) + \frac{1}{2} \sinh(\omega\tau_{th})\omega^2(\tau_s - \tau_{th})^2 \quad (25)$$

Inserting this approximation into eq 15 and iterating the solution up to the second order of $\Delta G + \lambda$, we find that

$$\tau_s \approx \tau_{th} \left(1 - \frac{\Delta G + \lambda}{\lambda_{q,c}} - \frac{M_3(\Delta G + \lambda)^2}{8(k_B T)^2 \lambda_{q,c}^3} \right) \quad (26)$$

Inserting this solution into eq 15 and keeping all the terms up to the second order of $(\Delta G + \lambda)$, we obtain an approximation for k_{sp} near $\Delta G = -\lambda$, which is denoted as $k_{sp,2}$ and has the following form:

$$k_{sp,2} = \frac{\Delta^2}{\hbar^2} \left(\frac{\pi\hbar^2}{(1 + Q^2)k_B T \lambda_{q,c}} \right)^{1/2} \exp \left\{ -\frac{(\Delta G + \lambda)^2}{4k_B T \lambda_{q,c}} \right\} \quad (27)$$

where

$$Q_2 \equiv -\frac{M_3(\Delta G + \lambda)}{4(k_B T \lambda_{q,c})^2} - \frac{M_3^2(\Delta G + \lambda)^2}{32(k_B T \lambda_{q,c})^4} + \frac{(\Delta G + \lambda)^2}{16(k_B T \lambda_{q,c})^3} \int d\omega J(\omega) \coth(\omega\tau_{th})(\hbar\omega)^4 \quad (28)$$

The approximation of eq 27 is different from the semiclassical approximation, eq 9, only by the additional term Q_2 in the preexponential factor. The two approximations become the same

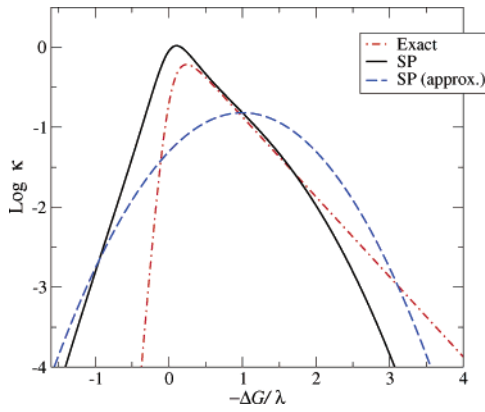


Figure 3. Logarithm (natural) of a dimensionless scaled rate κ versus $-\Delta G/\lambda$. κ is calculated by multiplying k or its approximations by $\hbar\sqrt{k_B T\lambda}/(\sqrt{\pi}\Delta^2)$. The units are such that $\hbar = \omega_c = k_B = 1$, and the temperature $T = 1/10$. “Exact” represents eq 1, evaluated through fast Fourier transform; “SP” represents the stationary-phase approximation, eq 27; and “SP(approx.)” represents eq 27 with the approximation of $Q_2 = 0$.

when $\Delta G = -\lambda$, where Q_2 vanishes. However, for $\Delta G + \lambda \neq 0$, eq 27 is expected to work better than eq 2. In Figure 3, we compare these two against the exact calculation of eq 1. The spectral density and the temperature are the same as those in Figure 1. We find that the performance of eq 27 is much more satisfactory than that of the semiclassical approximation, and that the inclusion of Q_2 is crucial for reproducing the correct ΔG derivative of the logarithmic rate near $\Delta G = -\lambda$.

Expanding all the terms in eq 27 with respect to $1/(k_B T)$, one can examine how it approaches k_M in the high-temperature limit. Expanding eqs 4 and 28 up to the lowest order of $1/(k_B T)$, we find that

$$\lambda_{q,c} \approx \lambda + \frac{M_3}{12(k_B T)^2} \quad (29)$$

$$Q_2 \approx -\frac{M_3(\Delta G + \lambda)}{4(k_B T)^2 \lambda^2} + \frac{M_3(\Delta G + \lambda)^2}{8(k_B T)^2 \lambda^3} \quad (30)$$

If the condition of eq 24 is satisfied, the above expressions show that $\lambda_{q,c} \approx \lambda$ and $Q_2 \approx 0$ as long as $\Delta G + \lambda$ is at most comparable to λ in magnitude, which is satisfied by the smallness of $(\Delta G + \lambda)/\lambda_{q,c}$, consistent with the assumption made in this subsection. These constitute the conditions under which eq 27 approaches the classical limit k_M .

C. Approximation for Equation 13 near $\Delta G = \lambda$. When $\Delta G - \lambda = 0$, $\tau_s = -\tau_{th}$ becomes a solution of eq 15. As long as $\Delta G - \lambda$ remains small, one can expand τ_s around $-\tau_{th}$ up to the second order of $\tau_s + \tau_{th}$ as follows:

$$\sinh(\omega\tau_s) \approx -\sinh(\omega\tau_{th}) + \cosh(\omega\tau_{th})\omega(\tau_s + \tau_{th}) - \frac{1}{2} \sinh(\omega\tau_{th})\omega^2(\tau_s + \tau_{th})^2 \quad (31)$$

Inserting this approximation into eq 15 and iterating the solution up to the second order of $\Delta G - \lambda$, we find that

$$\tau_s \approx -\tau_{th} \left(1 + \frac{\Delta G - \lambda}{\lambda_{q,c}} - \frac{M_3(\Delta G - \lambda)^2}{8(k_B T)^2 \lambda_{q,c}^3} \right) \quad (32)$$

Inserting this solution into eq 13 and keeping all the terms up to the second order of $\Delta G - \lambda$, we obtain an approximation

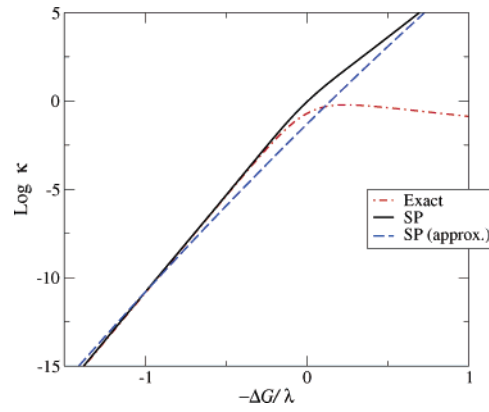


Figure 4. Logarithm (natural) of a dimensionless scaled rate κ versus $-\Delta G/\lambda$. κ is calculated by multiplying k or its approximations by $\hbar\sqrt{k_B T\lambda}/(\sqrt{\pi}\Delta^2)$. The units are such that $\hbar = \omega_c = k_B = 1$, and the temperature $T = 1/10$. “Exact” represents eq 1, evaluated through fast Fourier transform; “SP” represents the stationary-phase approximation, eq 33; and “SP(approx.)” represents eq 33 with the approximation of $Q_3 = 0$.

for k_{sp} near $\Delta G = \lambda$, which is denoted as $k_{sp,3}$ and has the following form:

$$k_{sp,3} = \frac{\Delta^2}{\hbar^2} \left(\frac{\pi \hbar^2}{(1 + Q_3)k_B T \lambda_{q,c}} \right)^{1/2} \times \exp \left\{ -\frac{(\Delta G - \lambda + 2\lambda_{q,c})^2}{4k_B T \lambda_{q,c}} + \frac{\lambda_{q,c} - \lambda}{k_B T} \right\} \quad (33)$$

where

$$Q_3 = \frac{M_3(\Delta G - \lambda)}{4(k_B T \lambda_{q,c})^2} - \frac{M_3^2(\Delta G - \lambda)^2}{32(k_B T \lambda_{q,c})^4} + \frac{(\Delta G - \lambda)^2}{16(k_B T \lambda_{q,c})^3} \int d\omega J(\omega) \coth(\omega) (\hbar\omega)^4 \quad (34)$$

In the above rate expression, eq 33, the Gaussian width factor $\lambda_{q,c}$ is the same as that in eq 27. However, eq 33 is different from eq 27 in that the Gaussian exponent is centered at $\lambda - 2\lambda_{q,c}$, and that there is an additional exponential factor and a slightly different term (Q_3) in the preexponential factor. Comparing eqs 28 and 34, one can easily show that $Q_3(\Delta G) = Q_2(-\Delta G)$. This equality is crucial for the detailed balance condition to hold between $k_{sp,2}$ and $k_{sp,3}$. That is, from eqs 27 and 33, we find that the following relation holds for an arbitrary value of ΔG :

$$\frac{k_{sp,3}(\Delta G)}{k_{sp,2}(-\Delta G)} = \exp \left(-\frac{\Delta G}{k_B T} \right) \quad (35)$$

Figure 4 compares eq 33 with the exact calculation of eq 1. Also shown is the rate with Q_3 neglected. The spectral density and the values of all the parameters are the same as those in previous figures. The results shown in Figure 4 confirm that eq 33 serves as a good approximation near $\Delta G = \lambda$ and that neglecting Q_3 degrades the accuracy of the approximation.

According to Figure 4, the errors of eq 33 become very large for $\Delta G < 0$. Thus, on the basis of this numerical test, it may not be clear whether eq 33 approaches the proper classical limit for all values of ΔG . This can be examined making the same analysis as that which has been made in the previous subsections. Expanding all the terms in eq 33 with respect to $1/(k_B T)$

and keeping terms up to the lowest order of $1/(k_B T)$, we find that

$$2\lambda_{q,c} - \lambda \approx \lambda + \frac{M_3}{6(k_B T)^2} \quad (36)$$

$$\lambda_{q,c} - \lambda \approx \frac{M_3}{12(k_B T)^2} \quad (37)$$

$$Q_3 \approx \frac{M_3(\Delta G - \lambda)}{4(k_B T)^2 \lambda^2} + \frac{M_3(\Delta G - \lambda)^2}{8(k_B T)^2 \lambda^3} \quad (38)$$

From the above expressions, it is clear that $2\lambda_{q,c} - \lambda \approx \lambda$ and $\lambda_{q,c} - \lambda \approx 0$ in the limit where eq 24 is satisfied. Provided that $\Delta G - \lambda$ remains at most comparable to λ in magnitude, this condition also implies that $Q_3 \approx 0$. Therefore, in the classical limit as specified above, eq 33 approaches k_M of eq 7.

D. An Interpolation Formula. We have gone through an elementary analysis of the stationary-phase approximation, eq 13, and derived closed-form rate expressions that are respectively valid near $\Delta G = 0$, $-\lambda$, and λ . The similarity of these three expressions suggests the possibility that a unified formula interpolating the three expressions may exist. Even though such an expression does not have a solid physical basis, it can still be important for a quantitative description of quantum ET or as a basis for developing a theory of quantum ET in low-temperature glassy media or protein environments.

Let us suppose that the interpolation formula can be expressed in the following form:⁶³

$$k_{sp} \approx \frac{\Delta^2}{\hbar^2} \left(\frac{\pi \hbar^2 W}{k_B T \lambda_{q,in}} \right)^{1/2} \exp \left\{ -\frac{(\Delta G + \lambda)^2}{4k_B T \lambda_{q,c}} \right\} \quad (39)$$

where $\lambda_{q,in}$ (expressed below) is introduced to account for the variation of the preexponential factor with ΔG , and W serves as an additional weighting factor. We assume that $\lambda_{q,in}$ is a quadratic function of $\Delta G/\lambda$ and impose that it reproduces the correct preexponential factors of the stationary-phase approximation at $\Delta G = 0$, $-\lambda$, and λ . Then, one can obtain the following expression:

$$\lambda_{q,in} = (\lambda_{q,c} - \lambda_{q,s}) \left(\frac{\Delta G}{\lambda} \right)^2 + \lambda_{q,s} \quad (40)$$

For W , we adopt the following functional form:

$$W = \frac{1}{1 + \alpha e^{\gamma \Delta G/\lambda}} \quad (41)$$

and assume that α and γ are positive. For a sufficiently large negative value of ΔG , W becomes unity. For a sufficiently large positive value of ΔG , it behaves like $e^{-\gamma \Delta G/\lambda}/\alpha$. That is, W contributes to the exponent of the rate in the normal region where the exponent of the semiclassical approximation becomes inaccurate. Assuming that γ is sufficiently large to ensure that $W \approx 1$ when $\Delta G = -\lambda$, we can determine α and γ so that eq 39 reproduces the stationary-phase rate expressions at $\Delta G = 0$ and λ . Solving the two resulting equations, we find that α and γ in eq 41 are given by

$$\alpha = e^{(\lambda_{q,c} \lambda_{q,t} - \lambda^2)/(2k_B T \lambda_{q,c})} - 1 \quad (42)$$

$$\gamma = \ln \left[\frac{e^{2\lambda(\lambda_{q,c} - \lambda)/(k_B T \lambda_{q,c})} - 1}{e^{(\lambda_{q,c} \lambda_{q,t} - \lambda^2)/(2k_B T \lambda_{q,c})} - 1} \right] \quad (43)$$

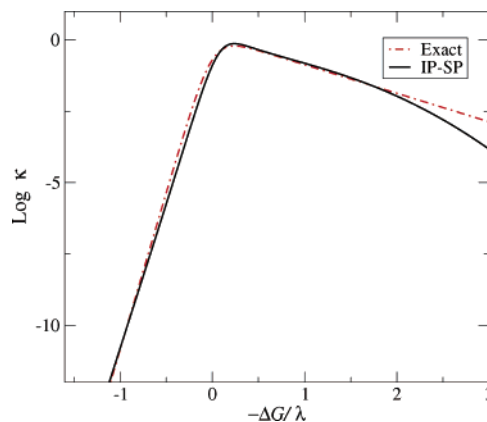


Figure 5. Logarithm (natural) of a dimensionless scaled rate κ versus $-\Delta/\lambda$. κ is calculated by multiplying k or its approximation by $\hbar\sqrt{k_B T \lambda}/(\Delta^2 \sqrt{\pi})$. The units are such that $\hbar = \omega_c = k_B = 1$, and the temperature $T = 1/10$. “Exact” represents the rate given by eq 1, which is calculated through fast Fourier transform, and “IP-SP” represents the interpolation formula, eq 39.

It is not clear whether the above expressions guarantee that α and γ are positive and real for arbitrary spectral density and temperature. However, in the high-temperature limit, it can be checked employing the expansions of $\lambda_{q,c}$ and $\lambda_{q,t}$ with respect to $1/(k_B T)$. That is, using eq 29 and the following expansion:

$$\lambda_{q,t} \approx \lambda - \frac{M_3}{48(k_B T)^2} \quad (44)$$

we find that

$$\alpha \approx \frac{M_3}{32(k_B T)^2} \quad (45)$$

$$\gamma \approx \ln\left(\frac{16}{3}\right) \quad (46)$$

up to the lowest order of $1/(k_B T)$. These expressions indeed show that α and γ are positive in the high-temperature limit. For low temperatures, the positivity of α and γ can be evaluated numerically given the spectral density.

For the model spectral density of eq 10, we calculated eq 39 under the same conditions used in the previous figures. The results (IP-SP) are shown in Figure 5. Comparison with the exact numerical calculation of eq 1 demonstrates that the interpolation formula provides an excellent approximation for the Fermi golden rule expression, eq 1, in all the three regions near $\Delta G = -\lambda$, 0, and λ . There is no significant degradation of its accuracy between these regions either. This shows that eq 39 indeed provides a reliable interpolation of the three expressions derived in the previous subsections.

E. Temperature Dependence. So far, we have tested the approximate rate expressions by varying ΔG at a fixed temperature, $T = 1/10$. In the present subsection, we examine how well the rate expressions account for the temperature dependence. For many experimental ET systems, the reaction free energy is in the range between 0 and $-\lambda$. Thus, we consider three representative values of ΔG within this region: 0, -0.5λ , and $-\lambda$. The range of temperature is such that $1 \leq 1/T \leq 20$. While ΔG and λ are, in general, free energies, in the present model study, we neglect any entropic contribution. (Note that λ (eq 3) is calculated assuming temperature-independent spectral density, $J_o(\omega)$, as given by eq 10.)

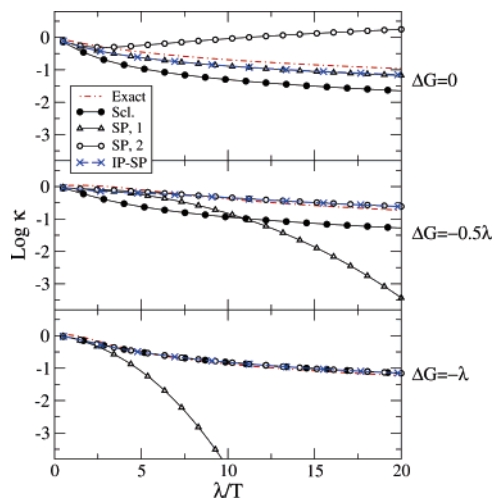


Figure 6. Logarithm (natural) of a dimensionless scaled rate κ versus $1/T$ at three values of ΔG : 0, -0.5λ , and $-\lambda$. κ is calculated by multiplying k or its approximation by $\hbar\sqrt{k_B T\lambda}/(\sqrt{\pi}\Delta^2)$. The units are such that $\hbar = \omega_c = k_B = 1$. “Exact” represents eq 1, calculated exactly through fast Fourier transform; “Scl.” represents the semiclassical approximation, eq 9; “SP,1” represents the stationary-phase approximation near $\Delta G = 0$, eq 17; “SP,2” represents the stationary-phase approximation near $\Delta G = -\lambda$, eq 27; and “IP-SP” represents the interpolation formula, eq 39.

We compare the semiclassical expression (eq 9), the two stationary-phase approximations (eqs 17 and 27), and the interpolation formula (eq 39) with the exact numerical evaluation of eq 1. The rate expression eq 33 is not reliable at the values of ΔG chosen above, and is not considered in the present test.

The results shown in Figure 6 confirm that all the quantum rate expressions approach the same classical rate in the high-temperature limit, and that each approximation works well at the values of ΔG where its derivation can be justified. The semiclassical approximation, eq 9, reproduces the correct temperature dependence reasonably well at $\Delta G = -\lambda$. However, its performance is not satisfactory at $\Delta G = -0.5\lambda$ or at $\Delta G = 0$. On the other hand, the performance of eq 27, which differs from the semiclassical approximation only in the preexponential factor, works well at both $\Delta G = -\lambda$ and $\Delta G = -0.5\lambda$. However, when $\Delta G = 0$, eq 27 again shows substantial deviation from the exact result, and even exhibits a qualitatively incorrect trend (the increase of rate with the decrease of temperature in comparison with the exact numerical results). Equation 17, the stationary-phase approximation near $\Delta G = 0$, works well when $\Delta G = 0$, as expected. However, for other values of ΔG , it deviates substantially from the exact numerical results in the low-temperature region.

Turning now to the interpolation formula, we find that eq 39 serves as the best approximation at all three ΔG regions. Although not shown here, we also tested the temperature dependence of the interpolation formula at $\Delta G = \lambda$ along with eq 33, and confirmed that these agree quite well with the exact evaluation of the rate. Thus the interpolation formula seems to serve as a reliable means for the study of temperature dependence as long as ΔG is in the region of $-\lambda \leq \Delta G \leq \lambda$ or does not depart from this region significantly.

IV. Summary

The motivation for the present paper was to derive simple closed-form quantum rate expressions that are more accurate than the semiclassical approximation. We used the more reliable stationary-phase approximation as the starting point, and

achieved our goal by first deriving three closed-form expressions that are respectively valid near three values of ΔG (0, $-\lambda$, and λ), and then devising a formula that can interpolate between the three expressions. Tests for a model Ohmic spectral density demonstrate the validity of our analysis and permit the performance of different approximations to be assessed. It was shown that the interpolation formula yields significant improvement relative to the semiclassical approximation or the Gaussian form expression derived by van Dyne and Fischer,³¹ and is more general than Tang’s expression,⁴³ which requires clear separation between quantum and classical baths.

The new expressions derived in the present paper are slightly more complicated than the semiclassical approximation. In particular, the rate expression near $\Delta G \approx -\lambda$ (eq 27), which differs from the semiclassical approximation only by an additional term (Q_2) in the preexponential factor, shows that substantial improvement of the latter is possible by a simple correction in the preexponential factor. It was also shown that the interpolation formula, eq 39, serves as a reasonably good approximation for the quantum ET rate, not only within the region of $-\lambda \leq \Delta G \leq \lambda$, but also somewhat outside of this region, as can be seen in Figure 5. The results presented in Figure 6 demonstrate that it serves as the best approximation for the study of temperature dependence as well. It is interesting to note that the interpolation formula requires only the three quantum reorganization energies defined by eqs 4–6 in addition to λ . This suggests that the information on the three quantum reorganization energies may be sufficient for reasonably accurate calculations of the quantum ET rate.

Because of its simplicity, the semiclassical approximation has been employed for the description of quantum ET rates in many systems and sometimes has become the starting point for more elaborate theories such as the Hoffman–Ratner theory¹⁹ for the ET rate in a medium going through glass transition. The essence of this theory is the assumption of a temperature-varying reaction free energy and reorganization energy under the constraint that $\Delta G + \lambda$ remains invariant. This phenomenological theory has recently been applied to the ET process in a bacterial light-harvesting complex 1 (LH1),⁴ and has been helpful in explaining the steep decrease of the ET rate below the glass transition temperature of the medium. However, considering the possible errors caused by the semiclassical approximation, this does not yet verify that the assumption of the Hoffman–Ratner theory is indeed valid for the LH1 system in the glassy medium. The use of the interpolation formula, eq 39, can be helpful in resolving such ambiguity.

For the development of a quantum ET theory in glassy media, not only a reliable rate expression, but also a detailed theoretical prescription for treating the temperature-dependent medium response is necessary. In addition, one must take account of complications due to spatial heterogeneity. Quite recently, Matyushov²⁰ presented an interesting approach to handle the issue of medium response. This theory starts at the level of the bath spectral density, unlike the Hoffman–Ratner theory, and employs a self-consistent approach where only the portion of spectral density with frequencies larger than the rate is used for the calculation of the reorganization energy. The resulting rate expression needs to be solved iteratively, employing a known functional form for the rate. Matyushov adopted the classical Marcus expression for this purpose. However, considering the significant quantum effects due to the medium, it is, in general, necessary to use a quantum ET expression. The interpolation formula, eq 39, may be appropriate for such purpose.

Finally, we would like to mention that, although the major focus of the present paper was ET theory, many of the new expressions obtained here can also be applied to excitation energy transfer³⁸ and condensed-phase linear spectroscopy,^{35,58,59} where the rate or the line shape involves the same type of Fermi golden rule expression.

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- (60) There is a typo in the rate expression provided in ref 31. Refer to eq 13 and the following paragraph of the present paper for the correct expression.
- (61) The classical limit is defined as the high-temperature limit where $\hbar\omega/(k_B T) \ll 1$ for all the ω with nonnegligible contribution to $J(\omega)$.
- (62) It should be noted that the term "reorganization" is used in a loose sense here, and that these quantum "reorganization" energies do not necessarily have clear physical interpretation.
- (63) It appears that this form provides a reasonable interpolation of the three stationary-phase approximations according to our numerical tests, but we cannot identify a clear physical basis for choosing this type of interpolation formula.