Electron transfer in the nonadiabatic regime: Crossover from quantum-mechanical to classical behaviour

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We study nonadiabatic electron transfer within the biased spin-boson model. We calculate the incoherent transfer rate in analytic form at all temperatures for a power law form of the spectral density of the solvent coupling. In the Ohmic case, we present the exact low temperature corrections to the zero temperature rate for arbitrarily large bias energies between the two redox sites. Both for Ohmic and non-Ohmic coupling, we give the rate in the entire regime extending from zero temperature, where the rate depends significantly on the detailed spectral behaviour, via the crossover region, up to the classical regime. For low temperatures, the rate shows characteristic quantum features, in particular the shift of the rate maximum to a bias value below the reorganization energy, and the asymmetry of the rate around the maximum. We study in detail the gradual extinction of the quantum features as temperature is increased.

I. INTRODUCTION

Electron transfer plays an important role in many chemical and biological reaction processes [1–5]. A prime example is the ultrafast primary electron transfer step in photosynthetic reaction centers, which is responsible for the high efficiency of the photosynthetic mechanism. The theory of electron transfer (ET) in chemical reactions goes back to Marcus [6] and Levich [7]. They were among the first who recognized the importance of the solvent environment. Since the donor and acceptor states are strongly solvated, the transfer of the electron entails a reorganization of the environment. This results in a free energy barrier separating reactants and products. The transition of the electron from the reactant to the product state can only take place if favorable bath fluctuations bring reactant and product states into resonance.

Electron transfer is conveniently discussed by considering the diabatic potential energy surfaces (PES) of each electronic state. In the classical limit, the transfer rate is determined by two factors. First, a Boltzmann factor with the activation energy $E_a$ required for bath fluctuations to the crossing region of the two diabatic PES. Second, an attempt frequency prefactor describing the probability for tunnelling once the levels are in resonance. The latter factor is mainly determined by the overlap between the electronic wave functions localized
on different redox sites. For large intersite coupling, the reaction is adiabatic, whereas for weak intersite coupling, the reaction is nonadiabatic. In this paper, we restrict ourselves to nonadiabatic electron transfer, where we have fast thermal fluctuations to the vicinity of the crossing region followed by a fast transversal of this region. Then the intersite coupling $\Delta$ can be treated in perturbation theory, which leads in lowest order to the Golden Rule formula for the rate, $k^+ \propto \Delta^2 \exp(-E_a/k_BT)$.

As the temperature is lowered to the quantum regime, nuclear tunnelling through the free energy barrier, which crucially depends on the detailed form of the spectral density, becomes effective and competes with thermal activation. We concentrate on spectral densities with a power law form at low frequencies, which has proven to be a useful characterization in many chemical and condensed matter applications. The appearance of quantum features in the ET rate with decreasing temperature has been repeatedly studied in the last decades (see Refs. [8–12] and references therein). However, a unified analytical treatment of the nonadiabatic case in the entire temperature regime is still missing.

The purpose of the present work is twofold. First, we give a detailed study of the quantum signatures for different spectral densities. The most characteristic quantum features are the shift of the rate maximum to a bias value below the classical reorganization energy, and the asymmetry of the rate around the maximum. Second, we discuss quantitatively the gradual extinction of the quantum effects as the temperature is tuned from the quantum to the classical regime. In Section II, we introduce the model and sketch the properties of the classical Marcus rate. In Section III, we review the important Ohmic case, for which the deep quantum regime can be described in analytic form. Special attention is paid to the situation of a large bias energy between the donor and acceptor state for nonzero temperature. To our knowledge, this case has not been studied systematically until now, except for some numerical results in Ref. [13]. In the remainder, we consider the rate in steepest descent ranging from the sub-Ohmic to the super-Ohmic case. General features are discussed in Section IV. In Section V, we study the rate at $T = 0$ and discuss the differences between the Ohmic and the non-Ohmic case. The two remaining sections are devoted to an analytic study of the crossover from quantum to classical behaviour. In Section VI, we concentrate on the case of small bias energies between the two redox sites. Finally, in Section VII, we consider the interesting strong bias regime, in which quantum features are most pronounced. We present a uniform description throughout the whole temperature range.

**II. THE MODEL**

As implied by the success of classical Marcus theory, the electron can be described in terms of two discrete states at all temperatures of interest. Modelling the solvent by a linearly responding heat bath, the proper Hamiltonian is the spin boson Hamiltonian [14–16]

$$H = -\frac{\hbar}{2}(\Delta \sigma_x - \epsilon \sigma_z) + \sum_\alpha \left[ \frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}m_\alpha \omega_\alpha^2 x_\alpha^2 \right] - \mu E \sigma_z.$$  

(1)

Here, $\sigma_z$ and $\sigma_x$ are Pauli spin matrices. Throughout, we put $\epsilon > 0$. The donor and acceptor states are the eigenstates of $\sigma_z$ with eigenvalues $+1$ and $-1$, respectively, and they differ by a bias energy $\hbar \epsilon$. Transitions between these localized states are induced by the
intersite or electronic coupling $\hbar \Delta$. The spin operator $\sigma_z$ is coupled linearly to the collective bath mode $\mu \mathcal{E} = (q_0/2) \sum_{\alpha} c_{\alpha} x_{\alpha}$, where $\mathcal{E}$ can be considered as a fluctuating dynamical polarization which vanishes on average, and $2\mu$ is the difference in the dipole moments of the two electronic states. The effects of the solvent are fully described by the spectral density $G(\omega) = (q_0^2/2\hbar) \sum_{\alpha} (c_{\alpha}^2/m_{\alpha} \omega_{\alpha}) \delta(\omega - \omega_{\alpha})$. Outer-sphere ET reactions are controlled by fluctuations in the solvent polarization which cover a wide frequency range. To model the solvent environment, we choose a smooth spectral density with a power law form at low frequencies and an exponential cutoff at high frequencies,

$$G(\omega) = 2\delta_s \omega^{1-s} \omega^s e^{-\omega/\omega_c}. \quad (2)$$

Here $\omega_c$ is a cutoff frequency for the bath modes and $\delta_s$ is a dimensionless coupling parameter. For convenience, we discriminate the reference frequency $\omega_{ph}$ from the cutoff frequency $\omega_c$. Ohmic or frequency-independent damping is described by $s = 1$, whereas the regimes $s > 1$ and $s < 1$ are referred to as super-Ohmic and sub-Ohmic damping.

For sufficiently high temperatures and/or strong damping, the system exhibits overdamped exponential relaxation towards the equilibrium state. Hence the dynamics in this regime is completely described by transition rates which obey the principle of detailed balance. In the nonadiabatic regime $\Delta \ll \omega_c$, the incoherent tunnelling rate from the donor to the acceptor state (forward rate) is given by the Golden Rule expression \[15]\,

$$k^+(\epsilon) = \frac{\Delta^2}{4} \int_{-\infty}^{\infty} dz e^{i\epsilon z - Q(z)}. \quad (3)$$

In Eq. (3), the system-environment coupling is considered in all orders, whereas the electronic coupling is treated in second order. The quantity $Q(z)$ is the twice integrated bath correlation function, $d^2Q(z)/dz^2 = (2\mu/\hbar)^2 \langle \mathcal{E}(z)\mathcal{E}(0) \rangle$, and is given by \[15,16]\,

$$Q(z) = \int_0^{\infty} d\omega \frac{G(\omega)}{\omega^2} \left\{ \coth \left( \frac{\hbar \omega}{2} \right) \left( 1 - \cos(\omega z) \right) + i \sin(\omega z) \right\}, \quad (4)$$

where $\beta = 1/k_B T$. The function $Q(z)$ is an analytic function of the complex time $z$ in the strip $0 \geq \text{Im} \ z > -\hbar \beta$ and obeys the symmetry relation $Q(-z - i\hbar \beta) = Q(z)$. Therefore, we can arbitrarily distort the integration contour in Eq. (3) inside this strip. We may choose, e.g., the contour $\mathcal{C}_\tau$ with constant negative imaginary part $0 \leq \tau < \hbar \beta$, as shown in Fig. 1.

![FIG. 1. The complex time plain z with three possible contours C_\tau.](image-url)
If we had derived the rate formula (3) with the alternative Im F-method instead of the Golden Rule approach, we would have directly obtained the contour $\mathcal{C}_\tau$ where $\tau$ is the width of the bounce (kink anti-kink pair) in imaginary time. The equivalence of these seemingly different approaches follows from the analytic properties of $Q(z)$. Putting $\tau = \hbar \beta / 2$ and $z = t - i\hbar \beta / 2$, the rate (3) is equivalently expressed as [17]

$$k^+(\epsilon) = \frac{\Delta^2}{4} e^{\hbar \beta \epsilon / 2} \int_{-\infty}^{\infty} dt \, e^{i \epsilon t} \, e^{-X(t)} = \frac{\Delta^2}{2} e^{\hbar \beta \epsilon / 2} \int_0^{\infty} dt \, \cos(\epsilon t) \, e^{-X(t)}.$$  (5)

The function $X(t)$ is real and symmetric in $t$,

$$X(t) \equiv Q(z = t - i\hbar \beta / 2) = \int_0^{\infty} d\omega \, \frac{G(\omega)}{\omega^2} \left[ \coth(\frac{1}{2} \hbar \beta \omega) - \frac{\cos(\omega t)}{\sinh(\frac{1}{2} \hbar \beta \omega)} \right].$$  (6)

In the representation (3), the detailed balance relation between the forward rate $k^+(\epsilon)$ and the backward rate $k^-(\epsilon) = k^+(\epsilon)$ is directly visible,

$$k^+(\epsilon) = e^{\hbar \beta \epsilon} k^-(\epsilon).$$  (7)

With the form (3), the integrations in Eqs. (4) and (6) can be performed exactly, yielding

$$Q(z) = 2\delta_s \Gamma(s - 1) \left( \frac{\omega_c}{\omega_{ph}} \right)^{s-1} \left\{ \left[ 1 - (1 + i\omega_c z)^{-s} \right] + 2(\hbar \beta \omega_c)^{1-s} \zeta(s - 1, 1 + \kappa) \right. \right.$$

$$- (\hbar \beta \omega_c)^{1-s} \left[ \zeta(s - 1, 1 + \kappa + i \frac{z}{\hbar \beta}) + \zeta(s - 1, 1 + \kappa - i \frac{z}{\hbar \beta}) \right] \left\} \right.$$  (8)

$$X(t) = 2\delta_s \Gamma(s - 1) \left( \frac{\omega_c}{\omega_{ph}} \right)^{s-1} \left\{ 1 + 2(\hbar \beta \omega_c)^{1-s} \zeta(s - 1, 1 + \kappa) \right. \right.$$

$$- (\hbar \beta \omega_c)^{1-s} \left[ \zeta(s - 1, 1 + \kappa + i \frac{t}{\hbar \beta}) + \zeta(s - 1, 1 + \kappa - i \frac{t}{\hbar \beta}) \right] \left\} \right.$$  (9)

Here, $\zeta(y, q)$ is Riemann’s generalized zeta function [18], $\Gamma(y)$ is Euler’s gamma function, and $\kappa = 1/\hbar \beta \omega_c$. For integer $s$, Eqs. (8) and (9) can be expressed in terms of polygamma functions. We shall refer to the case $\kappa \ll 1$ as the quantum limit, whereas the case $\kappa \gg 1$ describes the classical limit in which $k_B T$ is the largest energy scale of the problem. Note that for a high cutoff $\omega_c$, the quantum regime may extend up to quite high temperatures. Oppositely, for a very low cutoff, the classical regime reaches down to low temperatures.

In the classical limit $\kappa \gg 1$, the integral in Eq. (3) is dominated by the short-time regime, in which we can substitute the classical form $Q_{cl}(z)$ for Eq. (4),

$$Q_{cl}(z) = i \Lambda_{cl} z + (\Lambda_{cl}/\hbar \beta) z^2.$$  (10)

Here, $\hbar \Lambda_{cl}$ is the classical reorganization energy of the solvent, where

$$\Lambda_{cl} = \int_0^{\infty} d\omega \, \frac{G(\omega)}{\omega} = 2\delta_s \Gamma(s)(\omega_c/\omega_{ph})^{s-1} \omega_c.$$  (11)
The second equality holds for the spectral density (2). With Eq. (10), the calculation of the rate \( k^+ \) reduces to a Gaussian integration, giving the classic Marcus rate in the nonadiabatic limit

\[
k^+_{\text{cl}}(T, \epsilon) = \frac{\Delta^2}{4} \sqrt{\frac{\pi h \beta}{\Lambda_{\text{cl}}}} \exp \left\{ -\frac{h \beta}{4\Lambda_{\text{cl}}} (\epsilon - \Lambda_{\text{cl}})^2 \right\}.
\]

(12)

The influence of every bath is thus characterized by only one parameter, the classical reorganization energy, and the rate is insensitive to details of the spectral density. If the bias equals the reorganization frequency, \( \epsilon = \epsilon^* = \Lambda_{\text{cl}} \), the transfer is activationless, and the rate is maximal for fixed \( T \). Furthermore, the rate is symmetric around the maximum.

As the temperature is lowered to the quantum regime, nuclear tunnelling through the free energy barrier becomes effective. The quantum rate then shows some characteristic features which sensitively depend on the detailed form of the spectral density \( G(\omega) \). In the next section, we review the Ohmic case \( s = 1 \), in which the integral in Eq. (3) or (5) can be calculated in analytic form in the quantum regime. For non-Ohmic spectral densities, this is no longer possible, and we have to employ the method of steepest-descent.

### III. THE OHMIC RATE IN THE QUANTUM REGIME

In the Ohmic case \( s = 1 \), the spectral density (2) takes the form \( G(\omega) = 2K \omega e^{-\omega/\omega_c} \), where the dimensionless coupling strength \( \delta_i = K \) is often called Kondo parameter. By carefully performing the limit \( s \to 1 \) of the expressions (8) and (9), we obtain

\[
Q(z) = 2K \ln(1 + i\omega_c z) + 2K \ln \left( \frac{h \beta \omega_c \Gamma^2(1 + \kappa)}{\Gamma(1 + \kappa + iz/h\beta)\Gamma(1 + \kappa - iz/h\beta)} \right),
\]

(13)

\[
X(t) = 2K \ln \left( \frac{h \beta \omega_c \Gamma^2(1 + \kappa/2)}{\Gamma(1/2 + \kappa + it/h\beta)\Gamma(1/2 + \kappa - it/h\beta)} \right).
\]

(14)

In the quantum regime \( h \beta \omega_c \gg 1 \), the second term in Eq. (13) is simplified and we get

\[
Q(z) = 2K \ln(1 + i\omega_c z) + 2K \ln \left( \frac{\sinh(\pi z/h\beta)}{\pi z/h\beta} \right).
\]

(15)

The first term represents the correct \( T = 0 \) limit without any approximation. In the often employed scaling limit, the first term in Eq. (13) is approximated by \( 2K \ln(i\omega_c z) \). The scaling form for \( Q(z) \) is only justified if the contribution of the core region \( |z| \leq 1/\omega_c \) to the rate integral (3) is negligible. This is the case only if the bias is much smaller than the cutoff frequency, \( \epsilon \ll \omega_c \). The equivalent scaling form of \( X(t) \) reads

\[
X(t) = 2K \ln \left( \frac{h \beta \omega_c}{\pi} \cosh \left( \frac{\pi t}{h\beta} \right) \right).
\]

(16)

With Eq. (16), the rate (3) is calculated in analytic form as

\[
k^+(T, \epsilon) = \frac{\Delta^2}{4\omega_c} \left( \frac{h \beta \omega_c}{2\pi} \right)^{1-2K} \frac{\Gamma(K+i\beta \epsilon/2\pi)}{\Gamma(2K)} e^{\beta \epsilon/2},
\]

(17)
which is valid for \( k_B T, \hbar \epsilon < \hbar \omega_c \). The behaviour of this already well-known expression is discussed in Refs. [13,16]. We remark that the form (17) was originally obtained from the representation (3) using the scaling form of \( Q(z) \) [13,21]. In this representation, however, the rate integral (3) seems to exist only for \( K \leq \frac{1}{2} \), since the integrand is singular at the origin. Actually, this singularity is spurious due to the above analytic properties of \( Q(z) \), and therefore Eq. (17) is valid for all \( K \geq 0 \). In the representation (3) with Eq. (16), the singularity is far from the integration contour for all \( K \).

So far in the literature, little attention has been paid to the case where the bias is of the order of \( \omega_c \) or larger, and the bath is still quantum mechanical, \( \hbar \beta \omega_c \gg 1 \) [13]. If the bias is of the same order of magnitude as \( \omega_c \), most of the contribution to the integral (3) comes from the core region \( |z| \leq 1/\omega_c \). Then the scaling form of \( Q(z) \) is inappropriate and we have to use the expression (15). With this form, however, it is not possible to express the integral in (3) in analytic form for arbitrary temperatures. At zero-temperature, where \( Q(z) = 2K \ln(1 + i \omega_c z) \), the integration in (3) can be performed exactly, yielding [21,22]

\[
k^+(T = 0, \epsilon) = \frac{\pi \Delta^2}{2\omega_c} \frac{1}{\Gamma(2K)} \left( \frac{\epsilon}{\omega_c} \right)^{2K-1} e^{-\epsilon/\omega_c}.
\]  

The core region \( |z| \leq 1/\omega_c \) gives rise to the factor \( e^{-\epsilon/\omega_c} \). For \( \epsilon \ll \omega_c \), this factor is unity and we recover the \( T = 0 \) limit of Eq. (17). For a larger bias, the factor \( e^{-\epsilon/\omega_c} \) represents an essential modification of the \( T = 0 \) limit of the scaling result (17). For \( K > 1/2 \), the rate has a maximum when the bias equals the value \( \epsilon^* = (2K - 1)\omega_c = \Lambda_{cl} - \omega_c \). In the second form, we have used the reorganization frequency (11) in the Ohmic case, \( \Lambda_{cl} = 2K \omega_c \). Thus the position of the rate maximum is at a lower bias value compared to the classical regime, where \( \epsilon^* = \Lambda_{cl} \). The shift of the maximum is due to quantum mechanical nuclear tunnelling through the free energy barrier, and the relative shift \( \omega_c/\Lambda_{cl} = 1/2K \) is small for large coupling strength \( K \). For \( K \leq \frac{1}{2} \), no rate maximum exists. However, depending on the magnitude of the bias, electron tunnelling might be coherent and thus a rate description may be inappropriate in this coupling regime.

At finite temperature, the contribution of the core region to the integral (3) can not be given in analytic form. However, the exact low temperature expansion for arbitrary bias can be found. We proceed by writing Eq. (15) as \( Q(z) = 2K \ln(1 + i \omega_c z) + \delta Q(z) \). In the regime \( K k_B T \ll \hbar \epsilon \), we may expand \( \delta Q(z) \) into a power series of \( (z/\hbar \beta)^2 \),

\[
\delta Q(z) = K \frac{\pi^2}{3} \left( \frac{z}{\hbar \beta} \right)^2 + \mathcal{O} \left( \left( \frac{z}{\hbar \beta} \right)^4 \right).
\]  

Substituting the series (19) into the integral (3), we see that every term of the resulting series for \( \exp \left[ -\delta Q(z) \right] \) can be generated by suitable differentiations with respect to the bias. Thus, in principle, the full low temperature expansion can be constructed upon using Eq. (18). In leading order, we obtain the exponential correction

\[
k^+(T, \epsilon) = \exp \left[ K \frac{\pi^2}{3} \left( \frac{1}{\hbar \beta} \right)^2 \frac{\partial^2}{\partial \epsilon^2} \right] k^+(T = 0, \epsilon)
\]  

\[
= k^+(T = 0, \epsilon) \exp \left\{ \frac{\pi^2}{3} \frac{K}{(\hbar \beta)^2} \left[ -\frac{2K - 1}{\epsilon^2} + \left( \frac{1}{\omega_c} - \frac{2K - 1}{\epsilon} \right)^2 \right] \right\}
\]  

(21)
which varies as $\exp(aT^2)$. Depending on the parameters, the sign of $a$ can be positive or negative. The contribution $1/\omega_c$ in the round bracket comes from the core region. This term is negligible when the bias is considerably below $(2K - 1)\omega_c$, and in this regime Eq. (21) coincides with the low temperature expansion of the rate (17). For a stronger bias, however, this term is of crucial importance. The maximum of the rate (21) for $K > \frac{1}{2}$ is at $\epsilon = \epsilon^*$ where

$$
\epsilon^* = (2K - 1)\omega_c + \frac{1}{3} \frac{2K \omega_c}{2K - 1} \left( \frac{\pi k_B T}{\hbar \omega_c} \right)^2.
$$

(22)

With the onset of thermal activation at finite $T$, the rate maximum is shifted to a higher bias.

Let us now expand the rate expression (21) around the maximum, Eq. (22). In contrast to the classical formula (12), we now have an asymmetric distribution

$$
k^+(T, \epsilon) = k^+(T, \epsilon^*) \exp \left\{ - \frac{(\epsilon - \epsilon^*)^2}{2W^2 \omega_c^2} \left( 1 - A \frac{(\epsilon - \epsilon^*)}{\omega_c} + \mathcal{O} \left[ \frac{(\epsilon - \epsilon^*)^2}{\omega_c^2} \right] \right) \right\}.
$$

(23)

The dimensionless width $W$ and the asymmetry parameter $A$ are given by

$$
W^2 = (2K - 1) \left\{ 1 + \frac{2K}{3} \frac{2K - 2}{(2K - 1)^2} \left( \frac{\pi k_B T}{\hbar \omega_c} \right)^2 \right\},
$$

(24)

$$
A = \frac{2}{3(2K - 1)} \left\{ 1 - \frac{4K}{3} \frac{2K - 2}{(2K - 1)^2} \left( \frac{\pi k_B T}{\hbar \omega_c} \right)^2 \right\}.
$$

(25)

For $K \gg 1$, Eq. (23) is accurate over a wide bias range. Since $A > 0$ for $K > \frac{1}{2}$, the wing of the rate above the maximum is enhanced compared to the wing below the maximum. This is due to the smaller width of the free energy barrier in the inverted regime $\epsilon > \epsilon^*$. At $T = 0$, we have $W^2 = (2K - 1)$ and $A = 2/[3(2K - 1)]$. The width grows with increasing damping strength $K$, whereas the asymmetry decreases. For finite temperatures, thermal activation over the free energy barrier becomes possible. For $K > 1$, this leads to a widening of the distribution and a reduction of the asymmetry. The quantum features are reduced and the system behaves more “classically” with increasing temperature. In the regime $K < 1$, the behaviour is opposite: the width decreases and the asymmetry grows for finite temperatures. However, for $K < 1$ the representation (23) is only accurate in a small interval around $\epsilon^*$.

So far we have studied the Ohmic case in the quantum regime $\kappa \ll 1$. It is now interesting to see whether the quantum characteristics change qualitatively for a non-Ohmic spectral density.

**IV. EVALUATION OF THE RATE IN STEEPEST DESCENT**

For a general spectral density, it is not possible to calculate the rate (3) or (5) in analytic form. To evaluate the integral asymptotically, we choose the contour $C_s$ which passes through the saddle point $z_s = -i\bar{\tau}$ in the direction of steepest descent (cf. the discussion in Section II and Fig. 1). Putting

$$
F(z) = Q(z) - i \epsilon z,
$$

(26)
the saddle point $z_s$ is determined by the transcendental equation

$$F'(z_s) = 0,$$  \hspace{1cm} (27)

where the prime denotes differentiation with respect to the argument. Now, expanding $F(z)$ around $z_s$ up to second order,

$$F(z) = F(z_s) + \frac{1}{2}F''(z_s)(z - z_s)^2 + \mathcal{O}[(z - z_s)^4],$$  \hspace{1cm} (28)

we arrive at the steepest descent expression for the rate $[2,11]$,

$$k^+(T, \epsilon) = \frac{\Delta^2}{4} \left( \frac{2\pi}{F''(z_s)} \right)^{1/2} \exp[-F(z_s)].$$  \hspace{1cm} (29)

The quantities $F(z_s)$ and $F''(z_s)$ are positive real. Here, $\beta^{-1}F(z_s)$ is the “quantum activation free energy” of the donor state, and $F''(z_s)$ introduces quantum effects in the pre-exponential factor. As we shall find, the factor $F''(z_s)$ is responsible for the shift of the rate maximum to a bias value $\epsilon^*$ below $\Lambda_{cl}$. The leading correction to the formula (29) comes from the fourth order contribution in Eq. (28). This contribution is small when the condition

$$Q^{IV}(z_s)/8[Q''(z_s)]^2 \ll 1$$  \hspace{1cm} (30)

is fulfilled. Physically, this is the regime of multi-phonon emission processes.

In the absence of a bias, the transcendental equation (27) reduces to $Q'(z_s) = 0$. With the general form (4), the stationary point is then given by $z_s = -i\hbar\beta/2$. As the bias is increased, the stationary point moves from $z_s = -i\hbar\beta/2$ towards $z_s = 0$, and in general one has to solve the transcendental equation (27). The stationary point finally reaches the origin if the bias equals the classical reorganization frequency, $\epsilon = \Lambda_{cl} = -iQ'(0)$.

In the classical limit $\hbar\beta\omega_c \ll 1$, the stationary point is always near to the origin. Then the expansion (10) around $z = 0$ is justified for any bias.

V. ZERO TEMPERATURE RATE

In this section, we discuss the modifications of the quantum rate features when the spectral density is changed from Ohmic to sub-Ohmic and super-Ohmic.

For $T = 0$, the pair interaction (8) reduces to the form

$$Q(z) = 2\delta_s \Gamma(s - 1)(\omega_c/\omega_{ph})^{s-1}[1 - (1 + i\omega_c z)^{1-s}].$$  \hspace{1cm} (31)

Substituting Eq. (31) into Eq. (26), the saddle point is found in analytic form, $z_s = -i[(\Lambda_{cl}/\epsilon)^{1/s} - 1]/\omega_c$. Then the rate is obtained from Eq. (24) as

$$k^+(\epsilon) = \frac{\Delta^2}{4} \sqrt{\frac{2\pi}{s\Lambda_{cl}\omega_c}} \left( \frac{\Lambda_{cl}}{\epsilon} \right)^{1+s} \exp \left\{ -\frac{\epsilon}{\omega_c} + \frac{1}{s-1} \frac{\Lambda_{cl}}{\omega_c} \left[ s \left( \frac{\epsilon}{\Lambda_{cl}} \right)^{s-1} - 1 \right] \right\}. \hspace{1cm} (32)$$

The condition (30) for the validity of the form (32) reads

$$[2\delta_s \Gamma(s)]^{1/s}(\epsilon/\omega_{ph})^{(s-1)/s} = (\epsilon/\Lambda_{cl})^{(s-1)/s} \Lambda_{cl}/\omega_c \gg (s + 2)(s + 1)/8s.$$  \hspace{1cm} (33)
This roughly corresponds to the regime $\epsilon \leq \omega_{ph}$ in the sub-Ohmic case, $\epsilon \geq \omega_{ph}$ in the super-Ohmic case, and to $\delta_1 \equiv K \gg 1$ in the Ohmic case. It can easily be seen that the limit $s \to 1$ in Eq. (32) reproduces the Ohmic rate \cite{[13]} for $K \gg 1$. The rate (32) has a maximum when the bias takes the value $\epsilon^*$, which is determined by the transcendental equation

$$
(\epsilon^*/\Lambda_{cl})^{1-1/s} - (\epsilon^*/\Lambda_{cl}) = [(s + 1)/2s] (\omega_c/\Lambda_{cl}) .
$$

The expressions (32) – (34) hold for general $s$.

In the sub-Ohmic case $s < 1$, the formula (32) is valid down to $\epsilon = 0$. We have $k^+(\epsilon \to 0) \propto \epsilon^{-(s+1)/2s} \exp[-a_s(\Lambda_{cl}/\epsilon)^{(1-s)/s}]$. As a result of the high density of low-energy excitations, the barrier crossing is completely quenched for a symmetric system at zero temperature. In the limit $\omega_c \to \infty$, the position of the rate maximum is selfconsistently determined from Eq. (34) as

$$
\epsilon^* = \frac{2s}{(1 + s)} s/(1-s) [2\delta_1 \Gamma(s)]^{1/(1-s)} \omega_{ph} .
$$

In the descending flank of $k^+(\epsilon)$ above $\epsilon^*$, the multi-phonon emission processes gradually die out as $\epsilon$ is further increased. Then the steepest descent rate (32) ceases to be valid. For $\epsilon \gg \epsilon^*$, the influence of the environment is weak and emission of energy is determined by the one-phonon process \cite{[13]}.

The super-Ohmic case shows opposite behaviour. Here the low bias rate is determined by one- or few-phonon processes. With increasing $\epsilon$, multi-phonon processes come into operation and form the ascending flank of $k^+(\epsilon)$. For $\epsilon \geq \omega_{ph}$, the asymptotic multi-phonon expression (32) is valid. For $\Lambda_{cl} \gg \omega_c$, the position of the rate maximum is found from Eq. (34) as

$$
\frac{\epsilon^*}{\Lambda_{cl}} = 1 - \frac{s + 1}{2} \frac{\omega_c}{\Lambda_{cl}} + O\left(\frac{\omega_c^2}{\Lambda_{cl}^2}\right) ,
$$

which correctly reproduces the Ohmic result \cite{[23]}. For fixed $\omega_c/\Lambda_{cl}$, the value of $\epsilon^*/\Lambda_{cl}$ slopes down with increasing $s$. Expanding the rate around its maximum $\epsilon^*$ as in Eq. (23), we obtain for the width $W$ and the asymmetry parameter $A$

$$
W^2 = \frac{s \Lambda_{cl}}{\omega_c} \left[1 - \frac{s + 1}{2s} \frac{\omega_c}{\Lambda_{cl}} + O\left(\frac{\omega_c^2}{\Lambda_{cl}^2}\right)\right] ,
$$

$$
A = \frac{(s + 1) \omega_c}{3s \Lambda_{cl}} \left[1 + \frac{\omega_c}{\Lambda_{cl}} + O\left(\frac{\omega_c^2}{\Lambda_{cl}^2}\right)\right] .
$$

In the limit $s \to 1$, the width (37) reduces to the Ohmic form (24), and the asymmetry parameter is consistent with Eq. (25) for $K \gg 1$. Interestingly, the width grows and the asymmetry decreases with increasing $s$ for fixed $\omega_c/\Lambda_{cl}$.

**VI. QUANTUM TO CLASSICAL CROSSOVER FOR SMALL BIAS**

The ET rate for a symmetric system ($\epsilon = 0$) has been the subject of several works using different analytical approximations and numerical methods \cite{[9],[11],[13],[14]}. Here we study
the rate in the unbiased case for a general spectral density employing the steepest descent
method. We are particularly interested in the crossover from the quantum to the classical
regime. Moreover, we show how the procedure can be extended to the case of a small bias.

Since the stationary point is at \( z_s = \frac{-i \bar{\hbar} \beta}{2} \) for zero bias, it is natural to switch to the
representation (5), where the integrand is stationary at \( t_s = 0 \). Expanding the integrand of
the representation (6) about \( t = 0 \), we find

\[
X(t) = (\hbar \beta / 4) \Lambda_1 + (\Lambda_2 / \hbar \beta) t^2 + O(t^4),
\]

where the frequency scales \( \Lambda_1 \) and \( \Lambda_2 \) are given by

\[
\Lambda_1 = \frac{4}{\hbar \beta} \int_0^\infty d\omega \frac{G(\omega)}{\omega^2} \tanh(\frac{1}{4} \hbar \beta \omega),
\]

\[
\Lambda_2 = \frac{\hbar \beta}{2} \int_0^\infty d\omega \frac{G(\omega)}{\sinh(\frac{1}{2} \hbar \beta \omega)}. \tag{41}
\]

For the spectral density (2), we obtain the analytical expressions

\[
\Lambda_1 = 8 B_s (k_B T / \hbar) + b_s(\kappa) (k_B T / \hbar) (T / T_{\text{ph}})^{s-1}, \tag{42}
\]

\[
\Lambda_2 = a_s(\kappa) (k_B T / \hbar) (T / T_{\text{ph}})^{s-1}, \tag{43}
\]

\[
b_s(\kappa) = 16 \delta_s \Gamma(s-1) \left\{ \zeta(s-1, 1+\kappa) - \zeta(s-1, \frac{1}{2}+\kappa) \right\}, \tag{44}
\]

\[
a_s(\kappa) = 2 \delta_s \Gamma(s+1) \zeta(s+1, \frac{1}{2}+\kappa), \tag{45}
\]

where \( T_{\text{ph}} = \hbar \omega_{\text{ph}} / k_B \) and \( B_s = \delta_s \Gamma(s-1)(\omega_c / \omega_{\text{ph}})^{s-1} \). There follows from the forms (11),
(40), and (41) that \( \Lambda_{\text{cl}} \geq \Lambda_1 \geq \Lambda_2 \). In the limit \( \kappa \to \infty \), the energies \( \hbar \Lambda_1 \) and \( \hbar \Lambda_2 \) approach
the classical reorganization energy,

\[
\lim_{\kappa \to \infty} \Lambda_1 = \Lambda_{\text{cl}}, \quad \lim_{\kappa \to \infty} \Lambda_2 = \Lambda_{\text{cl}}. \tag{46}
\]

The limits (46) are found either from the integral representations or by substituting the
asymptotic expansion of the zeta function into Eqs. (12) and (43). In the quantum regime
\( \kappa \ll 1 \), the coefficient functions take the simpler form

\[
b_s(0) = 16 \delta_s \Gamma(s-1) [2 - 2^{s-1}] \zeta(s-1), \tag{47}
\]

\[
a_s(0) = 2 \delta_s \Gamma(s+1) [2^{s+1} - 1] \zeta(s+1). \tag{48}
\]

Substituting Eq. (43) into Eq. (5), the rate for zero bias is obtained as (10, 14)

\[
k^+(T, \epsilon = 0) = \frac{\Delta^2}{4} \sqrt{\frac{\pi \hbar \beta}{\Lambda_2}} e^{-\hbar \beta \Lambda_2 / 4}. \tag{49}
\]

This formula is a quantum generalization of the classical result (12) for \( \epsilon = 0 \). The quantum
features are included in the effective solvation energies \( \hbar \Lambda_1 \) and \( \hbar \Lambda_2 \). The energy \( \hbar \Lambda_2 / 4 \) plays
the role of a quantum activation free energy, which is below the classical value \( E_a = \hbar \Lambda_{\text{cl}} / 4 \)
because of nuclear tunnelling. The energy \( \hbar \Lambda_2 \) accounts for quantum effects in the attempt
frequency due to bath fluctuations. Both quantum effects lead to an enhancement of the rate over the classical value. The leading correction to the formula (49) arising from the $O(t^4)$-term in the expansion (39) is small when the condition

$$32\delta_s \left( \frac{T}{T_{ph}} \right)^{-1} \frac{[\Gamma(s+1) \zeta(s+1, \frac{1}{2} + \kappa)]^2}{\Gamma(s+3) \zeta(s+3, \frac{1}{2} + \kappa)} \gg 1 \quad (50)$$

is satisfied. Physically, this condition holds in the regime of multi-phonon processes. It is always fulfilled in the classical limit. In the quantum regime $\kappa \ll 1$, Eq. (50) corresponds in the Ohmic limit to the damping regime $K \gg 1$. In the super-Ohmic case, the condition (50) is met for temperatures well above $T_{ph}$, whereas for a sub-Ohmic bath, it is fulfilled when $T$ is fairly below $T_{ph}$.

For finite bias, the stationary point moves away from $t_s = 0$. However, for a small bias

$$\epsilon \ll (1 + 2\kappa)\Lambda_2, \quad (51)$$

the short-time expansion (39) for $X(t)$ can still be applied. The stationary point is located at $t_s = i\hbar \beta \epsilon / 2\Lambda_2$, and the rate (3) is found as

$$k^+(T, \epsilon) = \frac{\Delta^2}{4} \sqrt{\frac{\pi \hbar \beta}{\Lambda_2}} \exp \left\{ -\frac{\hbar \beta \Lambda_1}{4} + \frac{\hbar \beta \epsilon}{2} - \frac{\hbar \beta \epsilon^2}{4\Lambda_2} \right\}. \quad (52)$$

This expression describes the crossover from the classical to the quantum regime for general spectral densities. Corrections to the formula (52) are small if the conditions (50) and (51) are fulfilled. In the classical regime $\kappa \gg 1$, the condition (51) is satisfied even when the bias is very large. We see from Eq. (46) that the expression (52) reduces to the classical rate (12) as $\kappa \to \infty$. As the temperature is lowered to the quantum regime, the particular properties of the spectral density $G(\omega)$ become relevant which indicates that nuclear tunnelling becomes effective. The quantum effects are captured by the deviations of the effective solvation energies $\hbar \Lambda_1$ and $\hbar \Lambda_2$ from $\hbar \Lambda_{cl}$. However, the bias range (51) in which the rate formula (52) is valid shrinks as temperature is lowered. In the quantum regime $\kappa \ll 1$, the condition (51) reduces to $\epsilon \ll \Lambda_2 \propto T^s$. Hence the bias range goes to zero as $T \to 0$. In the quantum regime $\kappa \ll 1$, the formula (52) does not properly describe the rate around the maximum.

In the Ohmic case $s \to 1$, we obtain from Eqs. (12) and (13) in the quantum regime $\kappa \ll 1$

$$\Lambda_1 = (8K/\hbar \beta) \ln(\hbar \beta \omega_c / \pi), \quad \Lambda_2 = \pi^2 K/\hbar \beta, \quad (53)$$

and the rate expression (52) takes the form

$$k^+(T, \epsilon) = \frac{\Delta^2}{4\omega_c} \sqrt{\frac{\pi}{K}} \left( \frac{\pi}{\hbar \beta \omega_c} \right)^{2K-1} \exp \left\{ \frac{\hbar \beta \epsilon}{2} - \frac{1}{K} \left( \frac{\hbar \beta \epsilon}{2\pi} \right)^2 \right\}. \quad (54)$$

Now, the conditions (50) and (51) reduce to $K \gg 1$ and $\hbar \epsilon \ll \pi^2 K k_b T$. In this parameter regime, the steepest descent-rate (54) coincides with the previous expression (17).

For a larger bias than given by Eq. (51), the stationary point is no longer near to $t = 0$ and the expansion (39) cannot be employed any more. This case is studied in the next section.
VII. QUANTUM TO CLASSICAL CROSSOVER FOR STRONG BIAS

As the bias is further increased, the stationary point $z_s$ approaches the origin of the complex time plain, and for $\epsilon = \Lambda_{cl}$, we have $z_s = 0$. In general, for large bias and/or high temperature, the stationary point is near $z = 0$. To explore this regime in which quantum signatures are most pronounced, we expand the integral representation (4) of $Q(z)$ around $z = 0$ up to fourth order in $z$,

$$Q(z) = i\Lambda_{cl}z + \frac{c_2(\kappa)}{2!}(\omega_c z)^2 - i \frac{c_3}{3!}(\omega_c z)^3 - \frac{c_4(\kappa)}{4!}(\omega_c z)^4 + O(\omega_c z)^5. \tag{55}$$

The dimensionless coefficient functions $c_j(\kappa)$ are given by

$$c_2(\kappa) = \frac{1}{\omega_c^2} \int_0^\infty d\omega G(\omega) \coth\left(\frac{1}{2}\hbar\beta\omega\right),$$

$$c_3 = \frac{1}{\omega_c^3} \int_0^\infty d\omega \omega G(\omega),$$

$$c_4(\kappa) = \frac{1}{\omega_c^4} \int_0^\infty d\omega \omega^2 G(\omega) \coth\left(\frac{1}{2}\hbar\beta\omega\right). \tag{56}$$

For the spectral density (3), we readily obtain

$$c_2(\kappa) = s \left[ 1 + 2\kappa s + \zeta(s + 1, 1 + \kappa) \right] (\Lambda_{cl}/\omega_c),$$

$$c_3 = s(s + 1)(\Lambda_{cl}/\omega_c),$$

$$c_4(\kappa) = s(s + 1)(s + 2) \left[ 1 + 2\kappa s + 3\zeta(s + 3, 1 + \kappa) \right] (\Lambda_{cl}/\omega_c). \tag{57}$$

In earlier works, the analysis of the rate has been based on truncating the series (55) at order $z^2$ [9,12]. However, this crude approximation, which has been often termed “semi-classical”, fails to describe the actual shift of the rate maximum $\epsilon^* \neq \Lambda_{cl}$ and the asymmetric distribution around the maximum in the quantum regime $\kappa \approx 1$, as noticed already in Ref. [24]. In the sequel, we study the quantum effects of the rate related to terms of order $z^3$ and higher in Eq. (55).

In the bias regime

$$|\Lambda_{cl} - \epsilon| \ll \omega_c \frac{c_2(\kappa)/c_3(\kappa)}{c_2(\kappa)/c_3(\kappa)}, \tag{58}$$

the stationary point is obtained from Eq. (27) with Eq. (55) in the form of a series in $\Lambda_{cl} - \epsilon$. Up to second order, we find

$$z_s = -\frac{i}{\omega_c} \left(\frac{\Lambda_{cl} - \epsilon}{2c_3(\kappa)/c_2(\kappa)}\right) - \frac{i}{2\omega_c} \frac{c_3}{c_2} \left(\frac{\Lambda_{cl} - \epsilon}{\omega_c}\right)^2. \tag{59}$$

Then the rate is found in the form (29),

$$k^+(T, \epsilon) = \frac{\Delta^2}{4} \left(\frac{2\pi}{F''(z_s)}\right)^{1/2} \exp[-F(z_s)],$$

$$F(z_s) = \frac{1}{2c_2} \left(\frac{\Lambda_{cl} - \epsilon}{\omega_c}\right)^2 + \frac{c_3}{6c_2^2} \left(\frac{\Lambda_{cl} - \epsilon}{\omega_c}\right)^3,$$

$$F''(z_s) = \left[c_2 - \frac{c_3}{c_2} \left(\frac{\Lambda_{cl} - \epsilon}{\omega_c}\right) - \frac{1}{2} \left(\frac{c_3}{c_2}\right)^2 \left(\frac{\Lambda_{cl} - \epsilon}{\omega_c}\right)^2\right] \omega_c^2. \tag{60}$$
This rate expression together with Eq. (56) describes the full crossover from quantum-mechanical to classical behaviour for a general spectral density. It is valid if the bias condition (58) and the steepest descent condition (30), which approximately takes the form $c_4 / 8c_2^2 \ll 1$, are fulfilled. For $\kappa \gg 1$, we see from Eq. (56) that these conditions are fulfilled for any bias and spectral density, and the rate reduces to the classical result (12). For lower $\kappa$, the rate expression (56) shows substantial deviations from the classical behaviour. The quantum activation factor $\exp[-F(z_s)]$ of the rate alone would predict activationless transfer for $\epsilon = \Lambda_{cl}$. However, the rate maximum is actually shifted by the fluctuation factor $F''(z_s)$. We consistently obtain

$$\frac{\epsilon^*}{\Lambda_{cl}} = 1 - \frac{c_3 \omega_c}{2c_2 \Lambda_{cl}}.$$  \hspace{1cm} (61)

The rate around the maximum is again described by the form (23). The width $W$ and the asymmetry parameter $A$ are given by

$$W^2 = c_2 \left[ 1 + \frac{1}{2} \left( c_3^2 c_2^2 - c_4 c_2^2 \right) \right],$$  \hspace{1cm} (62)

$$A = \frac{c_3}{3c_2^2}.$$  \hspace{1cm} (63)

We emphasize that the expressions (61) – (63) together with Eq. (56) are valid for a general spectral density. In the following, we will restrict ourselves to the special form (17) of the coefficient functions $c_j$. Before discussing the quantum signatures in the parameters $\epsilon^*$, $W$, and $A$ in detail, we now consider the conditions (58) and (30) in the quantum regime $\kappa \ll 1$. First, the steepest descent condition (30) is approximately given by $\Lambda_{cl} \gg \omega_c$. This condition is practically always satisfied in the super-Ohmic case when $\omega_c \gg \omega_{ph}$, whereas in the Ohmic case, it corresponds to the regime $K \gg 1$. It is usually not fulfilled in the sub-Ohmic case, except for very strong coupling $2\delta s \Gamma(s) \gg (\omega_c/\omega_{ph})^{1-s}$. Secondly, the bias condition (58) takes roughly the form $|\Lambda_{cl} - \epsilon| \ll \Lambda_{cl}$, and thus at $T = 0$ we are confined to a narrow bias interval around $\Lambda_{cl}$ [25]. Importantly, the most interesting area around the rate maximum falls into this interval. It is easily verified that in this bias interval the $T = 0$ limit of the rate (56) reduces to the previous result (32).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.png}
\caption{$\epsilon^*/\Lambda_{cl}$ as a function of $\kappa$ for $\omega_c/\Lambda_{cl} = 0.05$. The solid, dashed, and dotted lines correspond to the cases $s = 1$, 2, and 3, respectively.}
\end{figure}
The position of the rate maximum, Eq. (61), is plotted as a function of $\kappa$ for different values of $s$ in Fig. 2. In the asymptotic low temperature regime, we find from Eq. (61)

$$\frac{\epsilon^*}{\Lambda_{cl}} = 1 - \frac{s + 1}{2} \frac{\omega_c}{\Lambda_{cl}} \left[ 1 - 2\zeta(s + 1) \left( \frac{k_B T}{\hbar \omega_c} \right)^{s+1} \right],$$

which correctly reproduces the $T = 0$ result, Eq. (30). The leading low-temperature corrections vary as $T^{s+1}$. For $s = 1$, the form (64) reduces to the earlier result (22) for $K \gg 1$. With increasing $\kappa$, the maximum $\epsilon^*$ is shifted upwards until it finally reaches the classical value $\Lambda_{cl}$. With increasing $s$, the approach to the classical limit is more gradual. As visible in Fig. 2 the deviations from the classical behaviour are more distinct for larger $s$ throughout the whole temperature range.

The width and the asymmetry parameter of the rate are displayed in Figs. 3 and 4.

![FIG. 3. The squared width $W^2$ as a function of $\kappa$ for $\omega_c/\Lambda_{cl} = 0.1$. The solid, dashed, and dotted lines correspond to the cases $s = 1, 2, \text{and } 3$, respectively. The thin solid line represents the classical component $W^2_{cl} = 2(\Lambda_{cl}/\omega_c)\kappa$. The difference between this straight line and the full squared width is the quantum component $W^2_{qm}$.]

At very low temperatures, the expressions (52) and (63) take the form

$$W^2 = \frac{s\Lambda_{cl}}{\omega_c} \left( 1 - \frac{s + 1}{2s} \frac{\omega_c}{\Lambda_{cl}} \right) \left[ 1 + 2\zeta(s + 1) \left( \frac{s^2 - 1}{2s} \frac{\omega_c}{\Lambda_{cl}} \right) \left( \frac{k_B T}{\hbar \omega_c} \right)^{s+1} \right],$$

$$A = \frac{(s + 1)\omega_c}{3s\Lambda_{cl}} \left[ 1 - 4\zeta(s + 1) \left( \frac{k_B T}{\hbar \omega_c} \right)^{s+1} \right].$$

Again, the $T = 0$ results (37) and (38) are correctly reproduced (26). With increasing $s$, the width grows, whereas the asymmetry decreases. The low temperature corrections vary as $T^{s+1}$. For $s \to 1$, we recover the Ohmic results (24) and (25) for $K \gg 1$. With increasing temperature, the asymmetry decreases and the width grows. However, the increase of the width is due to the “classical component” $W^2_{cl} = 2(\Lambda_{cl}/\omega_c)\kappa$ arising from thermal activation, whereas the “quantum component” $W^2_{qm}$ decreases. For this reason, the quantum effects are reduced with increasing temperature. In the limit $\kappa \to \infty$, the asymmetry finally drops down
to zero, and the width approaches the classical form $W_{cl}^2 = 2(\Lambda_{cl}/\omega_c)\kappa$. With increasing $s$, the curves in Figs. 3 and 4 approach the classical limits more gradually, and the deviations from the classical behaviour are more pronounced. This is in correspondence with the behaviour of $\epsilon^*$. Thus, with growing $s$, the quantum regime extends to higher temperatures. Clearly, this is due to the larger contribution of high frequency modes leading to an enhancement of nuclear tunnelling.

FIG. 4. The asymmetry parameter $A$ as a function of $\kappa$ for $\omega_c/\Lambda_{cl} = 0.1$. The solid, dashed, and dotted lines correspond to the cases $s = 1, 2,$ and $3$, respectively. Since $A > 0$, the wing of the rate above the maximum is enhanced compared to the wing below the maximum. In the quantum regime $\kappa \ll 1$, the deviations from the classical value $A = 0$ are more distinct for smaller $s$. This is in contrast to the behaviour of $\epsilon^*$ and $W^2$ for $\kappa \ll 1$ displayed in Figs. 2 and 3.

VIII. CONCLUSIONS

We have studied the nonadiabatic tunnelling rate in the biased spin-boson model within the Golden Rule formula. We have analyzed the quantum signatures of the rate in the position of the maximum $\epsilon^*$, the width $W$, and the asymmetry parameter $A$ for different spectral densities. In the Ohmic case, we have calculated the rate in analytic form at $T = 0$, and we have presented the leading low temperature corrections. Since the rate maximum is located in the strong bias regime, it has been essential to treat the bath correlation function beyond the scaling limit. For an Ohmic and non-Ohmic spectral density, we have investigated the entire quantum to classical crossover of the rate within steepest descent, and we have discussed the parameter bounds within which this approximation is justified. We wish to emphasize that the characteristic quantum features found are not artefacts of the steepest descent method. For the parameter regions displayed in Figs. 2 – 4, the deviations of the analytical expressions from numerical computations of the Golden Rule rate are negligibly small. The quantum signatures of the rate are gradually extincted with increasing temperature. We found that for fixed low temperature, $\kappa \ll 1$, the quantum features in the position of the maximum and the width are growing with increasing $s$. In contrast, the quantum signatures in the asymmetry parameter become less pronounced if we switch from Ohmic to super-Ohmic. At higher temperatures, $\kappa > 1$, the quantum signatures
in the parameters $\epsilon^*, W$, and $A$ are more distinct for larger $s$. Thus in the super-Ohmic case, the regime in which deviations from the classical behaviour are significant extends to higher temperatures than in the Ohmic or sub-Ohmic case.

Many of our results are not limited to the particular form (2) of the spectral density. They also apply to spectral densities with a peak-like structure at higher frequencies, which are relevant when inner-sphere reorganization or specific vibrational modes in the solvent are important. The quantum effects studied here are particularly pronounced for solvent modes with energy above the thermal energy. Finally, our study is also relevant for single charge transfer in ultrasmall junctions in which the electromagnetic environment plays the role of the solvent [27, 16].

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[25] With increasing temperature, the $T = 0$ conditions $\Lambda_{cl} \gg \omega_c$ and $|\Lambda_{cl} - \epsilon| \ll \Lambda_{cl}$ are softened.

[26] Actually, the form (66) at $T = 0$ gives Eq. (38) only in lowest order of $\omega_c/\Lambda_{cl}$. To reproduce the second order term in Eq. (38), we have to expand $Q(z)$ up to 5th order in $z$.

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