

Quantum Quadratic Brownian Oscillator Model for Absorption Lineshapes

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Abstract. The absorption lineshape of a two-level chromophore coupled quadratically to a collective Gaussian solvation coordinate with an arbitrary Brownian oscillator spectral density is calculated exactly using a path-integral representation of the dipole correlation function in Liouville space.

1. INTRODUCTION

Many optical and rate processes of molecules in solution may be described by a model of a two-electronic-level system coupled linearly to a collective harmonic bath coordinate representing the solvent. Marcus electron transfer theory^{1,2} and the multimode Brownian oscillator model of nonlinear spectroscopy³ are widely used examples of the applicability of this Spin Boson model.⁴ Linear coupling implies that the system may be represented by a displaced quadratic free-energy surface with the same curvature in both electronic states. In this model, the solvation coordinate responds linearly to the electronic excitation, and all of its nonlinear response functions vanish identically. One consequence of this strict linearity is the proportionality of the time-dependent Stoke shift $\langle \Delta E(t) \rangle$ and the energy gap correlation function $C(t)$. This manifestation of the celebrated Onsager's fluctuation dissipation relationships is satisfied experimentally in many systems, but clear deviations have been reported in other systems. For example, simulations conducted by Skaf and Ladanyi⁵ show differences between the two for water.^{5,6} In a previous paper,⁷ we showed that these observations may be explained by extending the multimode Brownian oscilla-

tor model for solvation dynamics by taking the energy gap to depend quadratically rather than linearly on the solvation coordinate. The model remains Gaussian and exactly solvable but the solvent response to electronic excitation becomes nonlinear, yielding a different time profile for $\Delta E(t)$ and $C(t)$.

In the present work, we calculate the linear absorption lineshape for the same quadratic Brownian oscillator model utilizing a path-integral approach in Liouville space. In the case of a solvation coordinate with an exponential correlation function, the calculation can be carried out by solving a linear integral equation using the Wiener-Hopf method. We propose a solution that can be easily implemented numerically for an arbitrary (e.g., stretched exponential) relaxation profile.

This paper is organized as follows. In Section 2, we present our model and develop the Liouville space path-integral calculation of the linear response function. Closed expressions for the linear optical response function are given. This quantity is calculated for an overdamped Brownian oscillator spectral density in Section 3, and technical details are given in the Appendices.

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2. LINEAR OPTICAL RESPONSE FOR THE QUADRATIC BROWNIAN OSCILLATOR MODEL

We consider a two-electronic-level system with the ground $|g\rangle$ and excited $|e\rangle$ states described by the Hamiltonian,

$$H = |e\rangle (H_e + \Omega) \langle e| + |g\rangle H_g \langle g| \quad (1)$$

where H_e and H_g are the excited and ground state Hamiltonians that depend on the nuclear (vibrational) degrees of freedom, and Ω is the two-level system frequency. We further define the collective solvation coordinate representing the electronic energy gap,

$$U \equiv H_e - H_g \quad (2)$$

The electronic gap U is quadratic in some collective nuclear coordinates $\{X_j\}$,

$$U = \sum_j A_j X_j + B_j X_j^2 \quad (3)$$

where A_j and B_j are coupling constants.

The linear absorption spectrum is given by

$$\sigma_a(\omega) = \frac{1}{\pi} \Re \int_0^\infty dt \exp\left[\frac{i}{\hbar}(\omega - \Omega)t\right] R(t) \quad (4)$$

In eq 4, the linear optical response function is

$$R(t) = \theta(t) \langle \exp_+ \left[-\frac{i}{\hbar} \int_0^t d\tau U(\tau) \right] \rangle \quad (5)$$

where

$$U(\tau) = e^{\frac{i}{\hbar} H_g \tau} U e^{-\frac{i}{\hbar} H_g \tau} \quad (6)$$

and $\theta(t)$ is a Heavyside step function. The "+" subscript denotes positive time-ordering and $\langle \dots \rangle$ stands for the ensemble averaging over nuclear degrees of freedom. The fluorescence spectrum $\sigma_f(\omega)$ is obtained simply by interchanging the indices g and e in eq 6.

Generally, the correlation function is given by

$$C_j(t) \equiv \langle X_j(\tau) X_j(0) \rangle = \int d\omega \tilde{C}_j''(\omega) \left[\coth\left(\frac{\hbar\omega}{2k_B T}\right) \cos\omega t - i \sin\omega t \right] \quad (7)$$

where T is temperature and k_B is the Boltzmann constant. All the relevant information about the bath degrees of freedom is contained in the spectral density $\tilde{C}_j''(\omega)$.^{3,4}

Optical lineshapes for high frequency underdamped nuclear coordinates with quadratic terms in the energy gap have been studied previously by many authors.⁸⁻¹³ In the present work, we compute the optical absorption

lineshapes for an arbitrary spectral density of the solvation nuclear coordinate.

The optical response can be calculated most conveniently in Liouville space. For any ordinary operator in Hilbert space, we introduce the tetradic superoperators Q_L (acting on the left (ket)), Q_R (acting on the right (bra)), defined as

$$Q_L \rho \equiv Q \rho, \quad Q_R \rho \equiv \rho Q \quad (8)$$

where ρ is any operator. Using eqs 3-8, the linear optical response function can be recast in the form

$$R_L(t) = \theta(t) \prod_j R_L^j \quad (9)$$

where

$$R_L^j = \langle \exp_{\mathcal{T}} \left\{ -\frac{i}{\hbar} \int_0^t d\tau [A_j X_{Lj}(\tau) + B_j X_{Lj}^2(\tau)] \right\} \rangle \quad (10)$$

$R_L^j(t)$ and hence, $R_L(t)$ may be evaluated by applying a path-integral representation^{14,15} for the Liouville-space correlation function in eq 10. In Appendix A, we derive the following expression for $R_L(t)$:

$$R_L(t) = \exp \left[-i \int_0^B d\xi \int_0^t d\tau L_\xi(\tau, \tau; t) - \frac{A^2}{2} \int_0^t d\tau'' \int_0^t d\tau' L_B(\tau'', \tau'; t) \right] \quad (11)$$

where the kernel $L_\xi(\tau'', \tau'; t)$ can be obtained by solving the linear integral equation:

$$L_\xi(\tau, \tau_0; t) + 2i\xi \int_0^t d\tau' C_{LL}(\tau - \tau') L_\xi(\tau', \tau_0; t) = C_{LL}(\tau - \tau_0) \quad (12)$$

and the correlation function $C_{LL}(\tau)$ is given in eq A2.

Equations 11 and 12 form a closed expression for R_L . In the next Section, we describe a numerical procedure for solving eq 12 for an arbitrary spectral density and compute the linear optical response for a multimode overdamped Brownian oscillator spectral density.

3. APPLICATION TO AN OVERDAMPED BROWNIAN OSCILLATOR

Equation 12 can be solved numerically for the kernel $L_\xi(\tau'', \tau'; t)$ with arbitrary correlation function, e.g., sum of stretched exponentials,

$$C(t-t') = \sum_j \tilde{\Delta}_j^2 e^{-\Lambda_j |t-t'|^\beta} \quad (13)$$

where

$$\tilde{\Delta}_j^2 = \Delta_j^2 - i\lambda_j \Lambda_j \quad (14)$$

with the linewidth parameter $\Delta_j^2 \equiv 2\lambda_j/\hbar\beta$,³ Λ_j^{-1} is the bath evolution timescale and $\lambda_j = \hbar/2m_j\omega_j^2$ is a system-bath coupling constant (fluctuation magnitude).

Calculation of the linear optical response for given values of parameters A and B involves solving the linear integral equation 12 for all values of parameter ξ that belong to segment $[0, B]$. This can be done by differentiating eq 12 with respect to ξ , yielding:

$$\frac{\partial}{\partial \xi} L_\xi(\tau, \tau_0; t) = -2iL_\xi^2(\tau, \tau_0; t) \quad (15)$$

L_ξ can be computed by solving eq 15 with the initial condition $L_\xi|_{\xi=0} = C_{LL}$.

In a numerical implementation, an integral operator is represented by a matrix, and eq 15 represents an equation for the propagation of this matrix. Note that the second term in the exponent in eq 11 involves L_ξ at $\xi = B$, whereas the first term involves L_ξ for all values of ξ in the form of an integral over ξ . This implies that we do not need to store the matrix elements of L_ξ for all $\xi \in [0, B]$, but only the current values of L_ξ and of the integral (i.e., in the limits from 0 to ξ). At each step of the propagation we need to evaluate $\text{Tr}[L_\xi]$, add it to the integral according to eq A15, and then calculate the next value of L_ξ .

In the special case of an exponentially relaxing nuclear coordinate, when $\beta = 1$, eq 12 can be solved analytically yielding a closed form expression for the linear optical response. In this paper, we consider the multimode overdamped Brownian oscillator spectral density,³

$$\tilde{C}^n(\omega) = \sum_{j=1}^N 2\lambda_j \frac{\omega \Lambda_j}{\omega^2 + \Lambda_j^2} \quad (16)$$

For this spectral density, the correlation function $C(t)$ becomes:

$$C(t) = \lambda_j \Lambda_j \cot\left(\frac{\beta \hbar \Lambda_j}{2}\right) e^{-\Lambda_j |t|} + \frac{4\Lambda_j \lambda_j}{\hbar \beta} \sum_{n=1}^{\infty} \frac{\nu_n e^{-\nu_n |t|}}{\nu_n^2 - \Lambda_j^2} - i\lambda_j \Lambda_j e^{-\Lambda_j |t|} \quad (17)$$

where $\nu_n \equiv 2\pi n/\hbar\beta$ are the Matsubara frequencies.^{3,16-18}

In the high temperature, $\beta\Lambda_j \ll 1$, limit eq 17 becomes

$$C(t) = \sum_j (\Delta_j^2 e^{-\Lambda_j |t|} - i\lambda_j \Lambda_j e^{-\Lambda_j |t|}) \quad (18)$$

The linear optical response for this correlation function can be computed using the Wiener-Hopf method outlined in Appendix A. R_L can be calculated for an arbitrary number of collective solvation coordinates X_j . Below we assume a single nuclear coordinate, i.e.,

$$U = AX + BX^2 \quad (19)$$

Technical details of the calculation are given in Appendix B. The linear response function is finally given by

$$R_L(t) = \theta(t) s^{-\frac{1}{2}} \exp\left[-\frac{A^2 \tilde{\Delta}^2}{\Lambda^2 s^3} (e^{-\Lambda s t} + \Lambda s t - 1)\right] + \frac{1}{2} (\text{Ei}[-2\Lambda s t] - \text{Ei}[-2\Lambda t]) \quad (20)$$

where $\text{Ei}(z)$ is the exponential integral defined by

$$\text{Ei}(z) \equiv -\int_z^\infty dt \frac{e^{-t}}{t} \quad (21)$$

where $z > 0$ and the principal value of the integral is taken. It has the following expansion:

$$\text{Ei}(x) = \gamma + \ln x + \sum_{n=1}^{\infty} \frac{x^n}{n \cdot n!} \quad (22)$$

In eq 22, $\gamma = 0.5772$ is the Euler constant. In eq 20, s is given by

$$s = \left(1 + \frac{4iB\tilde{\Delta}^2}{\Lambda}\right)^{1/2} \quad (23)$$

and

$$\tilde{\Delta}^2 = \Delta^2 - i\lambda\Lambda \quad (24)$$

Equation 20 for $R_L(t)$ is the main result of this paper. Note that when the collective electronic gap U (see eq 3) depends linearly on the nuclear coordinate X , i.e., setting $B = 0$ in eq 20, we obtain:

$$R(t) = \theta(t) \exp\left\{-\left[\frac{2\lambda k_B T}{\hbar \Lambda^2} - i(\lambda/\Lambda)\right](e^{-\Lambda t} + \Lambda t - 1)\right\} \quad (25)$$

Equation 25 can be obtained directly by using the second-order cumulant expansion of eq 5.^{3,11}

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APPENDIX A: LIOUVILLE SPACE CALCULATION OF THE LINEAR RESPONSE FUNCTION

The linear response function $R_L^j(t)$ (eq 10) can be expressed as a path integral that may be calculated exactly. Since the electronic energy gap U is given by a quadratic form eq 2, we rewrite eq 10 as eq A1 (in the forthcoming we set $\hbar = 1$ and suppress the index j but retain it whenever necessary)

$$R_L(t) = \int_{\mathcal{L}_t} D[X_L(\tau)] D[X_R(\tau)] \exp\left[-i\frac{A}{2} \int_0^t d\tau' X_L(\tau')\right] \times \exp\left[-\frac{1}{2} \int_0^t \int_0^t d\tau'' d\tau' \sum_{\alpha\beta} [M_{\alpha\beta}(\tau'', \tau') + 2Bi\delta_{\alpha L}\delta_{\beta R}\delta(\tau'' - \tau')] X_\alpha(\tau'') X_\beta(\tau')\right] \quad (A1)$$

Here, \mathcal{L}_t is defined as a direct sum of the spaces of left (L) and right (R) trajectories, i.e., $\mathcal{L}_t = \mathcal{L}_t^{(L)} \oplus \mathcal{L}_t^{(R)}$, and $D[X_L(\tau)] D[X_R(\tau)]$ denotes functional integration over space \mathcal{L}_t of pairs of ket and bra trajectories $X = (X_L(\tau), X_R(\tau))$ with $\tau \in [0, t]$, respectively. The indices α and β assume the values L and R. To arrive at eq A1, we have introduced a linear operator $M: \mathcal{L}_t \rightarrow \mathcal{L}_t$ defined on \mathcal{L}_t with the kernel $M_{\alpha\beta}(\tau'', \tau')$. The 2×2 matrix $M(\tau'', \tau')$ represents the dynamics of the collective coordinate X , and is expressed in terms of the Liouville space ground state correlation function,

$$M_{\alpha\beta}^{-1}(\tau'', \tau') \equiv C_{\alpha\beta}(\tau'' - \tau') \equiv \langle X_\alpha(\tau'') X_\beta(\tau') \rangle \quad (A2)$$

where $\langle \dots \rangle$ denotes the trace with respect to the ground state density matrix. Here, M_{LL}^{-1} (M_{RR}^{-1}) can be viewed as an operator in the space of the left (right) trajectories $\mathcal{L}_t^{(L)}$ ($\mathcal{L}_t^{(R)}$). We define a linear functional in \mathcal{L}_t ,

$$F^{(L)}(X) \equiv \int_0^t d\tau X_L(\tau) \quad (A3)$$

and matrix $M(B)$, which depends on parameter B ,

$$M_{\alpha\beta}(B) \equiv M_{\alpha\beta}(\tau'', \tau') \delta_{\alpha L} \delta_{\beta R} + 2Bi I_{\alpha\beta}(\tau'', \tau') \quad (A4)$$

where I is a linear operator in $\mathcal{L}_t^{(L)}$,

$$I_{\alpha\beta}(\tau'', \tau') \equiv \delta_{\alpha L} \delta_{\beta L} \delta(\tau'' - \tau') \quad (A5)$$

Using these definitions, eq A1 can be recast in the compact 2×2 operator form

$$R_L(t) = \int_{\mathcal{L}_t} D[X] \exp[-iAF^{(L)}(X)] \times \exp\left[-\frac{1}{2}(M_{\alpha\beta}(B)X, X)\right] \quad (A6)$$

where (\cdot, \cdot) denotes the following scalar product defined on \mathcal{L}_t

$$(X, X') \equiv \int_0^t d\tau [X_L'^*(\tau) X_L(\tau) + X_R'^*(\tau) X_R(\tau)] \quad (A7)$$

The Gaussian path integrals in eq A6^{14,15} can be carried out exactly, resulting in the following closed formal expression for R_L ,

$$R_L(t) = [\text{Det}M(B)]^{-1/2} \times \exp \left[-\frac{A^2}{2} \int_0^t d\tau'' \int_0^t d\tau' M_{LL}^{-1}(B, \tau'', \tau') \right] \quad (\text{A8})$$

We next expand the inverse matrix $M^{-1}(B)$ in powers of B and make use of eq A2. This gives, for the M_{LL}^{-1} -component,

$$M_{B,LL}^{-1}(t) = C_{LL}(t)(I + 2iBC_{LL}(t))^{-1} \quad (\text{A9})$$

In the above expression, C can be considered an operator in $\mathcal{L}_t^{(L)}$ with matrix elements $C_{LL}(\tau'', \tau') = C_{LL}(\tau'' - \tau')$.

In analogy with eq A9, we define a family of linear operators L_ξ that act in \mathcal{L}_t and depend on a parameter ξ

$$L_\xi(t) \equiv C_{LL}(t)(I + 2i\xi C_{LL}(t))^{-1} \quad (\text{A10})$$

We further use the identity^{19,20}

$$\text{Det}[M + 2i\xi I] = \text{Det}[M] \cdot \text{Det}[I + 2i\xi M_{LL}^{-1}] \quad (\text{A11})$$

where $\text{Det}[I + 2i\xi M_{LL}^{-1}]$ should be understood as a determinant in the $\mathcal{L}_t^{(L)}$ space. Making use of eq A9, and since $\text{Det}[M] = 1$, we obtain

$$\text{Det}[M + 2i\xi I^{(L)}] = \text{Det}[I + 2i\xi C_{LL}] \quad (\text{A12})$$

Substituting eqs A9, A10, and A12 into eq A8 and using the identity

$$\log \text{Det}[M] = \text{Tr} \log[M] \quad (\text{A13})$$

we obtain:

$$R_L(t) = \exp \left[-\frac{1}{2} \text{Tr} \log[I + 2iBC_{LL}(t)] - \frac{A^2}{2} \int_0^t d\tau'' \int_0^t d\tau' L_B(\tau'', \tau'; t) \right] \quad (\text{A14})$$

Equation A14 can alternatively be derived by expanding the exponent in eq A2, applying the Wick theorem, and grouping the resulting terms.^{20,21}

To recast R_L in a form suitable for numerical computations, we differentiate $\log[I + 2i\xi C_{LL}]$ with respect to ξ and integrate the resulting equation over x , which yields

$$\log[I + 2iBC_{LL}] = 2i \int_0^B d\xi L_\xi \quad (\text{A15})$$

Finally, substituting eq A15 into eq A14, we obtain eq 11 of the main text.

APPENDIX B: THE WIENER-HOPF METHOD

In this Section, we present the Wiener-Hopf method for solving the integral eq 12,

$$L_\xi(\tau, \tau_0; t) + 2i\xi \int_0^t d\tau' C(\tau - \tau') L_\xi(\tau', \tau'; t) = C(\tau - \tau_0) \quad (\text{B1})$$

Equation B1 should hold for all $\tau \in [0, t]$, and function $L(\tau)$ is defined on segment $[0, t]$. We can extend $L(\tau)$ to the entire real axis by requiring that

$$L(\tau, \tau_0; t) = 0 \text{ for } \tau_0, \tau \notin [0, t], \tau_0 < \tau \quad (\text{B2})$$

We can then recast eq B1 in a form

$$L_\xi(\tau, \tau_0; t) + 2i\xi \int_{-\infty}^{\infty} d\tau' C(\tau - \tau') L_\xi(\tau', \tau_0; t) = C(\tau - \tau_0) + F(\tau) \quad (\text{B3})$$

where

$$F(\tau) = 0 \text{ for } \tau \in [0, t] \quad (\text{B4})$$

With the requirements given in eqs B2 and B4, integral eq B3 is defined on the entire real axis. Equation B3, along with conditions (eqs B2 and B3), is equivalent to the original integral eq 13 defined for $\tau \in [0, t]$.

Equation 12 can be solved by switching to the frequency domain.

$$[1 + 2i\xi C(\omega)] L_\xi(\omega) = C(\omega) e^{i\omega\tau_0} + F(\omega) \quad (\text{B5})$$

Equation B4 allows the following representation for $F(\omega)$:

$$F(\omega) = F_-(\omega) + F_+(\omega) e^{i\omega t} \quad (\text{B6})$$

where $F_+(\omega)$ and $F_-(\omega)$ are holomorphic (analytic) functions in the upper ($\Im[\omega] > 0$) and lower ($\Im[\omega] < 0$) complex halfplanes, respectively. Combining eqs B5 and B6, we obtain:

$$L_\xi(\omega) = \frac{C(\omega) e^{i\omega\tau_0} + F(\omega)}{1 + 2i\xi C(\omega)} \quad (\text{B7})$$

To satisfy the requirement given by eq B2 in the time domain, we need to impose the following conditions in the frequency domain:

$L(\omega)$ is holomorphic for $\Im[\omega] > 0$

$$L(\omega)e^{-i\omega t} \text{ is holomorphic for } \Im[\omega] < 0 \quad (\text{B8})$$

Here we use the term "holomorphic function" to imply a holomorphic function decaying to zero as $\omega \rightarrow \infty$ not slower than ω^{-1} .

The Wiener-Hopf method is based on finding the functions $F_+(\omega)$ and $F_-(\omega)$ that are holomorphic in the upper and lower halfplanes such that function $L(\omega)$ given by eq B7 satisfies the constraints (eq B8). In our calculation, we assume that the correlation function $C(\omega)$ is a meromorphic function of ω (analytic in the entire domain, except possibly for some poles).

Using the representation (eq B6) for function $F(\omega)$, we expand $F_+(\omega)$ and $F_-(\omega)$ as

$$\begin{aligned} F_+(\omega) &= \sum_{j=1}^N \frac{A_j^+}{\omega + i\Lambda_j} \\ F_-(\omega) &= \sum_{j=1}^N \frac{A_j^-}{\omega - i\Lambda_j} \end{aligned} \quad (\text{B9})$$

where $\Re[\Lambda_j] > 0$, and A_j^+ , A_j^- are the coefficients chosen such that the zeros of the expression in the numerator exactly cancel the poles of the expression in the denominator of eq B7 (see Appendix B for more detail).

The solution of integral eq 12 for operator L_ξ in the frequency domain becomes

$$\begin{aligned} L_\xi(\omega) &= \left(1 + 2i\xi \sum_{j=1}^N \frac{2\lambda_j\Lambda_j}{\omega^2 + \Lambda_j^2} \right)^{-1} \times \\ &\sum_{j=1}^N \left(\frac{2\lambda_j\Lambda_j}{\omega^2 + \Lambda_j^2} e^{i\omega\tau_0} + \frac{A_j^+}{\omega + i\Lambda_j} e^{i\omega t} + \frac{A_j^-}{\omega - i\Lambda_j} \right) \end{aligned} \quad (\text{B10})$$

Inverse Fourier transforming $L_\xi(\omega)$ into the time domain and substituting it into eq 12, followed by integration over τ and ξ , we obtain the closed form expression for the linear optical response given by eq 20 in the main text.

APPENDIX C: DERIVATION OF EQ 20

In this Section, we use the Wiener-Hopf method presented in Appendix B to solve the integral eq 12 for the operator $L_\xi(\tau', \tau; t)$ in the frequency domain and calculate the linear optical response.

We first rewrite eq B9 in the form:

$$\begin{aligned} L_\xi(\omega) &= \frac{Q(\omega)}{P(\omega)} \sum_{j=1}^N \left(\frac{2\lambda_j\Lambda_j}{\omega^2 + \Lambda_j^2} e^{i\omega\tau_0} \right. \\ &\left. + \frac{A_j^+}{\omega + i\Lambda_j} e^{i\omega t} + \frac{A_j^-}{\omega - i\Lambda_j} \right) \end{aligned} \quad (\text{C1})$$

where $P(\omega)$ and $Q(\omega)$ are polynomials of ω , given by

$$\begin{aligned} Q(\omega) &\equiv \prod_{j=1}^N (\omega^2 + \Lambda_j^2) \\ P(\omega) &\equiv Q(\omega) + 2i\xi \sum_{j=1}^N 2\lambda_j\Lambda_j \prod_{j=1, j \neq k}^N (\omega^2 + \Lambda_j^2) \end{aligned} \quad (\text{C2})$$

The function $L_\xi(\omega)$ in eq C1 is generally meromorphic, rather than holomorphic. Note that the poles of the expression in the parenthesis inside the summation in eq C1 are cancelled by the zeros of the polynomial $Q(\omega)$. Also, as stated in Appendix A, in eq C1 the coefficients A_j^+ , A_j^- must be chosen in such a way that the zeros of the expression in the parenthesis exactly cancel the poles of the polynomial $P(\omega)$. This requirement yields the following linear system of equations for A_j^+ and A_j^- :

$$\sum_j S_{kj} A_j = -\frac{i}{2\xi} \exp \left[i\omega_k \left(\tau_0 - \frac{t}{2} \right) \right] \quad (\text{C3})$$

In eq C3, we have used the following notation. Latin indices assume the values $\pm 1, \pm 2, \dots, \pm N$; $A_j \equiv A_j^+$ for $j > 0$, $A_j \equiv A_j^-$ for $j < 0$, $\Lambda_{-j} = -\Lambda_j$, and ω_j for $j = \pm 1, \dots, \pm N$ are the roots of the polynomial $P(\omega)$.

The matrix S is given by

$$S_{kj} \equiv \frac{\exp \left[\frac{i}{2} \text{sign}[j] \omega_k t \right]}{\omega_k + i\Lambda_j} \quad (\text{C4})$$

where $[j]$ is 1 for $j > 0$, and -1 for $j < 0$. In deriving eqs C3 and C4, we made use of the fact that for any $k = \pm 1, \dots, \pm N$

$$1 + 2i\xi \sum_{j=1}^N \frac{2\lambda_j\Lambda_j}{\omega^2 + \Lambda_j^2} = 0 \quad (\text{C5})$$

Solving eq C3 for A_j yields:

$$A_j = -\frac{i}{2\xi} \sum_k (S^{-1})_{jk} \exp \left[i\omega_k \left(\tau_0 - \frac{t}{2} \right) \right] \quad (\text{C6})$$

and the solution of integral eq 12 assumes the final form:

$$L_\xi(\tau, \tau_0; t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega\tau} L_\xi(\omega, \tau_0; t) \quad (\text{C7})$$

where $L_\xi(\omega; \tau_0)$ is given by eq C2 with coefficients A_j^+ and A_j^- given by eq C6 for each j .

In the following calculation, we assume that the bath consists of one overdamped Brownian oscillator (see eq 19). In this case, the spectral density is reduced to the following expression

$$\tilde{C}''(\omega) = 2\lambda \frac{\omega\Lambda}{\omega^2 + \Lambda^2} \quad (\text{C8})$$

and eq C2 then becomes

$$L_\xi(\omega) = \frac{Q(\omega)}{P(\omega)} \left(\frac{2\tilde{\Delta}^2\Lambda}{\omega^2 + \Lambda^2} e^{i\omega\tau_0} + \frac{A^+}{\omega + i\Lambda} e^{i\omega t} + \frac{A^-}{\omega - i\Lambda} \right) \quad (\text{C9})$$

The poles of $P(\omega)$ are given by

$$\omega_{1,2} = \pm i\Lambda s \quad (\text{C10})$$

where s and $\tilde{\Delta}^2$ are defined in the main text (see eqs 23 and 24). Having found $\omega_{1,2}$, we now require that

$$\frac{2\tilde{\Delta}^2\Lambda}{\omega_{1,2}^2 + \Lambda^2} e^{i\omega_{1,2}\tau_0} + \frac{A^+}{\omega_{1,2} + i\Lambda} e^{i\omega_{1,2}t} + \frac{A^-}{\omega_{1,2} - i\Lambda} = 0 \quad (\text{C11})$$

such that

$$1 + \frac{4i\xi\tilde{\Delta}^2\Lambda}{\omega_{1,2}^2 + \Lambda^2} = 0 \quad (\text{C12})$$

Using eqs C11 and C12, we obtain:

$$A^+ = \frac{\Lambda(s^2 - 1)}{2\xi} \frac{(s+1)e^{\Lambda s\tau_0} + (s-1)e^{-\Lambda s\tau_0}}{(s+1)^2 e^{\Lambda s t} - (s-1)^2 e^{-\Lambda s t}} \quad (\text{C13})$$

and

$$A^- = -\frac{\Lambda(s^2 - 1)}{2\xi} \frac{(s+1)e^{\Lambda s(t-\tau_0)} + (s-1)e^{-\Lambda s(t-\tau_0)}}{(s+1)^2 e^{\Lambda s t} - (s-1)^2 e^{-\Lambda s t}} \quad (\text{C14})$$

Taking the Fourier transform of eq C10 as prescribed by eq C9, we obtain the solution of the integral eq12:

$$L(\tau, \tau_0; t) = \frac{\tilde{\Delta}^2}{s} e^{-\Lambda s|\tau + \tau_0|} + iA^+ \frac{s-1}{2s} e^{-\Lambda s|\tau + t|} + iA^- \frac{s+1}{2s} e^{-\Lambda s|\tau|} \quad (\text{C15})$$

with A^+ and A^- given by eqs C13 and C14.

Substituting eq C15 into the RHS of eq 11 and performing the integrations in the exponent, we finally obtain eq 20.