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Accuracy of second order perturbation theory in the polaron and variational polaron frames

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In the study of open quantum systems, the polaron transformation has recently attracted a renewed interest as it offers the possibility to explore the strong system-bath coupling regime. Despite this interest, a clear and unambiguous analysis of the regimes of validity of the polaron transformation is still lacking. Here we provide such a benchmark, comparing second order perturbation theory results in the original untransformed frame, the polaron frame, and the variational extension with numerically exact path integral calculations of the equilibrium reduced density matrix. Equilibrium quantities allow a direct comparison of the three methods without invoking any further approximations as is usually required in deriving master equations. It is found that the second order results in the original frame are accurate for weak system-bath coupling; the results deteriorate when the bath cut-off frequency decreases. The full polaron results are accurate for the entire range of coupling for a fast bath but only in the strong coupling regime for a slow bath. The variational method is capable of interpolating between these two methods and is valid over a much broader range of parameters.

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I. INTRODUCTION

In many open quantum systems, the coupling between the system and the bath can be considered as a small parameter. In this case, the application of second order perturbation theory leads to a master equation of Redfield or Lindblad type.¹ Their numerical implementation is straightforward and not computationally expensive. However, for many physical systems of current interest it has been shown that the weak coupling approximation is not justified. One example is the energy transfer process in photosynthetic complexes where the magnitude of the system-bath coupling is comparable to the electronic couplings.^{2–5} There are only a few non-perturbative techniques to obtain the numerically exact dynamics; examples include the hierarchy master equation,^{6,7} the quasi-adiabatic propagator path integral (QUAPI),^{8,9} and the multiconfiguration time-dependent Hartree approach.^{10–12} However, these methods are computationally demanding and also not trivial to implement.

Recently, a polaron transformed second order master equation^{13–18} has been derived to study the dynamics of open quantum systems at strong coupling. This approach transforms the total Hamiltonian into the polaron frame such that the system Hamiltonian is dressed by a polaron. The master equation is then obtained by applying perturbation theory to the transformed system-bath interaction term. This approach extends the regime of validity of the master equation to stronger system-bath coupling, provided that the electronic couplings (or tunneling matrix elements) are small compared to the typical bath frequency. When this condition is not fulfilled,

the polaron is too sluggish to accurately follow the system motion and the polaron transformation may perform worse than the standard master equation approach.

In order to partially overcome this difficulty, the variational method has been developed as a generalization of the polaron transformation.^{19–22} Instead of performing the full transformation, the variational polaron approach seeks for an optimal amount of transformation, depending on the properties of the bath. Thus it is able to interpolate between the strong and weak coupling regimes and to capture the correct behavior over a much broader range of parameters. Both the polaron and variational master equations have the attractive feature of being computationally economic (they have the same computational complexity as the Redfield equation) and are therefore suitable for studying large systems.

However, a thorough assessment of the accuracy of second order perturbation theory (2nd-PT) in the polaron and variational polaron frames is still lacking. It is not exactly clear how the accuracy depends on the properties of the bath, namely, the bath relaxation time and the coupling strength. One of the main goals of this work is to provide such a benchmark. Instead of studying the dynamics, here we focus on the equilibrium density matrix. Focusing on this quantity offers two key advantages. First, in the equilibrium case the second order perturbation is the only approximation involved. In the derivation of second order master equations, additional approximations generally must be invoked, such as factorized initial conditions and the Born-Markov approximation. These additional restrictions prevent a clear assessment of the isolated role of second order perturbation theory and the merits of the polaron transformation (Refs. 13–15, and 21 avoided the Born-Markov approximation though). Thus studying the equilibrium density matrix offers a direct comparison

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of the various perturbation methods. A second advantage of studying the equilibrium state is that it is much easier to obtain numerically exact results. Therefore, we are able to systematically explore a large range of the parameter space that is often not possible with other exact treatments of the dynamics.

In Sec. II A, the details of the spin-boson model used in the remainder of the text are outlined. Following this, the polaron transformation and its variational extension are applied to the Hamiltonian in Sec. II B. In Sec. II C, the second-order corrections to the equilibrium reduced density matrix are derived in the original, polaron, and variational polaron frames. In the ensuing section, results for the various perturbation theories are compared with exact numerical results from path integral calculations over a broad range of the parameter space. As expected, it is found that the second-order results in the original frame are accurate for small system-bath coupling and fast bath. The full polaron method is valid for the entire range of coupling for a fast bath. But for a slow bath, it is only accurate in the strong coupling regime. The variational method is capable of interpolating between these two methods and provides a much more accurate description.

II. THEORY

A. Spin-boson model

The spin-boson model is a paradigm for the study of quantum dissipative systems. It has been used to investigate the energy transfer in light harvesting systems,^{23,24} the problem of decoherence in quantum optics,²⁵ tunneling phenomena in condensed media,^{26,27} and quantum phase transitions.^{28–30} The spin-boson model consists of a two-level system coupled to a bath of harmonic oscillators. Its Hamiltonian can be written as (we set $\hbar = 1$)

$$\hat{H}'_{tot} = \frac{\epsilon}{2}\hat{\sigma}_z + \frac{\Delta}{2}\hat{\sigma}_x + \sum_k \omega_k \hat{b}_k^\dagger \hat{b}_k + \hat{\sigma}_z \sum_k g_k (\hat{b}_k^\dagger + \hat{b}_k), \quad (1)$$

where σ_i ($i = x, y, z$) are the usual Pauli matrices, ϵ is the energy splitting between the two levels, and Δ is the tunneling matrix element. The bath is modeled as a set of harmonic oscillators labeled by their frequencies, ω_k , and couplings to the two-level system denoted by g_k .

The properties of the harmonic bath are completely determined by the spectral density, $J(\omega) = \pi \sum_k g_k^2 \delta(\omega - \omega_k)$. Throughout the paper, we use a super-ohmic spectral density with an exponential cut-off,

$$J(\omega) = \frac{1}{2} \gamma \frac{\omega^3}{\omega_c^3} e^{-\omega/\omega_c}, \quad (2)$$

where γ is the system-bath coupling strength and has the dimension of frequency. The cut-off frequency is denoted by ω_c , and its reciprocal governs the relaxation time of the bath, $\tau \propto \frac{1}{\omega_c}$.

B. Polaron and variational polaron transformations

The polaron transformation is generated by the unitary operator

$$\hat{U} = \exp \left[\hat{\sigma}_z \sum_k \frac{f_k}{\omega_k} (\hat{b}_k^\dagger - \hat{b}_k) \right], \quad (3)$$

which displaces the bath oscillators in the positive or negative direction depending on the state of the two-level system. The parameter f_k determines the magnitude of the displacement for each mode. Setting $f_k = g_k$ corresponds to the full polaron transformation, whereas $f_k = 0$ corresponds to no transformation. The variational method allows us to determine an optimal value of f_k that lies in between these two limits, $0 \leq f_k \leq g_k$, making the transformation valid over a wider range of parameters.

Applying the transformation to the total Hamiltonian, we have

$$\begin{aligned} \hat{H}_{tot} &= \hat{U} \hat{H}'_{tot} \hat{U}^\dagger \\ &= \hat{H}_0 + \hat{H}_I, \end{aligned} \quad (4)$$

where the total free Hamiltonian is $\hat{H}_0 = \hat{H}_S + \hat{H}_B$. The transformed system Hamiltonian is given by

$$\hat{H}_S = \frac{\epsilon}{2}\hat{\sigma}_z + \frac{\Delta_R}{2}\hat{\sigma}_x + \sum_k \frac{f_k}{\omega_k} (f_k - 2g_k),$$

and the bath Hamiltonian remains unaffected, $\hat{H}_B = \sum_k \omega_k \hat{b}_k^\dagger \hat{b}_k$. The transformed interaction Hamiltonian becomes

$$\hat{H}_I = \hat{\sigma}_x \hat{V}_x + \hat{\sigma}_y \hat{V}_y + \hat{\sigma}_z \hat{V}_z, \quad (5)$$

where

$$\hat{V}_x = \frac{\Delta}{4} (\hat{D}_+^2 + \hat{D}_-^2 - 2B), \quad (6)$$

$$\hat{V}_y = \frac{\Delta}{4i} (\hat{D}_-^2 - \hat{D}_+^2), \quad (7)$$

$$\hat{V}_z = \sum_k (g_k - f_k) (\hat{b}_k^\dagger + \hat{b}_k), \quad (8)$$

and \hat{D}_\pm is the product of displacement operators, $\hat{D}_\pm = e^{\pm \sum_k \frac{f_k}{\omega_k} (\hat{b}_k^\dagger - \hat{b}_k)}$. The tunneling rate is renormalized by the expectation value of the bath displacement operators, $\Delta_R = B\Delta$, where

$$B = \langle \hat{D}_\pm^2 \rangle_{\hat{H}_B} = \frac{\text{tr}_B [\hat{D}_\pm^2 e^{-\beta \hat{H}_B}]}{\text{tr}_B [e^{-\beta \hat{H}_B}]} \quad (9)$$

$$= \exp \left[-2 \sum_k \frac{f_k^2}{\omega_k^2} \coth(\beta \omega_k / 2) \right]. \quad (10)$$

Note that the interaction term is constructed such that $\langle \hat{H}_I \rangle_{H_0} = 0$.

Following Silbey and Harris,^{19,20} we use the Bogoliubov variational theorem to determine the optimal values for the set

$\{f_k\}$. We first compute the Bogoliubov-Feynman upper bound on the free energy, A_B ,

$$A_B = -\frac{1}{\beta} \ln \text{tr}_{S+B} [e^{-\beta \hat{H}_0}] + \langle \hat{H}_I \rangle_{\hat{H}_0}. \quad (11)$$

Since $\langle \hat{H}_I \rangle_{\hat{H}_0} = 0$ by construction, the upper bound is solely determined by the free Hamiltonian. The variational theorem states that $A_B \geq A$ where A is the true free energy of H_{tot} . Therefore, we want to make this bound as small as possible by minimizing A_B with respect to $\{f_k\}$, i.e., $\frac{dA_B}{df_k} = 0$. The minimization condition leads to

$$f_k = g_k F(\omega_k); \quad (12)$$

$$F(\omega_k) = \left[1 + \frac{\Delta_R^2}{\omega_k \eta} \coth(\beta \omega_k / 2) \tanh(\beta \eta / 2) \right]^{-1}, \quad (13)$$

where $\eta = \sqrt{\epsilon^2 + \Delta_R^2}$.

In the continuum limit, the renormalization constant can be written as

$$B = \exp \left[-2 \int_0^\infty \frac{d\omega}{\pi} \frac{J(\omega)}{\omega^2} F(\omega)^2 \coth(\beta \omega / 2) \right]. \quad (14)$$

Since $F(\omega)$ is also a function of B , the above equation must be solved self-consistently.

C. Second order perturbation theory

This section is dedicated to finding the second-order correction to the equilibrium state of the system. The exact equilibrium reduced density matrix can be formally written as

$$\hat{\rho}_S = \frac{\text{tr}_B [e^{-\beta \hat{H}_{tot}}]}{\text{tr}_{S+B} [e^{-\beta \hat{H}_{tot}}]}. \quad (15)$$

Expanding the operator $e^{-\beta \hat{H}_{tot}}$ up to second order in \hat{H}_I , we have

$$e^{-\beta \hat{H}_{tot}} \approx e^{-\beta \hat{H}_0} \left[1 - \int_0^\beta d\beta' e^{\beta' \hat{H}_0} \hat{H}_I e^{-\beta' \hat{H}_0} + \int_0^\beta d\beta' \int_0^{\beta'} d\beta'' e^{\beta' \hat{H}_0} \hat{H}_I e^{-(\beta' - \beta'') \hat{H}_0} \hat{H}_I e^{-\beta'' \hat{H}_0} \right]. \quad (16)$$

The above expansion is similar to the Dyson expansion, with β treated as imaginary time.

Since $\langle \hat{H}_I \rangle_{\hat{H}_0} = 0$, the leading order correction to $\hat{\rho}_S$ is of second order in \hat{H}_I . Inserting the above expression into Eq. (15) and keeping terms up to the second order in \hat{H}_I , the system equilibrium state can be approximated as³¹⁻³³

$$\begin{aligned} \hat{\rho}_S &\approx \hat{\rho}_S^{(0)} + \hat{\rho}_S^{(2)} + \dots, \\ \hat{\rho}_S^{(0)} &= e^{-\beta \hat{H}_S} / Z_S^{(0)}, \\ \hat{\rho}_S^{(2)} &= \frac{\hat{A}}{Z_S^{(0)}} - \frac{Z_S^{(2)}}{(Z_S^{(0)})^2} e^{-\beta \hat{H}_S}, \end{aligned} \quad (17)$$

where

$$\begin{aligned} \hat{A} &= \sum_{n,m=x,y,z} \int_0^\beta d\beta' \int_0^{\beta'} d\beta'' C_{nm}(\beta' - \beta'') \\ &\quad \times e^{(\beta' - \beta'') \hat{H}_S} \hat{\sigma}_n e^{(\beta'' - \beta') \hat{H}_S} \hat{\sigma}_m e^{-\beta'' \hat{H}_S}, \\ Z_S^{(0)} &= \text{tr}_S [e^{-\beta \hat{H}_S}]; \quad Z_S^{(2)} = \text{tr}_S [\hat{A}], \end{aligned} \quad (18)$$

and $C_{nm}(\tau)$ is the bath correlation function in imaginary time,

$$C_{nm}(\tau) = \frac{\text{tr}_B [e^{\tau \hat{H}_B} \hat{V}_n e^{-\tau \hat{H}_B} \hat{V}_m e^{-\beta \hat{H}_B}]}{\text{tr}_B [e^{-\beta \hat{H}_B}]}. \quad (19)$$

The non-vanishing bath correlation functions are

$$C_{zy}(\tau) = -C_{yz}(\tau) \quad (20)$$

$$= i \Delta_R \int_0^\infty \frac{d\omega}{\pi} \frac{J(\omega)}{\omega} F(\omega) [1 - F(\omega)] \frac{\sinh(\frac{1}{2}(\beta - 2\tau)\omega)}{\sinh(\beta\omega/2)}, \quad (21)$$

$$C_{xx}(\tau) = \frac{\Delta_R^2}{8} (e^{\phi(\tau)} + e^{-\phi(\tau)} - 2), \quad (22)$$

$$C_{yy}(\tau) = \frac{\Delta_R^2}{8} (e^{\phi(\tau)} - e^{-\phi(\tau)}), \quad (23)$$

$$C_{zz}(\tau) = \int_0^\infty \frac{d\omega}{\pi} J(\omega) [1 - F(\omega)]^2 \frac{\cosh(\frac{1}{2}(\beta - 2\tau)\omega)}{\sinh(\beta\omega/2)}, \quad (24)$$

where

$$\phi(\tau) = 4 \int_0^\infty \frac{d\omega}{\pi} \frac{J(\omega)}{\omega^2} F(\omega)^2 \frac{\cosh(\frac{1}{2}(\beta - 2\tau)\omega)}{\sinh(\beta\omega/2)}. \quad (25)$$

It is useful at this point to analyze the behavior of the perturbation theory at strong coupling in the polaron frame. As seen from Eq. (14), when $\gamma \rightarrow \infty$ then $B \rightarrow 0$ and the system becomes incoherent since the coherent tunneling element vanishes. At the same time, $F(\omega) \rightarrow 1$ as $B \rightarrow 0$ so that all of the above correlation functions vanish, and hence also the second-order correction to $\hat{\rho}_S$. Therefore in this limit, the equilibrium density matrix is only determined by the energy splitting of the two levels, $\hat{\rho}_S \propto \exp(-\frac{\epsilon}{2} \beta \hat{\sigma}_z)$.

The full polaron result can be conveniently obtained by setting $F(\omega) = 1$; the only non-vanishing correlation functions in this case are C_{xx} and C_{yy} . The opposite limit of $F(\omega) = 0$ corresponds to performing no transformation and C_{zz} is the only non-zero correlation function. For comparison, below we will also include the results from these two limiting cases.

III. RESULTS AND DISCUSSIONS

In this section, we compare the results from 2nd-PT in the original [$F(\omega) = 0$], the polaron [$F(\omega) = 1$], and the variational polaron [$F(\omega)$ as in Eq. (13)] frames with those

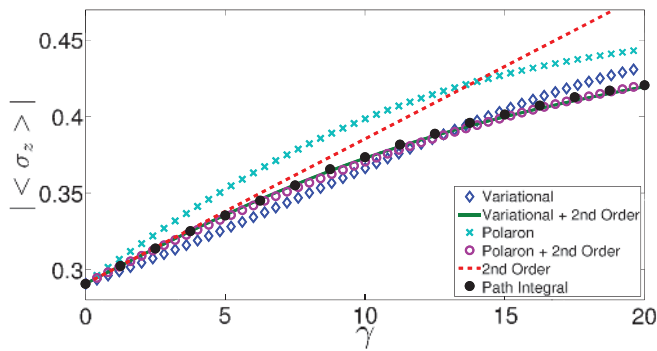


FIG. 1. Fast bath, $\omega_c > \Delta$. Comparison of the approximate methods with the exact path integral results as a function of the dissipation, γ , for $\omega_c = 5\epsilon$ and $\Delta = 3\epsilon$. Plotted are the values of $\langle \hat{\sigma}_z \rangle$ from the zeroth-order density matrix in the polaron frame (light blue crosses) and the variational polaron frame (dark blue diamonds), as well as from the density matrix in the original frame with the second-order correction (red dashed line), the polaron frame (purple empty circles), and the variational polaron frame (solid green line). The exact path integral results are shown as filled (black) dots.

from numerically exact imaginary time path integral calculations. We compute the expectation value, $\langle \hat{\sigma}_z \rangle$, since it is not affected by the transformation, $\langle \hat{U}^\dagger \hat{\sigma}_z \hat{U} \rangle = \langle \hat{\sigma}_z \rangle$. Therefore, this quantity allows us to make a direct comparison between the path integral results, which provide the density matrix in the original frame, and the (variational) polaron results. Results from the transformed zeroth-order density matrix, $\hat{\rho}_S^{(0)}$, which depends only on the renormalized system Hamiltonian \hat{H}_S , are also included. In the original frame, corrections to the off-diagonal elements of the equilibrium density matrix calculated within the polaron transformation appear already at first order in perturbation theory. Their computation, however, is substantially more involved and is a topic of ongoing work.

We first calculate $\langle \hat{\sigma}_z \rangle$ as a function of the dissipation strength for fast, slow, and adiabatic baths, assessing the accuracy of 2nd-PT for different bath cut-off frequencies. We then conclude this section by presenting phase diagrams of the relative errors of the various methods as functions of the dissipation strength and the bath cut-off frequency. This allows us to establish the regimes of validity of each approach across the entire range of bath parameters. Throughout the paper, we set $\epsilon = 1$ and $\beta = 1$.

A. Fast bath, $\omega_c > \Delta$

The value of $\langle \hat{\sigma}_z \rangle$ is plotted as a function of the dissipation strength, γ , in Fig. 1 for a fast bath, $\omega_c > \Delta$. First, it can be seen that the result from the usual 2nd-PT in the original frame (dashed line) is linearly dependent on γ . While this approach is accurate at small γ , it quickly degrades as the coupling increases. On the other hand, the results from 2nd-PT in the polaron (empty circles) and the variational polaron (solid line) frames are in excellent agreement with the exact path integral result (solid dots) over the entire range of dissipation. The zeroth-order result for $\langle \hat{\sigma}_z \rangle$ in the the polaron frame (crosses) tends to overestimate the correction, whereas the variational frame result (diamonds) provides at least a qualitatively correct description.

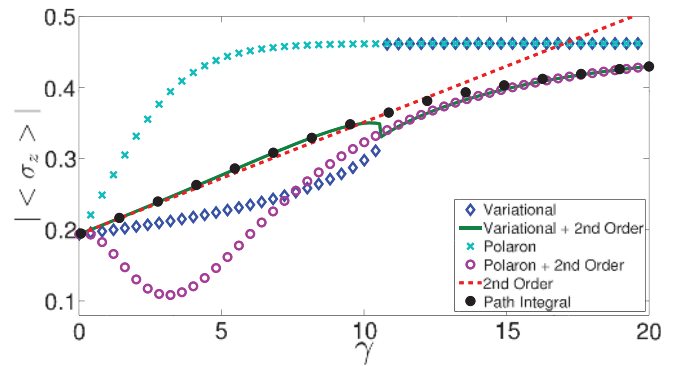


FIG. 2. Slow bath, $\omega_c < \Delta$. Comparison of the approximate methods with the exact path integral results as a function of the dissipation, γ , for $\omega_c = 1.5\epsilon$ and $\Delta = 5\epsilon$. Plotted are the values of $\langle \hat{\sigma}_z \rangle$ from the zeroth-order density matrix in the polaron frame (light blue crosses) and the variational polaron frame (dark blue diamonds), as well as from the density matrix in the original frame with the second-order correction (red dashed line), the polaron frame (purple empty circles), and the variational polaron frame (solid green line). The exact path integral results are shown as filled (black) dots.

B. Slow bath, $\omega_c < \Delta$

Figure 2 displays the opposite case, when the bath is slow as compared to the tunneling rate, $\omega_c < \Delta$. At small and intermediate γ , it can be seen that the polaron method with 2nd-PT fails to predict the correct behavior, while the usual 2nd-PT result in the original frame agrees well with the exact result. As with the case of the fast bath, at large γ , the polaron method provides an accurate description, while the original frame 2nd-PT breaks down. The variational polaron method (with 2nd-PT) interpolates between these two methods, providing accurate results over a large range of the dissipation strength. The failure of the full polaron method is due to the fact that the bath oscillators are sluggish and are not able to fully dress the system. Therefore, the full polaron displacement is no longer appropriate. It can also be seen that the second-order correction in the full polaron frame is huge at small γ (the difference between the crosses and open circles). This should cast doubt on the validity of 2nd-PT in this case since the perturbative correction should be small.

It can also be observed that there is a discontinuity in the variational result (both with and without 2nd-PT) at the critical point of $\gamma \approx 10.6$. The variational approach exhibits a rather abrupt transition from a small transformation [$F(\omega) \ll 1$] to the full polaron transformation [$F(\omega) \approx 1$]. This discontinuity, which is an artifact of the transformation rather than a physical phase transition, has been predicted by Silbey and Harris^{19,20} for a slow bath. The discontinuity comes from solving the self-consistent equation in Eq. (14). Over a certain range of dissipation strengths, there exist multiple solutions to the self-consistent equation. According to the variational prescription, the solution with the lowest free energy is selected. This causes a “jump” in the solution, as depicted in Fig. 3. It is also observed in Fig. 2 that the variational polaron result is least accurate around the transition point. Therefore, it will be worthwhile to look for a better variational criterion that removes this discontinuity, which can hopefully provide a uniformly accurate solution. One possibility is to include the second-order term (in H_I) to the free energy A_B . It has

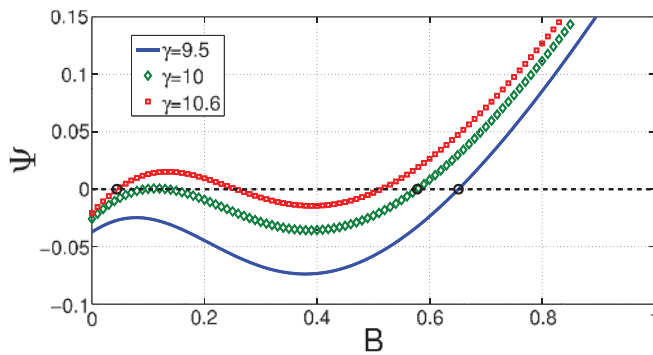


FIG. 3. Plot of the expression $\Psi = B - e^{-2 \int \frac{d\omega}{\pi} \frac{J(\omega)}{\omega^2} F(\omega)^2 \coth(\beta\omega/2)}$. The solutions to the self-consistent equation (14) are the points when $\Psi = 0$. At $\gamma = 9.5$, there is only one solution to the self-consistent equation. At $\gamma = 10$, multiple solutions start to develop, but the solution with the lowest free energy (denoted by the empty circle) is chosen. At the critical point of $\gamma = 10.6$, there is a “jump” in the lowest free energy solution which causes a discontinuity in the transformation.

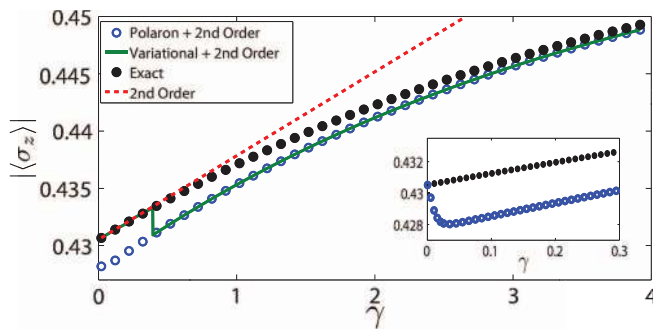


FIG. 4. $\omega_c \ll \Delta$. Comparison of the approximate methods with the exact result [from Eq. (26)] as a function of the dissipation, γ , for $\omega_c = 0.1\epsilon$ and $\Delta = 1\epsilon$. Plotted are the values of $\langle \hat{\sigma}_z \rangle$ from the density matrix with the second-order correction in the original frame (dashed red line), the polaron frame (empty blue circles), and the variational polaron frame (solid green line). The exact results are shown as filled (black) dots. The inset shows the small γ regime.

been shown in Ref. 28 that the correction can be important for a slow bath and its inclusion to the free energy calculations might improve the variational method. Additionally, an alternative ground state ansatz has been proposed in Ref. 34 that seems to be free of the discontinuity present in the Silbey-Harris approach.

C. Adiabatic bath, $\omega_c \ll \beta, \Delta$

In the adiabatic limit ($\omega_c \ll \beta$), the exact solution to the equilibrium state of the system can be obtained analytically. In this regime, the partition function is given by Ref. 35,

$$Z_S = \int_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi\chi}} \exp\left\{-\frac{x^2}{2\chi}\right. \\ \left. + \ln\left[2 \cosh[\beta\sqrt{(\Delta/2)^2 + (x + \epsilon/2)^2}]\right]\right\}, \quad (26)$$

where χ is the bath correlation function [in the original frame with $F(\omega) = 0$] in the adiabatic limit, $\chi = C_{zz}^{(0)} = \frac{2\gamma}{\pi\beta}$. The expectation value, $\langle \hat{\sigma}_z \rangle$, can be obtained from the partition function via the following relation:

$$\langle \hat{\sigma}_z \rangle = -\frac{2}{\beta} \frac{\partial}{\partial \epsilon} \ln Z_S. \quad (27)$$

In the regime where $\omega_c \ll \Delta$, the transition from $F(\omega) = 0$ to $F(\omega) = 1$ in the variational method is sharp, as seen in Fig. 4. Before the transition, the variational polaron result coincides with the exact result and that of perturbation theory in the original frame. In contrast, the full polaron result yields qualitatively incorrect results. Only at exactly $\gamma = 0$ does it produce the correct result (see inset of Fig. 4). After the transition, the variational result deviates from the exact result and becomes essentially the same as the full polaron result. As γ increases, results from both methods approach the exact result while the untransformed 2nd-PT breaks down as seen before.

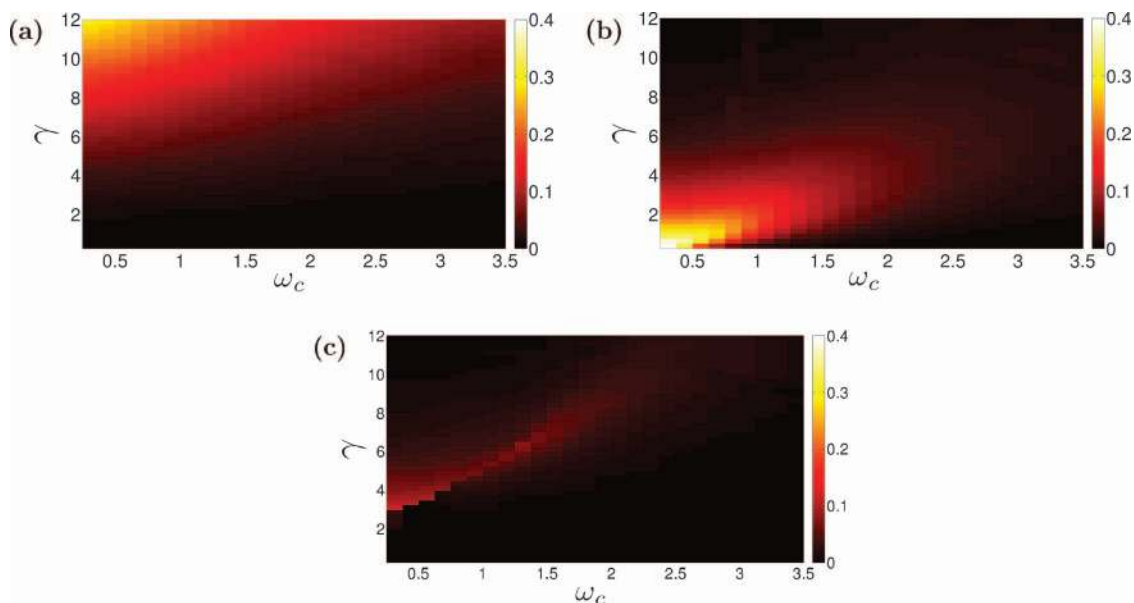


FIG. 5. At $\Delta = 3$, the relative errors of the second order perturbation theory as defined in Eq. (28) in (a) the original frame, (b) the full polaron frame, and (c) the variational polaron frame.

D. Relative errors

To get a better perspective of how the accuracy of 2nd-PT in different frames depends on the properties of the bath, we calculate the relative errors over the entire range of the bath parameters. The relative errors are defined as

$$\left| \frac{\langle \hat{\sigma}_z \rangle_{\text{Pert}} - \langle \hat{\sigma}_z \rangle_{\text{PI}}}{\langle \hat{\sigma}_z \rangle_{\text{PI}}} \right|, \quad (28)$$

where the subscripts ‘‘Pert’’ and ‘‘PI’’ denote the perturbative calculation and path integral calculation, respectively. Figure 5 displays the respective errors for the three methods as a function of the cut-off frequency and the coupling strength. As seen in Fig. 5(a), the usual 2nd-PT without transformation breaks down at large γ . It is also less accurate when the cut-off frequency is small, which corresponds to a highly non-Markovian bath. On the other hand, the 2nd-PT in the full polaron frame fails at small γ and ω_c [see Fig. 5(b)]. These two approaches provide complementary behavior as a function of the coupling strength; the polaron method is essentially exact for large γ , while the usual 2nd-PT is exact for small γ . The variational calculation is valid over a much broader range of parameters [see Fig. 5(c)], and essentially combines the regimes of validity of the full polaron result and 2nd-PT in the original frame. It is only slightly less accurate in the slow bath regime around the region where the discontinuity appears that was discussed above.

IV. CONCLUSIONS

In conclusion, we have provided a thorough assessment of the accuracy of the polaron and variational polaron methods. We compared the second order perturbation results in the polaron and variational polaron transformed frames with numerically exact path integral calculations of the equilibrium reduced density matrix. Focusing on the equilibrium properties allowed us to systematically explore the whole range of bath parameters without making any additional approximations as is generally required to simulate the dynamics. As expected, it is found that the standard perturbation results without the polaron transformation is only accurate for small coupling. The results deteriorate when the bath cut-off frequency decreases. On the other hand, the polaron results are accurate for the entire range of coupling for a fast bath ($\omega_c > \Delta$), whereas they are only accurate in the strong coupling regime when the bath is slow ($\omega_c < \Delta$). The variational method is capable of interpolating between the two methods and, therefore, is valid over a much broader range of parameters. It is only slightly less accurate around the region where the discontinuity appears.

The equilibrium properties presented here are not necessarily related to the accuracy of corresponding perturbative non-equilibrium dynamics. However, it should be noted that our findings are consistent with the results of Ref. 22 where the dynamics from the second order (variational) polaron master equation are compared with numerically exact QUAPI simulations for different tunneling strengths. The dynamical results fail, even at short times, in the same regime where the equilibrium properties fail. This consistency sug-

gests that the equilibrium results may indeed provide some indication of the accuracy of the dynamics.

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APPENDIX: IMAGINARY TIME PATH INTEGRAL

For Hamiltonians such as the spin-boson model where the bath is harmonic, the trace over the bath degrees of freedom in Eq. (15) may be performed analytically. In the path integral formulation this procedure leads to the well-known Feynman-Vernon influence functional.^{27,35–39} Using a Hubbard-Stratonovich transformation,^{27,35,37,40} it was shown that the influence functional may be unraveled by an auxiliary stochastic field. The ensuing imaginary time evolution may then be interpreted as one governed by a time-dependent Hamiltonian. Explicitly, the spin-boson model may be equivalently expressed as

$$\hat{H}(\tau) = \frac{\epsilon}{2} \hat{\sigma}_z + \frac{\Delta}{2} \hat{\sigma}_x + \hat{\sigma}_z \xi(\tau). \quad (A1)$$

All of the effects of the bath are accounted for by the colored noise term, $\xi(\tau)$, which obeys the autocorrelation relation

$$\langle \xi(\tau) \xi(\tau') \rangle = C_{zz}^{(0)}(\tau - \tau'), \quad (A2)$$

where $C_{zz}^{(0)}(\tau)$ is the correlation function given in Eq. (24) with $F(\omega) = 0$. The trace over the bath that was present in the original path integral formulation now corresponds to averaging the imaginary time dynamics over realizations of the noise. The auxiliary field is simply an efficient method of sampling the influence functional. Similar schemes for computing the real-time dynamics have recently shown promising results.^{41–43}

In practice, a sample of the reduced density matrix is propagated to the imaginary time β , where the time steps, $\delta\tau$, are determined by

$$\hat{\rho}_S(\tau + \delta\tau) = \exp[-\delta\tau \hat{H}(\tau)] \hat{\rho}_S(\tau), \quad (A3)$$

with the initial condition, $\rho(0) = I$. The primary benefit of this approach is that it generates the entire reduced density matrix from a single Monte Carlo calculation. Additionally, any form for the spectral density of the bath, $J(\omega)$, may be used. In our calculations, 10^8 (at small γ) to 10^{11} (at large γ) Monte Carlo samples are needed to achieve convergence. The details of the numerical implementation can be found in Ref. 40.

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