The simulation of electronic absorption spectrum of a chromophore coupled to a condensed phase environment: Maximum entropy versus singular value decomposition approaches

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We consider the problem of calculating the electronic absorption spectrum of a chromophore with intramolecular degrees of freedom coupled to a condensed phase environment. We approach this calculation in the framework of the imaginary-time path integral Monte Carlo techniques, and focus on the problem of the analytic continuation of the imaginary-time data to the real-time axis. Two alternative analytic continuation methods are considered: the maximum entropy method and the singular value decomposition method. An exactly solvable model is introduced to test the accuracy of these methods. Exact numerical results for the absorption spectra are compared to the spectra reconstructed by the analytic continuation methods; it is found that the singular value decomposition method gives systematically higher resolution than the maximum entropy method and is capable of reproducing the fine vibronic structure of the absorption spectrum. © *1997 American Institute of Physics.* [S0021-9606(97)51146-9]

I. INTRODUCTION

Numerous problems in chemical physics involve calculation of dynamic correlation functions in quantum systems.[1,2] For an isolated system with a few degrees of freedom, the correlation functions can be obtained from certain path integral techniques (e.g., numerical matrix multiplication[3,4]) or from the wave packet dynamics.[5] A more challenging situation occurs when the primary system is coupled to a condensed phase environment (''bath'') with essentially infinite number of degrees of freedom. Particular examples include: medium-induced electron transfer, dissipative tunneling, activated processes, and electronic spectroscopy of chromophores in crystals and in liquids. One possible strategy is to treat the bath dynamics classically, while retaining the quantum mechanical treatment of the primary system.[6] Mixed quantum-classical simulations of this type are suitable for certain problems, but, in general, do not give state-to-state transition probabilities accurately. In order to account for the quantum nature of the bath, some alternative methods have been employed, such as the time-dependent, self-consistent field approximation[7] or the cumulant expansion-based techniques.[8] The former method is based on the factorization of the system plus bath wave packet into wave packets for individual degrees of freedom, and the latter method employs truncation of the time evolution operator after the second-order term in the system–bath interaction. These approximations could limit the applicability of the above methods to relatively weak system–bath coupling.

Another possibility is to use path integral Monte Carlo (PIMC) techniques.[9–16] The direct Monte Carlo simulation of real-time quantum dynamics is extremely difficult due to the ''alternating weights'' problem. To avoid this difficulty, one can calculate the Euclidean-time correlation functions, and analytically continue these to the real-time axis.[17] While the PIMC simulation of imaginary time correlation functions is relatively straightforward, the analytic continuation is very difficult to perform numerically, because the solution of this ''inverse problem'' is extremely sensitive to the statistical noise in the simulation data. In recent years, two methods have been applied to problems of this type: the maximum entropy method[18–22] and the singular value decomposition (SVD) method.[23–25] The purpose of the present work is to test the applicability of these methods to the problem of calculating the electronic absorption spectrum of a chromophore coupled to a bath. We consider an exactly solvable model, where the relevant time correlation function (and, hence, the spectrum) can be computed exactly. This allows us to assess the accuracy of the two aforementioned analytic continuation methods in calculating the spectrum.

The paper is organized as follows. In Sec. II we present the expression for the electronic absorption spectrum, and discuss the problem of inverting the imaginary-time data to calculate the spectrum. In Sec. III we specify an exactly solvable model, which is used to assess the accuracy of the analytic continuation methods. The details of implementation of these methods are given in Sec. IV. In Sec. V we present the numerical results, and in Sec. VI we conclude.

II. ELECTRONIC ABSORPTION SPECTRUM AND THE INVERSION PROBLEM

We consider a chromophore with intramolecular degrees of freedom coupled to a condensed phase environment. We focus on a particular electronic transition, when the chromophore goes from its ground electronic state (denoted by $|0\rangle$) to the excited electronic state (denoted by $|1\rangle$). In the Born–Oppenheimer approximation, the total Hamiltonian can be written as

$$H=H_0|0\rangle\langle 0|+H_1|1\rangle\langle 1|, \tag{1}$$

where H_0 (H_1) is the Hamiltonian for the nuclear degrees of freedom of the system and the bath, corresponding to the

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motion on the Born–Oppenheimer potential surface when the chromophore is in its ground (excited) electronic state.

Within the electric dipole approximation, the normalized electronic absorption spectrum is given by the Fourier transform of the dipole–dipole time correlation function:

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dte^{i\omega t}C(t), \tag{2}$$

$$C(t)=\frac{\mathrm{Tr}[e^{-\beta H}e^{iHt/\hbar}\boldsymbol{\mu}e^{-iHt/\hbar}\boldsymbol{\mu}]}{\mathrm{Tr}[e^{-\beta H}\mu^2]}, \tag{3}$$

where $\beta=1/kT$, Tr$(\cdots)$ denotes the trace over all nuclear and electronic degrees of freedom, and $\boldsymbol{\mu}$ is the transition dipole operator.

Within the Condon approximation $\boldsymbol{\mu}$ does not depend on the nuclear coordinates, and can be written as follows:

$$\boldsymbol{\mu}=\boldsymbol{\mu}_{01}|0\rangle\langle 1|+\boldsymbol{\mu}_{10}|1\rangle\langle 0|. \tag{4}$$

Assuming the electronic energy gap between the excited and ground states to be much larger than kT, one can write approximately:

$$C(t)\approx\frac{\mathrm{Tr}_n[e^{-\beta H_0}e^{iH_0t/\hbar}e^{-iH_1t/\hbar}]}{\mathrm{Tr}_n[e^{-\beta H_0}]}, \tag{5}$$

where Tr$_n(\cdots)$ denotes the trace over the nuclear coordinates.

Once the dipole autocorrelation function is known, the electronic absorption spectrum can be obtained in a straightforward way via Eq. (2). However, exact calculation of $C(t)$ is possible only for a very limited number of simple models, e.g., when both H_0 and H_1 are quadratic (see below). In order to deal with anharmonic systems, one has to resort to simulation techniques, such as path integral Monte Carlo methods.

As mentioned in Sec. I, the direct evaluation of the real-time correlation function by PIMC methods is not feasible because of the phase oscillations. Instead, one can work with its analytic continuation to the imaginary axis defined according to: $G(\tau)=C(-i\tau)$, $0\leqslant\tau\leqslant\beta\hbar$. $G(\tau)$ and $I(\omega)$ are related by the two-sided Laplace transform.

$$G(\tau)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega I(\omega)e^{-\omega\tau}. \tag{6}$$

The major limitation of this approach stems from the fact that the Euclidean-time correlation function is defined on the negative imaginary time axis only up to $t=-i\beta\hbar$,[17] and the unavoidable statistical errors in this function limit the region of the complex plane where the analytic continuation can be performed with sufficient accuracy. Hence, it is important to study exactly solvable models, where the real-time correlation function (and its Fourier transform) can be obtained exactly, which then allows a test of the accuracy of the analytic continuation methods. In Sec. III we provide a description of such a model.

III. MODEL HAMILTONIAN AND MODEL SPECTRAL DENSITIES

In order to specify our model, we need to define the ground and excited state Born–Oppenheimer Hamiltonians in Eq. (1). In what follows, we consider a chromophore with a single intramolecular degree of freedom, which we denote by Q; the collection of the bath nuclear coordinates is labeled by q. Quite generally, one can write:

$$H_0=h_0(Q)+h_b(q)+V_0(Q,q), \tag{7}$$

$$H_1=h_1(Q)+h_b(q)+V_1(Q,q)+\hbar\omega_e, \tag{8}$$

where $h_0(Q)$ $[h_1(Q)]$ is the Hamiltonian for the vibrational coordinate of the system when it is in its ground (excited) electronic state, $h_b(q)$ is the bath Hamiltonian, and $V_0(Q,q)$ $(V_1(Q,q))$ is the system–bath coupling, which we assume to be different for the two electronic states of the chromophore; $\hbar\omega_e$ is the gas phase electronic transition of the chromophore, for convenience we set it equal to 0.

We now consider the following exactly solvable harmonic form of the above model. The vibrational Hamiltonians for the system are taken to be harmonic in both electronic states, but with different equilibrium positions Q_0 and Q_1, and (possibly) different frequencies ω_0 and ω_1. The bath is modeled by a collection of N harmonic oscillators, and the system–bath coupling is taken to be linear in both system and bath coordinates albeit with different coupling strengths for the two electronic states. The two Born–Oppenheimer Hamiltonians thus become (from now on we use atomic units)

$$H_0=-\frac{1}{2m}\frac{\partial^2}{\partial Q^2}+\frac{1}{2}m\omega_0^2(Q-Q_0)^2-\sum_i\frac{1}{2m_i}\frac{\partial^2}{\partial q_i^2}+\frac{1}{2}\sum_i m_i\omega_i^2q_i^2+\sum_i g_i^0(Q-Q_0)q_i, \tag{9}$$

$$H_1=-\frac{1}{2m}\frac{\partial^2}{\partial Q^2}+\frac{1}{2}m\omega_1^2(Q-Q_1)^2-\sum_i\frac{1}{2m_i}\frac{\partial^2}{\partial q_i^2}+\frac{1}{2}\sum_i m_i\omega_i^2q_i^2+\sum_i g_i^1(Q-Q_1)q_i. \tag{10}$$

In the above, m is the reduced mass of the system; index i (running from 1 to N_b) labels the bath normal modes q_i with frequencies ω_i and masses m_i; g_i^0 (g_i^1) are the coupling strengths for the ground (excited) state of the chromophore.

The harmonic model defined by Eqs. (9) and (10) is exactly solvable. In order to compute the real-time dipole autocorrelation function from Eq. (5), one can employ either the density matrix formalism of Kubo and Toyozawa[26] (based on Gaussian integrals), or the boson algebra technique of Balian and Brezin,[27] which allows evaluation of the thermal averages of exponentiated quadratic functions of phonon operators. In practice, both methods are limited to a finite number, N_b, of bath modes, and are essentially equivalent. Throughout the present work, we have utilized the Gaussian method of Kubo and Toyozawa.[26]

For the harmonic model considered here, the effect of the bath on the spectrum is completely determined by the two spectral densities defined as follows:

$$J_0(\omega)=\sum_i \frac{(g_i^0)^2}{2\omega_i}\,\delta(\omega-\omega_i), \tag{11}$$

$$J_1(\omega)=\sum_i \frac{(g_i^1)^2}{2\omega_i}\,\delta(\omega-\omega_i). \tag{12}$$

In this work we assume for simplicity that $J_0(\omega)$ and $J_1(\omega)$ have the same functional form, and differ only by an overall system–bath coupling strength, i.e., we write $J_0(\omega)=\rho_0 J(\omega)$ and $J_1(\omega)=\rho_1 J(\omega)$, where $J(\omega)$ is taken to be normalized according to: $\int_0^\infty d\omega J(\omega)=1$. We now introduce two model spectral densities $J(\omega)$—for acoustic and optical phonons, respectively.

The conventional choice of spectral density for acoustic phonons is the Debye model coupled with the deformation potential approximation.[28] This gives a spectral density which is proportional to ω^3, and has a sharp cutoff at the Debye frequency. For numerical convenience the model can be slightly modified[8] by introducing a smooth exponential cutoff:

$$J_{\mathrm{ac}}(\omega)=\frac{\alpha^4}{6}\,\omega^3\exp(-\alpha\omega). \tag{13}$$

Optical phonons are generally characterized by narrow dispersion. As a model for the spectral density, we have taken the following phenomenological form:[29]

$$J_{\mathrm{op}}(\omega)=\frac{3}{4\Delta^3}\,[\Delta^2-(\omega-\omega_{\mathrm{op}})^2] \times\theta[\omega-(\omega_{\mathrm{op}}-\Delta)]\,\theta[(\omega_{\mathrm{op}}+\Delta)-\omega], \tag{14}$$

where $\theta(x)$ is a step function. This is a parabolic spectral density peaked at ω_{op} with base linewidth 2Δ.

The numerical results for the electronic absorption spectra obtained with the two spectral densities specified above will be given in Sec. V.

IV. ANALYTIC CONTINUATION METHODS

Having defined a model for which the exact electronic absorption spectrum is known, we can assess the accuracy of the analytic continuation methods (maximum entropy and SVD) by applying them to this model. As discussed earlier, the imaginary-time correlation function data required as input for analytic continuation methods can be generated by PIMC simulations. These data are affected both by the systematic errors due to the discretization of path integrals, and by the statistical uncertainties present in any simulation data. In principle, these errors can be reduced by increasing the number of time slices in the path integrals, and by running longer PIMC simulations. However, it is important to emphasize that even when the exact imaginary-time data are available (as in the present case), one cannot expect the inversion procedure to produce the exact absorption spectra due to the bias introduced by the numerical implementation of the analytic continuation methods.

In this work, we have chosen to generate the imaginary time data by adding some random noise to the exact Euclidean-time correlation functions. The latter were calculated by the same method due to Kubo and Toyozawa[26] as their real-time counterparts. By decreasing the amplitude of the artificially added noise, one can eventually arrive at the best possible numerical solution of the inverse problem. We now give a brief account of the two analytic continuation methods employed in the present work.

A. Maximum entropy method

The maximum entropy method is based on well-established mathematical axioms from information and probability theories. In this method the inversion problem is reduced to maximizing the entropy of the spectrum (defined in the information theory sense) subject to a constraint on the value of the least-square deviation from the data. The method selects the positive spectrum to which corresponds the largest number of ways of reproducing the data; it also allows the introduction of prior known information about the solution through a default spectrum. When the method is applied to the PIMC data with the statistical noise in it, the necessary Lagrange multiplier can be determined self-consistently according to the classic maximum entropy scheme.[18] Since in the present work we use the exact Euclidean-time data with artificially added random Gaussian noise, we employ the historic maximum entropy scheme, where the Lagrange multiplier (the regularization parameter) is chosen by ensuring that the least-squares deviation from the data is equal to the number of observations. The implementation of the maximum entropy method has been described in detail in Ref. 21. The results of its application to the present problem of calculating the vibronic spectrum of a chromophore coupled to a bath will be given in Sec. V.

B. Singular value decomposition method

While the maximum entropy method is well-defined mathematically and requires minimal *a priori* information about the solution, there exists a more *ad hoc* approach to solving the inverse problems, which is based on the singular value decomposition method. Having the disadvantage of being much more problem specific in its implementation, the SVD method is generally characterized by a higher resolution compared to the maximum entropy approach.[25] Since the electronic absorption spectrum of a chromophore in a condensed phase environment can have relatively fine structure arising from individual vibronic transitions, it would be of interest to apply the SVD method to this problem and to compare the results with the maximum entropy solution.

One immediate difficulty in applying the SVD method to the present problem is due to the fact that the method by itself does not guarantee the positivity of the calculated spectrum. While certain regularization procedures have been proposed[23] which would restrict the SVD solution to positive values only, these procedures concomitantly reduce the resolution of the method, thus making its use as an alternative to maximum entropy much less justified. In order to avoid this problem, we use the SVD method to reconstruct not the absorption spectrum itself, but rather the difference between the fully quantum mechanical spectrum and the one calculated within the classical Franck–Condon approximation, i.e., when *all* the nuclear degrees of freedom (diatomic plus bath) are held fixed.[26,30,31] The calculation of the classical Franck–Condon spectrum reduces to a simple configuration space average; for the present all-harmonic model, this average can be performed analytically (analogously to the fully quantum mechanical case) by doing Gaussian integrals. The corresponding Euclidean-time correlation function can also be calculated, the difference $\Delta G(\tau)$ between the classical Franck–Condon function and the one obtained in the fully quantum mechanical treatment is related via the two-sided Laplace transform [cf. Eq. (6)] to the difference $\Delta I(\omega)$ between the classical Franck–Condon spectrum and the fully quantum mechanical spectrum:

$$\Delta G(\tau)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\Delta I(\omega)e^{-\omega\tau}. \tag{15}$$

In general, the sign of $\Delta I(\omega)$ alternates, and one can apply the SVD method in its original form (i.e., without the positivity constraint) to reconstruct $\Delta I(\omega)$ from $\Delta G(\tau)$. Adding $\Delta I(\omega)$ to the classical Franck–Condon spectrum, one obtains the fully quantum mechanical spectrum. The applicability of this approach to a more realistically anharmonic system relies on the assumption that the classical Franck–Condon spectrum for such a system can still be calculated in a relatively straightforward way.

The starting point for applying the SVD approach is to write Eq. (15) in the discretized form:

$$\Delta G(\tau_i)=\sum_j K_{ij}\Delta I(\omega_j), \tag{16}$$

with

$$K_{ij}=\frac{1}{2\pi}x_j\exp(-\tau_i\omega_j), \tag{17}$$

where the summation index j (going from 1 to N) labels the frequency points ω_j at which the solution is calculated, x_j are the suitably chosen quadrature weights, and the index i (going from 1 to M) labels the data points τ_i.

Introducing the transpose K^T of the matrix K, Eq. (16) can be written in the following matrix form:

$$\Delta\mathbf{I}(\omega)=(K^TK)^{-1}K^T\Delta\mathbf{G}(\tau) \tag{18}$$

The ill-posed nature of the inverse Laplace problem manifests itself in the fact that the matrix K^TK is nearly singular, and the solution of Eq. (18) is extremely unstable: small statistical noise in $\Delta G(\tau)$ is greatly amplified in the reconstructed spectrum $\Delta I(\omega)$. A common method for calculating the inverse of a nearly singular matrix is the singular value decomposition.[32] The singular eigenvectors associated with the smallest singular eigenvalues are highly irregular, and the SVD has to be combined with some smoothing procedure, e.g., Tikhonov regularization.[33] The latter amounts to solving Eq. (18) under a constraint of minimizing the norm of the solution or the norm of its derivative (possibly, a high-order one). This procedure smoothes out irregular features associated with the small singular eigenvalues, but can also smooth out the essential features present in the true (unknown) solution (this situation is analogous to the one mentioned earlier in the context of imposing the positivity constraint on the SVD algorithm). In order to circumvent this problem, the following approach[24,34,35] has been proposed: instead of expanding the solution in the singular eigenvectors of the matric K^TK [as is suggested by Eq. (18)], one expands $\Delta I(\omega)$ in a set of some known basis functions ϕ_i ($i=1,2,...,n$):

$$\Delta I(\omega_j)=\sum_i c_i\Phi_{ij}, \tag{19}$$

where $\Phi_{ij}=\phi_i(\omega_j)$, and c_i are the (unknown) expansion coefficients. With the above, Eq. (16) takes the form:

$$\Delta I(\omega)=\Phi(M^TM)^{-1}M^T\Delta G(\tau), \tag{20}$$

where $M=K\Phi$. Of course, the matrix M is also ill-conditioned, and solving Eq. (20) again requires using SVD combined with a smoothing procedure. However, in this case Tikhonov regularization has a very different effect from the case when it is combined with the standard SVD method.[24] On the basis of certain *a priori* knowledge about the qualitative features of the solution, one can construct the matrix Φ in such a way, that increasing the regularization parameter accentuates the desirable features of the solution, rather than simply making the solution smoother.[24]

Unfortunately, in contrast to the classic maximum entropy method, there is no well-defined prescription for choosing the regularization parameter. The prescriptions commonly used in the literature[34,35] are based on the χ^2 criterion similar to the one used in the historic Maximum Entropy scheme. Denoting by σ_i the uncertainties in the Euclidean-time data, χ^2 can be written as

$$\chi^2=\sum_{i=1}^{M}\frac{[\Delta G(\tau_i)-\Sigma_jK_{ij}\Delta I_{\mathrm{reg}}(\omega_j)]^2}{\sigma_i^2}, \tag{21}$$

where $\Delta I_{\mathrm{reg}}(\omega_j)$ is the spectrum obtained from Eq. (20) combined with the Tikhonov regularization procedure. In the present work we have found empirically that χ^2 has a pronounced minimum as a function of the regularization parameter; the value of χ^2 at this minimum is generally close to the number of observations M. In all cases studied, we have used the value of the regularization parameter corresponding to this minimum.

It follows from the above discussion that in order to apply the SVD analytic continuation method to the present problem we need to specify the set of basis functions ϕ_i. These functions have to be chosen in such a way that they can reproduce the essential qualitative features of the (expected) solution. Since the electronic absorption spectrum of a chromophore in a bath is generally characterized by some vibrational fine structure, we have chosen as our basis set the functions of Lorentzian form:

$$\phi_i(\omega)=\frac{\gamma_i}{(\omega-\omega_i)^2+\gamma_i^2}. \tag{22}$$

The peak positions ω_i are chosen randomly within the frequency range supporting the classical Franck–Condon spectrum, and the widths γ_i are also chosen randomly within ''reasonable'' limits. In fact, for the present all-harmonic model, both the peak positions and the widths can be calculated analytically.[36] However, for an anharmonic system such a calculation is generally not possible, and therefore we do not use the analytic results in constructing the basis functions. At the same time, by considering a harmonic Hamiltonian which approximates the anharmonic Hamiltonian of interest, one can at least obtain a rough estimate of the parameters referred to above, and thus impose certain limits on the range of these parameters. This is what we mean by reasonable limits in choosing randomly the widths of individual Lorentzian basis set functions.

Alternatively, one can choose other basis sets. For example with a Gaussian basis, a slightly larger number of basis functions are found to be needed to get the same kind of agreement with the exact spectrum.

V. NUMERICAL RESULTS

In performing the numerical calculations presented below we have used the following values for the parameters in Eqs. (9) and (10): $Q_0=0$, $Q_1=2$, $\omega_0=\omega_1=1$. For simplicity, we have taken $m=m_i=1$.

As mentioned earlier, the numerical calculations are limited to a finite number N_b of bath modes. In order to obtain the coupling coefficients which would mimic the appropriate continuous spectral density, the following procedure[37] was utilized: $J(\omega)$ was discretized evenly with an increment $\Delta\omega$, and the coupling coefficients were calculated according to

$$(g_i^0)^2=2\omega_i\rho_0 J(\omega_i)\Delta\omega,(g_i^1)^2=2\omega_i\rho_1 J(\omega_i)\Delta\omega. \tag{23}$$

In performing the calculations, we have checked for the convergence with respect to the number of modes by increasing N_b until no further change in the calculated spectra was observed. Typically, $N_b=30$ was found to be sufficient to achieve convergence.

To test the applicability of the analytic continuation methods, we have performed the calculations of the electronic absorption spectra for a variety of temperatures and coupling strength parameters both for acoustic and for optical phonons.

A. Acoustic phonons

The spectral density for acoustic phonons is given by Eq. (13); in performing the calculations we have taken $\alpha=5$. We further assume the overall system–bath coupling strength to be larger in the ground electronic state of the chromophore than in its excited state. Taking $\rho_0=0.125$ and $\rho_1=0.05$, we perform the calculations at the temperature $\beta=0.5$. The exact result for the fully quantum mechanical electronic absorption spectrum is shown in Fig. 1 together with the corresponding classical Franck–Condon absorption spectrum. The former spectrum has a pronounced fine vibronic structure, while the latter is a featureless single band. Nevertheless, the overall shapes of the two spectra are quite similar.

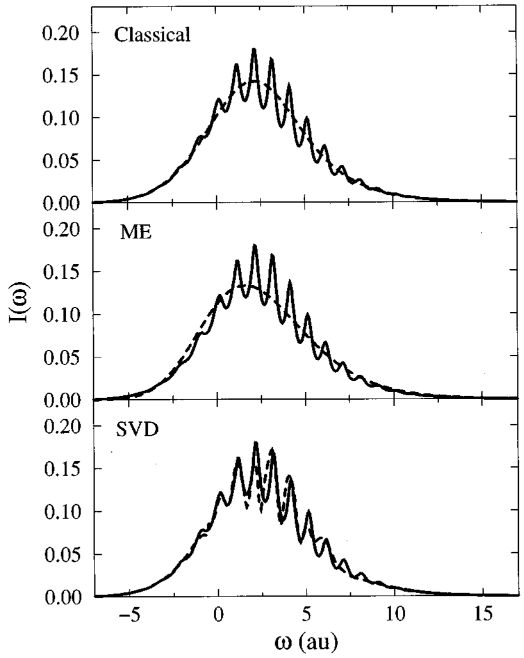

FIG. 1. The electronic absorption spectrum of the chromophore coupled to acoustic phonons. The solid line in all three panels is the fully quantum result. The dashed lines from top to bottom are as follows: (1) the classical Franck–Condon spectrum; (2) the spectrum reconstructed by the maximum entropy method; (3) the spectrum reconstructed by the singular value decomposition method.

The absorption spectra obtained by the maximum entropy and SVD analytic continuation methods as described in Sec. IV are also shown in Fig. 1 (the magnitude of random Gaussian noise added to the exact Euclidean-time data was taken to be 0.1%). The maximum entropy method reproduces well the overall shape of the absorption band, but does not capture the vibrational fine structure. The SVD method is characterized by a higher resolution, although not all positions and widths of individual peaks are reproduced quantitatively.

Similar calculations have been performed for other values of temperature and coupling strengths. As one would expect, raising the temperature and increasing the coupling strength produce the same qualitative effect: the real-time dipole autocorrelation function is damped faster, and the vibronic structure of the spectrum becomes less pronounced. For all sets of parameters studied, the performance of the two analytic continuation methods is similar to the case presented in Fig. 1, and we do not reproduce these results here.

B. Optical phonons

The spectral density for optical phonons is given by Eq. (14); in performing the calculations we have taken $\omega_{\text{op}}=1$

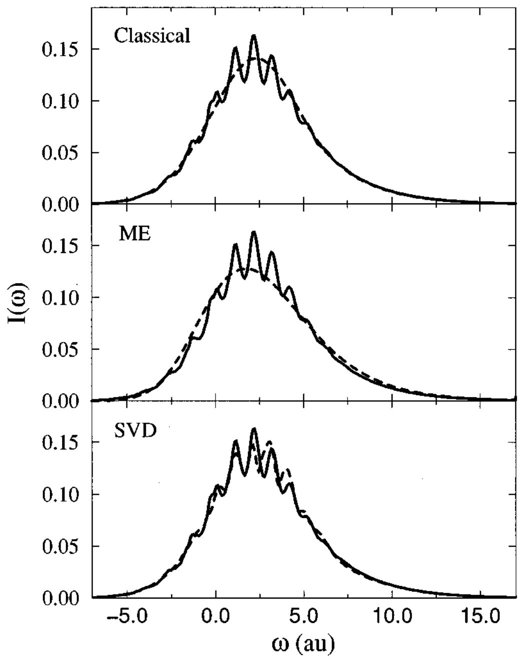

FIG. 2. The electronic absorption spectrum of the chromophore coupled to optical phonons. The solid line in all three panels is the fully quantum result. The dashed lines from top to bottom are as follows: (1) the classical Franck–Condon spectrum; (2) the spectrum reconstructed by the maximum entropy method; (3) the spectrum reconstructed by the singular value decomposition method.

and $\Delta=0.5$. Generally, one would expect the coupling of the chromophore to the optical phonons to be stronger as compared to the acoustic ones. Hence, we take $\rho_0=0.25$ and $\rho_1=0.10$. Setting $\beta=0.5$, we calculate the same quantities as described in Sec. V A, and show the results in Fig. 2. The general qualitative features are very similar to the case of acoustic phonons, although the fine structure of the quantum mechanical spectrum is somewhat less pronounced due to the enhanced chromophore–bath coupling. Once again, the maximum entropy method reproduces well the overall band shape, while the SVD method, in addition to that, captures the individual vibronic features (albeit not quantitatively).

VI. CONCLUDING REMARKS

In this paper we have considered the problem of calculating the electronic absorption spectrum of a chromophore with intramolecular degrees of freedom coupled to a condensed phase environment. The central quantity required for calculating this spectrum is the dipole time autocorrelation function, which can be obtained from path integral Monte Carlo simulations. While the real-time path integral calculations are extremely difficult, the imaginary-time correlation functions can be simulated in a straightforward way. Hence, the main focus of the present work has been the analytic continuation of the imaginary-time data to the real-time axis.

We have considered two alternative methods for performing the analytic continuation: the maximum entropy method and the singular value decomposition. The first method has a well-defined mathematical foundation in the information theory, while the second one is somewhat more *ad hoc* and problem specific. In order to assess the accuracy of these methods, we have studied an exactly solvable all-harmonic model, for which the absorption spectrum can be calculated exactly (numerically). For the purpose of testing the analytic continuation methods, we have used the exact imaginary-time data with artificially added random Gaussian noise. Two model spectral densities were introduced to model the effect of the environment on the chromophore's absorption spectrum: one appropriate for acoustic phonons, and the other—for optical ones. The calculations have been performed for a variety of temperatures and chromophore–bath coupling strengths. In all the cases studied, both analytic continuation methods reproduced well the overall shape of the absorption spectrum. The singular value decomposition method gives systematically higher resolution than the maximum entropy method, and is thus capable of reproducing to some extent the fine vibronic structure of the absorption spectrum.

The main focus of the present work has been to test the accuracy of two alternative analytic continuation methods for the problem of calculating the absorption spectra from the Euclidean-time correlation functions. As such, the exact imaginary-time data with artificially added random Gaussian noise have been used as input for the analytic continuation stage. A more stringent test of the above methods would involve ''real'' Euclidean-time data obtained from PIMC simulations, in which case a certain amount of cross correlations between different imaginary-time data points would be present.[21] As long as the condensed phase environment is modeled with a harmonic bath, in calculating the dipole time autocorrelation function the bath degrees of freedom can be integrated out analytically to give the Feynman–Vernon type influence functional.[38,36] The imaginary-time PIMC simulations can then be performed for an arbitrary (not necessarily harmonic) form of the chromophore's intramolecular potential energy. Carrying out such simulations and applying the analytic continuation methods to the simulated Euclidean-time correlation functions will be the subject of future investigations.[36]

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