Methods for simulating time correlation functions in quantum systems

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A review of the basic strategies that we have developed for the simulation of dynamic correlation functions in quantum systems is provided. Three methods are considered: (a) the analytic continuation of imaginary (thermal) time correlation functions to real times; (b) direct evaluation of thermally symmetrized version of the time correlation functions; (c) direct simulation of the power spectrum. All of these methods are based on the path integral representation of time correlation functions. The generalization of these methods for the computation of electronic spectrum, which involves the consideration of two potential energy surfaces, is also presented. We also discuss the approach based on numerical integration of an effective time-dependent Schrödinger equation for the simulation of electronic absorption and emission spectra for mixed quantum classical systems.

1. Introduction

Path integral Monte Carlo techniques have been exploited to determine equilibrium properties of manybody quantum systems in a variety of contexts [1,2] *. If exchange between identical quantum particles is neglected, then using a discretized version of the Feynman path integral representation of the canonical density matrix the partition function for a N-particle quantum system can be shown to be isomorphic to $N \times P$ particle classical system with P being the number of points used in the discretization scheme [3]. This allows one to use well-known numerical techniques, like Monte Carlo [4–6] or molecular dynamics methods [7] to simulate equilibrium properties of quantum systems. (For a discussion of nonergodicity problems in the molecular dynamics method see ref. [8].) A straightforward extension of this method, for problems where real-time quantum dynamics is needed, is difficult. The major reason for this difficulty is due to the presence of $e^{iHt/\hbar}$ involved in the dynamics which leads to the "alternating weights" problem. It has been shown that using the standard Metropolis Monte Carlo scheme, dynamical information in these systems may be obtained by evaluating the appropriate correlation functions in Euclidean time [9,24]. One can analytically continue Euclidean-time correlation functions in Laplace space to obtain the dynamical (real-time) correlation functions. This procedure is well known and the uniqueness of the analytic continuation for these problems has been shown by Baym and Mermin [10]. The obvious

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* For a recent review describing the use of quantum Monte Carlo methods in chemical physics, see ref. [1]. Reference [2] gives the application of quantum Monte Carlo methods to a variety of problems.

advantage of this method is that the evaluation of euclidean correlation functions is no more difficult that calculating the equilibrium properties of quantum systems. The major drawback with this method is that it is difficult to numerically perform the analytic continuation [9], and one needs extremely accurate estimates of the imaginary-time correlation functions. In order to avoid the analytic continuation, Behrman et al. [11] attempted a direct Monte Carlo importance sampling on the discretized path integral representation of the time correlation functions (TCF). However, because of the oscillatory factors involved, this method is at best accurate only for short times. Evaluation of dynamic correlation functions for short times can be accomplished as follows (see for example, ref. [12]): Expand the correlation function as a power series in time. The coefficients in this power series are then equilibrium moments which can be expressed in terms of path integrals in Euclidean time. Consequently, the moments can be readily computed by the path integral Monte Carlo technique. The moment method may be of interest in providing upper and lower bounds on time correlation functions. The drawback of this method is that very many moments are usually needed to represent intermediate time decay of correlation functions. Finally, short-time behavior may also be obtained from the application of the Gaussian wavepacket dynamics to quantum systems [13].

In this brief review we present several methods that we have developed for the simulation of TCF in quantum systems. The basis of most of these methods lies in path integral representation of the propagators, $e^{-H\tau}$, where H is the Hamiltonian of the system, and τ is in general complex. In the next section three different methods are presented for the simulation of TCF. The first method is based on the analytic continuation procedure [9], the second involves the direct simulation of the symmetrized version of the dynamic correlation functions [14]. Both these methods have been applied to simple problems and to certain nontrivial systems. The third method, which we present here for the first time, is an algorithm for a direct simulation of the power spectrum of the TCF. This method is a finite-temperature generalization of the algorithm due to Hirsch and Schrieffer [15] who presented the zero-temperature version some years ago.

In section 3 we consider the generalization of some of these techniques to the calculation of electronic spectra involving two potential surfaces. Two methods are presented. In the first one it is shown how path integral methods can be used for the computation of the electronic spectrum without invoking the familiar Franck–Condon approximation. The second method discusses the calculation of the spectrum of quantum systems interacting with a classical bath. A solution to the time-dependent Schrödinger equation using Gaussian wavepackets is discussed with emphasis on the simulation of electronic absorption and emission spectra of a diatomic molecule in a classical environment. The review is concluded with a few additional remarks in section 4.

2. Time correlation functions in quantum systems

In this section we consider the simulation of time correlation functions in quantum systems using the methods that we developed a few years ago. Some of these methods have been extended in new and novel ways by several investigators [16,17]. These improvements are not explicitly considered in this article. A partial review of these techniques may be found elsewhere [18]. In section 2.3 we present a new, but untested, method for the direct simulation of the frequency spectrum of finite temperature correlation functions.

2.1. Analytic continuation of thermal correlation functions

Consider a system specified by a Hamiltonian H, and let A be any quantum mechanical operator representing some dynamical quantity. The time correlation function $\langle A(t)A(0)\rangle$ is given by

$$C_{AA}(t) = \text{Tr}\langle e^{-\beta H}A(t)A(0)\rangle/\text{Tr } e^{-\beta H}, \tag{2.1}$$

where $A(t) = e^{iHt/\hbar} A(0) e^{-iHt/\hbar}$, and the temperature of the system T is given by β^{-1}/k_B with k_B being the Boltzmann constant. The Fourier transform or the power spectrum is defined by

$$C_{AA}(\omega) = \int_{-\infty}^{\infty} \left(\frac{d\omega}{2\pi}\right) e^{-i\omega t} C_{AA}(t) \, dt. \tag{2.2}$$

The basis of the method of the analytic continuation of the imaginary-time correlation function (the analog of the Wick rotation) lies in the observation that $C_{AA}(\omega)$ can be calculated directly from the knowledge of the spectral function or susceptibility $\chi''(\omega)$ [10]. Furthermore $\chi''(\omega)$ can be computed from the knowledge of the imaginary correlation function $C_{AA}(\lambda)$ with $0 \le \lambda \le \beta\hbar$. Specifically the susceptibility

$$\chi''(\omega) = i(1 - e^{-\beta\hbar\omega}) C_{AA}(\omega) \tag{2.3a}$$

can be expressed as

$$\chi''(\omega) = i[f(\omega + i\epsilon) - f(\omega - i\epsilon)], \tag{2.3b}$$

where the analytic function $f(Z)$ evaluated at the Matsubara frequencies $Z = Z_n = 2\pi n/(-i\beta\hbar)$ is given by

$$f(Z_n) = \frac{1}{i} \int_0^{\beta\hbar} d\lambda \, e^{Z_n\lambda} C_{AA}(\lambda). \tag{2.3c}$$

Thus to compute $\chi''(\omega)$ we analytically continue $f(Z_n)$ to all complex values of Z and use eq. (2.3b). Notice that the computation of $f(Z_n)$ requires the calculation of the Euclidean correlation function $C_{AA}(\lambda)$ given by

$$C_{AA}(\lambda) = \text{Tr}[\rho(\beta - \lambda/\hbar) A \rho(\lambda/\hbar) A] / \text{Tr} \, \rho(\beta), \tag{2.4a}$$

where

$$\rho(\beta) = e^{-\beta H}. \tag{2.4b}$$

The evaluation of $C_{AA}(\lambda)$ can be done in principle by path integral Monte Carlo methods [9]. This method was applied to obtain the spectra of two one-dimensional problems, namely the linear harmonic oscillator and the Morse oscillator. Although the results were encouraging it was pointed out that very accurate representation $C_{AA}(\lambda)$ for $0 \le \lambda \le \beta\hbar$ was required for a stable analytic continuation.

The above method has not been pursued in the chemical physics context. However, in the solid state physics community there have been some recent developments in devising better methods for analytically continuing the function $f(Z_n)$. These methods were suggested so that the numerical effect of noise (or round-off errors) that inevitably results in the evaluation of $C_{AA}(\lambda)$ is minimized. The first method was based on a least-squares fitting and was introduced by Schuttler and Scalapino [19]. Recently Jarrell and Biham [20] have provided a dynamic approach to obtain the spectral function $\chi''(\omega)$. This method is based on an expansion of $\chi''(\omega)$ in terms of a series of δ-functions

$$\chi''(\omega) = \sum_m A_m \delta(\omega - \omega_m), \tag{2.4}$$

where the real frequencies ω are chosen on a grid of spacing $\Delta\omega$. From eq. (2.3b) it follows that $\chi''(\omega)$ can be computed from the imaginary part of

$$f(Z_n) = \int_{-\infty}^{\infty} \frac{d\omega}{(2\pi)} \frac{\chi''(\omega)}{(Z_n - \omega)}. \tag{2.5}$$

using eqs. (2.3b) and (2.5) is easy to show that the coefficients A_m satisfy

$$\frac{\operatorname{Im} f(Z_n)}{\nu_n} = - \sum_{m=-\infty}^{+\infty} A_m/(\omega_m^2 + \nu_n^2), \tag{2.6}$$

where $\nu_n = 2\pi n/\beta\hbar$.

Jarrell and Binham [20] made the observation that the coefficients $\{A_m\}$ can be viewed as a steady-state solution of a dynamical equation in a fictious time such that eq. (2.6) is identically satisfied. To illustrate the origin of the dynamic equation let us assume that the grid for the real frequency ω_m is the same as the imaginary frequency ν_n. The simplest potential consistent with the steady-state eq. (2.6) is [20]

$$V\{A_m\} = V_1\{A_m\} + V_2\{A_m\}, \tag{2.7a}$$

where

$$V_1\{A_m\} = \frac{\operatorname{Im} f(Z_n)}{\nu_n} + \frac{1}{2}\sum_{n,m} \frac{A_m A_n}{(\omega_m^2 + \nu_n^2)} \tag{2.7b}$$

and

$$V_2\{A_m\} = \alpha_1\left(\sum_n A_n^{-1}\right)^p + \alpha_2\sum_n (A_{n-1} - 2A_n + A_{n+1})^2/(\Delta\omega)^4. \tag{2.7c}$$

It is clear that minimization of $V_1\{A_m\}$ with respect to A_m leads to eq. (2.7a). Since $V_1\{A_m\}$ is a quadratic potential in the space $\{A_m\}$ it has a single unique minimum. However it may not be easy to locate this minimum numerically if the space of coefficients $\{A_m\}$ is very large. The first term in eq. (2.7c) enforces the sum rule constraint on $\chi''(\omega)$ while the second term is introduced to prevent fluctuations in $\chi''(\omega)$ due to noisy data by making large gradients energetically unfavorable. The coefficients α_1 and α_2 are chosen so that once the constraints are satisfied, $V_1\{A_m\}$ dominates over $V_2\{A_m\}$ are always restricted to be positive, and this can be achieved by imposing infinite potential barriers whenever $\{A_m\}$ become less than zero. With these constraints the dynamics associated with $\{A_m\}$ becomes

$$\partial A_n/\partial t = -\partial V\{A_m\}/\partial A_n. \tag{2.8}$$

This corresponds to having a set of massless particles with dissipation, The solutions to eq. (2.6) corresponds to the fixed-point condition $\partial A_n/\partial t \equiv 0$. The resulting $\{A_n\}$ can be used to construct $\chi''(\omega)$. The above procedure was successfully applied to obtain $\chi''(\omega)$ for the symmetric Anderson model at low temperatures. Since the method automatically takes the various constraints into account and the spectral function is directly obtained using a sensible dynamics it is expected that one can obtain fairly accurate results using imaginary-time correlation function. It would be interesting to apply this to problems in chemical physics.

2.2. Direct evaluation

For several problems the direct evaluation of the dynamic correlation functions given by eq. (2.6) is of interest. The direct evaluation of $C_{AA}(t)$ for the case of spin-boson problems was first considered by Behrman et al. using path integral methods [11]. It is well known that the direct evaluation of $C_{AA}(t)$ by Monte Carlo technique is difficult because the time evaluation operator $e^{iHt/\hbar}$ is oscillatory. This leads to sampling configurations with negative weights and thus leads to numerical instability. Despite this for certain values of the parameter in the spin-boson problem Behrman et al. [11] were able to obtain results for the spin–spin correlation for relatively long times. Although this method has not been heavily used it

appears that recent advances, which use some variant of stationary phase Monte Carlo method, may enable evaluation of $C_{AA}(t)$ for times greater than $\beta\hbar$ [21].

Thirumalai and Berne [14] observed that instead of evaluating $C_{AA}(t)$ it should be more convenient from a simulation perspective to consider the symmetrized forms of the correlation function [22]

$$G_{AA}(t) = \frac{1}{Q}\text{Tr}\left\{ A\ e^{-H\tau/\hbar}A\ e^{-H\tau^*/\hbar} \right\},$$ (2.9a)

where

$$\tau = (\beta\hbar/2 - it).$$ (2.9b)

They pointed out that the simulation of $G_{AA}(t)$ should greatly reduce the phase cancellation problem [14], and hence it should be possible to directly evaluate real-time correlation functions for $t > \beta\hbar$. Using the cyclic invariance of the trace operation it is easy to show that

$$C_{AA}(t + i\beta\hbar/2) = G_{AA}(t)$$ (2.10)

and that $G(t)$ is a real function of t, i.e. $G(t) = G(-t)$. Consequently the Fourier transforms $G_{AA}(\omega)$ and $C_{AA}(\omega)$ are related by

$$C_{AA}(\omega) = e^{\beta\hbar\omega/2}G_{AA}(\omega).$$ (2.11)

If A is a position-dependent operator the coordinate representation of $G_{AA}(t)$ is

$$G_{AA}(t) = \frac{1}{Q}\int dx \int dx' A(x)A(x')\ |\langle x|e^{-H\tau}|x'\rangle|^2.$$ (2.12)

As an example Thirumalai and Berne [14] calculated the dipole–dipole correlation function of a proton moving in a bistable potential with parameters that correspond to a model for proton tunneling in H_2O_2. For the very low temperature considered by these authors only two lowest states contribute to $G_{\mu\mu}(t)$. Thus $G_{\mu\mu}(t)$ is given by

$$G_{\mu\mu} = \frac{1}{Q}\ |\mu_{12}|^2\ e^{-\beta(E_0+E_1)/2}\ \cos(\Delta\omega t/\hbar),$$ (2.13)

where μ_{12} is the transition dipole moment, and $\Delta\omega = (E_2 - E_1)|\hbar$ is the tunnel splitting. Using the numerical matrix multiplication (NMM) method [23] they were able to accurately compute $G_{\mu\mu}(t)$ for times of the order of 100 $\beta\hbar$. It should be emphasized that although NMM is free of statistical errors the method is applicable only to systems with a few degrees of freedom only [23]. Thus a true test of the direct simulation of $G_{\mu\mu}(t)$ should involve the computation of real-time correlation function for a nontrivial system.

We first argue why Monte Carlo methods should be stable for a direct evaluation of $G_{AA}(t)$. This can be appreciated by studying the explicit path integral form of $G_{AA}(t)$ [14]. In the coordinate representation we can write $G_{AA}(t)$ as

$$G_{AA}(t) = \frac{\int dx_1 \dots dx_{2p}A(x_1)F(x_1,\dots,x_{2p})A(x_{p+1})P(x_1, x_2,\dots,x_{2p})}{\int dx_1 \dots dx_{2p}F(x_1,\dots,x_{2p})P(x_2, x_2,\dots,x_{2p})}$$

$$\equiv \langle A(x_1)F(x_1,\dots,x_{2p})A(x_{p+1})\rangle / \langle F(x_1,\dots,x_{2p})\rangle,$$ (2.14)

where $F(x_1, \ldots, x_{2p})$ is the imaginary part arising from the propagator representation of $Q = e^{-H\tau} \cdot e^{-H\tau^*}$, and $P(x_1, x_2, \ldots, x_{2p})$ is the corresponding real part. The average $\langle \ldots \rangle$ indicated in eq. (2.14) is carried out with respect to $P(x_1, x_2, \ldots, x_{2p})$. The basic approach is to sample the configurations $(x_1, \ldots, x_{2p})$ from $P(x_1, x_2, \ldots, x_{2p})$ and compute the averages in eq. (2.14). Because F involves a phase factor that depends on the differences between functions of the sampled configurations it is expected that cancellations will result and that the average will be much more stable than would be the case for a direct attack on $C_{AA}(t)$. This was borne out in the study of the one-dimensional tunneling problem [14]. (The symmetrized versions of time correlation functions arise naturally in the reaction rate formalism for bimolecular reactions [24].) The above Monte Carlo algorithm has been pictorially interpreted by Behrman and Wolynes [25].

In an interesting paper Behrman and Wolynes [25] have used this basic algorithm to study the dynamics of a two-level system coupled to a dissipative bath. They have also discussed some additional advantages for considering the direct simulation of the correlation function $G_{AA}(t)$. They were able to obtain real-time dynamics of the spin–spin correlation function for long enough times to critically assess the validity of various approximate theories. Their conclusion was that real-time Monte Carlo algorithm is a practical tool to check analytical approximations. In addition it was pointed out that the Monte Carlo Algorithm could be greatly improved by using techniques such as importance sampling. In fact recently Doll and co-workers [18] have begun applying stationary phase Monte Carlo methods for the computation of the thermally symmetrized correlation functions. It is obvious that whatever advances one can make to make the calculations of $C_{AA}(t)$, these very same methods should work more efficiently when applied to $G_{AA}(t)$.

2.3. Direct simulation of the power spectrum

Sometime ago Hirsch and Schrieffer [15] proposed an algorithm for the direct simulation of the zero-temperature power spectrum of the time correlation function. This method was numerically tested by computing the vibrational spectra of simple models. Subsequently it was shown by Thirumalai et al. [26] that this method could in principle form the basis for using path integral methods for microcanonical ensemble. In particular we showed that path integral methods can be used to calculate quantum microcanonical rate constants for bimolecular reactions [24,27] for a given total energy of collision. In this section we show how this method can be generalized for the simulation of finite temperature power spectrum of TCF. The Fourier transform of the dynamic correlation function $C_{AB}(\omega)$, where A and B are any quantum mechanical operators, can be written using the eigenstates of H as

$$C_{AB}(\omega) = \frac{1}{Q} \sum_m \sum_n e^{-\beta E_n} A_{mn} B_{nm} \delta\left[\omega - (E_m - E_n)\right]. \tag{2.15}$$

The δ-function in the above equation can be expressed as a convolution

$$\delta\left[\omega - (E_m - E_n)\right] = \int ds\, \delta(\omega - E_m + s)\delta(s - E_n). \tag{2.16a}$$

With this $C_{AB}(\omega)$ becomes

$$C_{AB}(\omega) = \frac{1}{Q} \int ds \sum_m \sum_n e^{-\beta E_n} A_{mn} B_{nm} \delta(\omega - E_m + s)\delta(s - E_n). \tag{2.16b}$$

The algorithm for the direct simulation of $C_{AB}(\omega)$ is based on the Gaussian representation of the δ-function,

$$\delta(\omega - \alpha) = \lim_{\beta \to \infty} \frac{\sqrt{\beta_1}}{\pi} \exp\left[-\beta_1(\omega - \alpha)^2\right]. \tag{2.17}$$

In practice one uses a large but finite β_1 and this can be interpreted as a finite experimental resolution of the spectrum. The above identity allows one to write $C_{AB}(\omega)$ as

$$C_{AB}(\omega) = \lim_{\beta_1,\beta_2 \to \infty} \frac{\sqrt{\beta_1\beta_2}}{\pi Q} \int ds \ \mathrm{Tr}\{e^{-\beta H} e^{-\beta_1(H-(\omega-s))^2} A \ e^{-\beta_2(H-s)^2} B\} \tag{2.18a}$$

which in the coordinate representation becomes

$$C_{AB}(\omega) = \lim_{\beta_1,\beta_2 \to \infty} \frac{\sqrt{\beta_1\beta_2}}{\pi Q} \int ds \ dx \ dx' \ dx'' \rho(x, x'; \beta)\langle x' | e^{-\beta_1(H-(\omega+s))^2} | x'' \rangle$$

$$\cdot A(x'')\langle x'' | e^{-\beta_2(H-s)^2} | x \rangle B(x). \tag{2.18b}$$

Therefore $C_{AB}(\omega)$ can be evaluated by discretized path integral methods provided a suitable coordinate representation for the Gaussian operator is found. The Gaussian operators appearing in eq. (2.18) can also be evaluated using the Trotter formula, i.e.

$$e^{-\beta_1(H-\lambda)^2} = \left(e^{-\epsilon_1(H-\lambda)^2}\right)^L, \tag{2.19}$$

where $\epsilon_1 = \beta_1/L$. Inserting the resolution of unity in the coordinate representation the representation the matrix element of the Gaussian operator becomes

$$\langle x' | e^{-\beta_1(H-\lambda)^2} | x'' \rangle$$

$$= \int dq_1 \dots dq_L \langle x' | e^{-\epsilon_1(H-\lambda)^2} | q_1 \rangle \langle q_1 | e^{-\epsilon_1(H-\lambda)^2} | q_2 \rangle \cdots \langle q_L | e^{-\epsilon_1(H-\lambda)^2} | x'' \rangle. \tag{2.20}$$

For a large enough value of L, $\langle q_t | e^{-\epsilon_1(H-\lambda)^2} | q_{t+1} \rangle$ can be evaluated using the Trotter formula [15,26]

$$\langle q_t | e^{-\epsilon_1(H-\lambda)^2} | q_{t+1} \rangle \approx e^{-\frac{1}{2}\epsilon_1(V(q_t)-\lambda)^2} g(q_t, q_{t+1}) \ e^{-\frac{1}{2}\epsilon_1(V(q_{t+1})-\lambda)^2}, \tag{2.21a}$$

where $g(x, x')$ is given by

$$g(x, x') = \frac{1}{\pi} \int_0^\infty dp \ \cos p(x - x') \exp\left[-\epsilon_1\left(\frac{p^4}{4m^2} + \frac{p^2}{2m}[V(x) + V(x') - 2\lambda]\right)\right]. \tag{2.21b}$$

The integral in eq. (2.21b) cannot be done in closed form, and it has to be evaluated numerically. Substituting eqs. (2.21) into eq. (2.18) yields a complicated multidimensional integral which, in general, has to be evaluated by a Monte Carlo algorithm suitably designed for the negative weights that could arise from the short-time approximation to the Gaussian propagator, $\langle q_t | \exp(-\epsilon_1(H-\lambda)^2 | q_{t+1} \rangle$. In particular the integral $g(x, x')$ in eq. (2.21b) can have negative regions for certain values of x, x'. This will greatly depend on the potential.

So far this method has only been applied to simple problems [15]. Thirumalai et al. [26] used this basic method to calculate microcanonical reaction probability, expressed in terms of flux operators evaluated on a given energy shell, for the Eckart potential. The calculated values are in very good agreement with the exact results [26]. We also showed that the regions where the integrand in the multidimensional expression for the microcanonical rate constant becomes negative is small. Furthermore the degree of negative contribution to the weights appears to be negligible. For the general evaluation of $C_{AB}(\omega)$ one has to content with a $(P + 4L)$-dimensional integral where P is the number of discretized points in the density matrix $\rho(x, x'; \beta)$ and L is the number of discretization points for each Gaussian propagator. Because the negative weights for this method may not be as severe as for the direct computation of $C_{AB}(t)$ it should be worth applying this method to other nontrivial cases.

3. Simulation of electronic spectra

The electronic absorption spectrum $I(\omega)$ can be expressed as [28]

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, \exp(-i\omega t) C_{if}(t),$$

(3.1)

where $C_{if}(t)$ is the dipolar autocorrelation function which in the Born–Oppenheimer approximation for the transition from the electronic states i to f is given by

$$C_{if}(t) = \text{Tr}\left\{ \rho_i \mu_{if} \, e^{-iH_f t/\hbar} \mu_{if} \, e^{iH_i t/\hbar} \right\} / \text{Tr}\left\{ e^{-\beta H_i} \right\}.$$

(3.2)

We are assuming that the ground electronic state has a thermal distribution of vibrational states. The electronic transition moment is in general a function of the nuclear coordinates, H_i and H_f are the Hamiltonians corresponding to the upper and lower potential surfaces respectively. The density operator $\rho_i = e^{-\beta H_i} / \text{Tr} \, e^{-\beta H_i}$ is for the rot–vib states on the electronic surface i, and $\text{Tr}(\ldots)$ denotes the trace over these rot–vib states. In what follows we describe two methods to compute $I(\omega)$. The first method describes the extension of path integral techniques for computing TCF involving two potential surfaces and is in principle applicable to any situation. The second method is most suited for systems in which a few quantum degrees interact strongly with classical degrees of freedom.

3.1. Path integral methods

It was shown by Thirumalai and Berne [29] and independently by Coalson [30] that one can use the symmetrized version of $C_{if}(t)$ namely $G_{if}(t)$ for a direct simulation even when two different potential surfaces are involved. Following CTB we introduce the function [29,30]

$$G_{if}(t) = \text{Tr}\left\{ \rho_i \mu_{if}(R) \exp(-H_f \tau) \mu_{if}(R) \exp(-H_i \tau^*) \right\} / \text{Tr}\left\{ \exp(-\beta H_i) \right\}.$$

(3.3)

It can be easily shown that $C_{if}(t) = G_{if}(t - i\beta\hbar/2)$ and consequently $I(\omega)$ is related to the Fourier transform of $G_{if}(t)$ by

$$I(\omega) = e^{\beta\hbar\omega/2} G_{if}(\omega).$$

(3.4)

For reasoning similar to that given in section 2.2 it is more convenient to simulate $G_{if}(t)$ directly than $C_{if}(t)$. In the coordinate representation $G_{if}(t)$ becomes

$$G_{if}(t) = \int dR' \int dR \mu_{if}(R') \cdot \mu_{if}(R) \langle R | \exp(-H_f \tau) | R' \rangle \langle R' | \exp(-H_i \tau') | R \rangle.$$

(3.5)

Once the propagators are determined it is possible to evaluate the spectrum for any well-behaved functional form for the transition dipole moment $\mu_{if}(R)$, so that the usual Condon approximation, $\mu_{if}(R) \sim \mu_{if}(R_e) = \text{constant}$, need not be made. Here R_e denotes the equilibrium positions of the nuclei.

As an application we considered the computation of $I(\omega)$ for a model diatomic molecular discussed by Reimers et al. [31]. The spectra was calculated in the Condon approximation $\mu_{if}(R) = \mu_{if}(R_e) = \text{constant}$ and in the approximation $\mu_{if}(R) \propto (R - R_e)$. The calculated results for $I(\omega)$ in the Condon approximation are in excellent agreement with the numerically exact calculations presented by Reimers et al. [31]. For the case in which $\mu_{if}(R) \propto (R - R_e)$ Reimers et al. computed the band contour using Gaussian wavepacket dynamics by Fourier transforming only the initial decay of $C_{if}(t)$. Because of the truncation after only short times they did not observe any structure in the spectrum. However they noted that anharmonicity in the wavepacket propagation becomes more severe when the Condon approximation is

relaxed. We showed that the band contour obtained by our method is in very good agreement with the result reported by Reimers et al. [31]. In addition because of the stability of this method one can obtain $C_{if}(t)$ for sufficiently long times when applied to arbitrary potential surfaces and $\mu_{if}(R)$. Thus the detailed structure of the absorption spectrum could be resolved. We showed that for this model diatomic molecule considered by Reimers et al. relaxing the Condon approximation yields qualitatively different absorption cross-section. It appears that this method in conjunction with the stationary-phase Monte Carlo technique can be used for the computation of electronic spectrum in condensed phase systems.

3.2. Electronic spectrum in mixed quantum–classical systems

The formulation described in the previous subsection is valid in general, and follows from linear response theory. However there are many examples in chemical physics where one can treat part of the system involving very few degrees of freedom quantum mechanically, and the rest of the systems can be treated classically. Such systems are called mixed quantum–classical systems. Few of the physically interesting examples worthy of mention are electron transfer reactions in condensed phase, electronic spectroscopy in matrices, and mobility of an excess electron in classical fluids.

Thirumalai et al. [32] provided an algorithm for the treatment of a single quantum degree of freedom interacting with a classical solvent in the context of the calculation of absorption and emission spectra of a diatomic molecule in a cold matrix. This basic algorithm has been recently used in a variety of different problems where the strict conditions for which the method is applicable appears to be violated. Thus it is useful to emphasize once again the limits of applicability of the algorithm. Let the Hamiltonian of the systems on the two surfaces $H_{(f)}$ be

$$H_{i(f)} = T_Q + V_{i(f)}(Q) + V(Q, X) + H(P, X)$$
$$\equiv h_{i(f)}(Q, X) + H(P, X), \tag{3.6}$$

where T_Q is the kinetic energy operator the quantum degree of freedom, $V_{i(f)}(Q)$ is the electronic potential surface for the lower i [upper (f)] electronic states, $V(Q, X)$ is the potential of interaction between Q and X which for simplicity is taken to be independent of i or f, and $H(P, X)$ is the Hamiltonian for the classical degrees of freedom. The trace operation in eq. (3.2) is over both Q and X, formally let $\psi_{in}(Q, X)$ and $\psi_{fn}(Q, X)$ represent the stationary eigenstates of $h_i(Q, X)$ and $h_f(Q, X)$ with energies $E_{in}(X)$ and $E_{fn}(X)$ respectively. Here n labels the additional quantum numbers, (if any) required to specify the stationary state in a given electronic potential energy surface, i.e.

$$h_i(Q, X)\psi_{in}(Q, X) \equiv E_{in}(X)\psi_{in}(Q, X). \tag{3.7}$$

If the temperature is sufficiently low then we can assume that only the ground state ψ_{i0} of h_i contributes to the trace, then it is easy to show that

$$C_{if}(t) = \mathrm{Tr}_X \ e^{-\beta H(P,X)} \langle \phi_f(t) \,|\, \phi_i(t) \rangle / Q_0, \tag{3.8a}$$

where

$$Q_0 = \mathrm{Tr}_X \ e^{-\beta H(P,X)}, \tag{3.8b}$$

$$|\phi_i(t)\rangle \equiv \mu_{if} \ e^{-iH_i t/\hbar} |\psi_{i0}\rangle \tag{3.8c}$$

and

$$|\phi_f(t)\rangle \equiv e^{-iH_f t/\hbar}\mu_{if} |\psi_{i0}\rangle. \tag{3.8d}$$

The evaluation of $C_{if}(T)$ is further simplified if μ_{if} is independent of Q, although this is not always justified. Equation (3.6a) can be evaluated by propagating $|\psi_{i0}\rangle$ in the upper and lower surface for a time t and then evaluating the resulting overlap. The states $|\psi_{i(f)}(t)\rangle$ obey the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial r}|\phi_{i(f)}(t)\rangle = \left\{T_Q + V_{i(f)}(Q)V[Q, X(t)]\right\}|\phi_{i(f)}(t)\rangle, \tag{3.9}$$

where the potential $V[Q, X(t)]$ is a function of the classical trajectory $X(t)$, and hence is time dependent. The trajectory $X(t)$ is obtained by solving the classical equation of motion. Thirumalai et al. [32] showed using an earlier result due to Pechukas [33] that the time-dependent potential seen by the classical coordinates $X(t)$ is given by [34]

$$W_{cl}^{i(f)} = u[x(t)] + \langle \psi_{i(f)}(t)|V(Q, X(t))|\psi_{i(f)}(t)\rangle. \tag{3.10}$$

A few comments about the above equation are worth making: (a) The above algorithm based on eqs. (3.9) and (3.10) first used by Thirumalai et al. [32] for many-body systems is currently referred to as the adiabatic molecular dynamics. It is obvious the $W_{cl}^{i(f)}$ depends on the electronic surface. (b) The above form of equation for $W_{cl}^{i(f)}$ is necessary to ensure that total energy of the system is conserved [32] In order to derive the equations of motion (cf. eq. (3.10)), a certain transition-matrix element was evaluated using first-order perturbation theory. This is justified provided the propagation time step is sufficiently small. Since energy exchange between the classical and quantum degrees of freedom is proportional to the transition-matrix element, energy is conserved only to the lowest order in perturbation theory. (c) The derivation provided by us clearly demonstrates that this algorithm is valid only for adiabatic dynamics. If the states of the quantum degrees of freedom $\{\Psi_{i(f)}(Q, x)\}$ are coupled then modifications are required to account for such coupling. (For recent papers addressing curve crossing in condensed phases, see ref. [35].) In principle one can obtain the appropriate equations of motion following the method given in the appendix of the paper by Thirumalai et al. (d) Recently this basic algorithm has been used to study the adiabatic dynamics of localized states of an excess electron in molten salts [36], ammonia [37], and water clusters [38]. While this is interesting these authors have also attempted to obtain transport coefficients from the effective adiabatic dynamics. It is not clear that this procedure is equivalent to linear response theory which shows that for transport coupling between electronic states is required even when the thermodynamics is dominated by the ground state. Under these circumstances the above algorithm cannot be used. (e) Equations (3)–(9) and Hamilton's equation for $X(t)$ with the potential given by eq. (3.10) constitute a self-consistent set of equations for the mixed quantum–classical systems [32].

The numerical solution of the time-dependent Schrödinger equation can be done in several ways. In our original application we used a semiclassical approximation by using a Gaussian wavepacket to describe $\psi_{i0}(t)$ [13]. This ansatz is appropriate for the problem we considered namely the simulation of electronic absorption and emission spectra of Br_2 in an Ar matrix. The shortcomings of using Gaussian wavepacket techniques have already been discussed extensively. However our studies showed that certain qualitative features of the spectra commonly found in experiments could be theoretically simulated. In particular the low-resolution spectra we calculated for Br_2 in an Ar matrix was in accordance with the experimental findings [39]. Furthermore the emission spectrum displayed the vibrational progression seen in experiments.

Because of the limitations of wavepacket dynamics it is fruitful to solve the time-dependent Schrödinger's equation numerically. Recently Selloni et al. have used real-time fast Fourier transform propagator approach to evolve the time-dependent Schrödinger equation for the motion of the quantum degrees of freedom [36], and have obtained $X(t)$ by solving Newton's equation of motion. The resulting dynamic wavefunction is in a mixed state, and they use eq. (3.10) to calculate the forces on the classical degrees of freedom. It has been emphasized that eq. (3.10) assumes that the coupling between the electronic states are

zero [32]. Thus although the simulations of Selloni et al. are interesting the interpretation (specifically with respect to the calculation of transport quantities) of the results are difficult because of the inconsistent use of the algorithm. Nevertheless their method of solving eq. (3.9) may be useful for computing transport coefficients for mixed quantum–classical systems *after* a proper formulation of the problem in terms of effective eigenstates $\psi_{i(f)}(X, Q)$ is made.

4. Conclusions

In this article we have provided a brief assessment of the success of several methods that we have introduced for simulating time correlation functions in quantum and mixed quantum–classical systems. At present it is not clear that any one method is superior. It appears that the direct real-time simulations [11,14,25] have some obvious advantages over the analytic continuation method [9,19,20]. Clearly progress made to obtain spectral function from thermal correlation functions makes the analytic continuation technique quite practical [19,20]. It would also be interesting to test the method, we have suggested here for the first time in section 2.3, by applying to certain nontrivial cases.

Recent numerical developments [18] can be used to obtain efficient algorithms for the computation of electronic spectra using path integral techniques. It should be emphasized that the use of symmetrized version of TCF may not prove to be very advantageous when simulating electronic spectra [29,30]. The reason for this is that the arguments leading to phase cancellation presented in section 2.2 when applied to $G_{if}(t)$ show that if the potential surface for the electronic state is very different form the initial state then the imaginary part (corresponding to $F(X_1, \ldots, X_2)$ in eq. (2.14) could be highly oscillatory. This would result in large numerical errors in the simulation of $G_{if}(t)$.

Central to the simulation of quantum time correlation functions by path integral methods is the issue of sampling strategies. The introduction of new methods to cope with the alternating sign problem leads to use of sampling functions that are quite different than the usual Boltzmann factors encountered in classical Monte Carlo simulations. The representation of the quantum degrees of freedom by auxiliary classical degrees of freedom leads to the presence of additional time and length scales that have to be treated properly to ensure that simulations are properly converged. One strategy for circumventing the oscillatory problem arising in the direct real-time evaluation of dynamic correlation functions is the stationary phase Monte Carlo method [16–18]. This method essentially exploits the fact that most of the contribution to $C_{AA}(t)$ would arise when the phase obtained by collecting the imaginary part in a path integral representation of $C_{AA}(t)$ is stationary. Doll and co-workers have attempted some ways of locating these stationary phase regions using filtering functions. This method has only been applied to simple problems, and the generality of this promising technique is yet to be established. In an attempt to locate the stationary-phase region without resorting to the use of filtering functions Mak and Chandler [21] have used a distortion of the coordinate variables into the complex plane. The location of these stationary points was done by simulated annealing for the spin-boson problem. This method is clearly computationally intensive unless one has a-priori some idea of the location of the stationary phase regions. As pointed out by these authors for any complex problem it is reasonable to expect multiple solutions to the stationary-phase equation. If this proves to be the case the method may not prove to be too practical. In the absence of other methods these problems have to be resolved before one can hope for efficient methods for quantum simulation of time correlation functions based on path integral methods.

Acknowledgements

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