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Nonadiabatic effects in a method that combines classical and quantum mechanics

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We have included nonadiabatic effects in the calculation of the dynamical evolution of a system where a quantum particle in a double well is coupled to a classical oscillator. By performing an exponential resummation of the evolution operator we have included "polarization" effects (similar to the self-energy corrections for an electron that moves in a polarizable medium) which lead to a renormalization of the energy of the quantum particle. © 1996 American Institute of Physics. [S0021-9606(96)00210-4]

I. INTRODUCTION

Although molecular dynamics techniques for the study of systems with many degrees of freedom have been very successful, quantum effects like tunneling, interference and level quantization are often significant. However, a full quantum mechanical microscopic study becomes quickly impractical as the number of degrees of freedom increases. For this reason there has been intense interest in the development of methods that treat classically most of the degrees of freedom and quantum-mechanically only the few degrees of freedom that exhibit significant quantum effects.

This class of techniques originated in atomic scattering theory¹ and was further developed with the advent of "surface-hopping" methods,² in which typically the atoms move classically and a few electronic degrees of freedom undergo quantum transitions between levels in a potential dictated by the configuration of the classical atoms. Many workers³ have examined extensions and variations of surface-hopping methods. An interesting recent work is Ref. 4 where the authors examine the nonlocality in time and non-conservation of norm that is common to most surface-hopping methods and discuss some recent works⁵ in which algorithms have been proposed that address these problems.

In the next section we briefly review the computational scheme that is employed in mixed quantum-classical formalisms. We show that the initial implicit approximation in these schemes is the adiabatic approximation for the evolution operator. In Section III we calculate nonadiabatic corrections to the evolution operator and show that they lead to an extra effective potential in the Schrödinger equation for the quantum particle. In Section IV we examine numerically a simple model: a quantum particle in a double well is coupled to a classical oscillator. We calculate the energy splitting of the two lowest states using the adiabatic and nonadiabatic evolution operators and compare with the exact results. Finally we discuss the connection of these results with self-energy calculations for the polaron problem and with other nonadiabatic corrections that have been part of the standard mixed classical-quantum formalisms.

II. THE MIXED QUANTUM-CLASSICAL MECHANICS FORMALISM

Let us assume that we have a Hamiltonian of the form

$$H = h(x) + H_{\text{osc}}(\hat{R}) + f(x, \hat{R}). \quad (2.1)$$

Here, h contains the kinetic part for the quantum particle and the potential and depends only on x . H_{osc} is a harmonic oscillator Hamiltonian and depends only on \hat{R} (the hat means that \hat{R} is an operator, we wish to state this explicitly because eventually it will be approximated by a classical variable). Finally, f represents the coupling between the quantum particle and the oscillator and it is often assumed, although it is not necessary for our argument, that it is linear in \hat{R} and x .

We assume that the eigenfunction of the Hamiltonian (2.1) can be written in the following form:

$$\Phi = \psi(x; \hat{R}) \chi(\hat{R}), \quad (2.2)$$

where $\psi(x)$ is a wavefunction that describes the dynamics of the quantum particle and depends on \hat{R} , while $\chi(\hat{R})$ is the bath (i.e. oscillator) wavefunction.

A first attempt to describe the dynamics of the system is to employ the adiabatic approximation for the evolution operator

$$e^{-i(h+f+H_{\text{osc}})t} \simeq e^{-iH_{\text{osc}}t} e^{-i(h+f)t}, \quad (2.3)$$

i.e. we set the commutator $[h+f, H_{\text{osc}}]$ equal to zero. We let the operator of Eq. (2.3) act upon the state shown in Eq. (2.2):

$$e^{-iH_{\text{osc}}t} e^{-i(h+f)t} |\psi\rangle |\chi\rangle. \quad (2.4)$$

If we select the state $|\psi\rangle$ so that it is an eigenstate of $h+f$ with eigenvalue E_n (which is a function of \hat{R}), then Eq. (2.4) can be written as

$$|\psi_n\rangle e^{-i(H_{\text{osc}}+E_n(\hat{R}))t} |\chi\rangle. \quad (2.5)$$

Eq. (2.5) shows that the oscillator wavefunction evolves in time according to an effective Hamiltonian

$$H_{\text{eff}}(\hat{R}) = H_{\text{osc}} + E_n(\hat{R}). \quad (2.6)$$

Eq. (2.5) can also be understood in the sense of an iterating procedure: for given $R(t)$ we calculate ψ_n and $E_n(\hat{R})$

which is used in Eq. (2.6) for the calculation of $R(t+dt)$. This value $R(t+dt)$ is used for the calculation of a new pair ψ_n and $E_n(\hat{R})$ etc.

If the harmonic oscillator is treated classically, the equation of motion for the classical coordinate R can be written according to Eq. (2.6) as

$$M_R \ddot{R} = -\omega_R^2 R - \frac{\partial E_n}{\partial R}. \quad (2.7)$$

The conceptual difficulty with Eq. (2.7) is that one has to specify what happens to the classical coordinate when the quantum coordinate undergoes transitions between different states, since this would change the force $\partial E_n/\partial R$ that acts upon classical particle. Using the Hellman-Feynman theorem, the force on the classical oscillator can be written as⁵

$$\frac{\partial E_n}{\partial R} = \frac{\partial}{\partial R} \langle \psi_n | (h+f) | \psi_n \rangle = \left\langle \psi_n \left| \frac{\partial f}{\partial R} \right| \psi_n \right\rangle. \quad (2.8)$$

The philosophy of surface-hopping methods is to allow for the classical coordinate to react to quantum transitions of the quantum subsystem. For that purpose an ensemble of classical trajectories is introduced. The ratio of trajectories that evolve with the force $\partial E_n/\partial R$ (that corresponds to the quantum state n) is proportional to the probability that the state n is occupied. Then a “fewest switches” algorithm is introduced to determine when a transition takes place.⁵

A simpler alternative to the surface-hopping scheme, that is valid under certain conditions, is the “mean-trajectory” approximation. In this approximation the classical coordinate evolves along a unique trajectory under the influence of an average force. Instead of the expectation value in Eq. (2.8), the force is given by the mean value

$$\left\langle \phi \left| \frac{\partial f}{\partial R} \right| \phi \right\rangle, \quad (2.9)$$

where $\phi = \sum_n c_n \psi_n$ is the wavefunction of the system expanded in terms of the adiabatic eigenfunctions ψ_n . We shall come back later to the question of the validity of the mean-trajectory approximation.

The computational procedure is the following:

(i) For a given classical configuration R we find the eigenfunctions ψ_n of the Hamiltonian $h+f$. The choice of $h+f$ as the Hamiltonian that is diagonalized, is a consequence of the adiabatic approximation as shown in Eqs. (2.3)-(2.5).

(ii) The wavefunction of the system is expanded in terms of the adiabatic eigenfunctions ψ_n :

$$\phi = \sum_n c_n(t) \psi_n. \quad (2.10)$$

As the classical coordinate R evolves in time, the potential $f(R)$ changes and as a result the expansion coefficients c_n are time dependent. They satisfy the following system of coupled equations:⁶

$$i\dot{c}_k = \sum_j c_j \left(\langle \psi_k | (h+f) | \psi_j \rangle - i\dot{R} \langle \psi_k | \frac{\partial}{\partial R} | \psi_j \rangle \right). \quad (2.11)$$

The first term on the right-hand side is diagonal and is equal to $\epsilon_k \delta_{kj}$, where ϵ_k is the adiabatic energy eigenvalue. The second term is an off-diagonal coupling of the adiabatic eigenfunctions (the diagonal part of this term is equal to zero) and it is the nonadiabatic correction that is included in standard works that use mixed quantum-classical formalisms.^{2,5,6} It is interesting to note that Eq. (2.11) is formally identical to the equations for time-dependent perturbation theory for a problem with an unperturbed Hamiltonian $h+f$ and a time-dependent perturbation $-i\dot{R}\partial/\partial R$. In the next section we shall discuss a nonadiabatic correction to the diagonal part of Eq. (2.11), which leads to a renormalization of the adiabatic energy ϵ_k . Therefore, the nonadiabatic correction that we shall introduce in the next section has different physical meaning than the nonadiabatic correction that has been discussed by other authors.^{2,5,6}

(iii) The system of coupled equations Eq. (2.11) is solved simultaneously with an integration of the equation

$$M_R \ddot{R} = -\omega_R^2 R - \left\langle \phi \left| \frac{\partial f}{\partial R} \right| \phi \right\rangle \quad (2.12)$$

if the mean-trajectory approximation is used. If surface hopping methods are used, then Eq. (2.7) has to be integrated instead of Eq. (2.12).

III. NONADIABATIC CORRECTIONS

As the presentation in the last section showed, the calculational scheme outlined above makes use of the adiabatic approximation Eq. (2.3). Following our earlier work we expand the evolution operator and perform an exponential resummation⁷ to infinite order with respect to the operator H_{osc} . The result is (note that we have not yet taken the limit where the operator \hat{R} is treated as a classical variable)

$$e^{-i(h+f+H_{\text{osc}})t} \simeq e^{-i(h+f)t} e^{-iH_{\text{osc}}t} e^{i\sigma_1}, \quad (3.1)$$

where

$$i\sigma_1 = - \int_0^t dt' \int_0^{t'} dt'' e^{iH_{\text{osc}}t''} [H_{\text{osc}}, h+f] e^{-iH_{\text{osc}}t''} \quad (3.2)$$

contains the nonadiabatic corrections. We then use the fact $[H_{\text{osc}}, h] = [(1/2) M_R \omega_R^2 R^2, f] = 0$. If the degree of freedom \hat{R} has classical-like behavior, we can approximate it by its classical value. The transition to the classical limit will be carried out in two steps. First, we take the semiclassical limit, where \hat{R} is replaced by its average value $\langle \hat{R} \rangle$. Then, Eq. (3.2) can be written as

$$i\sigma_1 = \frac{i}{2M_R} \int_0^t dt' \int_0^{t'} dt'' e^{iH_{\text{osc}}t''} \times \left(\langle P \rangle \frac{\partial f}{\partial \langle R \rangle} + \frac{\partial f}{\partial \langle R \rangle} \langle P \rangle \right) e^{-iH_{\text{osc}}t''}. \quad (3.3)$$

We can interpret this equation as giving the time-evolved quantities $\langle \hat{R}_0(t) \rangle$, $\langle \hat{P}_0(t) \rangle$ in the Heisenberg picture. The subscript 0 means that \hat{R}_0 and \hat{P}_0 evolve according to the uncoupled equations of motion, since in Eq. (3.3) the expo-

nential operators are $\exp[\pm iH_M t]$ rather than $\exp[\pm i(f + H_M)t]$. After these changes of notation, σ_1 can be written as

$$i\sigma_1 = \frac{i}{M_R} \int_0^t dt' \int_0^{t'} dt'' \langle \hat{P}_0(t'') \rangle \frac{\partial f(x, \langle \hat{R}_0(t'') \rangle)}{\partial \langle \hat{R}_0 \rangle}. \quad (3.4)$$

Using Ehrenfest's theorem $\langle \hat{P}_0 \rangle / M_R = d\langle \hat{R}_0 \rangle / dt''$, the integration over t'' can be performed with the result

$$i\sigma_1 = -if(x, \langle \hat{R}_0(0) \rangle) + i \int_0^t dt' f(x, \langle \hat{R}_0(t') \rangle). \quad (3.5)$$

Using this result and the fact that $\hat{R}(0)$ is just the Schrödinger operator \hat{R} , the evolution operator for the quantum particle can be written as

$$e^{-i(h+f(x, \langle \hat{R} \rangle))t} e^{-if(x, \langle \hat{R} \rangle)t} e^{i \int_0^t dt' f(x, \langle \hat{R}_0(t') \rangle)}. \quad (3.6)$$

We now make the second step towards the classical limit, by replacing the mean value of the operator $\langle \hat{R} \rangle$ by the corresponding classical variable. Taking the time derivative of Eq. (3.6) leads to the following Schrödinger equation for the quantum subsystem (we repeat the steps of Eqs. (2.4,2.5)) which is the main result of the present paper:

$$i \frac{\partial \psi}{\partial t} = [h + f + \delta V] \psi$$

$$\delta V = f(x, R(t)) - f(x, R_0(t)), \quad (3.7)$$

where ψ , as in Eq. (2.2), is the wavefunction of the quantum subsystem. The effective potential δV need not be added to the usual mean-trajectory equation Eq. (2.12) for the following reason. Let us write the coupling term f as $f(x, R) \equiv cF(x, R)$ where c is a coupling constant. If we want to calculate ψ from Eq. (3.7) keeping up to quadratic in c terms, then it is sufficient when we evaluate $\delta V = c[F(R) - F(R_0)]$ to calculate R as R_0 plus a correction that is linear in c . The mean-trajectory equation (2.12) includes in R the linear in c corrections to R_0 , while if we include the term δV in Eq. (2.12) it will lead to corrections to R_0 that are quadratic in c and to corrections to ψ that are cubic in c , which can be ignored since the coupling constant c is usually taken to be small.

Equation (3.7) shows that besides the adiabatic Hamiltonian $h + f$, an extra effective potential δV has to be introduced to take into account the fact that R changes with time. To understand the physical meaning of this effective potential we look back at the mean trajectory equation Eq. (2.12) and note that the term $-\partial \langle f \rangle / \partial R$ plays the role of a frictional force, which while changing the classical trajectory from $R_0(t)$ to $R(t)$, produces work equal to

$$-\frac{\partial \langle f \rangle}{\partial R} \delta R. \quad (3.8)$$

This is the amount of energy that the oscillator lost as a consequence of its coupling with the reaction coordinate. Our result Eq. (3.7) shows that the additional term that has to be added to the adiabatic Hamiltonian $h + f$ is equal to (we make a Taylor expansion of $R(t)$ around $R_0(t)$)

$$f(R(t)) - f(R_0(t)) \approx \frac{\partial f(x, R)}{\partial R} \delta R. \quad (3.9)$$

The average of this term represents the amount of energy that the reaction coordinate gained, which is consistent with the amount of energy that the classical oscillator lost as shown in Eq. (3.8). In other words, our nonadiabatic correction $\exp[i\sigma_1]$ of Eq. (3.1) is the consistent correction for the wavefunction of the quantum coordinate so that energy is conserved.

It should be noted that in case we are performing a multi-time-step calculation and Eq. (3.7) gives the time development of the wavefunction from an intermediate value of time t_1 to t , the integral in Eq. (3.5) runs from t_1 to t and the uncoupled classical variable $R_0(t)$ is understood to have the initial condition $R_0(t_1) = R(t_1)$.

IV. NUMERICAL EXAMPLE

We shall study the problem defined by the following Hamiltonian:

$$H = \frac{p_x^2}{2m} + (ax^4 - bx^2) + \frac{p_R^2}{2M_R} + \frac{1}{2} M_R \omega_R^2 R^2 + cxR. \quad (4.1)$$

The first two terms represent a quantum particle in a symmetric double well. The ground state is symmetric and the first excited state antisymmetric. We shall call Δ_{01} the energy splitting between these two states. The quantum particle is coupled to a classical harmonic oscillator (next two terms in Eq. (4.1)) through a bilinear coupling term. The effect of the coupling is to reduce the energy splitting Δ_{01} .

We have used the following values for the parameters of the double well: $a = 0.0035$ and $b = 0.003$. These values correspond to a low barrier for which the energy splitting Δ_{01} is not very small. We chose a low barrier so that even when the coupling constant c is large, Δ_{01} does not become very small. The quantum particle has a mass equal to that of a hydrogen atom (1837 a.u.) while the classical oscillator has $M_R = 2000$ a.u.

The quantum version of the Hamiltonian (4.1) has been studied using the time-dependent self-consistent field approximation⁸ and by one of us⁹ by evaluating the exponential resummation Eq. (3.1) in the interaction picture. A coupling that is not bilinear was examined in Ref. 10.

We have calculated the survival probability of a Gaussian wavepacket centered in one well (in fact this wavepacket is equal to the difference between the symmetric ground state and the antisymmetric first excited state, plus a small mixing of higher excited states). This wavepacket decays after a time equal to π/Δ_{01} . The reason we have selected a low barrier (which leads to relatively large values for Δ_{01}) is in order to make the localized wavepacket decay at reasonable times. We assumed that the classical oscillator is initially at its equilibrium position and has kinetic energy equal to the zero-point energy of a quantum oscillator with the same frequency.

We describe the time evolution of the wavepacket with the following iterative scheme. For a give value of $R(t)$ we found the adiabatic eigenstates ψ_n by using a basis set of 16 harmonic eigenfunctions and using the EISPACK package to diagonalize the Hamiltonian Eq. (3.7). Then we used a Runge–Kutta routine¹¹ for the integration of the system of equations Eq. (2.11). We have neglected the off-diagonal nonadiabatic coupling in Eq. (2.11) since it is very small for this problem, mainly because we have solved for very small values of the coupling constant c , in particular 0–0.03.

Once we have found the coefficients $c_k(t)$ we proceed to the next time step. We use these values of $c_k(t)$ to calculate the force $\langle \phi | cx | \phi \rangle$ that appears in Eq. (2.12). Since Eq. (2.12) describes a forced harmonic oscillator it is easy to find analytically the value of $R(t+\Delta t)$, where Δt is chosen so that the integration of Eq. (2.11) by this time step proceeds smoothly. After we have found $R(t+\Delta t)$, we repeat the above calculation by finding the new adiabatic eigenfunctions ψ_n of the Hamiltonian $h+f(R)$.

We are now coming back to the question of the validity of the mean-trajectory approximation. The situation where it fails is when the quantum state ϕ consists of a part that is localized in the left well and a part that is localized in the right well. Then the force $\langle \phi | cx | \phi \rangle$, as calculated in the mean-trajectory approximation, is very close to zero. However, this is not correct since the quantum particle induces a nonzero force on the classical oscillator when it is in either state (*i.e.* centered at the left or right well). This is a situation where the averaging of the force over the possible quantum states does not make sense. However, in this paper we examined a case where this situation never arises. In particular, we started at time $t=0$ with a localized wavepacket in one well and since the barrier is low, it spreads smoothly towards the other well without getting into a state where the wavefunction consists of two localized wavepackets and is depleted in the region between the centers of the wells.

In problems where the barrier is high and the quantum particle makes transitions between localized states in deep nearly symmetric wells, surface-hopping techniques may be the only appropriate method. However, we would like to point out that even in such a case one could attempt a modified mean-trajectory approach by using a multi-configuration bath description, in the spirit of the multi-configuration time-dependent self-consistent field approach of Ref. 8.

We calculated the survival probability and found the time T for which the initial localized wavepacket decays. Then, the energy splitting is calculated from $\Delta_{01} = \pi/T$ (it should be noted that there are other dips in the survival probability that correspond to transitions between excited states). We have performed the calculation for two values of the classical oscillator frequency: $\omega_R = 0.007$ and 0.0136. For each case we repeated the calculation twice: first with the adiabatic Hamiltonian $h+f$ and then with the inclusion of the nonadiabatic correction δV as shown in Eq. (3.7). We performed the calculation for several values of the coupling constant c .

In Fig. (1) we show the decay times π/Δ_{01} as calculated by our adiabatic and nonadiabatic quantum-classical formal-

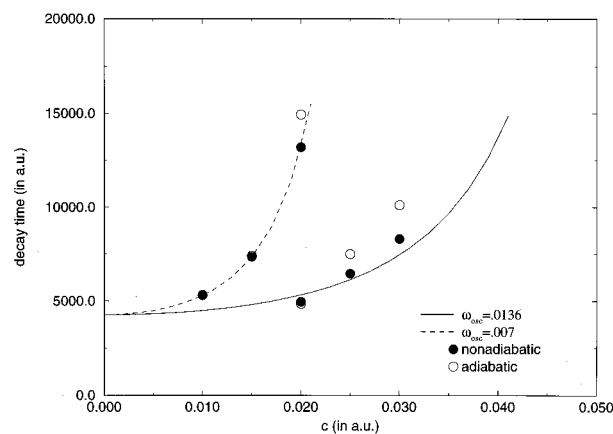


FIG. 1. Plot of decay times of a localized wavepacket as a function of the coupling constant c . We have performed the calculation for two values of the harmonic oscillator frequency. We show the results for both an adiabatic and a nonadiabatic calculation as discussed in the text. For weak coupling the adiabatic and nonadiabatic results are identical.

ism. Also shown are the exact results that are obtained by diagonalizing the full quantum Hamiltonian (with the harmonic oscillator initially in its ground state), finding the value of the energy splitting Δ_{01} and plotting π/Δ_{01} for various values of the coupling c . The results are not surprising. For a slow bath (harmonic oscillator) the adiabatic approximation works well. The same is true for a fast bath and weak coupling. As the coupling gets stronger the adiabatic result starts to fail. However, our nonadiabatic correction does shift the adiabatic result towards the exact answer.

V. DISCUSSION

We begin by reviewing briefly a standard model of many-body theory, the Fröhlich polaron.¹² In that model there are also two kinds of coordinates (fermionic and bosonic) but unlike the scheme discussed in this paper they are both quantum-mechanical. The Fröhlich polaron Hamiltonian describes the interaction of a single free-particle-like electron with longitudinal optical phonons and is of the form

$$H = h(x) + H_q + f(x, q), \quad (5.1)$$

where h is the free-electron Hamiltonian (x is a fermionic degree of freedom) and H_q is the phonon Hamiltonian (q are the bosonic degrees of freedom), essentially a collection of harmonic oscillators with the same (Einstein) frequency but different wavevectors. The interaction between x and q is represented by the coupling term $f(x, q)$.

Let's denote by ϵ_p the free-particle electronic energy. What is the single-particle energy E_p of the electron in the interacting system? The answer is not $E_p = \epsilon_p + f$ because the ions are not static. As the electron moves it polarizes the medium around it and this ionic motion acts back upon the electron, which has to drag the polarization cloud. This polarization effect is properly included in the following expression for the single-particle energy of the electron:

$$E_p = \epsilon_p + \text{Re} \Sigma_p, \quad (5.2)$$

where Σ is the self-energy of the electron (a detailed discussion of techniques for the calculation of the polaron self-energy can be found in Chapter 6 of Ref. 12).

Now we return to the single-particle Schrödinger equation Eq. (3.7) that describes the dynamics of the quantum particle. If the classical particle had not felt the effect of the coupling, it would be at the position $R_0(t)$. The influence of the quantum upon the classical particle is to force it to move to position $R(t)$. The difference $f(R(t)) - f(R_0(t))$ is the “polarization” potential energy due to the presence of the quantum particle at x and is analogous to the self-energy contribution to the electron energy in the polaron problem. It is worth noting that one way to calculate the self-energy of the polaron (the “linked-cluster” expansion¹²) is formally similar to the exponential resummation we have used as we have discussed elsewhere.¹³

In conclusion, we believe that the effective Hamiltonian $h + f$ represents the zeroth-order approximation and our effective Hamiltonian $h + f + \delta V$ takes into account the “polarization” drag effect, *i.e.* the fact that the quantum particle feels the reaction upon it created by the extra movement of the classical particle that itself caused.

We made this reference to the polaron to emphasize that the effect we have described in this paper is present in all interacting many-body systems (in the polaron case this effect is much more pronounced due to the long range of the Coulomb interaction). Therefore it should be taken into account whether one employs the mean-trajectory approximation or uses surface-hopping techniques since it is a correction to an approximation that was made at an earlier stage, as described in Eqs. (2.3)-(2.5). As we mentioned in Section II, this correction leads to a renormalization of the energy of the quantum particle. It is a correction to the *diagonal* term in Eq. (2.11) and is physically distinct from the off-diagonal

nonadiabatic coupling in Eq. (2.11) that was included in other works that use the mixed quantum-classical formalism.

Presently, we are working on the application of a mixed quantum-classical formalism to the study of proton transfer in proteins.

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