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Quantum Simulation of Reaction Dynamics by Density Matrix Evolution

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A density matrix evolution (DME) method to simulate the dynamics of quantum systems embedded in a classical environment is presented. The method is applicable when the quantum dynamical degrees of freedom can be described in a Hilbert space of limited dimensionality. The method is applied to the case of proton-transfer reactions in a fluctuating double-well potential [details are given in the following paper in this issue] and compared to other analytical and numerical solutions. The embedding of the quantum system within the classical system by using consistent equations of motion for the classical system with proper conservation properties is discussed and applied to the one-dimensional collision of a classical particle with a quantum oscillator.

1. Introduction

Simulations of reactive processes in the condensed phase that involve fast motion of light particles (electrons or protons), occurring under the influence of a fluctuating molecular environment, require dynamical simulation methods that combine a quantum mechanical treatment of a few degrees of freedom (possibly only one), while allowing a classical molecular dynamics (MD) simulation of the remainder of the system. Examples of such systems are electron or nuclear spins in a molecular fluid, proton transfer in double-well potentials, electron transfer from a donor to an acceptor molecule, and an embedded chromophore in an electromagnetic field and its optical relaxation.

Current MD methods, force fields, and computer power allow the realistic simulation of large molecular systems over times approaching nanoseconds. Therefore, the usual reduction of environmental effects to mean field and stochastic descriptions is not really required, and the full molecular details may be retained. The problem resides in the proper dynamical treatment of the essential quantum mechanical degrees of freedom and the proper description of the coupling between quantum and classical degrees of freedom.

We shall use the process of solvent-modulated proton transfer in an intramolecular hydrogen bond, where tunneling is important, as an example to demonstrate the proposed Density Matrix Evolution (DME) method. In an accompanying article,¹ we describe the application to hydrogen malonate in aqueous solution. Proton-transfer reactions have received considerable interest in the literature.^{2–4} Recently, Borgis *et al.*³ have treated the nonadiabatic proton transfer by a formalism that expresses the nonadiabatic reaction rate in terms of correlation functions of the quantum mechanical coupling and splitting parameters for the proton Hamiltonian.

Inclusion of quantum aspects in dynamic simulations can be accomplished in various ways. Path integral methods⁵ describe the quantum particle as a closed string of beads and equilibrate the quantum particle distribution per time step of the classical dynamics. The method has been applied to proton-transfer reactions in the solid state by Gillan.⁶ Although path integral simulations produce correct ensemble averages, they do not properly represent the dynamics of the quantum particle and cannot be regarded as quantum dynamical simulations. The Car–Parrinello method⁷ essentially solves the many-electron Schrödinger equation in the Born–Oppenheimer (*i.e.*, adiabatic) approximation for the ground state for every time step, using a

density functional Hamiltonian. This method can potentially simulate adiabatic reactions in the condensed phase involving electronic rearrangement in molecules but is not quantum dynamical either.

Complete solution of the time-dependent Schrödinger equation for one quantum particle in an environment of classical particles, involving evolution of the wave function, does provide a quantum dynamical simulation. Wave packet propagation⁸ falls into this category but is not suitable for double-well potentials if limited to Gaussian wave packets. The method of Selloni *et al.*⁹ to describe the wave function on a grid and solve the equations of motion by a split-operator technique is more general and could be employed for reactive processes. However, this method is restricted to instantaneous ground-state solutions; it requires that the gap between ground state and excited state is much larger than kT , and it is not clear how this method could deal with excited states of molecules rather than with a single quantum particle such as a solvated electron. Very recently, nonadiabatic transitions were incorporated into the method of Selloni *et al.* by the method of surface hopping.^{10,11} In the simulation of electrons, the method seems to correctly predict the probabilities for nonadiabatic transitions mainly because of the low probability of hopping as a result of the large energy gap.

Recently, Borgis *et al.*⁴ have computed the dynamics of a proton-transfer reaction in a simulated model environment including the stationary solution of the one-dimensional Schrödinger equation. However, they do not solve the time-dependent Schrödinger equation and hence only consider adiabatic motion. Thus, their method is similar in principle to path integral methods, except that dynamical quantities of the quantum subsystem have no physical meaning in the path integral method.

Most theories developed to treat reaction dynamics of quantum particles (protons, electrons) in the condensed phase^{3,12} do not simulate the quantum degrees of freedom explicitly but describe the effects of fluctuating terms in the Hamiltonian by expressing the latter in terms of mean field and stochastic properties. We follow a more straightforward approach by incorporating the dynamics of the quantum subsystem directly into the MD of the classical environment, similar to the method of Selloni *et al.*⁹ But instead of using a spatial grid, we describe the quantum subsystem in a Hilbert space of basis functions using the density matrix formalism. This allows the inclusion of excited states. Thus, we follow closely a formalism that is routinely used in the dynamics of spin systems¹³ but which to our knowledge has not been exploited yet in molecular simulations. A recent treatment of optical transition rates¹⁴ uses the density matrix evolution in the

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approximation of Redfield theory,¹⁵ which implies first-order rate constants for the time decay of the density matrix.

The dimensionality of the Hilbert space is kept as low as possible. Many problems, such as optical relaxation in a two-level system or tunneling in a double-well potential, require no more than two basis functions for a reasonably accurate description. If a higher dimensionality is needed, for example to include more excited states or vibrational degrees of freedom with a quantum character, the density matrix can be easily expanded. The computational effort increases with the cube of the number of basis functions used.

In section 2, we summarize the density matrix formalism and the derivation of rate constants. Explicit equations are derived for the case of a two-dimensional space. In section 3, analytical solutions for special cases are considered and compared with expressions derived by Borgis et al.³ for proton-transfer reactions. In section 4, a short summary is given of the results of a DME simulation of an intramolecular proton transfer in aqueous solution,¹ where the coupling from the quantum to the classical systems is assumed to be negligible during the short time that the DME is followed. Section 5 shows how in the case of strong coupling the equations of motions of the classical system must be modified; the one-dimensional collision of a classical atom with a quantum mechanical harmonic oscillator is simulated as an example. Section 6 discusses the results.

2. Density Matrix Evolution

Consider a system of particles with N classical degrees of freedom (with impulses p_1, \dots, p_N and coordinates q_1, \dots, q_N) which possesses an unspecified number of quantum degrees of freedom (the "quantum subsystem") in addition to the classical degrees of freedom. These quantum degrees of freedom are denoted ξ and may concern a single particle, a reaction coordinate, a vibrational coordinate, a set of electronic coordinates in an optical application, etc. At any configuration of the classical coordinates \mathbf{q} , the quantum subsystem obeys the time-dependent Schrödinger equation with a specified hamiltonian $\hat{H}(\mathbf{q})$. We assume that it is possible to define an orthonormal set of basis functions ψ_n on which the solutions of the Schrödinger equation can be expanded with sufficient accuracy. The basis functions may depend on the configuration \mathbf{q} , e.g., they may be defined relative to internal coordinates in a moving molecule, but the resulting time dependence is ignored on the time scale of the density matrix evolution.

We assume in this section that the perturbation of the classical system by the quantum subsystem is weak, so the classical Hamiltonian is independent of the quantum subsystem and hence the classical dynamics develops autonomously. In that case, $\mathbf{q}(t)$ and hence the hamiltonian $\hat{H}(\mathbf{q})$ can be generated from a classical MD simulation, without feedback from the quantum subsystem. This case corresponds to the usual assumption made in the study of nuclear spin systems in liquids, for which the density matrix formalism is perfectly suited. In section 5, we discuss the case that the weak-perturbation assumption is not fulfilled, as in most proton- and electron-transfer reactions and in optical and vibrational relaxation.

The solution $\Psi(\mathbf{q}, t)$ of the time-dependent Schrödinger equation can be expressed on the basis set as

$$\Psi(t) = \sum_n c_n(t) \psi_n \quad (1)$$

and the density matrix ρ is defined by

$$\rho_{nm} = c_n c_m^* \quad (2)$$

Note that in this definition the density matrix is not an ensemble average over the classical ensemble of the MD simulation but an instantaneous property attributed to a single quantum system.

The time evolution of the density matrix is given by

$$\dot{\rho} = \frac{i}{\hbar} [\rho, H] = \frac{i}{\hbar} (\rho H - H \rho) \quad (3)$$

where $H_{nm} = \langle n | \hat{H} | m \rangle$ is the Hamiltonian matrix, which may depend on the classical variables \mathbf{q} and hence on t . The expectation value $\langle A \rangle$ of an observable with operator \hat{A} and matrix A on the basis set used ($A_{nm} = \langle n | \hat{A} | m \rangle$) is given by

$$\langle A \rangle = \langle \text{Tr}(\rho A) \rangle \quad (4)$$

where brackets denote an average over the MD ensemble.

The diagonal elements ρ_{nn} represent the *population* of the n th state. Note that $\text{Tr}(\rho) = 1$ and that both ρ and H are hermitian. The off-diagonal elements represent phase factors.

Relation to the Rate Equation. We restrict ourselves to a two-state system denoted by R (the reactant state) and P (the product state). In the specific case of intramolecular proton transfer by tunneling, we assume at $t = 0$ the proton to reside in the reactant well R, and we wish to observe the rate at which the proton is transferred to the product well. So at $t = 0$ we choose $\rho_{11} = 1$ and all other elements of ρ zero, because there is no phase information at $t = 0$. The rate of transfer is given by ρ_{11} at small times. If we wish to compare with the macroscopic rate equation

$$\frac{dc_R}{dt} = -k c_R + k' c_P \quad (5)$$

where c_R and c_P are the populations in the reactant and product well, then we must solve the time dependence of ρ on a *coarse-grained time scale*:

$$k = - \frac{\langle \Delta \rho_{11} \rangle}{\Delta t} \quad (6)$$

where Δt is small on the reaction time scale but large on the time scale of the DMF, and $\langle \Delta \rho_{11} \rangle$ is averaged over the MD ensemble. Whether k can be thus defined must be observed from the numerical solution of the time evolution of $\langle \Delta \rho_{11} \rangle$; if this is not the case, the rate equation 5 cannot be valid.

Physical meaning can only be attached to the ensemble average of the diagonal elements of the density matrix. Therefore, the procedure is to solve $\rho_{11}(t)$ by solving the set of coupled equations 3 with $\rho_{11}(0) = 1$, starting at many points along the MD trajectory and averaging $\rho_{11}(t)$ over the obtained solutions. The starting points must be homogeneously distributed over the MD trajectory.

Practical Solution for the Two-State Case. For the two-state case, described by two basis functions, it is convenient to define a variable

$$z = \rho_{11} - \rho_{22} \quad (7)$$

instead of ρ_{11} and ρ_{22} , since $\rho_{11} + \rho_{22} = 1$. The variable z indicates the population difference between the reactant and product state: $z = 1$ if the system is completely in the reactant state and $z = -1$ if it is in the product state. We then have the complex variable ρ_{12} and the real variable z obeying the equations

$$\dot{\rho}_{12} = (i/\hbar) \{ \rho_{12} (H_{22} - H_{11}) + z H_{12} \} \quad (8)$$

$$\dot{z} = (2i/\hbar) \{ \rho_{12} H_{12}^* - \rho_{12}^* H_{12} \} \quad (9)$$

where we have used the hermitian property of ρ and H . Equations 8 and 9 imply that the quantity $4\rho_{12}\rho_{12}^* + z^2$ is a constant of the motion since the time derivative of that quantity vanishes. Thus, if we define a real vector

$$\mathbf{r} = (x, y, z) \quad (10)$$

with

$$x = \rho_{12} + \rho_{12}^* = 2\text{Re}(\rho_{12}) \quad (11)$$

$$y = (1/i)(\rho_{12} - \rho_{12}^*) = 2\text{Im}(\rho_{12}) \quad (12)$$

then the length of that vector is a constant of the motion. The

motion of \mathbf{r} is restricted to the surface of a sphere with unit radius if $\rho_{11}(0) = 1$. This result is well-known in the quantum dynamics of a two-spin system.¹³

The equations for the time evolution of \mathbf{r} can now be written as

$$\dot{x} = y\omega_z - z\omega_y \quad (13)$$

$$\dot{y} = z\omega_x - x\omega_z \quad (14)$$

$$\dot{z} = x\omega_y - y\omega_x \quad (15)$$

or

$$\dot{\mathbf{r}} = \mathbf{r} \times \boldsymbol{\omega} \quad (16)$$

where $\boldsymbol{\omega}$ is a real vector describing the Hamiltonian, defined as

$$\omega_x = (1/\hbar)(H_{12} + H_{12}^*) = (2/\hbar)\text{Re}(H_{12}) \quad (17)$$

$$\omega_y = (1/\hbar)(H_{12} - H_{12}^*) = (2/\hbar)\text{Im}(H_{12}) \quad (18)$$

$$\omega_z = (1/\hbar)(H_{11} - H_{22}) \quad (19)$$

Since the z -component of \mathbf{r} indicates the difference in population of the two states, the rate constant of eq 6 relates to the coarse-grained time derivative of z as follows:

$$k = -\frac{\langle \Delta z \rangle}{2\Delta t} \quad (20)$$

The vector $\boldsymbol{\omega}$ is a time-dependent function determined by the classical motions of the system. ω_z produces a rotation in the x,y -plane, and ω_x rotates the vector in the y,z -plane.

In the case of a transfer reaction in a double-well potential, H_{12} is real and hence $\omega_y = 0$; ω_x is a coupling parameter between the two well states, equal to $2C/\hbar$ in the notation of Borgis et al.,³ and ω_z is the angular frequency corresponding to the energy difference between the two lowest quantum levels in each state. The latter is related to the difference in the ground-state levels of reactant and product states ($-\Delta H/\hbar$ in the notation of ref 3).

3. Analytical Solutions

Although we propose to find the solutions of $\mathbf{r}(t)$, and hence the rate constant, by solving the density matrix evolution directly from eqs 3 or 13–15 using the simulated behavior of $\boldsymbol{\omega}(t)$, it is useful to express solutions in terms of the stochastic behavior of $\boldsymbol{\omega}$ and compare with the result given by Borgis et al.³ Let us first consider the case of stationary $\boldsymbol{\omega}$ in order to obtain some insight into the processes involved. The stationary case is not of interest in fluids, where the solvent reorientation is in general not slow compared to the reaction rate.

If $\boldsymbol{\omega}$ is stationary, the solution of $\dot{\mathbf{r}} = \mathbf{r} \times \boldsymbol{\omega}$ with $\mathbf{r}(0) = (0,0,1)$ is given by a rotation around the $\boldsymbol{\omega}$ -axis with angular frequency

$$\omega = (\omega_x^2 + \omega_y^2 + \omega_z^2)^{1/2} \quad (21)$$

In the case that $\omega_y = 0$, the components of \mathbf{r} are given by

$$x = (\omega_x \omega_z / \omega^2)(1 - \cos \omega t) \quad (22)$$

$$y = (\omega_x / \omega) \sin \omega t \quad (23)$$

$$z = 1 - (\omega_x^2 / \omega^2)(1 - \cos \omega t) \quad (24)$$

Figure 1 shows the stationary behavior of $\mathbf{r}(t)$ for the cases $\omega_z \gg \omega_x$ and $\omega_x \gg \omega_z$. In the former case, there is no effective tunneling, but in the latter case the well-known oscillation between the two states by tunneling is shown. So, in the stationary limit of slow fluctuations of the classical degrees of freedom, the population difference $\langle z \rangle$ behaves according to

$$\langle z \rangle = 1 - \langle \omega_x^2 / \omega^2 \rangle + \langle (\omega_x^2 / \omega^2) \cos \omega t \rangle \quad (25)$$

where averages are taken over the classical ensemble. Thus, the population difference decays to a value $1 - \langle \omega_x^2 / \omega^2 \rangle$, which can be close to 1 if solvent stabilization is significant. In that case

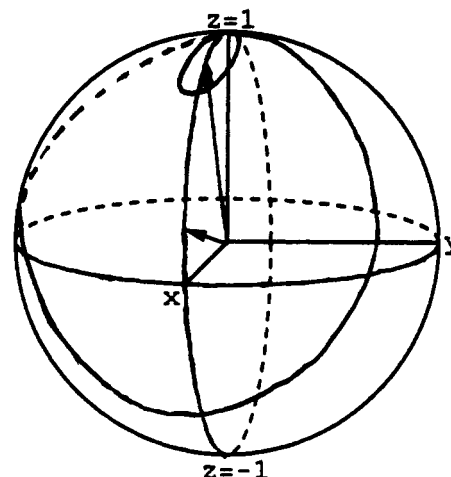


Figure 1. Stationary behavior (constant $\boldsymbol{\omega}$) of the unit vector \mathbf{r} , which represents the density matrix. z is the relative population difference between the P and R states; the projection on the x,y -plane determines the phase of the off-diagonal element. The small ellipse represents the case where the energy difference is large compared to the coupling and no tunneling occurs; the large ellipse represents the tunneling case with a coupling large compared to the energy difference.

there is no effective proton transfer if the solvent dynamics is not taken into account. The last term in eq 25 represents a decay function which depends on the distribution functions of ω_x and ω_z ; for the case that $\omega_x \ll \omega_z$, and both have independent Gaussian distributions, the decay is a cosine at the average ω_z , damped with a Gaussian.

In the general case, $\boldsymbol{\omega}$ is a fluctuating function of time, and eq 16 is now a stochastic vector equation, which can be solved analytically for the case that the fluctuations of ω_x decay fast on the macroscopic time scale of the population change $\langle z \rangle$. This is the limit considered by Borgis et al.,³ in magnetic resonance relaxation, this is the limit in which the Redfield theory¹⁵ is applicable. Then we may take $z = 1$ and solve for $y(t)$ from the equations for x and y (we consider again the case $\omega_y = 0$):

$$\dot{x} = \omega_z(t)y \quad (26)$$

$$\dot{y} = -\omega_z(t)x + \omega_x(t) \quad (27)$$

The solution for y can be obtained by the following substitution:

$$w(t) = (x + iy) \exp[i\varphi(t)] \quad (28)$$

where

$$\varphi(t) = \int_0^t \omega_z(t') dt' \quad (29)$$

From eqs 26 and 27, it follows that $\dot{w} = i\omega_x \exp(i\varphi)$, with $w(0) = 0$. From

$$y = \text{Im}\{w \exp(-i\varphi)\} = \text{Im}[i \exp\{-i\varphi(t)\} \int_0^t \omega_x(t') \exp\{i\varphi(t')\} dt'] \quad (30)$$

we find the solution

$$y(t) = \int_0^t \omega_x(t') \cos\{\varphi(t) - \varphi(t')\} dt' \quad (31)$$

This solution can be inserted into the equation for z (eq 15)

$$\dot{z} = -\omega_x y \quad (32)$$

and solved for the ensemble average:

$$\langle \dot{z}(t) \rangle = -\int_0^t \langle \omega_x(t) \omega_x(t') \cos\{\varphi(t) - \varphi(t')\} \rangle dt' \quad (33)$$

Substituting $\tau = t - t'$, using stationarity and reversibility for the fluctuations of ω_x and ω_z , and assuming fast decay of the autocorrelation function of ω_x which allows extension of the

integral to infinity, we then obtain

$$k = -1/2 \langle \dot{z} \rangle = 1/2 \int_0^\infty d\tau \langle \omega_x(0) \omega_x(\tau) \cos\varphi(\tau) \rangle \quad (34)$$

which is equivalent to the equation of Borgis et al.³ for the case that the modulation of the hydrogen bond length is comprised in the classical motion. Equation 34 can be further approximated by a cumulant expansion.³

4. Application to Proton Transfer

The DME method was applied¹ to calculate the rate of proton tunneling in the intramolecular double-well hydrogen bond of hydrogen malonate in aqueous solution. One hydrogen malonate molecule was simulated in a bath of 255 water molecules by classical MD during 100 ps after equilibration. A basis set consisting of two orthonormalized Gaussians was used, which represent the reaction and product state. The DME was repeatedly followed during 60 fs, starting with a diagonal density matrix with $\rho_{11} = 1$ from many (25 000) different starting points in the trajectory, and then averaged. Thus, the initial rate constants of tunneling were determined and found to be in reasonable agreement with the approximate analytical theory.

This treatment of proton transfer is still approximate; it concerns only the initial rate of transfer because no coupling from the quantum system to the classical system was incorporated in the classical MD. In the following section, we describe how this coupling can be realized.

5. Classical System Dynamics in the Case of Strong Coupling

Thus far we have (as have others³) only considered the *weak coupling* case: the classical environment is considered to have autonomous dynamics. This neglects any dynamical response of the classical system to changes in the quantum system. While for a proton-transfer reaction with weak electrostatic coupling to the solvent this may be a valid approximation, in the case of strong solvent polarization or in the case of an optical transition to a state with significantly different force field parameters for the classical system, this approximation may severely break down.

In the following, we show how the response of the classical system can be incorporated into the mixed dynamics. The most important requirement is that energy is conserved over the total system.

The total system is described by a Hamiltonian $H_{\text{tot}}(\mathbf{p}, \mathbf{q}, \pi, \xi)$, where π denotes the momenta conjugate to the quantum degrees of freedom ξ . Now we assume that a proper set of orthonormal basis functions $\psi_n(\xi)$ has been defined. Replacing ξ and π by their corresponding operators, \hat{H} is represented by a matrix with elements

$$H_{nm}(\mathbf{p}, \mathbf{q}) = \langle n | \hat{H}(\mathbf{p}, \mathbf{q}, \hat{\pi}, \hat{\xi}) | m \rangle \quad (35)$$

which can be evaluated for any configuration \mathbf{p}, \mathbf{q} of the classical coordinates. Using this Hamiltonian matrix, the density matrix ρ evolves according to eq 3 simultaneously with the classical system. The latter evolves from the Hamilton equations of motion, in which the derivatives of the classical Hamiltonian are replaced by their expectation values:

$$\dot{q}_i = \text{Tr} \left(\rho \frac{\partial H(\mathbf{p}, \mathbf{q})}{\partial p_i} \right) \quad (36)$$

$$\dot{p}_i = -\text{Tr} \left(\rho \frac{\partial H(\mathbf{p}, \mathbf{q})}{\partial q_i} \right) \quad (37)$$

Here \mathbf{H} is the Hamiltonian matrix of eq 35. With these equations of motion, the total energy $E = \text{Tr}(\rho \mathbf{H})$ is conserved:

$$\begin{aligned} \frac{dE}{dt} &= \text{Tr}(\dot{\rho} \mathbf{H} + \rho \dot{\mathbf{H}}) = \text{Tr}(\dot{\rho} \mathbf{H}) + \text{Tr} \left(\rho \sum_i \frac{\partial \mathbf{H}}{\partial p_i} \dot{p}_i + \right. \\ &\quad \left. \rho \sum_i \frac{\partial \mathbf{H}}{\partial q_i} \dot{q}_i \right) = \text{Tr} \left(\frac{i}{\hbar} [\rho, \mathbf{H}] \mathbf{H} \right) + \sum_i \dot{p}_i \text{Tr} \left(\rho \frac{\partial \mathbf{H}}{\partial p_i} \right) + \\ &\quad \sum_i \dot{q}_i \text{Tr} \left(\rho \frac{\partial \mathbf{H}}{\partial q_i} \right) = \frac{i}{\hbar} \text{Tr}(\rho \mathbf{H} \mathbf{H} - \mathbf{H} \rho \mathbf{H}) + \sum_i \dot{p}_i \dot{q}_i - \\ &\quad \sum_i \dot{q}_i \dot{p}_i = 0 \quad (38) \end{aligned}$$

The first term $\text{Tr}(\rho \mathbf{H} \mathbf{H} - \mathbf{H} \rho \mathbf{H})$ vanishes because the trace of a matrix product is invariant for cyclic exchange:

$$\text{Tr}(\rho \mathbf{H} \mathbf{H}) = \sum_{ijk} \rho_{ij} H_{jk} H_{ki} = \sum_{ijk} H_{ki} \rho_{ij} H_{jk} = \text{Tr}(\mathbf{H} \rho \mathbf{H}) \quad (39)$$

The equations of motions, eqs 36 and 37, are easily solved numerically but require the computation of all matrix elements of the forces that involve ξ (eq 37). On the other hand, eq 36 is usually simple: for Cartesian coordinates the equations are independent of ξ and reduce to $\dot{q}_i = p_i/m_i$. The classical equations 36 and 37 do not contain ξ explicitly, which means that ξ must be treated as a constraint in each step of the classical dynamics. The methods for numerical solution of constraint dynamics are well established.¹⁶

We shall now show by simulation of the simple collinear collision of a classical particle with a harmonic quantum oscillator that the method works. This problem has been treated extensively in the literature by various approximations up to a full quantum mechanical treatment.¹⁷ Elsewhere, we shall address the equilibrium of a quantum oscillator (such as a nitrogen molecule) in a bath of classical particles (such as argon atoms) and show that the quantum oscillator attains its proper Boltzmann occupation of quantum levels.

Consider a quantum particle with mass m and a classical particle with mass M with Hamiltonian

$$H = \frac{\pi^2}{2m} + \frac{p^2}{2M} + \frac{1}{2} k \xi^2 + V(|x - \xi|) \quad (40)$$

For the interparticle potential $V(r)$, we have taken the form

$$V(r) = A e^{-br} \quad (41)$$

For the basis functions, we have chosen the wave functions ψ_0 and ψ_1 for the ground and first excited state of the harmonic oscillator with mass m and force constant k . The quantum particle was initially put into the ground state with $\rho_{11} = 1$ and all other $\rho_{ij} = 0$; the classical particle was initially placed at a large distance x_0 and given a velocity v_0 toward the quantum particle. The numerical values chosen were as follows: $m = 1$ u; $M = 40$ u; $k = 84.92$ kcal/mol⁻¹ Å⁻², corresponding to a wavenumber of 1000 cm⁻¹ or $\hbar\omega = 2.86$ kcal/mol for the unperturbed oscillator; $x_0 = 5$ Å; and $v_0 = 9$ Å/ps, corresponding to an initial kinetic energy of 5.303 kcal/mol. The interparticle interaction parameters were $A = 1.0 \times 10^5$ kcal/mol and $b = 4$ Å⁻¹. The classical and density matrix equations of motion were solved by a fourth-order Runge-Kutta integrator using a time step of 0.05 fs over a total time of 1.0 ps. The matrix elements were computed analytically, which is possible with this functional form of the potential. In general, the matrix elements can best be computed from a series expansion.

Figure 2 shows the reflection of the classical particle with a velocity inversion after 322 fs. During the collision, energy is temporarily transferred to the oscillator, as is shown in Figure 3 (the population difference $\rho_{11} - \rho_{22} = 0.6205$ at the turning point, corresponding to a "population" of the excited state of 19%), but it is completely returned to the colliding particle. The eigenvalues change from the unperturbed value of 2.86 to 4.26

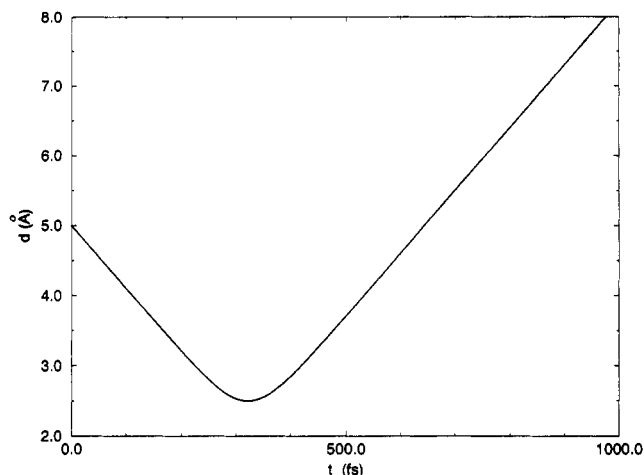


Figure 2. Distance between classical and quantum particle (expectation value) during the simulation of a collinear collision of a heavy classical particle ($m = 40$) with a light quantum oscillator ($m = 1$), starting at a distance of 5 Å and a velocity of 9 Å/ps. The collision turning point is at 322 fs.

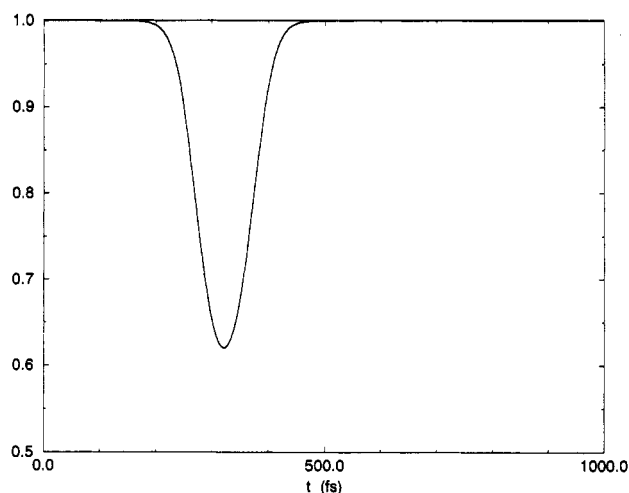


Figure 3. Population difference between ground and excited state $\rho_{11} - \rho_{22}$ of the quantum oscillator during the collision.

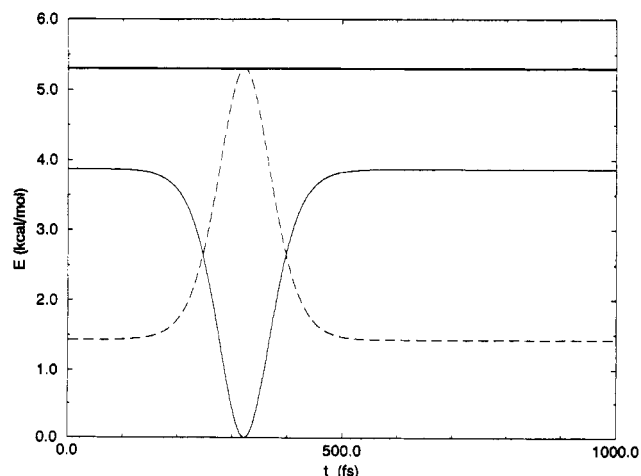


Figure 4. Energy changes during the collision. Thin solid line: kinetic energy of the classical particle. Broken line: total potential plus quantum energy. Thick line: total energy.

kcal/mol during the collision for $E_2 - E_1$. The total energy is very well conserved: the total energy before the collision was 5.3029, at the turning point 5.3026, and after the collision 5.3023 kcal/mol. Figure 4 shows the kinetic energy of the classical particle, the quantum energy (i.e., the trace over the Hamiltonian including the kinetic energy of the quantum particle and the total potential energy), and the sum of both.

6. Discussion and Conclusion

The DME treatment given above seems to be readily applicable to simulations of complex systems, in which a limited number of degrees of freedom must be treated by quantum dynamics. The method is suitable for cases where the wave function can be expanded in a limited number of basis functions. The DME method has no problems with nonadiabatic transitions and with inclusion of excited states. It is the method of choice to simulate transfer processes of electrons or protons between well-definable states, to simulate vibrational energy transfer in collision processes or in the condensed phase, or to simulate optical excitation and relaxation in complex molecular systems. It is not the method of choice when the wave function can develop into highly delocalized shapes like a solvated electron, which would require a large number of basis functions, or when we deal with many quantum particles, as in the density functional Car-Parrinello dynamics.

We have considered the case of the nonadiabatic quantum transition in a quantum system embedded in a classical environment (such as a proton or electron transfer or an optical or vibrational transition) from the point of view of direct dynamic simulation. We have considered a two-level system, appropriate for proton transfer along a hydrogen bond, in more detail. We have also shown how the quantum systems react back to the classical system and demonstrated the equations of motion that conserve total energy for a simple case.

Future work will be directed toward more complex applications, including reaction dynamics. A challenging field of application is the study of relaxation of optically excited states. The force field, as needed for the classical dynamics, describing the excited state will be different from that describing the ground state; it will be much more difficult to determine and will require high-quality quantum mechanical calculations. On the other hand, the DME method easily incorporates an external field (as a laser field) and can simulate optical dephasing and pulse echo experiments.

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References and Notes

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