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The Schrödinger equation with friction from the quantum trajectory perspective

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Similarity of equations of motion for the classical and quantum trajectories is used to introduce a friction term dependent on the wavefunction phase into the time-dependent Schrödinger equation. The term describes irreversible energy loss by the quantum system. The force of friction is proportional to the velocity of a quantum trajectory. The resulting Schrödinger equation is nonlinear, conserves wavefunction normalization, and evolves an arbitrary wavefunction into the ground state of the system (of appropriate symmetry if applicable). Decrease in energy is proportional to the average kinetic energy of the quantum trajectory ensemble. Dynamics in the high friction regime is suitable for simple models of reactions proceeding with energy transfer from the system to the environment. Examples of dynamics are given for single and symmetric and asymmetric double well potentials. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4788832]

I. INTRODUCTION

Quantum molecular dynamics with dissipation, relevant to many processes in chemistry, physics, and biology, is a long-standing theoretical challenge. [1] Dissipation describes interaction of the actively rearranging "system" with the "bath," representing the environmental degrees of freedom. With few exceptions, the numerically exact simulations of such quantum processes occurring in condensed phase, have been performed, using path integral Monte Carlo methods for models consisting of a low-dimensional system coupled to a bath of harmonic oscillators. [2,3] Inclusion of friction directly into the Schrödinger equation may be viewed as a simple way to mimic the effect of energy transfer from the system to the environment while limiting quantum dynamics calculations to the system degrees of freedom. Such picture is simplistic, yet it might be useful for some processes. For example, the quantum transition state theory of dissipative tunneling reproduces measurement of the H/D motion on Pt(111) surface with few adjustable parameters. [4]

The force of friction, often taken for processes in condensed phase[5] as linear in velocity of a particle, is most straightforwardly incorporated into equations of motion of a classical particle, characterized by position x_t and momentum p_t,

$$\frac{dp_t}{dt} = -\left.\frac{dV(x)}{dx}\right|_{x=x_t} - \gamma p_t, \quad \frac{dx_t}{dt} = \frac{p_t}{m}. \tag{1}$$

The trajectory evolves under the influence of an external potential $V(x)$, which is a function of the Cartesian coordinate x; parameter γ denotes the friction coefficient.

In this paper, the friction-generating term for the time-dependent Schrödinger equation (TDSE) is obtained from analogy between classical mechanics and the Madelung-de Broglie-Bohm formulation of TDSE. [6–8] The friction term depends on the phase of the evolving wavefunction. The resulting TDSE is nonlinear; the time-dependent wavefunction conserves normalization, while the total energy of the wavefunction decreases with time to the zero-point energy value. On a finite time-scale in the high friction regime such quantum evolution may represent a reactive system losing energy to the environment. The formalism is presented in Sec. II. Some examples including the parabolic and double wells, and discussion are given in Sec. III followed by conclusions.

II. FORMALISM

For simplicity, we consider one-dimensional Schrödinger equation in Cartesian coordinates, $-\infty < x < \infty$, and work in atomic units,

$$\iota \frac{\partial}{\partial t}\psi(x, t) = \hat{H}\psi(x, t). \tag{2}$$

The wavefunction $\psi(x, t)$ is considered normalizable. Multidimensional generalization of the quantum trajectory formalism can be found in Ref. 9. The Hamiltonian of the system is

$$\hat{H} = -\frac{1}{2m}\frac{\partial^2}{\partial x^2} + V(x). \tag{3}$$

The equivalent, *hydrodynamic* or *quantum trajectory* (also Bohmian) formulation of the TDSE (2)[8] is based on a polar form of the wavefunction expressed in terms of real amplitude $A(x, t)$ and phase $S(x, t)$,

$$\psi(x, t) = A(x, t)\exp(\iota S(x, t)). \tag{4}$$

Using Eq. (4), the conventional TDSE (2) yields a system of two equations,

$$\frac{\partial S}{\partial t} = -\frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2 - (V + U), \tag{5}$$

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$$\frac{\partial A^2}{\partial t} = -\frac{1}{m}\frac{\partial S}{\partial x}\frac{\partial A^2}{\partial x} - \frac{A^2}{m}\frac{\partial^2 S}{\partial x^2}. \tag{6}$$

Function U,

$$U(x,t) = -\frac{1}{2mA}\frac{\partial^2 A}{\partial x^2} \tag{7}$$

is the quantum potential entering evolution equations on par with the external classical potential $V(x)$, and formally generating all quantum-mechanical effects. Equation (6) is an equation of continuity of the wavefunction density $A^2(x,t)$; Eq. (5) connects quantum and classical mechanics once the gradient of the wavefunction phase is associated with the trajectory momentum,

$$p(x,t) = \frac{\partial S(x,t)}{\partial x}. \tag{8}$$

Differentiation of Eq. (5) defines time-evolution of $p(x,t)$,

$$\frac{\partial p}{\partial t} = -\frac{p}{m}\frac{\partial p}{\partial x} - \frac{\partial}{\partial x}(V+U), \tag{9}$$

which in the Lagrangian frame-of-reference gives Newton's equation of motion for the quantum trajectory (x_t, p_t),

$$\frac{dp_t}{dt} = -\frac{\partial}{\partial x}(V+U)\bigg|_{x=x_t}, \tag{10}$$

$$\frac{dx_t}{dt} = \frac{p_t}{m}. \tag{11}$$

(An interested reader may find overviews of theory and implementations based on quantum trajectories in Refs. 10 and 11.) By analogy with classical Eq. (1), the friction term γp is subtracted from the right-hand-side of Eq. (10) leading to

$$\frac{\partial p}{\partial t} = -\frac{p}{m}\frac{\partial p}{\partial x} - \frac{\partial}{\partial x}(V+U) - \gamma p. \tag{12}$$

(Other functional forms of friction may be introduced at this step.) Integrating Eq. (12) with respect to x using Eq. (8), the evolution of S with friction becomes

$$-\frac{\partial S}{\partial t} = \frac{p^2}{2m} + V + U + \gamma S + C(t). \tag{13}$$

The constant of integration $C(t)$ can be defined on physical grounds: the overall phase of a wavefunction should not affect its evolution, including wavefunctions describing eigenstates. This requirement is satisfied by the choice,

$$C(t) = -\gamma\langle S(x,t)\rangle. \tag{14}$$

Together with Eq. (6) unchanged by friction, the conventional TDSE with friction becomes

$$\iota\frac{\partial}{\partial t}\psi(x,t) = \hat{H}\psi(x,t) + \gamma(S - \langle S\rangle)\psi(x,t), \tag{15}$$

where

$$S = \arg\psi(x,t). \tag{16}$$

A similar equation termed the Schrödinger-Langevin equation has been proposed for a Brownian particle.[12] The expression includes random potential term and is obtained from the Langevin equation for the Heisenberg operators. The idea of quantum trajectory evolution with friction has been used for

the Caldeira-Leggett equation for the density matrix[13] and, with *ad hoc* friction, to stabilize the numerical implementation of the quantum trajectory formulation of Eqs. (7), (10), and (11).[14,15] Equation (15) derived above has simple form and, being directly related to the quantum and classical Newton's equations of motion, allows straightforward analysis and interpretation of its solutions.

The TDSE (15) is nonlinear due to the friction term dependent on the evolving wavefunction. The time-evolution of $\psi^*(x,t)$ is

$$-\iota\frac{\partial}{\partial t}\psi^*(x,t) = (\hat{H} + \gamma(S - \langle S\rangle))\psi^*(x,t). \tag{17}$$

The wavefunction dissipates energy and evolves into the ground state of the system, similar to the imaginary time evolution with the quantum Boltzmann operator, i.e., to thermal cooling of a wavefunction.[16,17] Unlike the imaginary time evolution, friction does not change the wavefunction norm, $N = \langle\psi(t)|\psi(t)\rangle$:

$$\frac{dN}{dt} = \iota\int\psi[\hat{H}\psi^* + \gamma(S - \langle S\rangle)\psi^*]dx - \iota$$

$$\times\int\psi^*[\hat{H}\psi + \gamma(S - \langle S\rangle)\psi]dx = 0. \tag{18}$$

The total energy of the system, E, decreases with time until the systems comes to rest. Note that with the definition of Eq. (14) the explicit contribution of the friction term to the total energy is zero,

$$E = \langle\psi(t)|\hat{H} + \gamma(S - \langle S\rangle)|\psi(t)\rangle = \langle\psi(t)|\hat{H}|\psi(t)\rangle. \tag{19}$$

Differentiation of Eq. (19) with respect to time gives

$$\frac{dE}{dt} = \iota\int\psi^*(\hat{H} + \gamma(S - \langle S\rangle))\hat{H}\psi dx - \iota$$

$$\times\int\psi^*\hat{H}(\hat{H} + \gamma(S - \langle S\rangle))\psi dx = \iota\gamma\langle[S,\hat{H}]\rangle. \tag{20}$$

Integration by parts simplifies the expression to

$$\frac{dE}{dt} = -\frac{\gamma}{m}\int\left(\frac{\partial S}{\partial x}\right)^2|\psi|^2 dx = -\frac{\gamma\langle p^2\rangle}{m}. \tag{21}$$

Equation (21) gives a simple visualization of the wavefunction dynamics with friction. Decrease of the total energy due to friction is proportional to the classical kinetic energy of the system, $K = \langle p^2\rangle/(2m)$, associated with the momenta of quantum trajectories p defined by Eq. (8). The total energy stops changing once the systems comes to rest, i.e., the quantum trajectories do not move: $p = 0$. Formally, any eigenstate is characterized by the zero momentum p, however application of the nonlinear friction term to a non-eigenstate wavefunction adds a mixture of eigenstates at each timestep until the lowest energy state is reached.

Let us verify that dynamics with friction reduces a general wavefunction to the ground state (for symmetric $V(x)$, to the lowest energy state of the same symmetry as $\psi(x,0)$). Consider the short-time evolution of a wavefunction initially

comprised of the ground state, ϕ_0, and the first excited state, ϕ_1, of a harmonic oscillator of unit mass and frequency,

$$\hat{H} = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + \frac{x^2}{2}, \hat{H}\phi_n = \frac{1}{2}\left(n + \frac{1}{2}\right)\phi_n, n = 0, 1. \quad (22)$$

The initial wavefunction has a small contribution of ϕ_1 added to ϕ_0,

$$\psi(x, 0) = \frac{1}{\sqrt{1 + d^2}}(\phi_0(x) + \iota d\phi_1(x)). \quad (23)$$

The phase of $\psi(x, 0)$ is ($\Im$ denotes the imaginary part)

$$S(x, 0) = \int \Im\left(\psi^{-1}\frac{\partial}{\partial x}\psi\right) dx = \arctan(d\sqrt{2}x). \quad (24)$$

The constant of integration may be left unspecified because $\langle S \rangle$ is subtracted from S in Eq (15). For the wavefunction and phase given by Eqs. (23) and (24), $\langle S \rangle = 0$. Expanding the time-dependent solution to Eq. (15) through the first orders in time increment t and coefficient d and projecting the result onto the eigenstates ϕ_0 and ϕ_1 we find that the relative population of the excited state ϕ_1,

$$\eta(t) = \frac{|\langle\phi_1|\psi(x, t)\rangle|^2}{|\langle\phi_0|\psi(x, t)\rangle|^2} = d^2(1 - 2\gamma t) + O(d^2 t^2) \quad (25)$$

is lower than its initial value, $\eta(0) = d^2$. Therefore, in the course of dynamics with friction a wavefunction evolves to the lowest energy eigenstate (of the symmetry of the system if applicable).

III. EXAMPLES

A. Dynamics of a Gaussian wavepacket with friction

The dynamics of a Gaussian wavepacket with friction has analytical solution, particularly simple for a coherent Gaussian wavepacket evolving according to Eq. (15) in the potential $V = w^2 x^2/2$ for particle $m = 1$. The wavefunction has the following form:

$$\psi(x, t) = \left(\frac{w}{\pi}\right)^{1/4} \exp\left(-\frac{w}{2}(x - q_t)^2 + \iota p_t(x - q_t) + \iota s_t\right). \quad (26)$$

The time-dependence of the parameters q_t, p_t, and s_t is defined by the equations

$$\frac{dq_t}{dt} = p_t, \frac{dp_t}{dt} = -w^2 q_t - \gamma p, \frac{ds_t}{dt} = \frac{p_t^2}{2} - \frac{w^2 q_t^2}{2} - \frac{w}{2}. \quad (27)$$

The wavepacket phase is

$$S(x, t) = p_t(x - q_t) + s_t, \quad (28)$$

and the friction term in TDSE is

$$\gamma(S - \langle S \rangle) = \gamma p_t(x - q_t). \quad (29)$$

Taking for simplicity $w = 1$ for general initial wavepacket conditions $\{q_0, p_0\}$ in case of low friction,

$$\gamma < 2, \gamma^\dagger = \sqrt{4 - \gamma^2}, \quad (30)$$

q_t exhibits oscillations as it evolves toward the bottom of the potential well,

$$q_t = \frac{q_0}{\gamma^\dagger}e^{-\gamma t/2}\left(\gamma \sin(\gamma^\dagger t/2) + \gamma^\dagger \cos(\gamma^\dagger t/2)\right)$$
$$+ \frac{2p_0}{\gamma^\dagger}e^{-\gamma t/2}\sin(\gamma^\dagger t/2). \quad (31)$$

In case of high friction,

$$\gamma > 2, \gamma^\dagger = \sqrt{\gamma^2 - 4}, \quad (32)$$

the center of the wavepacket q_t slides toward the bottom of the well without changing sign,

$$q_t = \frac{q_0}{\gamma^\dagger}e^{-\gamma t/2}\left(\gamma \sinh(\gamma^\dagger t/2) + \gamma^\dagger \cosh(\gamma^\dagger t/2)\right)$$
$$+ \frac{2p_0}{\gamma^\dagger}e^{-\gamma t/2}\sinh(\gamma^\dagger t/2). \quad (33)$$

For $\gamma = 2$,

$$q_t = e^{-t}(q_0(1 + t) + p_0 t), \quad (34)$$

convergence of q_t to the minimum of the well and of the wavepacket energy to the ZPE value is the fastest.

Time-dependence of the total energy and of the average position for an initially displaced coherent wavefunction ($q_0 = 1$, $p_0 = 0$) for several values of the friction parameter are shown on Fig. 1. Fig. 2 shows positions of the quantum trajectories as functions of time for low and high friction regime: the trajectories drift toward stationary values with or without oscillations, respectively. The positions of the trajectories become stationary in consistency with the quantum trajectory perspective on dynamics. For an eigenstate, the quantum and classical potentials add up to a constant, thus the total force
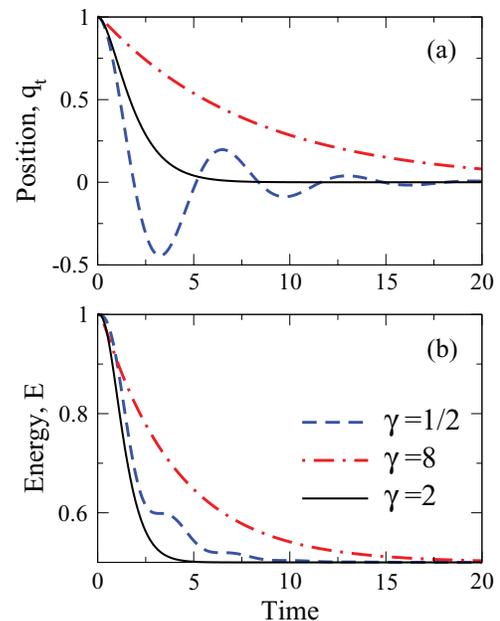

FIG. 1. Gaussian dynamics with friction in the parabolic well: position of the center of the wavepacket (a) and its total energy (b) as functions of time. Results are shown for the regimes of low ($\gamma = 1/2$, blue dashed) high ($\gamma = 8$, red dotted-dashed) friction and for the regime of exponential convergence ($\gamma = 2$, black solid line) on both panels.
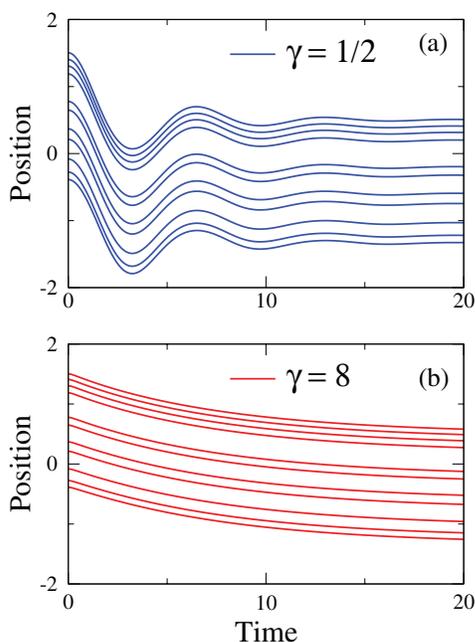
FIG. 2. Gaussian dynamics with friction in the parabolic well: positions of quantum trajectories as functions of time in the regimes of low ($\gamma = 1/2$ on panel (a)) and high ($\gamma = 8$ on panel (b)) friction.

acting on the trajectories is zero, and the wavefunction phase is independent of the coordinates, thus the trajectory momenta are equal to zero.

Let us remark at this point that the TDSE with friction of Eq. (15) does not include thermal fluctuations due to interaction of the environment with the system, therefore describing dynamics of a pure quantum state. The hydrodynamic description of quantum densities in phase space, which includes full dissipation (friction and random force), has been given in Ref. 18. For a coherent state of a harmonic oscillator, the hydrodynamic phase space formulation yields trajectories shown for example on Fig. 4 in Ref. 18, equivalent to those of Fig. 2.

B. Dynamics with friction in the double well

Dynamics in a double well, which is often used as a model potential for the reaction coordinate coupled to bath modes, is implemented numerically. Equation (15), where the friction term is a time-dependent function, has been solved using the split-operator propagator and an equidistant grid.[19,20] The reconstruction of the wavefunction phase from $\psi(x, t)$ adds certain complications. The wavefunction phase defined by Eq. (16) is a discontinuous function, which should be made continuous. We use the following expression to determine $S(x, t)$:

$$S(x, t) = \arctan\left(\frac{\Im(\psi(x, t))}{\Re(\psi(x, t))}\right), \quad (35)$$

and remove the "jumps" by shifting $S(x, t)$ by $\pm\pi$ if the values for two adjacent grid points are discontinuous (if the values differ by more than ± 2, in the example below). The overall additive constant in $S(x, t)$ is left unspecified since it is cancelled once the $\langle S \rangle$ is subtracted from $S(x, t)$ in Eq. (15).
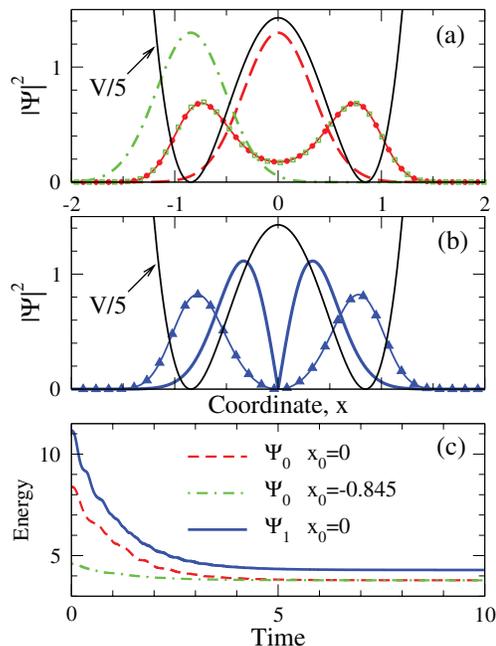

FIG. 3. Dynamics with friction in the double well V given by Eq. (36). (a) Initially Gaussian functions centered on a barrier (red dashed) or in the left well (green dotted-dashed) evolve to the ground state; the final wavefunction densities are shown with red circles and green squares, respectively. (b) Symmetric initial wavefunction with one node (blue solid line) evolves to the excited state (blue triangles). The potential, divided by a factor of 5 is shown on panels (a) and (b). (c) Time-dependence of the total energy for the wavefunctions shown on (a) and (b).

Besides the discontinuity issue, the reconstructed $S(x, t)$ is inaccurate in the regions of very low wavefunction amplitude. This problem is mitigated by the fact that in Eq. (15) the friction term multiplies ψ, but the errors may accumulate with time.

We have considered the double-well potential of Ref. 21 used in a number of subsequent numerical studies,

$$V(x) = x^2(ax^2 - b) + \frac{b^2}{4a}. \quad (36)$$

The parameter values are $a = 14$ $E_h a_0^{-4}$ and $b = 20$ $E_h a_0^{-2}$; the particle mass is $m = 1$ a.u. Fig. 3 presents some results for the propagation with friction coefficient $\gamma = 1$, carried out for 5000 time-steps to the final time of $t = 10$ a.u. The grid of 1024 points spanned the range of 6 a_0. The considered initial wavefunctions are

$$\psi_0(0) = N_0 \exp\left(-\alpha(x - x_0)^2\right), \quad (37)$$

$$\psi_1(0) = N_1 \exp\left(-\alpha(x - x_0)^2\right)(1 - 2\alpha(x - x_0)). \quad (38)$$

The value for the width parameter, $\alpha = 4.47$ a_0^{-2}, is defined by the frequency of the wells. Fig. 3(a) shows the initial and final wavefunction densities for $\psi_0(0)$ centered on the barrier top, at $x_0 = 0$, and in the left "reactant" well, at $x_0 = -0.845$ a_0. The final densities are the same for both values of x_0 and describe the ground state of this system. The initial and final densities for the initial state with the node, $\psi_1(0)$, centered at the barrier top is shown on Fig. 3(b). In this symmetric setup, the final density describes

TABLE I. Calculation of the ground state of the asymmetric double well given by Eq. (39). The first column lists the asymmetry parameter c. E_{DVR} is the lowest energy obtained from the Hamiltonian matrix diagonalization. E_γ is the wavefunction energy at $t = 10$ a.u. obtained from dynamics with friction $\gamma = 1$. ΔV is the difference between the two minima of the potential. P_{RHS} is the probability of a particle in its ground state to be in the right well (in the positive half-plain).

c [$E_h a_0^{-1}$]	E_{DVR} [E_h]	E_γ [E_h]	ΔV [E_h]	P_{RHS}
0	3.7830	3.7833	0	0.5000
0.1	3.7734	3.7732	0.1690	0.3701
0.25	3.7274	3.7277	0.4226	0.2227
0.5	3.6003	3.6006	0.8451	0.1042
1.0	3.2769	3.2773	1.6901	0.0388

the first excited state of odd symmetry. The total energies for the wavefunctions, shown on Fig. 3(c) as functions of time, converge to the appropriate energy eigenvalues. The wavefunction norms remain equal to 1 in the course of propagation. We have numerically checked that the shifted $\psi_1(0)$ ($x_0 \neq 0$) converges to the ground state confirming the analysis of Eqs. (22)–(25).

Let us introduce an asymmetry to the double well potential by adding a linear term to the potential of Eq. (36),

$$V(x) = x^2(ax^2 - b) + \frac{b^2}{4a} + cx. \tag{39}$$

The purpose of the asymmetric well example is to examine the effect of friction, not to present the dynamics with friction as a way of finding eigenstates. The effect of the asymmetry parameter, whose values were set to $c = \{0.1, 0.25, 0.5, 1.0\}$ $E_h a_0^{-1}$, on the ground state energy is shown in Table I. The difference between the two minima of the potential and the probability for a particle in its ground state to be in the right half-plain, defined by Eq. (40), are listed in the last two columns. This probability changes from 37% to 4% as the asymmetry increases. The initial wavefunction, defined by Eq. (37) with parameters $\alpha = 1$ a_0^{-2}, $x_0 = 0$, has been evolved up to $t = 10.0$ a.u. with the friction coefficient of $\gamma = 1$. The propagation time was sufficiently long for $\psi(x,t)$ to evolve to the ground state of the system. The final wavefunctions are shown on Fig. 4 with symbols placed on the lines showing the exact eigenfunctions obtained using a conventional discrete variable representation.[22] The agreement of the ground state functions and energies (Table I) obtained from dynamics with friction with exact results is very good (four digits). We note, however, that convergence of the wavefunction to the ground state can be slow and numerically unstable if the friction coefficient is high (at least, in our simple numerical implementation). This is especially noticeable when the eigenstate is highly asymmetric or if the ground/excited state splitting is very small.

As mentioned above, the double well often serves as a model potential for the reaction coordinate coupled to the bath modes of motion. However, without this coupling dynamics in the reactive degrees of freedom cannot properly describe a reactive process or rearrangement, since oscillations of the wavefunction density persist in time. Friction acting on a characteristic for the process timescale, may serve as a
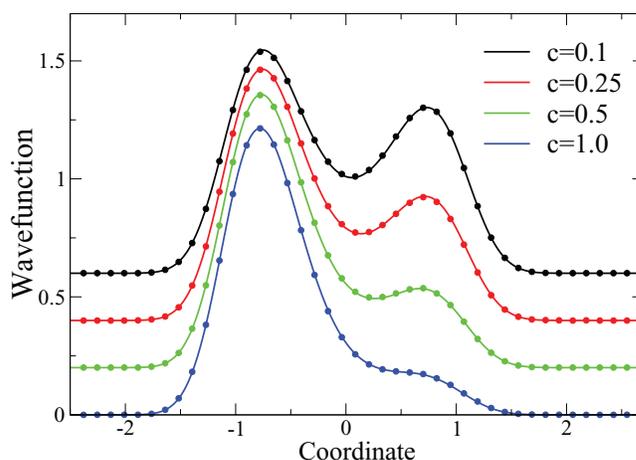

FIG. 4. Dynamics with friction in the asymmetric double well given by Eq. (39) for the asymmetry parameter values $c = \{0.1, 0.25, 0.5, 1.0\}$. The ground eigenstates obtained using Hamiltonian matrix diagonalization are shown with lines. The wavefunctions obtained from dynamics with friction $\gamma = 1$ at $t = 10$ a.u. are shown with circles. The curves are shifted in the vertical axis by 0.2 for clarity.

simple way of modeling a completed reaction (not rigorously, since in the limit of infinite time the wavefunction decays to the ground state), of estimating isotope effects, barrier parameters, etc.

Figures 5 and 6 illustrate this point. Panels (a, c, e) of Fig. 5 show the reaction probabilities,
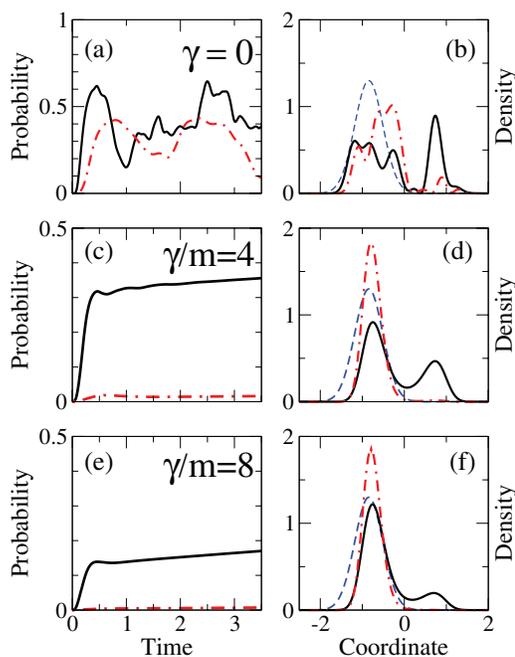
$$P(t) = \int_0^\infty |\psi(x,t)|^2 dx, \tag{40}$$

FIG. 5. Reaction probabilities in the double well potential given by Eq. (36). Panels (a), (c), and (e) show the probabilities $P(t)$ of Eq. (40) for $\gamma = 0, 4, 8$ as functions of time. Panels (b), (d), and (f) show the wavefunction densities $|\psi(x,t)|^2$ at $t = 5$ a.u. for $\gamma = 0, 4, 8$. On all panels results for the hydrogen, $m = 1$, are shown with black solid line, results for the deuterium, $m = 2$, with the red dotted-dashed. Blue dashed line indicates $|\psi(x,0)|^2$ for the $m = 1$ calculations.
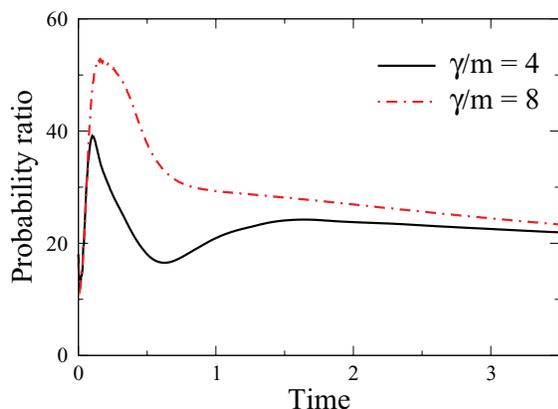
FIG. 6. The ratio of the reaction probability for the hydrogen ($m = 1$) to that of deuterium ($m = 2$) for the friction coefficients $\gamma/m = 4$ (solid line) and $\gamma/m = 8$ (dashed line).

for a particle initially localized in the left well in the course of dynamics without and with friction. On each panel, the initial wavefunction was defined by Eq. (37) for $x_0 = -0.845$ a_0 and α describing a Gaussian approximation to the eigenstate of the left well for $m = 1$ (hydrogen) and $m = 2$ (deuterium). Panels (b, d, f) of Fig. 5 show the corresponding wavefunction densities at $t = 3.5$ a.u. Without the friction, the oscillations in probability persist in time making it impossible to analyze, for example, the isotope effect. With the friction included some general estimates can be made. Averaging the probabilities over the second half of the time interval shown on Fig. 6, the isotope effect on reactivity defined as $\kappa = P_H/P_D$, is $\kappa = 23.02 \pm 0.63$ and $\kappa = 25.37 \pm 1.23$ for the friction coefficients of $\gamma/m = 4$ and $\gamma/m = 8$, respectively. The uncertainty of the estimated κ is 3% and 5%. The two values of κ are close to each other in this case.

IV. CONCLUSIONS

We have provided a derivation of the time-dependent Schrödinger equation with friction from the quantum trajectory formulation of TDSE, based on the analogy between equations of motion for the classical and quantum trajectories. The friction term depends on the wavefunction phase. The resulting TDSE is nonlinear, norm-conserving, and the total energy has a simple time-dependence: it decays to the lowest energy of the appropriate symmetry (if applicable), and the rate of decay is proportional to the average kinetic energy of the quantum trajectories. Unlike the Langevin and master equations incorporating temperature and describing evolution of mixed quantum states,[12,18,23] the TDSE with friction given of Eq. (15) does not contain the fluctuation (random force) term. It has classical rather than statistical mechanics as its classical limit—defined as the quantum potential set to zero—and describes pure quantum states. The friction term (with positive friction constant γ) introduces phenomenological irreversible energy loss from the system to the environment. At infinite time, a wavefunction undergoing dynamics with friction evolves into the ground state of the system. When considered at finite times relevant to reaction processes the TDSE with friction may be useful for the development of simple

models for reactions in condensed phase, with the quantum trajectory perspective providing an intuitive visualization of dynamics.

The numerical implementation of the friction term within a conventional grid-type formulation of Eqs. (15) and (16) is in general challenging because the phase of the wavefunction, $S(x, t) = \arg \psi(x, t)$ has to be made continuous, and errors may accumulate with time due to inaccuracies in the phase in the low density regions. We have used the most straightforward definition of extracting the wavefunction phase using inverse trigonometric functions, which required appropriate shifts beyond the range of the usual principal value. In many dimensions, this may become cumbersome, as it will be done dimension by dimension. Alternatively, one could solve equations of motion for the quantum trajectories with friction and compute the phase $S(x_t)$ along a quantum trajectory $\{x_t, p_t\}$ according to

$$\frac{dS(x_t)}{dt} = \frac{p_t^2}{2m} - (V + U)|_{x=x_t} - \gamma(S(x_t) - \langle S(x_t)\rangle), \quad (41)$$

or in the Eulerian frame-of-reference according to Eq. (13). If the time-propagation is based on the fast Fourier transform, one can also use ∇S computed in the momentum space to reconstruct a continuous S.

Conceptually, the most appealing solution would be to actually evolve the quantum trajectories and compute S from the Hamilton-Jacobi Eq. (41). Because of the continuity equation of the probability density, exact quantum trajectories do not go into the regions of low density and the S changes in time continuously. Without the friction, the quantum trajectories are known to be numerically unstable[24,25] because of the singularities in the quantum potential U, defined in Eq. (7), near the wavefunction nodes. This behavior, formally a consequence of the polar form of the wavefunction Eq. (4), is a general feature of exact quantum trajectory dynamics. However, the friction has been shown[14] to stabilize the trajectory dynamics and may alleviate problems of implementation of Eq. (7) or of Eq. (35), or its equivalent forms, because the friction suppresses interference effects, i.e., the node development. In particular, the numerical methodology developed for the quantum hydrodynamics equations with artificial viscosity[26] should be well suited for solving the TDSE with friction.

To conclude, while the TDSE with friction does not include temperature, and thus does not fully describe two-way interaction with the environment, it may be useful for the development of simple models for reactions in condensed phase, with the quantum trajectory perspective providing an intuitive visualization of dynamics.

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