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Quantum dynamics with Bohmian trajectories: energy conserving approximation to the quantum potential

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Abstract

The Schrödinger equation can be solved in terms of quantum trajectories evolving under the influence of quantum potential. We present a method of computing the quantum potential by approximating the non-classical component of the momentum operator, such that the total energy of a closed system is conserved. A case of special interest is *linearized quantum force* with analytical parameters and correct average value. This method is computationally cheap and exact for locally quadratic potentials. We illustrate its efficiency and accuracy by computing the photodissociation spectrum of ICN and the wavepacket transition probability for H_3 in two dimensions.
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Description of quantum mechanical effects within trajectory-based approaches is highly desirable for multi-dimensional problems of nuclear dynamics. Formulation of the Schrödinger equation in terms of *quantum trajectories* [1] serves as a convenient framework to achieve this goal. The wavefunction of a system is represented in a set of ‘particles’ that move according to the classical equation of motion and carry along certain density. The non-local quantum character enters this formulation through the *quantum potential*, which depends on the density and its derivatives. Quantum potential governs the dynamics of the ‘parti-

cles’ along with the classical external potential. Since solution of the Schrödinger equation is based on trajectories, rather than grid points, the scaling bottleneck is avoided. In the last few years, several practical ways of using quantum trajectories have been suggested [2–8]. Application to several model multi-dimensional problems, where a small number of trajectories was used, is encouraging. However, for general problems accurate implementation of this formulation with rapidly varying quantum potential might be very tedious. Illustrative examples of complicated quantum trajectories can be found in [9,10], where trajectories are used as an interpretive tool.

Recently, we have introduced the idea of using approximate quantum potentials [11,12] that provide practical and accurate description of quantum effects in semiclassical systems. With approximate

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quantum potentials derived from the global fit of density we could balance numerical effort vs. level of description of quantum effects by choosing the number of fitting Gaussian functions. Complete basis of fitting functions gives exact quantum potential and full quantum description, while zero functions gives a classical limit. An intermediate number of functions can be considered as a semiclassical description with a single fitting function reproducing exact quantum dynamics of a Gaussian wavepacket in a locally quadratic potential. In principle, the accuracy of the fit controls the degree in which semiclassical description approaches exact quantum dynamics. This was illustrated for one-dimensional scattering on a barrier for which accurate transmission probabilities were obtained. However, the total energy of the system was not conserved and the non-linear fitting was not straightforward. In this Letter, we provide a different approach to determine approximate quantum potential. This new method, based on the optimal fit within a trial function to the log-derivatives of density, which is a ‘non-classical’ momentum, *conserves total energy* in a closed system. A simple implementation with a linear trial function described below is rigorous, free of adjustable parameters and cheap. Optimal parameters are found from the first and second moments of distribution of trajectories, whose weights are constant in time. The resulting quantum force is linear. Procedure is formulated solely in terms of summation over trajectories. The new method provides exact quantum description for the quadratic potential problem, as do successful approximate time-dependent methods, and is capable of describing quantum effects for general semiclassical systems. As an illustration we calculate the photodissociation spectra of ICN and the probability of the wavepacket transmission for H_3 in two dimensions using a few hundred trajectories.

Let us consider a quantum system described in N -dimensional Cartesian coordinates with the Hamiltonian $\hat{H} = \hat{\mathbf{P}}^\dagger M^{-1} \hat{\mathbf{P}}/2 + V$, where M is a diagonal matrix of masses, $\{M_{nn}\} = m^{(n)}$ (super-script indexes are used to label dimensions; sub-script indexes are used to label trajectories). Substituting $\psi(\vec{x}, t) = A(\vec{x}, t) \exp(\frac{i}{\hbar} S(\vec{x}, t)) = \sqrt{\rho(\vec{x}, t)} \exp(iS(\vec{x}, t)/\hbar)$ where amplitude $A(\vec{x}, t)$ and phase

$S(\vec{x}, t)$ are real functions, into the time-dependent Schrödinger equation and making a transformation into the Lagrangian frame of reference, one obtains

$$\frac{dS(\vec{x}, t)}{dt} = \frac{\vec{p}^T M^{-1} \vec{p}}{2} - V - U, \quad (1)$$

$$\frac{d\rho(\vec{x}, t)}{dt} = -\vec{\nabla} \cdot \vec{v} \rho(\vec{x}, t), \quad (2)$$

where U ,

$$U = -\frac{\hbar^2}{2} \frac{\vec{\nabla}^T M^{-1} \vec{\nabla} A(\vec{x}, t)}{A(\vec{x}, t)}, \quad (3)$$

is a non-local time-dependent quantum potential, and momentum, $\vec{p} = M\vec{v} = \vec{\nabla} S(\vec{x}, t)$ is defined as in classical mechanics. Eq. (1) is the Hamilton–Jacobi equation describing dynamics of a trajectory in the presence of a classical potential V and a quantum mechanical potential U . Position and momentum of a trajectory, $\vec{x} = \vec{x}(t)$ and $\vec{p} = \vec{p}(t)$, are defined by Hamilton’s equations of motion.

The difference between action of a quantum operator \hat{P} on a wavefunction and that of \vec{p} is

$$(\hat{P} - \vec{p})\psi(\vec{x}, t) = -i\hbar A(\vec{x}, t)^{-1} \vec{\nabla} A(\vec{x}, t) \psi(\vec{x}, t).$$

The result, $-i\hbar \vec{\nabla} A(\vec{x}, t)/A(\vec{x}, t)$, is imaginary and on the order of \hbar . It can be interpreted as a non-classical component of \hat{P} vanishing in the $\hbar \rightarrow 0$ limit, while \vec{p} is its classical component. The non-classical momentum is proportional to the curvature of the amplitude or density and this is the object that we will use below,

$$\vec{r}(\vec{x}, t) = 2 \frac{\vec{\nabla} A(\vec{x}, t)}{A(\vec{x}, t)} = \frac{\vec{\nabla} \rho(\vec{x}, t)}{\rho(\vec{x}, t)}. \quad (4)$$

The quantum potential $U(\vec{x}, t)$, which is on the order of \hbar^2 , can be considered as a non-classical contribution to the kinetic energy operator, though it enters equations of motion on equal footing with $V(\vec{x})$. We will use $\hbar = 1$ below.

Eq. (2) is a continuity equation for the density, which is normalizable and conserved in a closed system, $\int \rho(\vec{x}, t) d\vec{x} = 1$. Initial density $\rho(\vec{x}, 0)$ is discretized in a set of ‘particles.’ A certain amount of density within a volume element $\delta\vec{x}_i(t)$ is

associated with the i th trajectory. This quantity – the weight of a trajectory $w_i = \rho(\vec{x}_i)\delta x_i$ – remains constant in the course of dynamics [12], allowing an easy evaluation of average values without reconstruction of $\psi(\vec{x}, t)$. Using constant weights and conservation of the total energy in a closed quantum system, we obtain an important property of quantum potential

$$\frac{dE}{dt} = \int \frac{\partial U(\vec{x}, t)}{\partial t} \rho(\vec{x}, t) d\vec{x} = 0. \quad (5)$$

Another property of quantum potential following from its definition (3) is that it exerts *zero* average force. As follows from Eq. (3), quantum potential does not depend on the amplitude of a wavefunction, only on its curvature. Accurate numerical evaluation of derivatives needed for quantum potential in the low amplitude regions of space becomes problematic, when fitting or interpolating $\rho(\vec{x}, t)$. Therefore, we will look for the optimal approximation to $\bar{r}(\vec{x}, t)$ rather than to $\rho(\vec{x}, t)$. Each component is approximated by a function $g^{(n)}(\vec{x}, \vec{s})$, that is a specified function of \vec{x} with time-dependent parameters \vec{s} . Vector \vec{s} is a combined list of parameters of all $g^{(n)}$ s. In general, the dimensionality K of \vec{s} is not related to the dimensionality N of \vec{x} . For each dimension we define a functional, which after integration by parts and discretization in terms of trajectories form can be expressed as

$$\begin{aligned} I^{(n)} &= \int \left(r^{(n)}(\vec{x}, t) - g^{(n)}(\vec{x}, \vec{s}) \right)^2 \rho(\vec{x}, t) d\vec{x} \\ &\approx I_0^{(n)} + \sum_i w_i \left(2 \frac{\partial g^{(n)}(\vec{x}_i, \vec{s})}{\partial x^{(n)}} + g^{(n)}(\vec{x}_i, \vec{s})^2 \right), \end{aligned} \quad (6)$$

where $I_0^{(n)}$ abbreviates a term that does not depend on \vec{s} . Neither $\rho(\vec{x}, t)$ nor its derivatives are needed for determination of approximate $\bar{r}(\vec{x}, t)$. The optimal values of \vec{s} are found from minimization of a functional I ,

$$I = \sum_{n=1}^N \frac{I^{(n)}}{m^{(n)}}, \quad (7)$$

by solving a system of K equations,

$$\frac{\partial I}{\partial s^{(k)}} = 0, \quad k = 1, \dots, K. \quad (8)$$

The mass factors were introduced in order to relate I to the corresponding quantum potential. Once we solve Eq. (8), approximate quantum potential can be expressed in terms of $g^{(n)}(\vec{x}, \vec{s})$

$$\begin{aligned} \tilde{U} &= - \sum_{n=1}^N \frac{1}{8m^{(n)}} \left(g^{(n)}(\vec{x}, \vec{s})^2 + 2 \frac{\partial g^{(n)}(\vec{x}, \vec{s})}{\partial x^{(n)}} \right), \\ \langle \tilde{u} \rangle &= - \frac{1}{8} \left(I - \sum \frac{I_0^{(n)}}{m^{(n)}} \right). \end{aligned} \quad (9)$$

If \tilde{U} is evaluated at the optimal values of \vec{s} defined by Eq. (8) and used as quantum potential, the total energy of the system is conserved, since Eq. (5) is satisfied

$$\begin{aligned} \int \frac{\partial \tilde{U}}{\partial t} \rho(\vec{x}, t) d\vec{x} &= \sum_{k=1}^K \int \frac{\partial \tilde{U}}{\partial s^{(k)}} \rho(\vec{x}, t) d\vec{x} \frac{ds^{(k)}}{dt} \\ &= - \frac{1}{8} \sum_{k=1}^K \frac{\partial I}{\partial s^{(k)}} \frac{ds^{(k)}}{dt} = 0. \end{aligned} \quad (10)$$

The simplest functional form of $g^{(n)}$ s is a monomial in \vec{x} derivable from the Gaussian density. Introducing a symmetric matrix of the widths parameters A and a vector \vec{x}_0 , where the center of a Gaussian density is located,

$$\rho(\vec{x}, t) \approx \left(\frac{\det(A)}{\pi} \right)^{N/2} \exp \left(- (\vec{x} - \vec{x}_0)^T A (\vec{x} - \vec{x}_0) \right). \quad (11)$$

Note here, that we do not restrict the actual density to a Gaussian. We simply look for the best linear approximation of $\bar{r}(\vec{x}, t)$ as outlined above, that is consistent with a Gaussian density and results in a linearized quantum force (LQF). If Eq. (11) becomes too inaccurate, matrix elements of A and the resulting \tilde{U} go to zero and dynamics becomes purely classical. With $g^{(n)}$ s derived from Eq. (11) the functional (7) becomes

$$\begin{aligned} I(\vec{s}) &= \int \left((\vec{x} - \vec{x}_0)^T A^T M^{-1} A (\vec{x} - \vec{x}_0) \right. \\ &\quad \left. - \text{Tr}(AM^{-1}) \right) \rho(\vec{x}, t) d\vec{x}, \end{aligned} \quad (12)$$

up to a term independent on parameters. In this case, the list of parameters \vec{s} is comprised of $N(N+1)/2$ elements of A and of N elements of \vec{x}_0 . Minimization of this functional gives a unique solution,

$$\vec{x}_0 = \int \vec{x} \rho(\vec{x}, t) d\vec{x}; \quad A = \frac{1}{2} B^{-1}, \quad (13)$$

where B is the matrix of the second moments $b_{ij} = \int (x^{(i)} - x_0^{(i)})(x^{(j)} - x_0^{(j)}) \rho(\vec{x}, t) d\vec{x}$. These approximate quantum potential and quantum force have several attractive features. From the point of view of implementation: (i) optimization has a simple analytical solution; (ii) the first and second moments of the density distribution in terms of trajectories are found as a summation over trajectories, $\vec{x}_0 = \sum_i w_i \vec{x}$ and $b_{ij} = \sum_i (x^{(i)} - x_0^{(i)})(x^{(j)} - x_0^{(j)}) w_i$; (iii) this is the only addition to classical trajectory propagation. From the theoretical point of view: (i) time-evolution of a Gaussian wavepacket in a locally quadratic potential is solved exactly (including correlated density); (ii) the total energy is conserved; the average quantum force is zero; (iii) since \tilde{U} is based on approximation of the non-classical momentum, which is small in the semiclassical limit, we expect that it can adequately describe dominant quantum effects.

As an illustration we applied the LQF approximation to a benchmark test for nuclear dynamics – calculation of the transmission probability for collinear H_3 system, and to photodissociation of a collinear ICN, which is also a standard model for evaluation of approximate propagation methods. The purpose of our testing is twofold: to check the numerical efficiency of LQF and to probe the quality of description it provides.

The hydrogen exchange in the collinear H_3 system, $H_A + H_B H_C \rightarrow H_A H_B + H_C$, is a standard test problem in nuclear dynamics. It is a stringent test for approximate methods, since in a system of light nuclei the quantum effects are significant. As a first application, we compute the transition probability of a wavepacket as a function of its initial kinetic energy in the translational degree of freedom. The system is described in Jacobi coordinates where the kinetic energy is diagonal. The details on the Hamiltonian, coordinates and po-

tential surface are the same as in [13]. We start by defining a wavefunction $\psi(0) \sim \exp(-\alpha_1(R - R_0)^2 - \alpha_2(r - r_0)^2 + i p_0(R - R_0))$, where r is the $H_B H_C$ distance and R is the translational degree of freedom – the distance between H_A and the diatomic. $\psi(0)$ is placed in the reactant region of the potential surface. It is a wavepacket incoming toward the interaction region. Values of the parameters in atomic units (the unit of time is 918 a.u.) are $R_0 = 4.5$, $r_0 = 1.3$, $\alpha_1 = 4$, $\alpha_2 = 9$ and $p_0 = [-15, -1]$. The initial conditions for quantum trajectories are chosen on a rectangular grid. A cut-off is imposed on trajectory weights, $w_i > 10^{-5}$. The trajectories are either transmitted to the reactant region or reflected back into the product region in a course of the dynamics under the influence of a classical and quantum potentials. The transmission probability is a sum over trajectories in the product region $P = \sum_i w(i)$ at time t_{\max} when the bifurcation of the wavepacket is complete (completed in 180 steps at $t_{\max} = 1.8$). We obtain converged probabilities for a range of p_0 by propagating 941 trajectories for each value of p_0 . The run-time of a single wavepacket propagation is less than a second. The results are compared with the quantum mechanical calculations performed with the split-operator method [14] on the 128×128 grid and with the ‘classical’ quantum trajectories result, where quantum potential was set identically to zero. The comparison is presented on Fig. 1. The classical probabilities

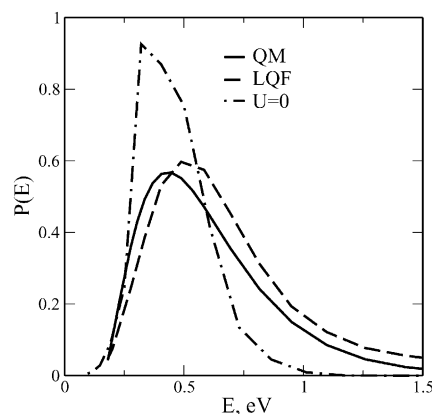


Fig. 1. Transmission P of a wavepacket for H_3 system as a function of initial energy E .

substantially differ from the quantum result. Presence of LQF accounts for the zero-point energy effect and gives spread in energy to the trajectories. LQF probabilities are in overall good agreement with the quantum results, which is encouraging since they are obtained, essentially, with the effort of classical propagation for a system with strong quantum effects.

The second example is photodissociation of ICN. We follow works of Brown and Heller [15] and Coalson and Karplus [16], where collinear ICN was treated within the Beswick–Jortner model [17]. A wavepacket representing an ICN molecule is excited by a laser from the ground to the excited electronic state, where it dissociates into I and CN. We use the Hamiltonian and the Jacobi coordinate system as described in [16]. An initial wavefunction $\psi(0) \sim \exp(-\alpha_1(y-y_0)^2 - \alpha_2(x-x_0)^2 + 2\alpha_{12}(y-y_0)(x-x_0))$ is defined as the lowest eigenstate of the ground electronic surface with zero momentum. The ground state potential is composed of two harmonic potentials in CN and CI stretches. Thus, $\psi(0)$ is a correlated Gaussian wavepacket in the Jacobi coordinates located on the repulsive wall of the excited surface. The photodissociation cross-section is computed from

the Fourier transform of the wavepacket auto-correlation function $C(t)$ as $\sigma(\omega) = \omega \Re(\int C(t) \exp(i\omega t) dt)$. For real $\psi(0)$ $C(t)$ can be expressed as a sum over trajectories

$$C(t) = \langle \psi(0) | \psi(t) \rangle = \langle \psi(t/2) | \psi(t/2) \rangle = \sum_i w_i \exp(2itS_i). \quad (14)$$

Calculation is performed for two values of the repulsion parameter describing direct dissociation (system I) and a predissociation (system II). The calculation set-up is similar to our first example. Trajectories, sampling $|\psi(0)|^2$, are assigned weights and zero initial momenta and phase. Propagation of 103 and 130 trajectories (for systems I and II, respectively) were sufficient to obtain the cross-sections shown in Fig. 2. For system I agreement between the exact quantum and LQF results is excellent for both $C(t)$ and $\sigma(\omega)$. For system II the wavepacket performs two CN oscillations before dissociating. Auto-correlation function and spectrum exhibit more structure. There is a difference in the third maximum of $C(t)$, which translates into a small negative error in the low-energy spectrum, that could be reduced by

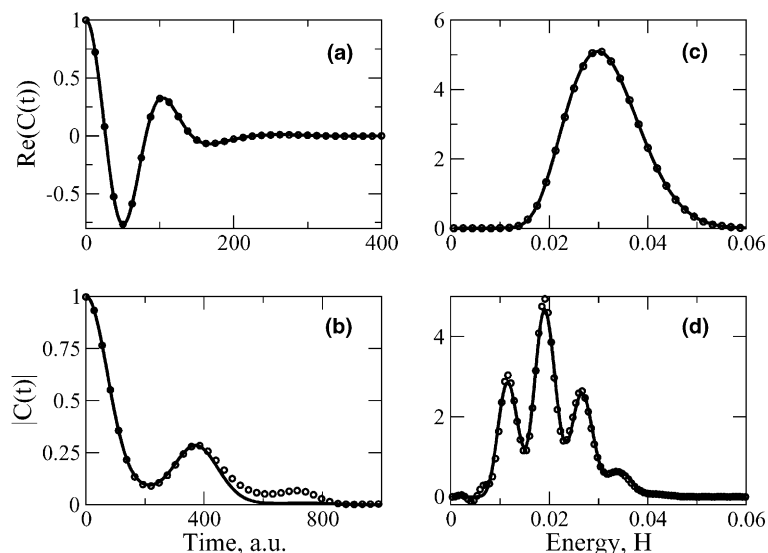


Fig. 2. Photodissociation cross-section of ICN: (a) and (b) show the correlation function for systems I and II; (c) and (d) show the cross-section for systems I and II. Quantum results are plotted with solid lines; LQF results are shown with circles.

damping of $C(t)$ or high-resolution spectral method [18,19]. The rest of the spectrum agrees with the quantum result very well.

In conclusion, we have described a new approach to approximation of quantum dynamics. Our method is based on trajectory propagation in the presence of approximate quantum potential and has full quantum mechanics as a limit of highly accurate quantum potential and many trajectories. Quantum potential is determined from the optimal fit of the non-classical component of the momentum operator, restricted by a trial function. This strategy generates quantum potential conserving the total energy. As its simplest implementation we use a linear trial function for the non-classical momentum in many dimensions, that produces LQF and can be related to an approximation of density in terms of a single correlated Gaussian. The equations for optimal parameters are solved analytically in terms of the first and second moments of the trajectory distribution and is formulated solely in terms of constant weights of trajectories. LQF is exact for a Gaussian wavepacket in any parabolic potential, and in addition to the energy conservation satisfies a criterion for the average quantum force to be zero. LQF can be viewed as a simple model of quantum dynamics. Its implementation is computationally cheap and approaches pure classical trajectory propagation, even in the limit of many dimensions. Our numerical applications to the collinear hydrogen exchange reaction and to the photodissociation of ICN suggest that LQF can accurately describe dominant quantum effects in semiclassical systems of heavy particles. Future multi-dimensional applications will show if LQF is a viable model for molecular dynamics. Presented results, wavepacket transmission probability and

spectra, were extracted directly from the trajectory weights and phases. Efficient reconstruction of the wavefunction and calculation of arbitrary wavefunction overlaps without loss of accuracy is one of our future goals. More sophisticated trial functions are also of great interest, since they will provide a systematic way of going from classical to exact quantum dynamics.

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