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A Chebyshev expansion of hydrodynamical fields for ultrafast vibrational wave packet dynamics

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ABSTRACT

A computational method based on the Chebyshev polynomial expansion of the hydrodynamical fields is applied to the quantum trajectory modeling of the one-dimensional vibrational dynamics. The spatial derivatives of the fields are computed using the Chebyshev polynomial recursion, and they are subsequently used to numerically integrate the equations of motion for the fluid particles. The performance of the proposed algorithm is assessed via the comparison with the analytical solutions for the time evolution of a Gaussian wave packet on harmonic potential, and with the results of quantum wave packet propagation on an anharmonic potential. The scheme is found to provide an accurate representation of both the molecular density and the quantum potential, even if low-order truncated expansions are used. The quantum trajectory propagation using the Chebyshev expansion method yields results in close agreement with the corresponding benchmarks, regarding both the time-dependent molecular distributions and the computed observables.

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1. Introduction

The emergence and the subsequent development of time-resolved spectroscopic techniques have triggered, during the last decades, a large number of experimental and theoretical investigations of dynamical processes at the molecular scale [1,2]. These investigations allow the identification of the mechanisms of fundamental physical and chemical phenomena, to elucidate the energy redistribution pathways and to translate the experimental signals into an explicit picture of the underlying atomic motion. The research on time-dependent processes at the microscopic level is also stimulated by the possibility to use the insight provided by these studies in the design of novel nanoscale devices, or to achieve the long-endeavored goal to steer chemical reactions in specific directions.

Quantum mechanical phenomena are at the essence of any first-principle description of the microscopic structure of matter. A variety of phenomena such as particle delocalization and interference, tunneling, non-adiabatic transitions, geometric phases, etcetera, are ubiquitous in the theoretical modeling of the structural and dynamical properties of atomic and molecular systems. In particular, time-dependent wave packet propagation schemes have been extensively used in the study of numerous dynamical problems in chemical physics [3,4]. Several numerical techniques have been developed to tackle the quantum molecular dynamics. Typically, those methods make use of standard bases or single variable representation schemes [5–7], and they become computationally very demanding for systems with many dimensions. Therefore, they are unsuitable for systems with more than a few atoms. A possible route to sidestep the exponential scaling of the computational cost of rigorous quantum mechanical calculations as the system size increases, is the development of alternative methodologies in which a different set of equations is solved (rather than solving the Schrödinger equation explicitly). To this purpose, significant effort has been devoted to include quantum effects in trajectory-based approaches (e.g., semiclassical initial value representations) [8–10].

The introduction of the quantum trajectory method (QTM) by Lopreore and Wyatt [11] lead to a renaissance of the interest in trajectory-based formulations of quantum mechanics. Both the time-independent [12–14] and the time-dependent [15–19] versions of the Schrödinger equation can be solved using quantum trajectories. The method can be regarded as a numerical implementation of the Madelung's or hydrodynamical formulation, where the time-dependent Schrödinger equation is rewritten as a set of Euler equations of a fluid (i.e., the equation of continuity

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and the conservation of momentum). Within this formulation, the wave function is represented as a set of "fluid particles" whose position and momenta evolve according to Newton-like equations of motion (EOM). The information of the probability amplitude and the phase of the wave function is carried along these trajectories, and the state vector can be synthesized at any point in time from these data. The non-local quantum effects enter in the dynamics through the quantum potential, which depend on the curvature of the wave function. It is responsible for every individual trajectory to feel the effect of the others at each time step. The quantum trajectory approach takes the advantage of the linear scaling, with the dimensionality of the system, of trajectory-based formulations (in contrast to the propagation of quantum wave packets via the standard basis or the discrete variable representations). However, the QTM may deviate from the linear scaling depending on the algorithm used to approximate the quantum potential.

In spite of the apparent simplicity of the hydrodynamical formulation, the numerical propagation of the quantum trajectories is very challenging. In the last two decades, rather robust computational methods to solve the quantum trajectory EOM (which combine numerical techniques like local least-square fit, regridding, implicit averaging, adaptative and moving grids, among others) have been developed, and those methods have been applied to a variety of problems such as model scattering reactions [11,20–25], non-adiabatic [26–28] and imaginary-time [29] dynamics. Furthermore, other applications to the modeling of quantum–mechanical phenomena explored the use of approximate expressions for the quantum potential [30,31], or the introduction of an artificial frictional force [32–34]. Such methodologies often lead to an over-smoothing of the actual quantum potential, which improves the stability of the integration of the EOM for the fluid particles at the expense of describing quantum mechanical effects only approximately.

In this contribution, we implement a numerical method for the solution of the hydrodynamical EOM. The scheme is subsequently applied to the description of **spatially localized** vibrational dynamics, in particular to the evolution of a wave packet on a harmonic and on a Morse potential. The numerical implementation is based on the representation of the logarithm of the density and the phase fields using Chebyshev polynomials. Chebyshev expansions of a variety of functions of the Hamiltonian have been used extensively in quantum dynamical calculations [35–39], and they are extended this way to the quantum trajectory modeling of the molecular dynamics. Chebyshev polynomials are chosen because of their property of being the best interpolation polynomials in the minimax sense. In the Chebyshev expansion, the truncation error is smoothly spread out throughout the interpolated interval. As a consequence, the Chebyshev approximation exhibits the smallest maximum deviation from the interpolated function (among all polynomials of the same degree). Furthermore, the elimination of edge instabilities by using a variable radius of support in the moving least squares method, which becomes larger in the vicinity of the edges [32], suggests the suitability of using global interpolating functions to compute the derivatives in the hydrodynamical formulation. Likewise, the recurrence relations obeyed by Chebyshev polynomials allow the straightforward computation of the derivatives of the hydrodynamical fields.

The present method could also be extended to the propagation of molecular wavepackets on multiple potential energy surfaces. In the case of several potential energy surfaces with negligible non-adiabatic couplings, the same equations of motion are obtained for the uncoupled fields evolving on each surface. In the presence of significant non-adiabatic effects, the Chebyshev representation of the tensor fields can be straightforwardly implemented in the generalization of the quantum-trajectory equations of motion for non-adiabatic dynamics [40].

The paper is organized as follows. First, the hydrodynamical formulation of quantum mechanics is briefly introduced in Section 2, and the numerical scheme proposed for the solution of the hydrodynamical equations is described. The results of the application of the computational method to the time-evolution of a wave packet on a quadratic and on a Morse potential are presented and discussed in Section 3. Finally, in Section 4, some remarks are given.

2. Theoretical methodology

2.1. Hydrodynamical formulation of quantum mechanics

In the hydrodynamical formulation of quantum mechanics, the wave function is written in polar form $\Psi(\vec{r},t) = e^{C(\vec{r},t)+iS(\vec{r},t)/\hbar}$, where $C(\vec{r},t)$ and $S(\vec{r},t)$ are real valued functions. Inserting this *ansatz* in the time-dependent Schrödinger equation, and after separating the real and imaginary parts, the hydrodynamical equations of motion read:

$$\frac{\partial \rho(\vec{r},t)}{\partial t} + \nabla \cdot \left(\rho \frac{\nabla S}{m}\right) = 0, \tag{1}$$

$$-\frac{\partial S}{\partial t} = \frac{1}{2m}(\nabla S)^2 + V(\vec{r},t) + Q[\rho(\vec{r},t)]. \tag{2}$$

Since $\rho(\vec{r},t) = e^{2C(\vec{r},t)}$ represents the probability density in the quantum fluid, Eq. (1) can be identified as the continuity equation, with $\nabla S/m$ it representing the velocity field of the fluid particles of mass m. On the other hand, Eq. (2) resembles the Hamilton–Jacobi equation of classical mechanics, although it includes the additional term:

$$Q(\vec{r},t) = -\frac{\hbar^2}{2m}\left[(\nabla C)^2 + (\nabla^2 C)\right], \tag{3}$$

known as the de Broglie–Bohm or the quantum potential. Hence, in the QTM, the density and the action fields are propagated along a swarm of trajectories which evolve, according to the laws of classical mechanics, on the potential surface resulting from the addition of the contributions V (due to the interaction forces) and Q. As it was mentioned above, the quantum potential depends on the curvature of the density profile, and it brings all the quantum mechanical effects in the formulation. The divergence of the quantum potential for vanishing densities, and the stiffness of the resulting EOM in regions where rapid spatial variations of the probability density are present (e.g., close to ripples in the density profile), constitute the main factors hindering the numerical integration of the coupled partial differential equations of quantum hydrodynamics. In the present work, this problem is alleviated by implementing a trajectory-reallocation scheme and conventional regularization techniques, as will be described bellow.

Exploiting the mathematical equivalence of the various formulations of classical mechanics, the EOM (1) and (2) can be recast (in the Lagrangian reference frame) into the set of equations:

$$\frac{dS}{dt} = \frac{1}{2m}(\nabla S)^2 - V(\vec{r},t) - Q[C(\vec{r},t)], \tag{4}$$

$$\frac{d\vec{r}}{dt} = \frac{\nabla S}{m}, \tag{5}$$

$$\frac{dC}{dt} = -\frac{\nabla^2 S}{2m}. \tag{6}$$

The validity of expressions (4) and (5) immediately follows from identifying the field S with the action of classical particles of mass m, moving on the total external potential $V + Q$, whereas Eq. (6) enforces norm conservation. The change in the argument of the quantum potential stress the fact that expression (3) allows to compute Q directly from the function $C(\vec{r},t)$, without any explicit reference to the molecular density $\rho(\vec{r},t)$ or the wave function $\Psi(\vec{r},t)$. On

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