Quantum Trajectories from a Discrete−Variable Representation Method†

María Fernanda González,‡ Xavier Giménez,‡ Javier González-Aguilar,§ and Josep Maria Bofill*,§

Departament de Química Física i Centre especial de Recerca en Química Teòrica and Departament de Química Orgànica i Centre especial de Recerca en Química Teòrica, Universitat de Barcelona i Parc Científic de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain

Received: March 21, 2007; In Final Form: June 8, 2007

A method for obtaining quantum trajectories from a discrete−variable representation computation of the quantum potential is presented. The method exploits the linearity of the Schrödinger equation, deals smoothly with the quantum potential singularities, and readily performs the time propagation up to fairly large total elapsed times. A one-dimensional test of the general *n*-dimensional formulation is included.

I. Introduction

Formulating quantum mechanics (QM) in terms of the mathematical elements of classical mechanics (CM), namely, positions, trajectories, velocities, action and forces, has remained an exciting open question since the early quantum days. A notorious attempt in this regard was performed by Madelung[1] and de Broglie[2,3] in the late 1920s and by Bohm in the early 1950s,[4,5] who developed an exact reformulation of QM in terms of the basic CM elements. As expected, the resulting structure of the primary equations, trajectories, action, as well as forces, show outstanding differences, as compared to the "traditional" classical case.[6] According to this formulation, the main difference between CM and QM resides in the force. Whereas in CM the force is just the minus gradient of the potential at the current particle's location (i.e., the Newtonian force), in QM the force is the usual Newtonian force plus a new term, the quantum force, which arises from the time-dependent quantum mechanical density. Thus, within this view, the QM dynamics is seen to arise simply from a different potential than that described by CM. In addition, it is a well-known result that this mathematical formulation of QM, in terms of classical elements, shows the same structure as the equations of classical hydrodynamics. Hence, this QM formulation is often known as the hydrodynamic formulation of QM (HQM).[7] The primary objects generated by the HQM equations (trajectories) are actually termed quantum trajectories (QT) or, equivalently, Bohmian trajectories (BT).[6]

An appealing aspect of the QTs is their deterministic nature, even though physically orthodox conclusions are recovered only after averaging over a sufficiently complete swarm of trajectories. As expected, the HQM formulation does not eliminate the intrinsic nonlocality of QM; it is actually embedded within the quantum force. However, the very concept of trajectory may be, at first sight, misleading in this regard, for it is obtained from a scalar field dependent upon the instantaneous positions. One has to recall the continuity equation, to infer that the particle's density is obtained after integration along the complete configuration space, for each time increment. This view, based on a joint analysis of a pair of coupled differential equations, may be simplified. The authors have recently shown that the quantum force can be formulated solely in terms of integrals of the action function derivatives evaluated along the QT.[8] This result clearly shows that a QT, at any position and time, depends not only on the initial position and time, as occurs in CM, but also on the whole history of the trajectory, up to the current position and time. Hence, this formulation might be regarded as a novel form to address the nonlocality problem in purely classical terms.

An important consequence of nonlocality emerges in the computational evaluation of QTs. First, this nonlocality means computational overload. The quantum force is time-dependent, so it has to be updated at each time increment. Moreover, it is obtained from the particle's density, so it requires a full configuration space integration.[9] Second, the quantum force expression is prone to singularities whenever the density shows a nodal point in configuration space. These difficulties are manifest either in the original formulation of the quantum force, as proposed by Bohm,[4,5] or in the author's integral expression.[8]

Nevertheless, the last decades have witnessed outstanding theoretical and algorithmic advances concerning QT computations.[9−15] The QT method (QTM) has been applied, for instance, in molecular photodissociation,[16] tunneling in a double well potential,[17] scattering of quantum trajectories from an Eckart barrier,[10] reflections on a downhill ramp potential,[13]quantum resonances in one-dimensional chemical reactions,[18] as well as other interesting physical chemistry − chemical physics problems.[19] The contributions of Bob Wyatt in this field cannot be overemphasized. Wyatt triggered a new impetus, starting in 1999, when he and his coworkers proposed a general technique, and several variants of it, to numerically solve the hydrodynamic equations of motion. This method is based on the association of bohmian particles to discretized fluid elements, where each fluid element follows the influence of both classical and quantum forces.[10] A previous, close algorithm is due to Weiner and coworkers,[20,21] which resorts to the Lagrangian hydrodynamic method. New, more recent improvements have been introduced in the discretized fluid elements technique. For instance, distributed approximated functionals on the grid are used to

† Part of the special issue "Robert E. Wyatt Festschrift".

* To whom correspondence should be addressed. E-mail: jmbofill@ub.edu.

‡ Departament de Química Física i Centre especial de Recerca en Química Teòrica.

§ Departament de Química Orgànica i Centre especial de Recerca en Química Teòrica.

10.1021/jp072237o CCC: $37.00
Published on Web 08/15/2007

facilitate the computation of the derivatives that appear in the equations of motion.[22] In addition, this approach has been applied to both uniform and nonuniform grids. However, a main difficulty in this algorithm is the "edge problem", which may be stated as the difficulties in keeping the simultaneous accuracy of the fit and derivatives near the grid edges.

A very recent variant for the computation of QTs is that of Goldfarb et al.[23] These authors provide a derivation of the equations of bohmian mechanics with the aid of plane waves and complex actions.[24] However, the QTs thus obtained are defined in the complex plane. Consequently, even though the computational efficiency may be superior and full quantum mechanical results are obviously reproduced, the nature of the method somewhat departs from the original spirit of the HQM, which resorts to just classical quantities.

In this paper, a new method for extracting the hydrodynamic quantum trajectories from the theory is presented. The method is rooted to the core of the HQM theory.[6] It is then useful, in this regard, to recall the original postulates as originally stated by Madelung,[1] de Broglie,[2,3] and Bohm:[4,5](a) every physical system is formed by a set of point particles that moves in space and time under the guidance of a complex wave function; (b) the wave function satisfies the time-dependent Schrödinger equation (TDSE); (c) the velocity of each point particle, which in fact characterizes the corresponding QT, is equal to the derivative with respect to the position of the real phase function of the complex wave function. (d) the probability to find a particle of the ensemble corresponding to the physical system, at any position and time, is given by the square modulus of the wave function at this position and time.

One may conclude, from a strict point of view, that the HQM model does not eliminate the complex wave function from the theory. On the contrary, it is actually its first basic element. The complex wave function, along with positions, trajectories, action, forces, and densities, conforms to the whole set of elements that appear in this alternate but rigorous QM formulation.

One may ask whether the above ontological statements may be translated into an operational procedure. In other words, is it possible to use the wave function as a first step to compute densities and afterwards get the evolution of the physical system under the HQM model? The prospective answer may be supported by the fact that there exist a variety of stable techniques to solve the TDSE,[25] which provide the complex wave function and, in turn, the real phase function. Moreover, well-known techniques are available to obtain the complex wave function as linear combinations of analytical expressions for the real phase function. Thus, the position derivative of this phase function should provide the velocity of the trajectory in a straightforward manner. Once this velocity is available, one should get the corresponding trajectory with no difficulties using some standard integration techniques. From the computational point of view, this procedure is thought to be a feasible and stable integration technique of QTs because analytic expressions are used through the whole process.

One of the methods widely used to integrate the Schrödinger equation (SE), which appears to satisfy the above requirements, is the discrete variable representation (DVR) method, formulated in the context of molecular systems by Light and co-workers,[26] which in turn was based on earlier works by Harris et al.,[27] Dickinson and Certain,[28] and Shizgal and Blackmore.[29] Colbert and Miller derived, in detail, an interesting class of DVR, usually termed "sinc DVR".[30] In particular, the authors provided analytic expressions for the kinetic energy operator in terms of the grid increment after performing, in closed form, the summations implicit in the standard DVR formulation for a primitive basis consisting of particle-in-a-box eigenfunctions.

In the present study, the sinc DVR is introduced in the TDSE. A very simple matrix algorithm results. Then, the separation of real and imaginary parts in the complex wavefunction leads to a systematic derivation of the bohmian particle equations of motion in terms of the basic DVR ingredients. Consequently, we have been able to formulate a DVR-based algorithm for the integration of QTs, where each bohmian particle is initially associated to a discrete position of the DVR mesh. Finally, integration algorithms are introduced to follow the particle's time-dependence on the DVR grid. The method is especially suited for dealing with the quantum potential singularities, for no explicit use is made of the quantum potential and, in addition, the quantities computed at the grid elements are refreshed at each time increment.

To our knowledge, it is the first attempt of producing QTs from the wavefunction. The main equations are thus derived, computationally implemented, and tested for a benchmark, one-dimensional system. The scaling of the method, as presently formulated, is typical of basis set methods, so improving the scaling performances of presently existing methods has not been an issue in the present work. One may expect alternate formulations of the DVR technique to arise for multidimensional systems, such as the time-dependent correlated DVR,[31,32] to properly address the exponential growth of the necessary computational effort.

This paper is organized as follows. In section II we outline a brief summary of the DVR method. Section III introduces, in detail, the proposed algorithm to evaluate QTs, and some computational results are reported in section IV. Finally, section V concludes this paper.

II. The DVR Technique

In this section we briefly summarize the definition and properties of the DVR functions and its application. This technique has been reviewed extensively many times.[33,34] However, making the paper self-contained demands a brief summary of the essential features, which are shown below. The technique is based on the use of continuous functions, satisfying the properties of being position eigenfunctions associated to a grid. These functions become strongly localized in the points of the grid once a primitive basis is linearly transformed to diagonalize the position operator. Such functions define a DVR that was popularized in the realm of molecular physics some time ago by Light and co-workers.[26] One form of starting the derivation consists in specifying a set of orthogonal polynomials ($\{P_n(x)\}$) along with a weighting function ($w(x)$) such that we get eq 1.

$$\int_{x_i}^{x_f} P_m(x) w(x) P_n(x)\, dx = \delta_{mn} \tag{1}$$

Following Light,[26,33,34] we introduce the so-called finite basis representation (FBR) functions ($\{\phi_n(x)\}$), where $\phi_n(x) = (w(x))^{1/2} P_n(x)$. With this set of functions, the overlap integrals are evaluated exactly in a N-point Gaussian quadrature ($\{x_\mu\}_{\mu=1}^{N}$);

$$\int_{x_i}^{x_f} \phi_m(x)\phi_n(x)\, dx = \sum_{\mu=1}^{N} \frac{w_\mu}{w(x_\mu)} \phi_m(x_\mu)\phi_n(x_\mu) = \sum_{\mu=1}^{N} w_\mu P_m(x_\mu) P_n(x_\mu) = \delta_{mn} \tag{2}$$

where $\{w_\mu\}_{\mu=1}^N$ is the set of quadrature Gaussian weights. Now we can calculate the coordinate matrix of the FBR basis functions in an exact manner in the same quadrature because the N-point Gaussian quadrature is exact up to the $2N$ order;

$$\chi_{mn} = \int_{x_i}^{x_f} \phi_m(x) x \phi_n(x)\, dx = \sum_{\mu=1}^{N} \frac{w_\mu}{w(x_\mu)} \phi_m(x_\mu) x_\mu \phi_n(x_\mu) = \sum_{\mu=1}^{N} \phi_m(x_\mu) \sqrt{\frac{w_\mu}{w(x_\mu)}}\, x_\mu \sqrt{\frac{w_\mu}{w(x_\mu)}}\, \phi_n(x_\mu) = \sum_{\mu=1}^{N} T^{T}_{m\mu} x_\mu T_{\mu n} \quad (3)$$

where the superscript T indicates transposed. In matrix form, eq 3 can be written as $\mathbf{X} = \mathbf{T}^T\mathbf{X}_D\mathbf{T}$, where $\mathbf{X}_D$ is the diagonal matrix, and the diagonal elements are $\{x_\mu\}_{\mu=1}^N$, the set of DVR points. Notice that in eq 2, $\mathbf{T}^T\mathbf{T} = \mathbf{I}$, where matrix $\mathbf{I}$ is the unit matrix of dimension N. This fact permits us to rewrite the latter matrix expression as an eigenvalue equation, $\mathbf{X}\mathbf{T}^T = \mathbf{T}^T\mathbf{X}_D$. Now, using the definition of the $\mathbf{T}$ matrix given in eq 3, we introduce in a natural way the definition of DVR functions ($\{u_\mu(x)\}_{\mu=1}^N$) of the grid of DVR set of points ($\{x_\mu\}_{\mu=1}^N$), namely eq 4.

$$u_\mu(x) = \sum_{n=1}^{N} T^{T}_{n\mu} \phi_n(x) = \sum_{n=1}^{N} \phi_n(x_\mu) \sqrt{\frac{w_\mu}{w(x_\mu)}}\, \phi_n(x) \quad (4)$$

Because the $\mathbf{T}$ matrix is a unitary (orthonormal if the functions are real) matrix, we obtain one of the important properties of the DVR functions (eq 5).

$$u_\mu(x_\nu) = \sum_{n=1}^{N} T^{T}_{n\mu} \phi_n(x_\nu) = \sum_{n=1}^{N} \phi_n(x_\mu) \sqrt{\frac{w_\mu}{w(x_\mu)}}\, \phi_n(x_\nu) = \sum_{n=1}^{N} T^{T}_{n\mu} T_{\nu n} \sqrt{\frac{w(x_\nu)}{w_\nu}} = \delta_{\mu\nu} \sqrt{\frac{w(x_\nu)}{w_\nu}} \quad (5)$$

The above set of properties of DVR functions are obtained by considering both eqs 4 and 5. The DVR functions are continuous and differentiable functions with respect to x everywhere in the domain $x_i \le x \le x_f$. In addition, if we consider a DVR function, say $u_\mu(x)$, then this function takes a value of zero at all DVR points except in both the DVR point (x_μ) and the rest of the domain. Finally, using eq 5 we show that the set of DVR functions are orthogonal (eq 6).

$$\int_{x_i}^{x_f} u_\mu(x) u_\nu(x)\, dx = \sum_{\alpha=1}^{N} \frac{w_\alpha}{w(x_\alpha)} u_\mu(x_\alpha) u_\nu(x_\alpha) = \sum_{\alpha=1}^{N} \delta_{\mu\alpha}\delta_{\nu\alpha} = \delta_{\mu\nu} \quad (6)$$

In practical terms, the selection of the FBR basis set depends on the boundary conditions of the problem under consideration. In fact, the accuracy of the Gaussian quadrature, which is the basis of the present derivation, is given for periodic functions and an equally spaced grid. In this case, $w(x) = 1$ and $w_\nu = L/(2N+1)$, where $L = x_f - x_i$ is the length of the domain, and $2N+1$ is the number of basis functions. Notice that the set of DVR points ($\{x_\mu\}_{\mu=1}^{2N+1}$) are defined in eq 7.

$$x_\mu = \frac{L}{2N+1}(\mu - N - 1) \qquad \mu = 1,...,2N+1 \quad (7)$$

The elements of the $\mathbf{T}$ matrix transformation, defined in eq 3, now take the values shown in eq 8.

$$\mathbf{T}_{\mu n} = \sqrt{\frac{L}{2N+1}} \phi_n(x_\mu) \quad (8)$$

In this way, any type of function ($f(x)$) defined in the domain $x_i \le x \le x_f$ can be expanded by using the DVR basis functions;

$$f(x) = \sum_{\mu=1}^{N} g_\mu u_\mu(x) \quad (9)$$

where, using eq 5, we can evaluate the set of expansion coefficients, $g_\mu = (w_\mu/w(x_\mu))^{1/2} f(x_\mu)$. If the function to be expanded is defined in a M-dimensional domain with periodic boundary conditions ($f(\mathbf{x})$) where, $\mathbf{x}^T = (x^1, ..., x^M)$, then M-dimensional DVR functions are formed as a product of one-dimensional DVR functions, $\{u_\mu^J(x^J)\}_{\mu=1}^{N_J}$, for $\forall\ J = 1, ..., M$, and are used to build the expansion shown in eq 10;[35]

$$f(\mathbf{x}) = \sum_{\mu=1}^{N_1} ... \sum_{\nu=1}^{N_M} g_{\mu...\nu} u_\mu^1(x^1) ... u_\nu^M(x^M) \quad (10)$$

where $\{g_{\mu...\nu}\}_{\mu=1,...,\nu=1}^{N_1,...,N_M}$, is the set of expansion coefficients. Proceeding as before, each coefficient takes the value shown in eq 11;

$$g_{\mu...\nu} = \left(\frac{w_\mu^1}{w^1(x_\mu^1)}\right)^{1/2} \cdots \left(\frac{w_\nu^M}{w^M(x_\nu^M)}\right)^{1/2} f(\mathbf{x}_{\mu...\nu}) \quad (11)$$

where $\mathbf{x}_{\mu...\nu}{}^T = (x_\mu^1, ..., x_\nu^M)$. Finally, because the DVR functions are continuous and analytically defined in all of the domain, as given in eq 4, then we can evaluate the derivatives of the function $f(\mathbf{x})$ expanded in the sets of DVR basis functions, namely eq 12, at any point of the domain.

$$\frac{\partial f(\mathbf{x})}{\partial x^J} = \sum_{\mu=1}^{N_1} \cdots \sum_{\tau=1}^{N_J} \cdots \sum_{\nu=1}^{N_M} g_{\mu...\tau...\nu} u_\mu{}^1(x^1) \cdots \frac{du_\tau^J(x^J)}{dx^J} \cdots u_\nu^M(x^M) \quad (12)$$

At a DVR point, say $\mathbf{x}_{\alpha...\beta...\gamma}$, the above partial derivative takes the value shown in eq 13.

$$\left.\frac{\partial f(\mathbf{x})}{\partial x^J}\right|_{\mathbf{x}=\mathbf{x}_{\alpha...\beta...\gamma}} = \left(\frac{w^1(x_\alpha^1)}{w_\alpha{}^1}\right)^{1/2} \cdots \left(\sum_{\tau=1}^{N_J} g_{\alpha...\tau...\gamma} \left.\frac{du_\tau^J(x^J)}{dx^J}\right|_{x^J=x_\beta^J}\right) \cdots \left(\frac{w^M(x_\gamma^M)}{w_\gamma^M}\right)^{1/2} \quad (13)$$

An important class of DVR functions, used in the present work, is that proposed by Colbert and Miller.[30] It may be regarded as an infinite order (finite difference on infinite uniform grids) formulation of the Hamiltonian. This formulation is based on the use of particle-in-a-box functions. The corresponding representation on the grid is such that the number of functions goes to infinity as the range becomes infinite. In this case, because the grid is equally spaced, $w(x_\nu^J) = 1$, $w_\nu^J = L_J/(2N_J + 1) = \Delta x^J$ for $\forall\nu$, Δx^J is the difference for the J

coordinate, and $L_J = x_f^J - x_i^J$ is the length of the domain of this J coordinate. The final DVR functions obtained in this way form an infinite basis of the following functions.

$$u_\mu^J(x^J) \rightarrow \mathrm{sinc}_\mu(x^J) = \frac{\sin(\pi(x^J - x_\mu^J)/\Delta x^J)}{\pi(x^J - x_\mu^J)} \qquad (14)$$

where, in this case, we take $x_\mu^J = \mu\Delta x^J$, $\mu = 0, \pm1, \pm2, ...$; with the sinc basis functions introduced in eq 14, the quantum Hamiltonian takes a very simple structure, namely eq 15;[30]

$$\mathbf{H}_{x_\alpha^1 x_\beta^1,...,x_\mu^M x_\nu^M} = \sum_{I=1}^{M} \mathbf{K}_{x_\gamma^I x_\kappa^I} \prod_{\substack{J=1 \\ J\neq I}}^{M} \delta_{x_\eta^J x_\epsilon^J} + V(\mathbf{x}_{\alpha...\mu}) \prod_{J=1}^{M} \delta_{x_\eta^J x_\epsilon^J} \qquad (15)$$

where $V(\mathbf{x})$ is the potential function and $\mathbf{K}_{x_\gamma^I x_\kappa^I}$ is an element of the matrix kinetic operator,

$$\mathbf{K}_{x_\gamma^I x_\kappa^I} = \frac{\hbar^2(-1)^{\gamma-\kappa}}{2m\Delta x^I} \begin{Bmatrix} \pi^2/3 & \gamma = \kappa \\ 2/(\gamma-\kappa)^2 & \gamma \neq \kappa \end{Bmatrix} \qquad (16)$$

where m is the mass of the particle, and $\hbar$ is Planck's constant. In practical applications it is not possible to use an infinite basis because we have only a finite set of DVR points. In this situation the Hamiltonian does not possess the same simple mathematical structure than that given in eqs 15 and 16. However because of its simplicity in both the structure of the basis functions and the Hamiltonian represented in this basis, we take this type of DVR as a basic tool for evaluating the QTs.

III. The Integration of Bohmian Trajectories Using a Discrete Variable Representation Algorithm

In this section we present the mathematical basis for the BTs, or QTs, integration technique. We start with a brief discussion of the main HQM equations, because it is the required starting point of the present formulation. The complex wave function $\Psi(\mathbf{x}, t)$ can be expressed in polar form (eq 17).

$$\begin{aligned}\Psi(\mathbf{x}, t) &= R(\mathbf{x}, t)\exp\left(\frac{i}{\hbar}S(\mathbf{x}, t)\right) \\ &= R(\mathbf{x}, t)\cos(S(\mathbf{x}, t)/\hbar) + iR(\mathbf{x}, t)\sin(S(\mathbf{x}, t)/\hbar) \\ &= \Psi_{\mathrm{real}}(\mathbf{x}, t) + i\Psi_{\mathrm{imag}}(\mathbf{x}, t)\end{aligned} \qquad (17)$$

As it is known, this expression for the complex wave function leads to a real amplitude function that takes the form of eq 18a,

$$R(\mathbf{x}, t) = (\Psi_{\mathrm{real}}{}^2(\mathbf{x}, t) + \Psi_{\mathrm{imag}}{}^2(\mathbf{x}, t))^{1/2} \qquad (18a)$$

whereas the real phase function is given by eq 18b.

$$S(\mathbf{x}, t) = \hbar \arctan\left(\frac{\Psi_{\mathrm{imag}}(\mathbf{x}, t)}{\Psi_{\mathrm{real}}(\mathbf{x}, t)}\right) \qquad (18b)$$

The wave function given in eq 17 is taken as the solution of the Schrödinger equation.

$$i\hbar\frac{\partial\Psi(\mathbf{x}, t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla_{\mathbf{x}}{}^2 + V(\mathbf{x})\right)\Psi(\mathbf{x}, t) = H(\mathbf{x})\Psi(\mathbf{x}, t) \qquad (19)$$

Now, inserting eq 17 into eq 19 and separating into real and imaginary parts, we obtain the field equations for the real functions $R(\mathbf{x}, t)$ and $S(\mathbf{x}, t)$.[1−5,7] The real part results in eq 20a, which is the so-called the Hamilton−Jacobi equation.[6]

$$\frac{\partial S(\mathbf{x}, t)}{\partial t} + \frac{\nabla_{\mathbf{x}}^T S(\mathbf{x}, t)\nabla_{\mathbf{x}} S(\mathbf{x}, t)}{2m} + V(\mathbf{x}) - \frac{\hbar^2}{2m}\frac{\nabla_{\mathbf{x}}{}^2 R(\mathbf{x}, t)}{R(\mathbf{x}, t)} = 0 \qquad (20a)$$

The imaginary part in the expression (eq 20b) is the conservation, or continuity, equation.[6]

$$\frac{\partial R^2(\mathbf{x}, t)}{\partial t} + \nabla_{\mathbf{x}}^T\left(\frac{R^2(\mathbf{x}, t)}{m}\nabla_{\mathbf{x}} S(\mathbf{x}, t)\right) = 0 \qquad (20b)$$

According to the coupled partial differential equations (20a,b), the real functions $R(\mathbf{x}, t)$ and $S(\mathbf{x}, t)$ are codetermined by one another. Now we introduce a point particle of mass m that follows the trajectory $\mathbf{x} = \mathbf{x}(t)$. To this aim, we assume that at each point of space and time the tangent vector to the particle trajectory passing through this point $(\mathrm{d}\mathbf{x}/\mathrm{d}t\,|_{\mathbf{x}=\mathbf{x}(t)})$ is proportional to the vector field $(\nabla_{\mathbf{x}} S(\mathbf{x}, t))$ with the proportional factor $1/m$. These trajectories are orthogonal to the surfaces $S(\mathbf{x}, t) = constant$ and may be found by integration of the differential equation given by eq 21.

$$\left.\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t}\right|_{\mathbf{x}=\mathbf{x}(t)} = \left(\frac{1}{m}\right)\nabla_{\mathbf{x}} S(\mathbf{x}, \tau)\Big|_{\substack{\mathbf{x}=\mathbf{x}(t) \\ \tau=t}} \qquad (21)$$

Solving eq 21 requires setting the initial position $\mathbf{x}_0 = \mathbf{x}(t_0)$. Because the tangent vector of the trajectory, at each point of the trajectory, is proportional to a gradient vector that belongs to the field of gradient vectors of the surface $S(\mathbf{x}, t)$, we propose (1) to obtain the real phase function $(S(\mathbf{x}, t))$ through eqs 17−19 and (2) to get from this surface the field of gradient vectors, $\nabla_{\mathbf{x}} S(\mathbf{x}, t)$. Finally, the corresponding set of trajectories is obtained by integration of eq 21 rather than solving the pair of coupled partial differential equations (20a,b). With this strategy, we might avoid solving a system of partial differential equations, which is very often plagued with numerical instabilities, as mentioned in the introduction.

When the quantum Hamiltonian $H(\mathbf{x})$, given by eq 19, is time-independent, it is well-known that the wave function at time t $(\Psi(\mathbf{x}, t))$ is derived from the wave function at the initial time t_0 $(\Psi(\mathbf{x}, t_0))$ through the operator action shown in eq 22;

$$\Psi(\mathbf{x}, t) = \exp\left(-\frac{i}{\hbar}H(\mathbf{x})(t - t_0)\right)\Psi(\mathbf{x}, t_0) \qquad (22)$$

which is the integrated form of eq 19.[36] According to eq 22, $\Psi(\mathbf{x}, t)$ may be known if we expand both $\Psi(\mathbf{x}, t_0)$ and the exponential term in a series of eigenfunctions of $H(\mathbf{x})$. Let us assume that the spectrum of the $\mathbf{H}$ matrix associated to the $H(\mathbf{x})$ operator, in a given representation, is discrete and nondegenerate, and we denote such by $\{E_n, \mathbf{v}_n\}$, the set of eigenpairs. Moreover, if $\mathbf{f}(t)$ and $\mathbf{f}(t_0)$ denote the complex wave functions $\Psi(\mathbf{x}, t)$ and $\Psi(\mathbf{x}, t_0)$ in this representation, respectively, then eq 22 must be written as shown in eq 23.

$$\mathbf{f}(t) = \exp\left(-\frac{i}{\hbar}\mathbf{H}(t-t_0)\right)\mathbf{f}_0 = \sum_{n=1}\mathbf{v}_n \exp\left(-\frac{i}{\hbar}E_n(t-t_0)\right)\mathbf{v}_n^T\mathbf{f}_0 = \sum_{n=1}\mathbf{v}_n\{\cos(E_n(t-t_0)/\hbar) - i\sin(E_n(t-t_0)/\hbar)\}\mathbf{v}_n^T\mathbf{f}_0 \quad (23)$$

If we take the **H** matrix given in eq 15, then the time evolution equation (23) is represented in the sinc DVR basis as shown in eq 24.

$$\Psi(\mathbf{x},t) = \sum_{\alpha=1}^{N_1}\ldots\sum_{\beta=1}^{N_J}\ldots\sum_{\gamma=1}^{N_M}\sum_{\Xi=1}^{N_T}\left\{u_\alpha{}^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}\mathbf{L}_{\alpha\ldots\beta\ldots\gamma,\Xi}\exp\left(-\frac{i}{\hbar}E_\Xi(t-t_0)\right)\times\sum_{\mu=1}^{N_1}\cdots\sum_{\tau=1}^{N_J}\ldots\sum_{\nu=1}^{N_M}\mathbf{L}^T_{\Xi,\mu\ldots\tau\ldots\nu}\Psi(\mathbf{x}_{\mu\ldots\tau\ldots\nu},t_0)\right\} \quad (24)$$

where $N_T = N_1 + \ldots + N_J + \ldots + N_M$, $z_{\alpha\ldots\beta\ldots\gamma} = (w^1/w^1(x^1{}_\alpha))^{1/2}\ldots(w^J/w^J(x^J{}_\beta))^{1/2}\ldots(w^M/w^M(x^M{}_\gamma))^{1/2}$, and we have assumed that the DVR points along each coordinate are equally spaced. In eq 24, $\{E_\Xi, \mathbf{L}_\Xi\}_{\Xi=1}^{N_T}$ represents the set of eigenpairs of the Hamiltonian matrix given in eq 15. Substituting eq 17 in the right-hand part of eq 24, after some rearrangement we obtain eq 25;

$$\Psi(\mathbf{x},t) = \sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M}u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}\sum_{\Xi=1}^{N_T}\mathbf{L}_{\alpha\ldots\beta\ldots\gamma,\Xi}(\mathbf{a}_\Xi(t)+i\mathbf{b}_\Xi(t)) = \sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M}u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}(\mathbf{c}_{\alpha\ldots\beta\ldots\gamma}(t) + i\mathbf{d}_{\alpha\ldots\beta\ldots\gamma}(t)) \quad (25)$$

where the explicit form of the elements of the time-dependent vectors, $\mathbf{a}(t)$ and $\mathbf{b}(t)$, is given by eqs 26a,b;

$$\mathbf{a}_\Xi(t) = \sum_{\mu=1}^{N_1}\cdots\sum_{\tau=1}^{N_J}\cdots\sum_{\nu=1}^{N_M}\mathbf{L}^T_{\Xi,\mu\ldots\tau\ldots\nu}R(\mathbf{x}_{\mu\ldots\tau\ldots\nu},t_0)\cos\left(\frac{S^0_\Xi(\mathbf{x}_{\mu\ldots\tau\ldots\nu},t)}{\hbar}\right) \quad (26a)$$

$$\mathbf{b}_\Xi(t) = \sum_{\mu=1}^{N_1}\cdots\sum_{\tau=1}^{N_J}\cdots\sum_{\nu=1}^{N_M}\mathbf{L}^T_{\Xi,\mu\ldots\tau\ldots\nu}R(\mathbf{x}_{\mu\ldots\tau\ldots\nu},t_0)\sin\left(\frac{S^0_\Xi(\mathbf{x}_{\mu\ldots\tau\ldots\nu},t)}{\hbar}\right) \quad (26b)$$

where $S^0_\Xi(\mathbf{x}_{\mu\ldots\tau\ldots\nu}, t) = S(\mathbf{x}_{\mu\ldots\tau\ldots\nu}, t_0) - E_\Xi(t-t_0)$. Finally, from eq 25 we have the expressions for both the $R(\mathbf{x}, t)$ and the $S(\mathbf{x}, t)$ functions, eqs 27a,b, respectively.

$$R(\mathbf{x},t) = [(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M}u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}\mathbf{c}_{\alpha\ldots\beta\ldots\gamma}(t))^2 + (\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M}u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}\mathbf{d}_{\alpha\ldots\beta\ldots\gamma}(t))^2]^{1/2} \quad (27a)$$

$$S(\mathbf{x},t) = \hbar\arctan\frac{(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M}u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}\mathbf{d}_{\alpha\ldots\beta\ldots\gamma}(t))}{(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M}u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}\mathbf{c}_{\alpha\ldots\beta\ldots\gamma}(t))} \quad (27b)$$

Notice again that the tensors $\mathbf{c}_{\alpha\ldots\beta\ldots\gamma}(t)$ and $\mathbf{d}_{\alpha\ldots\beta\ldots\gamma}(t)$ are only functions of t. The derivative of $S(\mathbf{x}, t)$ with respect to a coordinate, say x^J, will correspond to an element of the $\nabla_\mathbf{x}S(\mathbf{x}, t)$ vector, namely eq 28.

$$\frac{\partial S(\mathbf{x},t)}{\partial x^J} = \hbar\left\{\left(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M}u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}\mathbf{c}_{\alpha\ldots\beta\ldots\gamma}(t)\right)\times\left(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M}u_\alpha^1(x^1)\ldots\frac{\mathrm{d}u_\beta^J(x^J)}{\mathrm{d}x^J}\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}\mathbf{d}_{\alpha\ldots\beta\ldots\gamma}(t)\right) - \left(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M}u_\alpha^1(x^1)\ldots\frac{\mathrm{d}u_\beta^J(x^J)}{\mathrm{d}x^J}\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}\mathbf{c}_{\alpha\ldots\beta\ldots\gamma}(t)\right)\times\left(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M}u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M)z_{\alpha\ldots\beta\ldots\gamma}\mathbf{d}_{\alpha\ldots\beta\ldots\gamma}(t)\right)\right\}R^{-2}(\mathbf{x},t) \quad (28)$$

Now, taking into account eq 21 and eq 28, one obtains the QT by integration. We propose, through the integration process, the following procedure: let us assume that a point of the trajectory is $\mathbf{x}_0 = \mathbf{x}(t_0)$. Then the trajectory itself can be represented by a Taylor series in t expanded about $\mathbf{x}_0$;

$$\mathbf{x}(t) = \mathbf{x}(t_0) + \frac{\mathrm{d}\mathbf{x}(t)}{\mathrm{d}t}|_{t=t_0}(t-t_0) + \frac{1}{2}\frac{\mathrm{d}^2\mathbf{x}(t)}{\mathrm{d}t^2}|_{t=t_0}(t-t_0)^2 + \ldots = \mathbf{x}(t_0) + \left(\frac{1}{m}\right)\nabla_\mathbf{x}S(\mathbf{x},\tau)|_{\mathbf{x}=\mathbf{x}(t_0)\tau=t_0}(t-t_0) + \frac{1}{2}\left(\frac{1}{m}\right)\frac{\mathrm{d}(\nabla_\mathbf{x}S(\mathbf{x},\tau))}{\mathrm{d}t}|_{\mathbf{x}=\mathbf{x}(t_0)\ \tau=t_0}(t-t_0)^2 + \ldots \quad (29)$$

where eq 21 has been used. In eq 29 the term $\mathrm{d}(\nabla_\mathbf{x}S(\mathbf{x}, \tau))/\mathrm{d}t$, at the point $\mathbf{x} = \mathbf{x}(t)$ and $\tau = t$, is evaluated as shown in eq 30;

$$\frac{\mathrm{d}}{\mathrm{d}t}(\nabla_\mathbf{x}S(\mathbf{x},\tau)) = \left(\frac{1}{m}\right)[\nabla_\mathbf{x}\nabla_\mathbf{x}^TS(\mathbf{x},\tau)](\nabla_\mathbf{x}S(\mathbf{x},\tau)) + \nabla_\mathbf{x}\frac{\partial S(\mathbf{x},\tau)}{\partial t} \quad (30)$$

where eq 21 has been used. The term in brackets appearing in the right-hand side part of eq 30 is computed by derivation of eq 28 with respect to **x**. Finally, the term $\partial S(\mathbf{x}, \tau)/\partial t$, which represents the negative energy of the trajectory at the point $\mathbf{x} = \mathbf{x}(t)$ and $\tau = t$ is obtained by derivation of eq 27b with respect to t (eq 31);

$$\frac{\partial S(\mathbf{x}, t)}{\partial t} = \hbar\left\{\left(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M} u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M) z_{\alpha\ldots\beta\ldots\gamma}\mathbf{c}_{\alpha\ldots\beta\ldots\gamma}(t)\right)\times \left(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M} u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M) z_{\alpha\ldots\beta\ldots\gamma}\frac{\partial \mathbf{d}_{\alpha\ldots\beta\ldots\gamma}(t)}{\partial t}\right) - \left(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M} u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M) z_{\alpha\ldots\beta\ldots\gamma}\frac{\partial \mathbf{c}_{\alpha\ldots\beta\ldots\gamma}(t)}{\partial t}\right)\times \left(\sum_{\alpha=1}^{N_1}\cdots\sum_{\beta=1}^{N_J}\cdots\sum_{\gamma=1}^{N_M} u_\alpha^1(x^1)\ldots u_\beta^J(x^J)\ldots u_\gamma^M(x^M) z_{\alpha\ldots\beta\ldots\gamma}\mathbf{d}_{\alpha\ldots\beta\ldots\gamma}(t)\right)\right\} R^{-2}(\mathbf{x},t) \quad (31)$$

where

$$\frac{\partial \mathbf{c}_{\alpha\ldots\gamma}(t)}{\partial t} = \sum_{\Xi=1}^{N_T}\mathbf{L}_{\alpha\ldots\gamma,\Xi}\frac{\partial \mathbf{a}_\Xi(t)}{\partial t} = \frac{1}{\hbar}\sum_{\mu=1}^{N_1}\cdots\sum_{\nu=1}^{N_M}\sum_{\Xi=1}^{N_T}\mathbf{L}_{\alpha\ldots\gamma,\Xi}E_\Xi\mathbf{L}^T_{\Xi,\mu\ldots\nu}R(\mathbf{x}_{\mu\ldots\nu}, t_0)\sin\left(\frac{S_\Xi{}^0(\mathbf{x}_{\mu\ldots\nu}, t)}{\hbar}\right) \quad (32)$$

and

$$\frac{\partial \mathbf{d}_{\alpha\ldots\gamma}(t)}{\partial t} = \sum_{\Xi=1}^{N_T}\mathbf{L}_{\alpha\ldots\gamma,\Xi}\frac{\partial \mathbf{b}_\Xi(t)}{\partial t} = -\frac{1}{\hbar}\sum_{\mu=1}^{N_1}\cdots\sum_{\nu=1}^{N_M}\sum_{\Xi=1}^{N_T}\mathbf{L}_{\alpha\ldots\gamma,\Xi}E_\Xi\mathbf{L}^T_{\Xi,\mu\ldots\nu}R(\mathbf{x}_{\mu\ldots\nu}, t_0)\cos\left(\frac{S_\Xi{}^0(\mathbf{x}_{\mu\ldots\nu}, t)}{\hbar}\right) \quad (33)$$

At each integration step we take the time interval $t - t_0$, such that the value of the derivative (m d$\mathbf{x}(t)$/dt) obtained by derivation of eq 29 with respect to t coincides, until some tolerance, with the actual value of the derivative of the function $S(\mathbf{x}, t)$ with respect to **x** evaluated at this new point using eq 28. This procedure provides the desired solution in a manner such that numerical stability is taken into account.

IV. Numerical Implementation

Equations 26−29 provide the basic formulas for the numerical implementation of the present algorithm. These formulas have been translated into a computational code. The proper numerical implementation requires, however, providing additional details, mainly concerning the actual computation of trajectories (i.e., the position as a function of time).

The practical implementation starts discretizing the full configuration space. This discretization is identical to that performed for the computation of the quantum mechanical density, thus covering the whole configuration space. The computation of quantum trajectories requires considering an initial swarm of bohmian particles (i.e., the grid positions are ascribed to a bohmian particle, but only to those positions where the density at the initial time is different from zero). In practice, this means that bohmian particles are given to discrete points where the associated density is higher than a tolerance value.

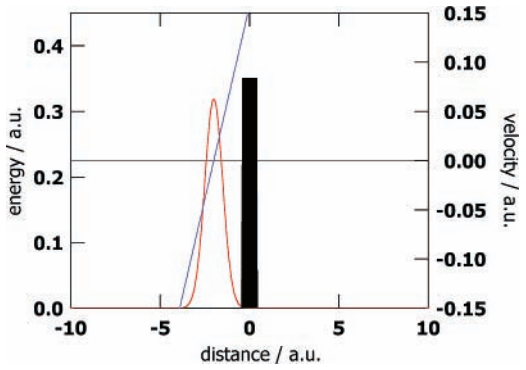

Figure 1. Statement of the problem used as a numerical test. An initial coherent-state wavepacket (red trace) is set to collide against a square potential energy barrier (filled black trace). The wavepacket's central momentum is 15 a.u., whereas the mass is one-fifth of the proton mass. The collision proceeds from left to right. The blue trace corresponds to the initial velocity (right vertical axis), as a function of position (i.e., in practice, the initial condition for each quantum trajectory). This velocity is calculated (see text) from the time zero flux divided by the t_0 density.

Next, an initial momentum is given to each bohmian particle. These momenta are obtained from the computation of the time zero-quantum flux, associated to our quantum mechanical initial state. This quantity is very easy to compute because it is a by-product of the original DVR method, as applied to the computation of the time-dependent wave function. Figure 1 shows the results of the computation of this quantum flux for a system described by a coherent state, minimum uncertainty initial state. The t_0 local flux is described by a linear function, whose slope is proportional to the central momentum of the initial wavepacket. It is thus a function, which is consistent with common practice in previous studies with quantum trajectories.

The following step consists of applying eqs 26−29 so that the positions are updated by the corresponding time increments. Each initial position, as stated above, corresponds to a DVR position. However, as a result of the action of the equations of motion, the following position will hardly correspond to any discretized point of the DVR grid. Consequently, the complete set of quantities, which are required for the computation of the position time increment, have to be interpolated from the information available at each DVR grid position.

At this point, any of the interpolation procedures available in the literature might be of use. Among them, one especially suited is the DVR−FBR transformation of the wavefunction amplitude, because the primary quantity computed here is the wavefunction. Nevertheless, it has been shown that in simple applications a linear interpolation algorithm between successive DVR points suffices. It is important to note, in this regard, that the DVR grid is time-independent (i.e., is fixed through the initial conditions) concerning the grid increment and the grid size. Then, the bohmian particles are considered to evolve on the grid. A possibility is to switch to time-dependent, moving grids, but this is left for future work.

In practice, the integration starts by selecting a given DVR point, which initially coincides with a bohmian particle. Then, the quantities in eq 29, up to second-order, are computed for a given time increment. This means computing the time-dependent wave function in terms of their related quantities as shown above. Because these quantities develop the original wavefunc-

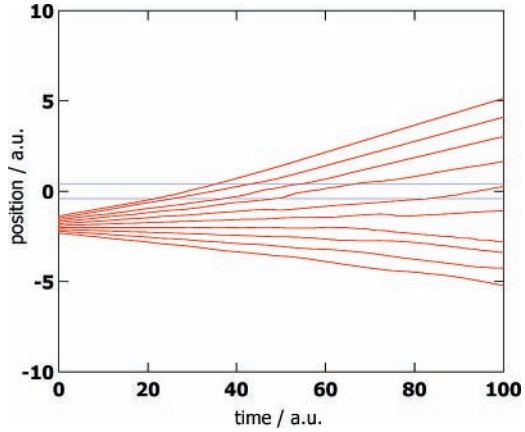

Figure 2. A sample of 10 quantum trajectories; red traces are for a wavepacket collision against a square potential barrier problem. The initial positions correspond to initial DVR grid positions, even though one may sample intermediate positions from a FBR−DVR transformation. The horizontal blue traces correspond to the square barrier limits along the vertical position axis. The center of the wavepacket is located at $x = -2$ and has a momentum of 15 a.u. This means that it has an energy of 0.3064 a.u., which should be compared to the barrier height of 0.35 a.u. Actually, the last particle showing transmission (when looking at the red traces from top to bottom), does it by tunneling, because it has an initial energy lower than the potential barrier.

tion in terms of a large summation of simple terms, the time-dependence is expected to be described accurately. Actually, as the original basis increases in size, this time-dependence will become more accurate (i.e., a better description of the problem is given by the DVR grid).

Figure 2 shows an application of the present technique, namely a collision of a coherent state wavepacket against a square potential energy barrier. It is thus an open, scattering problem, which is usually more demanding than standard, bounded systems. A swarm of 10 quantum trajectories, sampling the initial wavefuntion density around its maximum, is shown for illustrative purposes to confirm that the present new technique leads to the correct results. Results of Figure 2, leading to converged results, have been obtained after dividing the whole configuration space into 200 discretized, equally spaced positions. Each trajectory is integrated individually, from nonlocal information concerning the wavefunction amplitude and its real phase, the action, as well as their spatial and temporal derivatives. The time spanned corresponds to 100 atomic time units. It has been computed using a time increment of 0.5 au, so that the whole trajectory required just 200 points during the integration process.

V. Conclusions

A new method for obtaining quantum trajectories has been presented. The derivation has started from a revision of the basic postulates of the bohmian mechanics because the method is considered to be firmly rooted to them. In particular, the starting point is the fact that a wavefunction is associated to a deterministic time-evolution of the system. The wavefunction amplitude-based computation of trajectories benefits from the linearity of the Schrodinger equation, an advantage that is fully exploited because the final equations are obtained after a systematic use of an initial linear expansion. This method is in contrast to those based on the wavefunction density, which do not permit tracking of the linearly expanded wavefunction phase up to the final equations of motion.

Next, the paper discusses how the DVR may provide an adequate framework for the formulation of the method as an efficient manner of translating the original linear expansion to a practical computation of discrete quantities, in terms of discrete increments both in time and position.

The derivation develops the wavefunction in terms of its real and imaginary parts and thereafter introduces the DVR expansion on it. It ultimately leads to a set of linear equations in which the real and imaginary parts are evaluated separately, in terms of primary DVR quantities.

The time propagation is considered afterwards. This is expressed here in terms of the basic guidance equation of bohmian mechanics, incorporated within the present expanded formulation in terms of the DVR basis. It results in a basic appearance of the action function as well as its position and time derivatives, which are performed in a very simple manner in actual applications, thanks to the DVR expansion. These quantities are computed exclusively on the original DVR grid. However, they are required at positions that fall within DVR points. In actual applications where the grid is sufficiently fine-grained, one may simply linearly interpolate the grid information to update for intergrid quantities. In more demanding, multi-dimensional cases, one has to resort to more sophisticated interpolation algorithms, such as the DVR−FBR transformation. This is why the present DVR derivation has insisted in its relation to the FBR.

The initial conditions for the bohmian trajectories are chosen so that the local quantum flux is computed on the DVR grid. This provides a natural method for selecting the initial momenta for the bohmian particles for an initial coherent state wavepacket, which fully coincides with common practice when computing quantum trajectories by other methods. Finally, the feasibility of the method has been made explicit by the computation of quantum trajectories for a collision of a coherent state wavepacket against a square potential energy barrier. Results fully coincide with those from other methods.

Acknowledgment. Financial support from the Spanish Ministerio de Ciencia y Tecnología, DGI project CTQ2005-01117/BQU, and in part from the Generalitat de Catalunya, projects 2005SGR-00111 and 2005SGR-00175, is fully acknowledged. M.F.G. gratefully thanks the Ministerio de Ciencia y Tecnología for a predoctoral fellowship.

References and Notes

(1) Madelung, E. *Z. Phys*. **1926**, *40*, 322.
(2) de Broglie, L. *C. R. Acad. Sci. Paris* **1926**, *183*, 447.
(3) de Broglie, L. *C. R. Acad. Sci. Paris* **1927**, *184*, 273.
(4) Bohm, D. *Phys. Rev*. **1952**, *85*, 166.
(5) Bohm, D. *Phys. Rev*. **1952**, *85*, 180.
(6) Holland, P. R. *The Quantum Theory of Motion*; Cambridge University Press: New York, 1993.
(7) Takabayasi, T. *Prog. Theor. Phys*. **1952**, *8*, 143; **1953**, *9*, 187; **1954**, *11*, 341; **1955**, *14*, 283.
(8) González, M. F.; González, J.; Bofill, J. M.; Giménez, X. *J. Math. Chem*., in press.
(9) Wyatt, R. E. *Quantum Dynamics with Trajectories*; Springer: New York, 2005.
(10) Lopreore, C. L.; Wyatt, R. E. *Phys. Rev. Lett*. **1999**, *82*, 5190.
(11) Wyatt, R. E. *Chem. Phys. Lett*. **1999**, *313*, 189.
(12) Wyatt, R. E. *J. Chem. Phys*. **1999**, *111*, 4406.
(13) Lopreore, C. L.; Wyatt, R. E. *Chem. Phys. Lett*. **2000**, *325*, 73.
(14) Wyatt, R. E.; Lopreore, C. L.; Parlant, G. *J. Chem. Phys*. **2001**, *114*, 5113.
(15) Wyatt, R. E.; Na, K. *Phys. Rev. E* **2002**, *65*, 016702.
(16) Sales Mayor, F.; Askar, A.; Rabitz, H. A. *J. Chem. Phys*. **1999**, *111*, 2423.
(17) Bittner, E. R. *J. Chem. Phys*. **2000**, *112*, 9703.
(18) Derrickson, S. W.; Bittner, E. R.; Kendrick, B. K. *J. Chem. Phys*. **2005**, *123*, 054107.
(19) Sanz, A.; Borondo, F.; Miret-Artés, S. *Phys. Rev. B* **2000**, *61*, 7743.
(20) Weiner, J. H.; Partom, Y. *Phys. Rev*. **1969**, *187*, 1134.
(21) Weiner, J. H.; Askar, A. *J. Chem. Phys*. **1971**, *54*, 1108; **1971**, *54*, 3534.

(22) Wyatt, R. E.; Kouri, D. J.; Hofman, D. K. *J. Chem. Phys*. **2000**, *112*, 10730.
(23) Goldfarb, Y.; Degani, I.; Tannor, D. J. *J. Chem. Phys*. **2006**, *125*, 231103.
(24) Leacock, R. A.; Padgett, M. J. *Phys. Rev. D* **1983**, *28*, 2491.
(25) Kosloff, R. *J. Phys. Chem*. **1988**, *92*, 2087.
(26) Light, J. C.; Hamilton, I. P.; Lill, J. V. *J. Chem. Phys*. **1985**, *82*, 1400.
(27) Harris, D. O.; Engerholm, G. G.; Gwinn, W. D. *J. Chem. Phys*. **1965**, *43*, 151.
(28) Dickinson, A. S.; Certain, P. R. *J. Chem. Phys*. **1968**, *49*, 4209.
(29) Shizgal, B.; Blackmore, R. *J. Comput. Phys*. **1984**, *55*, 313.
(30) Colbert, D. T.; Miller, W. H. *J. Chem. Phys*. **1992**, *96*, 1982.
(31) Dawes, R.; Carrington, T., Jr. *J. Chem. Phys.* **2004**, *121*, 726; **2005**, *122*, 134101.
(32) Van Harrevelt, R.; Manthe, U. *J. Chem. Phys.* **2005**, *123*, 064106.
(33) Light, J. C. Discrete variable representations in quantum dynamics. In *Time-Dependent Quantum Molecular Dynamics*; Plenum-Press: New York, 1992.
(34) Light, J. C.; Carrington, T., Jr. *Adv. Chem. Phys*. **2000**, *114*, 263.
(35) Liu, Y.; Yarne, D. A.; Tuckerman, M. E. *Phys. Rev. B* **2003**, *68*, 125110.
(36) Messiah, A. *Mecánica Cuántica*; Tecnos: Madrid, 1965 (spanish translation of the 1962 french version).