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An Iterative Finite Difference Method for Solving the Quantum Hydrodynamic Equations of Motion

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I. INTRODUCTION

The quantum hydrodynamic equations of motion associated with the de Broglie-Bohm[1–5] description of quantum mechanics describe a time evolving probability density whose “fluid” elements evolve as a correlated ensemble of particle trajectories. These equations are intuitively appealing due to their similarities with classical fluid dynamics and the appearance of a generalized Newton’s equation of motion in which the total force contains both a classical and quantum contribution. However, the direct numerical solution of the quantum hydrodynamic equations (QHE) is fraught with challenges: the probability “fluid” is highly-compressible, it has zero viscosity, the quantum potential (“pressure”) is non-linear, and if that weren’t enough the quantum potential can also become singular during the course of the calculations. Collectively these properties are responsible for the notorious numerical instabilities associated with a direct numerical solution of the QHE. The most successful and stable numerical approach that has been used to date is based on the Moving Least Squares (MLS) algorithm.[6–8] The improved stability of this approach is due to the repeated local least squares fitting which effectively filters or reduces the numerical noise which tends to accumulate with time. However, this method is also subject to instabilities if it is pushed too hard. In addition, the stability of the MLS approach often comes at the expense of reduced resolution or fidelity of the calculation (i.e., the MLS filtering eliminates the higher-frequency components of the solution which may be of interest).

Recently, a promising new solution method has been developed which is based on an iterative solution of the QHE using finite differences.[9] This method (referred to as the Iterative Finite Difference Method or IFDM) is straightforward to implement, computationally efficient, stable, and its accuracy and convergence properties are well understood. A brief overview of the IFDM will be presented followed by a couple of benchmark applications on one- and two-dimensional

Eckart barrier scattering problems.

II. METHODOLOGY

In the de Broglie-Bohm description of quantum mechanics, the complex wave function is written in polar form $\psi(\mathbf{x}, t) = \exp[C(\mathbf{x}, t)] \exp[iS(\mathbf{x}, t)/\hbar]$ and substituted into the time dependent Schrödinger equation. The velocity field is defined as $\mathbf{v}(\mathbf{x}, t) = \nabla S/m$ where m is the mass. The resulting quantum hydrodynamic equations (QHE) are given by (in a fixed Eulerian frame)

$$\frac{dC}{dt} = -\frac{1}{2} \nabla \cdot \mathbf{v} - \mathbf{v} \cdot \nabla C, \quad (1)$$

$$m \frac{d\mathbf{v}}{dt} = -\nabla(V + Q) - m \mathbf{v} \cdot \nabla \mathbf{v}. \quad (2)$$

The classical potential is denoted by V and the quantum potential Q is given by

$$Q = -\frac{\hbar^2}{2m} (\nabla^2 C + |\nabla C|^2). \quad (3)$$

The classical and quantum forces are given by $\mathbf{f}_c = -\nabla V$ and $\mathbf{f}_q = -\nabla Q$, respectively. The probability density is $\rho = e^{2C}$ and the quantum trajectories are obtained by solving the equation $\dot{\mathbf{x}} = \mathbf{v}$.

The IFDM is based on an iterative solution (Newton's method) of the non-linearly coupled QHE using an implicit second-order central differencing in both space and time. A "control volume" approach is used for which the velocity grid is "staggered" relative to the spatial grid. The use of a staggered velocity grid is important in order to prevent the appearance of spurious oscillations in the numerical solutions.[10] In one-dimension, the x coordinate is discretized using a set of N computational cells with centers located at x_j where $j = 0, \dots, N+1$ and width Δx . The velocities $v_{j+1/2}$ are defined on the "cell walls" which lie half-way between the cell centers (i.e., $x_{j+1/2} = (x_j + x_{j+1})/2$). The time coordinate is discretized using a set of evenly spaced time intervals t_n ($n = 0, 1, \dots$) separated by Δt .

The 2nd-order finite difference expressions for the QHE (Eqs. 1 and 2) are given by[9]

$$\begin{aligned} (C_j^{n+1} - C_j^n)/\Delta t = & - \left[(v_{j+3/2}^{n+1} - v_{j-1/2}^{n+1}) + (v_{j+1/2}^{n+1} - v_{j-3/2}^{n+1}) \right. \\ & \left. + (v_{j+3/2}^n - v_{j-1/2}^n) + (v_{j+1/2}^n - v_{j-3/2}^n) \right] / (16 \Delta x) \\ & - \left[(v_{j+1/2}^{n+1} + v_{j-1/2}^{n+1})(C_{j+1}^{n+1} - C_{j-1}^{n+1}) \right. \\ & \left. + (v_{j+1/2}^n + v_{j-1/2}^n)(C_{j+1}^n - C_{j-1}^n) \right] / (8 \Delta x), \end{aligned} \quad (4)$$

and

$$m(v_{j+1/2}^{n+1} - v_{j+1/2}^n)/\Delta t = (f_{j+1/2}^{n+1} + f_{j+1/2}^n)/2 - m \left[v_{j+1/2}^{n+1}(v_{j+3/2}^{n+1} - v_{j-1/2}^{n+1}) + v_{j+1/2}^n(v_{j+3/2}^n - v_{j-1/2}^n) \right] / (4 \Delta x), \quad (5)$$

where $f = f_c + f_q$ denotes the *total* force. Equations 4 and 5 are solved iteratively by rewriting these two equations as

$$f_1(C, v) = C_j^{n+1} - C_j^n - \Delta t \text{RHS}_{\text{Ceq}}, \quad (6)$$

$$f_2(C, v) = v_{j+1/2}^{n+1} - v_{j+1/2}^n - \Delta t \text{RHS}_{\text{veq}}/m, \quad (7)$$

where RHS_{Ceq} and RHS_{veq} denote the right-hand-side of Eqs. 4 and 5, respectively. Using an abbreviated notation where $C = C_j^{n+1}$ and $v = v_{j+1/2}^{n+1}$, Newton's method in two variables consists of expanding f_1 and f_2 in a Taylor series expansion with respect to $C = C_o + \Delta C$ and $v = v_o + \Delta v$ where C_o and v_o represent an initial guess (typically the solution from the previous time step: $C_o = C^n$ and $v_o = v^n$)

$$f_1(C, v) = f_1(C_o, v_o) + \frac{\partial f_1}{\partial C} \Delta C + \frac{\partial f_1}{\partial v} \Delta v, \quad (8)$$

$$f_2(C, v) = f_2(C_o, v_o) + \frac{\partial f_2}{\partial C} \Delta C + \frac{\partial f_2}{\partial v} \Delta v. \quad (9)$$

By setting $f_1(C, v) = 0$ and $f_2(C, v) = 0$, the ΔC and Δv can be expressed in terms of the known quantities $f_1(C_o, v_o)$ and $f_2(C_o, v_o)$ and their derivatives with respect to C and v . Analytic expressions for the derivatives of f_1 and f_2 with respect to C and v can be derived by taking the appropriate derivatives of Eqs. 6 and 7.[9] Once the ΔC and Δv are computed, the values of C and v are updated and these updated values become the new guess (i.e., the C_o and v_o). Equations 8 and 9 are then solved for new values of ΔC and Δv and the process is repeated until convergence is achieved. In practice, the absolute values of the ΔC , Δv , f_1 , and f_2 are monitored until all four are simultaneously less than some user specified convergence threshold at all of the grid points. The converged C and v are now the correct values at the future time step t_{n+1} . The time index is incremented $n \rightarrow n + 1$ and the process is repeated to find the values of C and v at the next time step and so on. The iterative solution method converges exponentially with respect to the iteration count which typically varies between 10 - 20 iterations depending upon the size of the time step (Δt) and the desired level of convergence. At each time step, the values of the C_0 , C_{N+1} , $v_{-1/2}$, and $v_{N+3/2}$ at the edges of the grid are determined by applying the appropriate finite-difference expressions for the Gaussian-like boundary conditions: $\partial^2 C / \partial x^2 = \text{constant}$ and $\partial^2 v / \partial x^2 = 0$.[9]

A stability analysis of the IFDM was performed using the method of truncation error analysis.[9] In this approach, Taylor series expansions of the C and v with respect to Δx and Δt are substituted into the finite difference Eqs. 4 and 5 and the truncation error terms (i.e., the terms multiplying Δx^2 and Δt^2) are explicitly derived. Some of these error terms represent numerical diffusion and take the form $\gamma_v \partial^2 v / \partial x^2$ and $\gamma_C \partial^2 C / \partial x^2$ (the explicit functional forms for γ_v and γ_C are given in Ref. 9). The effective diffusion coefficients are given by $\Gamma_v = \Delta t^2 \gamma_v$ and $\Gamma_C = \Delta t^2 \gamma_C$ which can be positive or negative and can also change sign during the course of the calculation. Even a temporary occurrence of a negative diffusion coefficient can lead to instabilities and a complete breakdown of the calculations. To ensure a stable propagation, the overall diffusion coefficient must remain positive. This can be accomplished using the well-known hydrodynamic technique called “artificial viscosity”.[11–13] In this approach, a positive diffusion term with the *same functional form* as that derived in the truncation error analysis is introduced into the finite difference equations. The positive diffusion coefficient multiplying this new diffusive term is chosen large enough to ensure that the overall diffusion coefficient is always positive so that the propagation will remain stable. In other words, the overall diffusion (truncation error + artificial viscosity) is always dissipative or stabilizing. It is important to note that the diffusive artificial viscosity term is of the *same* order in Δt^2 as the truncation error. Thus, the stability of the calculation can be maintained even as the grid spacing and time step are decreased (i.e., the resolution of the calculation is increased).

III. APPLICATIONS

The IFDM has been applied to three different test cases: (1) a one-dimensional free Gaussian wave packet, (2) a one-dimensional Gaussian wave packet scattering off an Eckart barrier, and (3) a two-dimensional Gaussian wave packet scattering off an Eckart barrier coupled with a harmonic oscillator potential in the other degree of freedom.[9, 14, 15] The IFDM results for these three different applications were compared to the results of two other numerical methods: the Crank-Nicholson algorithm[11] (which is based on a finite difference solution of the time-dependent Schrödinger equation) and the MLS/ALE approach[8] (which is another quantum hydrodynamic method). These comparisons provide an initial assessment of the convergence properties, numerical accuracy, computational efficiency, and stability of the IFDM.

The accuracy of the IFDM solution for the one-dimensional free Gaussian wave packet was found to be in excellent agreement with the analytic result with an average percent difference of less than $5 \times 10^{-5} \%$ using a grid spacing of $\Delta x = 0.05$ au. In contrast the Crank-Nicholson method required a much smaller grid spacing of $\Delta x = 0.0005$ au to obtain an average percent difference

of $6 \times 10^{-3}\%$. This is due to the fact that the Crank-Nicholson algorithm is directly solving for the highly oscillatory real and imaginary parts of the wave function. The accuracy of the 4-th order MLS/ALE solution for the free Gaussian wave packet was found to be similar to the IFDM. The stability of the IFDM was verified out to the edges of the fixed (Eulerian) grid where the probability density is extremely small $\rho < \exp(-40,000)$.

For the one- and two-dimensional Eckart barrier tunneling problems, the IFDM transmission probabilities were found to be in excellent agreement with both the Crank-Nicholson and MLS/ALE methods. In all three applications, the IFDM proved to be more computationally efficient than either the Crank-Nicholson or MLS/ALE approach. For the one-dimensional Eckart barrier tunneling problem, the IFDM transmission probabilities were computed 1.8 and 6.9 times faster than those computed using the Crank-Nicholson and MLS/ALE methods, respectively.[9] For the two-dimensional Eckart barrier tunneling problem, the IFDM transmission probabilities were computed in 15 minutes compared to the 1 hour required by the ALE/MLS approach.[15]

The latest version of the IFDM requires no filtering of the second derivative of C in the evaluation of the quantum force.[15] The original version used a moving window average of $\partial^2 C / \partial x^2$ to help reduce the numerical noise and improve stability.[9] We have found that this window averaging can be eliminated all together by simply increasing the artificial viscosity coefficient to $\nu_o^1 = 1 \times 10^5$ and truncating the fixed (Eulerian) grid to some reasonable value of the density (i.e., $\rho > 1 \times 10^{-8}$). A “smart” Eulerian grid is then implemented which “activates” or adds new edge points to the grid when the density at the edge point increases above a user specified threshold (i.e., $\rho > 1 \times 10^{-8}$). The values of C and v at the edge point are initialized in a stable way by using a finite difference representation of the appropriate Gaussian like boundary conditions at the edge (i.e., $\partial^2 C / \partial x^2 = \text{constant}$ and $\partial^2 v / \partial x^2 = 0$). These modifications not only improve the accuracy and resolution of the method by eliminating the window averaging of the second derivative of C , they also significantly improve the computational efficiency of the method by reducing the size of the grid. The calculations are performed only at those “active” Eulerian grid points where the density is significant. In this way, the fixed Eulerian grid is optimized so that it exhibits similar computational advantages as a Lagrangian or ALE grid.

IV. CONCLUSIONS AND FUTURE WORK

The Iterative Finite Difference Method (IFDM) is a promising new approach for the direct numerical solution of the quantum hydrodynamic equations of motion.[9] The set of non-linearly coupled finite differenced quantum hydrodynamic equations are solved iteratively at each time step using Newton’s method. The IFDM converges exponentially with respect to the iteration count and is

second order accurate in both space and time. The stability of the method was investigated using truncation error analysis and the functional form of the potentially negative (unstable) numerical diffusion terms were identified. The stability of the IFDM is ensured by introducing a positive (stabilizing) numerical diffusion term (“artificial viscosity”) into the finite difference equations. This stabilizing term is of the same order as the errors which are already present in the calculation. Thus, the stability of the method can be maintained even as the resolution of the calculation is increased. The methodology was briefly reviewed and the results of several initial benchmark calculations discussed. These initial applications show that the IFDM is computationally efficient, stable, and numerically accurate. Recent improvements to the IFDM include the elimination of all filtering or averaging of the second derivative of C and a truncation of the fixed (Eulerian) grid. A “smart” Eulerian grid is used for which the calculations are performed only at active grid points which contain significant probability density.

In its present form, the IFDM does not solve the “node problem” (i.e., the singularities in the quantum potential and force which can occur in the regions where the density approaches zero due to the interference effects in the reflected component of a wave packet scattering off a barrier).[16] However, an important feature of the IFDM is that it remains stable even in the presence of nodes which allows the propagation to continue and accurate transmission probabilities can be computed. Also, the artificial viscosity technique can be used to mitigate the “node problem” by preventing the formation of nodes (at the expense of smoothing out the solution in the region near the node).[8, 9] Future work will include investigation of a possible analytic treatment of the “node problem” within the IFDM, its extension to higher dimensions, and most importantly its application to real molecular systems.

V. ACKNOWLEDGMENTS

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- [1] L. de Broglie, C. R. Acad. Sci. Paris. **183**, 447 (1926); **184**, 273 (1927).
 - [2] D. Bohm, Phys. Rev. **85**, 166 (1952); **85**, 180 (1952).
 - [3] P. R. Holland, “The Quantum Theory of Motion”, Cambridge University Press, New York, 1993.

- [4] R. E. Wyatt, "Quantum Dynamics with Trajectories: Introduction to Quantum Hydrodynamics", Springer, New York, 2005.
- [5] "Quantum Trajectories", edited by P. K. Chattaraj, CRC Press/Taylor & Francis Group, 2010.
- [6] C. Lobreore and R. E. Wyatt, Phys. Rev. Lett. **82**, 5190 (1999).
- [7] R. E. Wyatt, Chem. Phys. Lett. **313**, 189 (1999).
- [8] B. K. Kendrick, J. Chem. Phys. **119**, 5805 (2003).
- [9] B. K. Kendrick, J. of Molec. Struct: THEOCHEM **943**, 158 (2010).
- [10] S. V. Patankar, "Numerical Heat Transfer and Fluid Flow", Hemisphere Publishing Co., New York, 1980.
- [11] W. H. Press, B. P. Flannery, S. A. Teukolsky, W. T. Vetterling, "Numerical Recipes; The Art of Scientific Computing", Cambridge University Press, New York, 1986.
- [12] J. VonNeumann and R. D. Richtmyer, J. Appl. Phys. **21** (1950) 232.
- [13] E. Scannapeico and F. H. Harlow, Los Alamos National Laboratory report LA-12984, (1995).
- [14] D. K. Pauler and B. K. Kendrick, J. Chem. Phys. **120** (2004) 603.
- [15] B. K. Kendrick, unpublished.
- [16] R. E. Wyatt and E. R. Bittner, J. Chem. Phys. **113** (2000) 8898.