Quantum Dynamics using Trajectories in Python

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1 Abstract

In this paper we will see the application of Bohmian mechanics to a few simple systems. Those being the free wave-packet and the harmonic oscillator, which were chose due to their numerical stability. The equations of motion are integrated in the arbitrary Lagrangian-Eularian frame-of-reference, with the velocity of the grid points chose to maintain their uniformity. The spatial derivatives are evaluated using the Moving Weighted Least Squares fitting procedure. All codes were developed in the Python programming language using the Matplotlib, NumPy, and SciPy libraries and can be readily adapted for realistic molecular potentials.

2 Introduction

Bohmian mechanics is an ontological interpretation of quantum theory, meaning that it concerns itself with describing what is in the world. It states that there are particles with well-defined position and momentum in nature. It was first presented by Louis de Broglie in 1927 and completed by David Bohm in 1952. It recieved little attention since the work of David Bohm in 1952 until approximately 2000. It has since been used extensively to develop numerical methods for time-dependent qunatum mechanics amoung other applications.

3 Theory

We can start by considering the theory, beginning with the position-representation of wavefunction in polar form

$$\psi = Re^{iS/\hbar} = e^{C+iS/\hbar} \tag{1}$$

Where R is the amplitude of the wavefunction $R = |\psi|$, S is its phase $S = \hbar(\ln\psi - \ln\psi^*)/2i$, and C is the C-amplitude $C = \ln R$. We insert this wavefunction in polar form into the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{-\hbar^2}{2m}\nabla^2\psi + V\psi \tag{2}$$

After some manipulations and separation into real and imaginary parts to get the following set of coupled differential equations

$$\frac{\partial C}{\partial t} = -\frac{1}{2m}\left[\nabla^2 S + 2\vec{\nabla}C\cdot\vec{\nabla}S\right] \tag{3}$$

$$\frac{\partial S}{\partial t} = -\left[\frac{|\vec{\nabla}S|^2}{2m} + V + Q\right] \tag{4}$$

So, we see that Equation (4) is the classical Hamilton-Jacobi equation with an additional term, Q, where $Q = -\frac{\hbar^2}{2m}\left[\nabla^2 C + |\vec{\nabla}C|^2\right]$. The classical Hamilton-Jacobi equation is solved to obtain the velocity field on configuration space, given by $\vec{\mathbf{v}} = \vec{\nabla}S/m$, for the propagation of classical trajectories. Similarly, we can associate the quantum Hamilton-Jacobi equation with this velocity field for the propagation of quantum trajectories. The additional term, the quantum potential, introduces all the quantum effects into the dynamics of these particles.

The C-amplitude is used rather than R as it avoids division by a very small number in the quantum potential. We can convert to a moving frame of reference by using the material derivative

$$\frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + \frac{\mathrm{d}\vec{\mathbf{r}}}{\mathrm{d}t}\cdot\vec{\nabla} \tag{5}$$

Where $\frac{\mathrm{d}\vec{\mathbf{r}}}{\mathrm{d}t}$ is the velocity of the reference frame. Substituting Equation (5) into Equations (3)-(4) gives us

$$\frac{\mathrm{d}C}{\mathrm{d}t} = (\frac{\mathrm{d}\vec{\mathbf{r}}}{\mathrm{d}t} - \vec{\nabla}S/m) \cdot \vec{\nabla}C - \frac{\nabla^2 S}{2m} \tag{6}$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = (\frac{\mathrm{d}\vec{\mathbf{r}}}{\mathrm{d}t} - \vec{\nabla}S/m) \cdot \vec{\nabla}S + \frac{|\vec{\nabla}S|^2}{2m} - V - Q \tag{7}$$

These are the equations of motion whose frame of reference depends on the value of $\frac{\mathrm{d}\vec{\mathbf{r}}}{\mathrm{d}t}$. There are a few cases that are relevant — the first being when $\frac{\mathrm{d}\vec{\mathbf{r}}}{\mathrm{d}t} = 0$, this is the fixed frame of reference, which is called "Eularian". The second case being the "Lagrangian", this is when the grid points move along quantum trajectories at the flow velocity of the quantum fluid, i.e. $\frac{\mathrm{d}\vec{\mathbf{r}}}{\mathrm{d}t} = \vec{\mathbf{v}}$. Finally when we have $\frac{\mathrm{d}\vec{\mathbf{r}}}{\mathrm{d}t} \neq \vec{\mathbf{v}} \neq 0$ that is an "arbitrary Lagrangian-Eularian" (ALE) frame-of-reference. The latter case was used in my numerical calculations.

This is as when quantum trajectories are calculated in the Eularian frame-of-reference it takes a much larger grid. When quantum trajectories are obtained in the Lagrangian frame, the trajectories move to areas of high probability density, so numerical derivatives necessary cannot be accurately obtained. So, in the ALE frame, grid velocities can be chosen so improve numerical accuracy with the same number of grid points as the Lagrangian frame.

4 Methods

4.1 ψ

I utilized the following initial wavefunction

$$\psi(x,0) = \Big(\frac{\alpha_0}{\pi}\Big)^{1/4} \exp\Big[-\frac{\alpha_0}{2}(x-x_0)^2 + ik_0(x-x_0)\Big] \tag{8}$$

Where we have $\alpha_0 = .5$ to set the width of the packet, the wavenumber $k_0 = 3$ in both cases, and the center of the wave packet $x_0 = 0$.

4.2 $\frac{\partial^n}{\partial x^n}$

Using the methods of Robert E. Wyatt, solving the hydrodynamic equations in using the ALE frame-of-reference consists of propagating a set of N grid

points that are initially distributed uniformly around the centroid of the wavepacket. The hydrodynamic fields and trajectories are integrated concurrently, done with the LSODA algorithm, which is a switching algorithm that can adapt to the stiffness encountered in the equations of motion.

Evaluating the quantum potential is especially difficult in both the Lagrangian and ALE frames. The quantum potential requires derivatives of the C-amplitude, which is used here because it can be locally approximated with a quadratic polynomial for a wave packet that is initially Gaussian, making it well-suited to polynomial interpolation or fitting for calculation of the spacial derivatives. I used the Moving Weighted Least Squares (MWLS) to approximate the C-amplitude and phase sampled at the N grid points. The MWLS method can be formulated by Taylor expanding around point x_k evaluated at a nearby point x to the M^{th} order

$$f(x) = \sum_{i=0}^{M} f^{(i)}(x_k)(x - x_k)^i \tag{9}$$

Now using a weighted sum of square errors for the above function evaluated at N data points

$$\Omega_k = \sum_{j=1}^{N} \omega(x_j - x_k) \left(f_j - \sum_{i=0}^{M} f^{(i)}(x_k)(x_j - x_k)^i \right)^2 \tag{10}$$

Where $\omega(x_j - x_k)$ is a weighting function, which can take the form

$$\omega(x_j - x_k) = \exp\left[-\alpha(x_j - x_k)^2\right] \tag{11}$$

In our case the parameter $\alpha = 1$. Now taking the derivative of the above equation with respect to $f^{(i)}$ and setting it to zero allows us to obtain

$$\mathbf{B}^T\mathbf{W}\mathbf{B}\vec{\mathbf{c}} = \mathbf{B}^T\mathbf{W}\vec{\mathbf{f}} \tag{12}$$

Where the vector $\vec{\mathbf{c}}$ is an N dimensional column vector whose elements are given by $c_i = f^{(i)}(x_k)$, $\vec{\mathbf{f}}$ is similar but it contains our points to be fit to. The matrix $\mathbf{B}$ with dimensions $N \times M$ with elements $B_{i,j} = (x_i - x_k)^j$. Finally, we have the weight matrix $\mathbf{W}$ which is $N \times N$ with elements $W_{i,j} = \omega(x_j - x_k)\delta_{i,j}$. We can solve Equation (22) for $\vec{\mathbf{c}}$ to get our approximated function and it's derivatives at a given point x_k, therefore, the system of equations must be solved N times for N points.

4.3 V

The classical potential utilized is given as V, has the following form

$$V = ax^2 \tag{13}$$

Where $a = 0, 2$ for our two cases of the free wave packet and the harmonic oscillator.

5 Results

In both cases atomic units are used. The time increments are $dt = 0.005$ and extend from $t = 0$ to $t = 5$. The number of grid points used is $N = 25$ and they are uniformly spaced between $x = -2$ and $x = 2$.

5.1 Free Wave Packet

The results obtained for this situation can be seen here in Figure 1

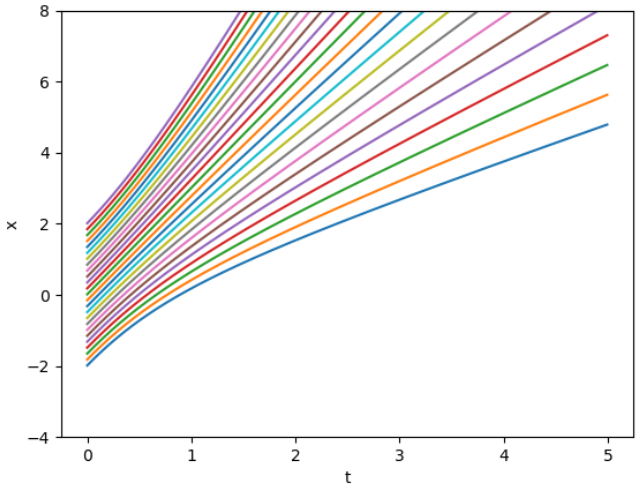

Figure 1: Quantum trajectories in ALE frame corresponding to the free wave packet

Here we see the characteristic spreading in the wave packet through the dynamics seen in the increasing space between trajectories.

5.2 Harmonic Oscillator

The results for the harmonic oscillator are given as

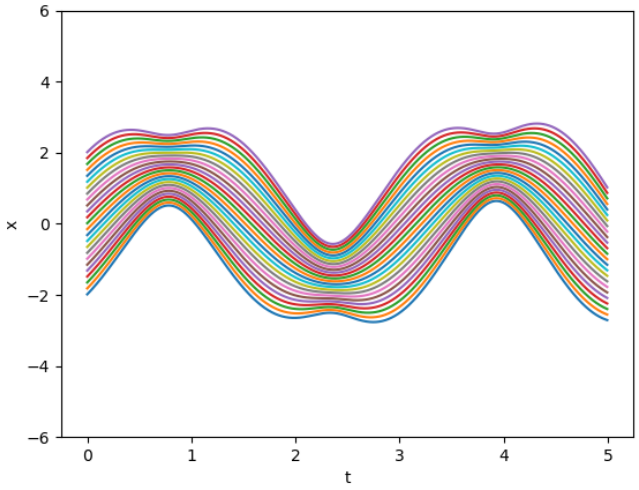

Figure 2: Quantum trajectories in ALE frame corresponding to the harmonic oscillator

The so-called "breathing" at the turning points of the harmonic oscillator when a non-coherent state is propagated is seen here.

6 Conclusion

In our simulations of simple model systems we saw results characteristic of what is expected using only 25 grid points. The method works very well in these situations but, in anharmonic potentials, where ripples in the density form, it becomes very difficult to obtain numerical spatial derivatives. In these systems that are very pertinent for molecular dynamics of realistic molecular systems, it may be necessary to lessen the quantum forces at nodes of the wavefunction or to integrate a hybrid of Equations (6)-(7) and the moving-path transform of the Schrödinger equation. Future directions would be obtaining more accurate or efficient approximations to the quantum potential. Through developing this program, I learned a great amount about

molecular dynamics and Python programming. Thank you for reading my paper.

References

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