Kernel density estimation-based solution of the nuclear Schrödinger equation

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A B S T R A C T

Solving the time-dependent Schrödinger equation for nuclear motion remains a challenge. Despite novel approaches based on Bohmian mechanics, the long-time stability and generalization to multiple dimensions remains an open question. In the present work a method based on an ensemble of classical particles instead of a wave function is employed to evolve the system. Quantum effects are introduced through forces derived from the quantum potential $Q$ and the necessary derivatives are obtained from a density estimate using kernel density estimation. Application of the procedure to typical 1- and 2-dimensional problems yields good agreement with numerically exact solutions and favourable scaling with the number of particles is found.

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1. Introduction

In recent years the de-Broglie–Bohm formulation of quantum mechanics, i.e. Bohmian mechanics, has attracted increased attention [1]. While the essential aspects of Bohmian mechanics date back to ideas by de Broglie [2] and Bohm [3], it was not until the development of the quantum trajectory method (QTM) that interest in the de-Broglie–Bohm formulation intensified [4]. In QTM, the probability density $\rho$ is discretized into a set of ‘fluid elements’ and the equations of the hydrodynamic formulation of quantum mechanics [5] are used to propagate the wave function.

Since $\rho$ appears in the denominator, the quantum potential $Q$ (see Eq. (5)) undergoes rapid variations over short length scales in nodal regions and becomes singular at the exact positions of nodes. In practice, similar problems occur also in regions of ‘pseudo nodes’ where $\rho \neq 0$ but there are kinks in the velocity field [6]. Large oscillating quantum forces compromise the numerical stability of the QTM [7]. These numerical challenges were addressed in various ways including e.g. the introduction of artificial viscosity into the hydrodynamic equations [6], which prevents $Q$ from becoming singular or the use of a covering wave function to avoid developing nodes before they cause problems [7].

Here, a novel computational approach – conceptually different from the usual implementation of Bohmian mechanics – is presented. It is based on the de-Broglie–Bohm formulation, but an ensemble of ‘virtual particles’ following Newton’s equations of motion is used. The virtual particles in KDE are conceptually different from the fluid elements used in QTM and related approaches in that they are defined by their position and velocity, while the fluid elements in QTM carry additional amplitude and phase information used to reconstruct the hydrodynamic fields by a fitting procedure. Although fluid elements are often referred to as ‘computational particles’, they rather are grid points of a moving grid in QTM and related methods. In KDE no fitting of the hydrodynamic fields is necessary which makes the method computationally efficient, numerically stable and allows comparatively long propagation times. Furthermore, KDE in its present implementation eliminates the node problem and makes it suitable for mixed quantum-classical nuclear dynamics which is of interest for future applications in atomistic simulations.

2. Formal development

The formal development starts from the Madelung ansatz [5]

$$\psi(x, t) = R(x, t) \exp(iS(x, t)/\hbar)$$

for the wave function where $R(x, t)$ and $S(x, t)$ are the real-valued amplitude and action, respectively. Substituting $\psi$ in the time dependent Schrödinger equation (TDSE) (Eq. (1))

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(x, t)\right] \psi(x, t)$$

(1)
and separating real and imaginary parts, the quantum Hamilton–Jacobi equation [3] is obtained

$$-\frac{\partial S}{\partial t} = \frac{1}{2m}(\nabla S)^2 + V - \frac{\hbar^2}{2m} \nabla^2 R$$

(2)

Eq. (2) is identical to the classical Hamilton–Jacobi equation except for the last term, which is commonly referred to as the quantum potential $Q$.

$$Q = -\frac{\hbar^2}{2m} \nabla^2 R$$

(3)

The quantum potential and the associated quantum force $f_Q = -\nabla Q$ derived from it give rise to all quantum effects, including tunnelling, zero point energy and interference [6]. Thus, if the quantum potential was known, it would be possible to use Newton’s equations of motion instead of the TDSE to follow the time evolution according to [3]

$$m\ddot{x} = -\nabla[V + Q] = f_c + f_Q$$

(4)

where $f_c$ is the classical and $f_Q$ the quantum force.

Substituting $R = \sqrt{\rho}$ in Eq. (3) the expressions for $Q$ and $f_Q$ in terms of the density $\rho$ are [8]

$$Q = \frac{\hbar^2}{8m} \left[ \frac{(V\rho)^2}{\rho^2} - 2V^2 \rho \right]$$

(5)

$$f_Q = \frac{\hbar^2}{4m} \left[ \frac{\nabla^3 \rho}{\rho} - \frac{\nabla(V\rho) \cdot \nabla\rho}{2\rho^2} - \left( \frac{\nabla^2 \rho}{\rho} - \frac{\nabla \rho \cdot \nabla^2 \rho}{\rho^2} \right) \nabla \rho \right]$$

(6)

It is not necessary to embrace the interpretation of $\rho$ as a particle density as physical reality. Instead, the notion of virtual particles may simply be regarded as a computational tool to solve the TDSE.

Since it is impossible to evolve an infinite number of particles according to Eq. (4) and the evaluation of the quantum potential and force according to Eqs. (5) and (6) requires knowledge of the particle density $\rho$, an efficient way to estimate $\rho$ is required. For convenience the following description is for a single physical particle in one dimension but extensions to multiple dimensions are straightforward.

In Statistics, the method of kernel density estimation (KDE) [9,10] is a non-parametric way to estimate the probability density function from finite data samples. An estimate $\hat{\rho}$ for the true density $\rho$ using $N$ virtual particles with corresponding positions $x_i$ is afforded by

$$\hat{\rho}(x) = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{h_i} k \left( \frac{x - x_i}{h_i} \right)$$

(7)

where $h_i$ is the bandwidth and the kernel $k$ is a non-negative function that integrates to unity and has zero mean. By construction, the estimate $\hat{\rho}$ integrates to unity and probability is thus always conserved. Here, a Gaussian kernel (Eq. (8)) gave the best results.

$$k(x) = \frac{1}{\sqrt{2\pi}} e^{-x^2/2}$$

(8)

The bandwidth $h_i$ is crucial for the quality of the estimate $\hat{\rho}$ [11]. For this work, a point-wise estimator using a different $h_i$ for each sample point $x_i$ was found to be best.

First, a pilot estimate needs to be constructed where all $h_i$ in Eq. (7) are set equal to a fixed bandwidth $h_{\text{pilot}}$. A common way to choose $h_{\text{pilot}}$ is to minimize the mean integrated squared error (MISE) between the estimate $\hat{\rho}$ and the true $\rho$.

$$\text{MISE}(h) = E \int (\hat{\rho}(x) - \rho(x))^2 \, dx$$

(9)

Under weak assumptions [9,10] for $\rho$ and $k$ the asymptotically optimal bandwidth $(N \to \infty)$ is given by [12]

$$h_{\text{opt}} = \left[ \frac{\int k(x)^2 \, dx}{N \int k^2(x) \, dx} \right]^{1/5}$$

(10)

Usually, Eq. (10) cannot be evaluated directly since $\rho$ is unknown. However, here the initial $\rho$ is specified by the boundary conditions (see below). In a dynamics simulation $h_{\text{pilot}}$ needs to be updated since Eq. (10) is only used for $t=0$. Although there are multiple ways to choose a bandwidth for unknown probability densities [12,13], a faster method is desirable for a dynamics simulation where a new $h_{\text{pilot}}$ is needed at every time step.

The following updating scheme for $h_{\text{pilot}}$ was found to provide robust results:

$$h_{\text{pilot}}(t + \Delta t) = \left( \frac{G(t - \Delta t)}{G(t)} \right)^{1/d} h_{\text{pilot}}(t)$$

(11)

where $G(t)$ and $G(t - \Delta t)$ are the geometric means $G = \left( \prod_{i=1}^{N} \hat{\rho}(x_i) \right)^{1/N}$ at the current and previous time step (see Eq. (12)) and $d$ is the number of dimensions. Pilot bandwidths for the first and second time step are set equal to $h_{\text{opt}}$. As the initial distribution of particles evolves, the pilot bandwidth needs to adapt (spread or shrink) for a robust estimate of $\hat{\rho}$. The geometric mean was found to be a good measure for that.

To reduce the bias, $h_{\text{pilot}}$ is scaled according to Abramson’s square root law [14] to obtain a scaled bandwidth $h_i$ for each particle

$$h_i = \sqrt{\frac{G_i}{\hat{\rho}_i}} h_{\text{pilot}}$$

(12)

where $\hat{\rho}_i$ is the pilot estimate at the individual particle positions $x_i$.

Then, a new estimate is obtained from the scaled $h_i$ and used to calculate $Q$ and $f_Q$. The derivatives in Eqs. (5) and (6) are calculated analytically. The $r$th derivative of $\hat{\rho}$ is

$$\frac{d^r}{dx^r} \hat{\rho}(x) = \frac{1}{N} \sum_{i=1}^{N} (-1)^r \frac{1}{h_i^{r+1}} H_r \left( \frac{x - x_i}{h_i} \right) k \left( \frac{x - x_i}{h_i} \right)$$

(13)

where $H_r$ is the $r$th Hermite polynomial.

Although multivariate versions of KDE are known [15], we use a simple product of one-dimensional Gaussian kernels (Eq. (8)) sharing the same bandwidths for our two-dimensional example. This greatly simplifies higher-dimensional kernel density estimation and was found to be sufficient for the investigated problem. A main advantage of KDE is that the true particle density can be estimated without any computationally expensive fitting which usually involves solving a system of linear equations. It is thus conceptually different from the method developed by Garashchuk et al [16] where the density is a sum of Gaussians, but their parameters have to be calculated at every time step and the number of Gaussians changes during the simulation.

3. Applications

To start an actual simulation the initial $x_i$ are required. For this, Monte-Carlo sampling can be used, but it is more efficient to choose them directly according to the initial density. In one dimension this can be easily achieved by distributing the integral of the normalized density into intervals of magnitude $1/N$ and placing a single particle in each interval. In multiple dimensions the problem is known as optimal quantization and several algorithms to find a so-called $N$-quantizer are available [17–19].

Alternatively, an arbitrary distribution of particles is subjected to a short equilibration before running the actual dynamics. During
the equilibration, the only force acting on the ensemble is the equilibrating force $f_{eq}$ given by

$$f_{eq}(t) = -\frac{m}{\tau} \nabla \left( \hat{\rho}(t) - \rho \right)$$

(14)

where $m$ is the particle mass, $\hat{\rho}$ the current density estimate, $\rho$ the target density and $c$ an arbitrary constant selected such that time integration is stable using the chosen time step. Particle velocities are set to 0 after every step and the equilibration is run until all positions have reached a stable point. For the two-dimensional model problem in this work, the initial $x_i$ were chosen using an $N$-quantizer obtained by Lloyd’s method [18] followed by an equilibration as described above.

The algorithm with known particle positions and velocities at time $t$ is as follows.

1. Generate a pilot estimate according to Eq. (7) using $h_{\text{pilot}}$ then scale all bandwidths according to Eq. (12).
2. Calculate $f_{eq}$ acting on each particle according to Eq. (8).
3. Integrate the equation of motion ((4)) from time $t$ to $t + \Delta t$ (in this work, a Velocity-Verlet integrator [20] is used).
4. Update $h_{\text{pilot}}$ according to Eq. (11).
5. Return to step 1 until the desired total time $t$ is reached.

The above techniques are used to solve two previously investigated problems. One is the scattering of a particle from a 1-dimensional Eckart barrier [4,6], the other one is the scattering of a harmonic oscillator from an Eckart barrier [21]. Tunnelling probabilities were obtained by counting the fraction of virtual particles passing the barrier maximum. All values are given in atomic units unless specified otherwise.

1-dimensional Eckart Barrier: The scattering of a particle of mass $m = 2000 \, m_e$ from an Eckart Barrier given by

$$V(x) = \frac{V_0}{\cosh^2(a(x-x_0))}$$

(15)

where $V_0 = 8000 \, \text{cm}^{-1} \, (0.992 \, \text{eV})$ is the height of the barrier, $a = 0.4 a_0^{-1}$ determines the width and $x_0 = 7 a_0$ is the location of the maximum was considered first. The initial density

$$\rho(x, 0) = \sqrt{\frac{\beta}{\pi}} \exp(-\beta x(x-x_0)^2)$$

(16)

is a Gaussian with width $\beta = 4 a_0^2$, initially centred at $x_0 = 2 a_0$. The initial particle velocities are $v_i = \sqrt{2E_{\text{kin}}/m}$ for different values of $E_{\text{kin}}$. The equation of motion (Eq. (4)) was integrated using a Velocity-Verlet integrator [20] with $\Delta t = 0.34 \, \text{a.u.}$ until $\text{int} = 150 \, \text{fs}$ (tunnelling probabilities converge long before the end of the simulation for all energies $E_{\text{kin}}$).

For $N = 1$ the system behaves purely classically, whereas quantum effects become more pronounced with increasing $N$. A good estimate compared to exact results is obtained using as few as $N = 100$ particles. Table 1 shows the tunnelling probabilities for a range of kinetic energies and varying number of virtual particles $N$. The absolute error remains almost constant across the entire range of energies for a given $N$.

![Figure 1. Tunnelling probability in dependence of available kinetic energy. The solid black line with circles shows the results obtained using the KDE approach with $N = 2000$ particles and the grey (red) dashed line with crosses shows the exact results obtained using the Crank–Nicolson algorithm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)

Table 1

<table>
<thead>
<tr>
<th>$E_{\text{kin}}$ (eV)</th>
<th>$N = 1$</th>
<th>$N = 100$</th>
<th>$N = 500$</th>
<th>$N = 1000$</th>
<th>$N = 2000$</th>
<th>C.N.</th>
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<td>0.00000</td>
<td>0.00000</td>
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<td>0.00100</td>
<td>0.02380</td>
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</tr>
<tr>
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<td>0.01000</td>
<td>0.04200</td>
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</tbody>
</table>

Figure 1. Tunnelling probability in dependence of available kinetic energy. The solid black line with circles shows the results obtained using the KDE approach with $N = 2000$ particles and the grey (red) dashed line with crosses shows the exact results obtained using the Crank–Nicolson algorithm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

<table>
<thead>
<tr>
<th>$x_0/d_0$</th>
<th>$N = 100$</th>
<th>$N = 200$</th>
<th>$N = 500$</th>
<th>$N = 1000$</th>
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<td>0.532</td>
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<td>0.510</td>
<td>0.510</td>
<td>0.506</td>
<td>0.507</td>
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</table>
**Figure 2.** Snapshots at different times for the scattering from an Eckart barrier ($V_0 = 0.992$ eV) with an initial kinetic energy of the wave packet of 0.8 eV. The grey (red) solid line shows the results obtained using the Crank–Nicolson algorithm and the black solid line shows density estimate using $N = 300$ virtual particles. The shape of the Eckart barrier is shown by the dotted black curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Partially bound state:** In order to model the potential energy curve of a bound state, the 1-d Eckart barrier is combined with one half of a harmonic oscillator, giving the potential

\[
V(x) = \begin{cases} 
\frac{V_0}{\cosh^2(a(x-x_0))} & x \geq x_0 \\
\frac{V_0}{\cosh^2(a(x-x_0))} + \frac{1}{2}k(x-x_0)^2 & x < x_0 
\end{cases}
\]

(19)

with $k = 0.002$ and $x_0 = 2a_0$. All other parameters for the Eckart barrier and the initial density (given by Eq. (16)) are the same as for the 1-d scattering problem, discussed above.

The initial particle velocities are $v_i = \sqrt{2E_{\text{kin}}/m}$ with $E_{\text{kin}} = 0.8$ eV and the equations of motion integrated with Velocity-Verlet [20] and a time step of $\Delta t = 5.17$ a.u. until $t = 1000$ fs. Tunnelling probabilities were again obtained by counting the fraction of virtual particles that passed the barrier maximum $x_b$. In order to treat this problem, a slight variation to the bandwidth selection described earlier was required. The particle ensemble is separated into a ‘trapped’ and a ‘transmitted’ part and bandwidths are assigned to both parts individually. The $\hbar_{\text{pilot}}$ for the transmitted part is initialized (to the current value of $\hbar_{\text{pilot}}$ for the trapped part) once the first particle crosses the barrier maximum. This is necessary since the transmitted part spreads out quite significantly and lowers the geometric mean of the density estimate. Since $\hbar_{\text{pilot}}$ evolves according to Eq. (11), this leads to an unphysical broadening of the trapped part if the bandwidth is not calculated for both parts individually.

**Figure 3.** Density estimate ($N = 1000$) for the 2D wave packet given by Eq. (18) scattering from the potential given by Eq. (17) at different time steps. The wave packet starts from $x = -2.5a_0$ and moves to the right. The density is overlaid on the contours of the potential energy surface. Contours of the potential energy are equally spaced between: 0 dark grey (blue) to 0.07 grey (red). Contours of the densities start from $\rho = 0.2$ (black outline) in dark grey (blue) to the maximum value in grey (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Figure 4.** Tunnelling probability as a function of time from the KDE approach (black solid line) and the Crank–Nicolson (CN) algorithm (grey (red) solid line). The results obtained using KDE approach deviate qualitatively and quantitatively from the numerically exact results. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
transform (IFGT) [22], which achieve linear scaling for the summation of Gaussians and are exact to a chosen precision. Although the IFGT was not employed in this work, it will be useful for the application to systems that require a larger number of virtual particles $N$.

Numerical problems encountered with the QTM or similar schemes are effectively eliminated, although capturing interferences is currently not possible. Also, the method is computationally more efficient than grid-based methods. Future improvements concern the selection of the bandwidths $h_i$. Other bandwidth selection methods were tested and allow to capture interferences. However, they have to be adapted in a problem-specific manner and are only numerically stable for a limited time interval. Therefore it is reasonable to expect that a more sophisticated, parameter-free choice of the bandwidth will allow the description of interference effects and generally improve the accuracy of the method.

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