Trajectory guided gaussian basis method

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1 Gaussian Basis

One possible way to solve time-dependent Schrödinger equation is to expand the initial wavepacket as a linear combination of basis functions. Gaussian basis with fixed width is becoming popular in recent years.

$$g_m(x,t) = \sqrt[4]{\frac{a}{\pi}} \exp\left(-\frac{\alpha}{2}(x-q_m(t))^2 + \imath p_m(t)(x-q_m(t)\right) \tag{1}$$

$$|\psi_0\rangle = \sum_{n=1,\ldots,N} c_n(t=0)|g_n(q_n,p_n,t=0)\rangle \tag{2}$$

$$\langle g_m|\psi_0\rangle = \sum_n c_n\langle g_m|g_n\rangle, \quad m=1,...,N. \tag{3}$$

where N is the number of basis used to project the initial wavepacket.

Initial coefficients $c_n(0)$ can be obtained by solving the matrix equation

$$\mathbf{Mc} = \mathbf{b} \tag{4}$$

where

$$\mathbf{M}_{mn} = \langle g_m|g_n\rangle, \quad \mathbf{b} = \{\langle g_1|\psi_0\rangle, \ldots, \langle g_n|\psi_0\rangle\}. \tag{5}$$

Normalization of the wavepacket is conversed in the propagation.

$$N = \langle\psi|\psi\rangle = \sum_{mn}\int dx\ \boldsymbol{c}_m^*\mathbf{M}_{mn}\boldsymbol{c}_n, \tag{6}$$

$$\frac{dN}{dt} = 0 \tag{7}$$

It can be proved by using the Hermitian property of hamiltonian $\mathbf{H}$. Define

$$\boldsymbol{c} = \{c_1, c_2, \ldots, c_N\} \tag{8}$$

and

$$\boldsymbol{\phi} = \{g_1(q_1, p_1), \ldots, g_N(q_N, p_N)\}, \tag{9}$$

Wavefunction at time t can be written as

$$\psi(x,t) = \boldsymbol{c}^T(t)\boldsymbol{\phi}(t) \tag{10}$$

if we substitute Eq. (10) into time-dependent Schrödinger equation , propagation of the initial wavepacket can be transformed into the evolution of the coefficients $c_n(t)$ and the motion of $(p_n(t), q_n(t))$ of gaussian wave packets. The equations for evolution of $\boldsymbol{c}$ will be

$$\imath\mathbf{M}\dot{c} = (\mathbf{H} - \imath\dot{\mathbf{M}})\boldsymbol{c}, \tag{11}$$

where

$$\dot{\mathbf{M}}_{mn} = \langle g_m | \dot{g_n} \rangle \tag{12}$$

and $\mathbf{H}$ is the hamiltonian matrix,

$$\mathbf{H}_{mn} = \langle g_m | -\frac{\hbar^2}{2m}\nabla^2 + V(x) | g_n \rangle. \tag{13}$$

Potential energy is expanded into second-order Taylor series at position of each trajectory

$$V(x) = V(q_n) + \nabla V(q_n)(x - q_n) + \frac{\nabla^2 V(q_n)}{2}(x - q_n)^2 + O((x - q_n)^3) \tag{14}$$

Substituting Eq. (14) to Eq. (11) and ignore the third-order term, we will obtain

$$\mathbf{H}_{mn} = \langle g_m | d_0 + d_1(x - q_n) + d_2(x - q_n)^2 | g_n \rangle. \tag{15}$$

$$d_0 = V(x_n) - \frac{p_n^2 - \alpha}{2m}, \quad d_1 = -\nabla U(x_n), \quad d_2 = \frac{1}{2}\left(\nabla^2 V(x_n) - \frac{\alpha^2}{m}\right) \tag{16}$$

2 System

Quantum effects can be incorporated into the dynamics of parameter trajectories of gaussian basis. At first beginning, linear quantum force(LQF) is being used to the evolution of trajectories, and Morse Oscilator for H_2 is being tested. The initial wavefunction is set as

$$\psi(x,0) = \sqrt[4]{\frac{2\alpha_0}{\pi}} \exp(-\alpha_0(x - x_0)^2 + \imath p_0(x - x_0)) \tag{17}$$

We set $x_0 = 1.4,\ \alpha_0 = 9.16$. Atomic units are used if not specified throughtout the paper.

Because of the inefficiency of LQF of quantum trajectories, some trajectories will diverge. We introduce a parameter $cutoff$ to solve this problem. Trajectories which run out of $cutoff$ ($x(i) > cutoff$) are abondoned.

3 Approximate the wavefunction at each time step with one guassian

Approximate $\psi(x,t)$ with one guassian $g(\alpha(t), x_0(t))$ at each time step. Fitting with a guassian is transformed into fitting $ln\psi(x,t)$ polynomials $f(x) = ax^2 + bx + c$

Instead of using the classical force at the center of gaussian wavepacket,

4 Ehrenfest trajectories

Ehrenfest trajectories was firstly brought out to prevent trajectories from crossing as it averages the force acted on every trajectory. Each Ehrenfest trajectory is experiencing the same force. Quantum tunnelling effects is covered in a different way, but Ehrenfest approximation won't delocalize the wavefunction. The equations of motion (EOM) for Ehrenfest trajectories are as follows:

$$\dot{q} = \frac{p}{m} \tag{18}$$

$$\dot{p} = \langle -\frac{\partial V}{\partial x} \rangle \tag{19}$$

5 Problems

To describe a scattering system, the transmitted wavefunction will be spread out in space, wich is difficult to describe with few sharp gaussians.

6 Probability expansion - Another way to update coefficients

In de Broglie-Bohm formulation of quantum mechanics, there are two coupled equations, one is the so-called quantum Hamilton-Jacobi equation(QHJE), the other is continuity equation. QHJE defines "exact" quantum trajectories, moving under external "real" force and "virtual" quantum force, except for coherent state under harmonic well, where quantum potential is a constant, i.e. wavefunction keeps its shape through propagation.

Computation of exact quantum potential needs the knowledge of the amplitude of wavefunction, which is extremely hard to compute numerically. Certain approximations has to be made about the "hard" term.

On the other hand, continuity equation defines the weight of quantum trajectories, which is a constant i.e. no time dependence, in Lagrangian frame of reference.

Continuity equation in principle is a way to propagate density. So we can expand $\rho(x,t)$ in terms of basis functions $\phi(x;x_i)$, which is decided by the position of evolving trajectories x_i,

$$\rho(x,t) = \sum_i c_i \phi_(x; x_i) \tag{20}$$

If we substitute this expansion into continuity equation, we will obtain

$$\sum_i \dot{c}_i \phi_{ji} + \sum_i c_i \langle \phi_j | \nabla v | \phi_i \rangle = 0 \tag{21}$$

where

$$\phi_{ji} = \langle \phi_j | \phi_i \rangle \tag{22}$$

We can propagate this equation simultaneously while evolving quantum trajectories with linear quantum force (LQF). If written in matrix form, we will get

$$\mathbf{M}\dot{\boldsymbol{c}} = -\mathbf{G}\boldsymbol{c} \tag{23}$$

where

$$M_{ji} = \langle \phi_j | \phi_i \rangle, \quad G_{ji} = \langle \phi_j | \frac{\nabla p}{m} | \phi_i \rangle \tag{24}$$

Matrix G elements cannot be obtained directly, it seems necessary to do a polynomial (or other basis) fitting to get derivative of momentum, we can also add an equation of motion for the first-order derivative to the propagation, but then we need second-order derivative of potential, which is also hard to get.

7 Complex quantum trajectory approach

Complex Hamilton-Jacobi equation

$$\psi(x,t) = \exp\left(\frac{\imath}{\hbar} S(x,t)\right) \tag{25}$$

$$S_t + \frac{S_x}{2m} + V = \frac{\imath\hbar}{2m} S_{xx} \tag{26}$$