

Quantum molecular dynamics with dissipation

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I. INTRODUCTION

Quantum molecular dynamics with dissipation, relevant to many processes in chemistry, physics, and biology, is a long-standing theoretical challenge. Dissipation describes interaction of the system with the bath, representing the environmental degrees of freedom. With few exceptions, the numerically exact simulations of such quantum processes occurring in condensed phase, have been performed, using path integral Monte Carlo methods for models consisting of a low-dimensional system coupled to a bath of harmonic oscillators.^{2,3} Inclusion of friction directly into the Schrödinger equation may be viewed as a simple way to mimic the effect of energy transfer from the system to the environment while limiting quantum dynamics calculations to the system degrees of freedom. Such picture is simplistic, yet it might be useful for some processes. For example, the quantum transition state theory of dissipative tunneling reproduces measurement of the H/D motion on Pt(111) surface with few adjustable parameters.

The force of friction, often taken for processes in condensed phase as linear in velocity of a particle, is most straightforwardly incorporated into equations of motion of a classical particle, characterized by position x_t and momentum p_t ,

$$\frac{dp_t}{dt} = -\frac{dV(x)}{dx} - \gamma p_t|_{x=x_t}, \quad \frac{dx_t}{dt} = \frac{p_t}{m}. \quad (1)$$

The trajectory evolves under the influence of an external potential $V(\mathbf{x})$, which is a function of the Cartesian coordinate, \mathbf{x} , parameter γ denotes the friction coefficient. The friction term for the time-dependent Schrödinger equation (TDSE) can be incorporated into the de Broglie-Bohm formulation of TDSE. The friction term depends on the velocity of each quantum trajectory. The resulting TDSE is nonlinear; the time-dependent wavefunction conserves normalization, while the total energy of the wavefunction decreases with time to the zero-point energy value. The new equations of motion with friction term for quantum trajectories in the Lagrangian frame of reference are as follows:

$$\frac{dp}{dt} = -\frac{\partial}{\partial x}(V + U) - \gamma p \quad (2)$$

$$\frac{dx}{dt} = -\frac{p}{m} \quad (3)$$

Integrating Eq. (14) with respect to x , the evolution of $S(x, t)$ with friction becomes

$$-\frac{\partial S}{\partial t} = \frac{p^2}{2m} + V + U + \gamma S + C(t). \quad (4)$$

The constant of integration $C(t)$ is defined in ??, the overall phase of a wavefunction should not affect its evolution, including wavefunctions describing eigenstates. This requirement is satisfied by the choice,

$$C(t) = -\langle S(x, t) \rangle. \quad (5)$$

Together with continuity equation unchanged by friction, the conventional TDSE with friction becomes

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \hat{H} \psi(x, t) + \gamma(S - \langle S(x, t) \rangle) \psi(x, t). \quad (6)$$

II. GLOBAL LINEAR APPROXIMATION TO NONCLASSICAL MOMENTUM

Quantum potential, U , is responsible for all quantum mechanical effects. We use the QT formalism as a well-defined semiclassical propagation method by making a single approximation to the quantum potential. The essential idea is to get AQP from the global linear least-squares fitting of the nonclassical component of the momentum operator [?],

$$r_\alpha(\mathbf{x}, t) = \frac{\nabla_\alpha A(\mathbf{x}, t)}{A(\mathbf{x}, t)} \approx \tilde{r}_\alpha(\mathbf{x}, t) \quad (7)$$

at each time step in small basis $\mathbf{f}(\mathbf{x})$, which is analytically determined. We use greek letters α, β, \dots to label an arbitrary degree of freedom.

$$U \approx \sum_\alpha \frac{-\hbar^2}{2m} (\tilde{r}_\alpha \cdot \tilde{r}_\alpha + \nabla_\alpha \tilde{r}_\alpha). \quad (8)$$

The least-squares fitting [?] minimizes $\sum_\alpha \langle (r_\alpha - \tilde{r}_\alpha)^2 \rangle$, where \tilde{r}_α is represented in a linear basis $f(\mathbf{x})$

For a two dimensional system, $\mathbf{f}(\mathbf{x})$ can be arranged as a vector $(1, x, y)$, so the approximate nonclassical momentum component is expressed as

$$\tilde{r} = \mathbf{C}\mathbf{f}, \quad (9)$$

where \mathbf{C} is a matrix of coefficients, which solves the matrix equation

$$2\mathbf{S}\mathbf{C} + \mathbf{B} = 0. \quad (10)$$

The matrices are defined by the outer product of vectors

$$\mathbf{S} = \langle \mathbf{f} \otimes \mathbf{f} \rangle, \quad \mathbf{B} = \langle \nabla \otimes \mathbf{f} \rangle^T \quad (11)$$

which, when expanded, are

$$\mathbf{S} = \begin{pmatrix} \langle 1 \rangle & \langle x \rangle & \langle y \rangle \\ \langle x \rangle & \langle x^2 \rangle & \langle xy \rangle \\ \langle y \rangle & \langle xy \rangle & \langle y^2 \rangle \end{pmatrix}, \quad \mathbf{B} = \begin{pmatrix} \langle 0 \rangle & \langle 0 \rangle \\ \langle 1 \rangle & \langle 0 \rangle \\ \langle 0 \rangle & \langle 1 \rangle \end{pmatrix} \quad (12)$$

The approximate quantum potential defined by Eqs. 8-11 is simply a quadratic function of \mathbf{x} yielding a linear quantum force (LQF) for every trajectory. This approximation rigorously conserves energy and is exact for Gaussian wavepackets, but does not presume that $\psi(\mathbf{x}, t)$ is necessarily a Gaussian wavefunction. (Some other methods about approximations of quantum potential can be found in Refs [? ? ? ? ? ?].) This simple approximation gives basic QM effects, such as wavepacket bifurcation, moderate tunneling and zero-point energy. [?]

While studying quantum dissipation, theoretically, the wavefunction will decay to the ground state, which means the quantum force, $\nabla U(\mathbf{x}, t)$, will cancel the classical force so that the momentum of quantum trajectories will stay 0. For an anharmonic system, take, $V(x) = \frac{x^2}{2} + \lambda x^4$, the linear quantum force ($-\nabla U = \frac{1}{2m}(r\nabla r + \nabla^2 r)$) does not have the corresponding x^3 term to balance classical force. To solve the problem, one possible solution is to add more flexibility to the formula of quantum force. A straightforward method is to increase the basis size for the approximations of non-classical momentum.

III. EULERIAN FRAME OF REFERENCE

There is an alternative frame of reference that can be used in the propagation of trajectories, which is the so called Eulerian frame. The equations of motion can be obtained through, the relationship of the rate of change for quantities in these two frame of references can be expressed in the following equation

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{\alpha} m_{\alpha}^{-1} \nabla_{\alpha} S \nabla_{\alpha} \quad (13)$$

Substitute this equation into the equations of motion in Lagrangian frame of reference, we can obtain

$$\frac{\partial p}{\partial t} = -\frac{p\nabla p}{m} - \nabla(V + U) - \gamma p. \quad (14)$$

$$\frac{\partial x}{\partial t} = 0 \quad (15)$$

$$(16)$$

IV. CLASSICAL FORCE

A pre-calculated potential describing the interaction of two helium atoms $V(r^2)$ is used to compute the potential for the whole system. The position vector \vec{r}_{ij} between two helium atoms is defined as:

$$\vec{r}_{ij} = -d\vec{r}_i + \vec{d}_{ij} + d\vec{r}_j, \quad (17)$$

where $d\vec{r}_i$, $d\vec{r}_j$ are displacement vectors for atom i and j ,

$$d\vec{r}_i = \frac{dx_i}{|dr_i|}\vec{x} + \frac{dy_i}{|dr_i|}\vec{y} + \frac{dz_i}{|dr_i|}\vec{z}. \quad (18)$$

Since the interaction of two helium atoms is expressed as a function of the square of the distance between two atoms, we need to use chain rule to compute the force on helium atoms,

$$\frac{\partial V}{\partial dx_i} = \frac{\partial V}{\partial r_{ij}^2} \frac{\partial r_{ij}^2}{\partial dx_i}, \quad (19)$$

$$r_{ij}^2 = (-dx_i + x_{ij} + dx_j)^2 + (-dy_i + y_{ij} + dy_j)^2 + (-dz_i + z_{ij} + dz_j)^2, \quad (20)$$

$$\frac{\partial r_{ij}^2}{\partial dx_i} = 2(-dx_i + x_{ij} + dx_j). \quad (21)$$

Finally, we get

$$\frac{\partial V}{\partial dx_i} = 2(-dx_i + x_{ij} + dx_j) \frac{\partial V}{\partial r_{ij}^2} \quad (22)$$

V. LONG-RANGE INTERACTIONS CORRECTION

Long-range interactions are calculated in the same way as for the short-range interactions. The long-range interaction for each atom is approximated by a polynomial $P_{N_b}(x, y, z)$ on the basis of,

$$\mathbf{b} = \{1, x, y, z, x^2, y^2, z^2, xy, yz, xz\}^T, \quad (23)$$

$$P_{N_b}(x, y, z) = \mathbf{b}^T \mathbf{c} \quad (24)$$

. We set up a three-dimensional grid of the displacements of atom on space and for each point (x_i, y_i, z_i) , we obtain the value of the long-range interaction $V_l(x_i, y_i, z_i)$ which is convergent to the number of atoms being used for the computation. Finally, we will get $N_p = N_x \times N_y \times N_z$ values and use these values to obtain the coefficients

$$\mathbf{c} = \{c_1, c_2, \dots, c_{N_b}\}^T \quad (25)$$

before the each basis term. N_b is the number of basis terms, which in this case is 10. The coefficients can be obtained by solving the matrix equation

$$\mathbf{M}\mathbf{c} = \mathbf{V}_l, \quad (26)$$

where \mathbf{M} is an $N_p \times N_b$ matrix, for each line, the elements are

$$\mathbf{M}(i, j = 1, \dots, N_b) = \{1, x_i, y_i, z_i, x_i^2, y_i^2, z_i^2, x_i y_i, y_i z_i, x_i z_i\}. \quad (27)$$

and \mathbf{V}_l is the vector of the interaction values at all points,

$$\mathbf{V}_l(i) = V_l(x_i, y_i, z_i). \quad (28)$$

Since it is an overdetermined system, the matrix equation is solved under Least-Squares algorithm.

VI. EQUATIONS OF MOTION FOR (x, p, r)

Starting from continuity equation

$$\frac{\partial \rho(\mathbf{x}, t)}{\partial t} + \nabla \cdot \left(\rho(\mathbf{x}, t) \frac{\mathbf{p}}{m} \right) = 0 \quad (29)$$

substitute $\rho = A^2$ into the continuity equation, we will obtain

$$2A\partial_t A + \sum_{\alpha} (2A\nabla_{\alpha} A m_{\alpha}^{-1} p_{\alpha} + A^2 \nabla_{\alpha} p_{\alpha} m_{\alpha}^{-1}) = 0 \quad (30)$$

divide by $2A^2$,

$$\partial_t \log A = - \sum_{\alpha} \left(\nabla_{\alpha} \log A p_{\alpha} m_{\alpha}^{-1} + \frac{\nabla_{\alpha} p_{\alpha}}{2m_{\alpha}} \right) \quad (31)$$

use partial derivative operator ∇_{α} operate on both sides of the last equation and notice $r_{\alpha} = \nabla_{\alpha} \log A$, we will get

$$\dot{r}_{\alpha} = - \left(\sum_{\beta} \frac{\nabla_{\alpha} p_{\beta}}{m_{\beta}} r_{\beta} + \sum_{\beta} \frac{\nabla_{\alpha} \nabla_{\beta} p_{\beta}}{2m_{\beta}} \right) \quad (32)$$

Then in Lagrangian frame of reference, the exact equations of motion for (x, p, r) will be

$$\dot{x}_\alpha = \frac{p_\alpha}{m_\alpha} \quad (33)$$

$$\dot{p}_\alpha = -\nabla_\alpha (V(\mathbf{x}) + U(\mathbf{x}, t)) \quad (34)$$

$$\dot{r}_\alpha = -\left(\sum_\beta \frac{\nabla_\alpha p_\beta}{m_\beta} r_\beta + \sum_\beta \frac{\nabla_\alpha \nabla_\beta p_\beta}{2m_\beta} \right) \quad (35)$$

where

$$\tilde{U}(x, t) = \sum_\alpha (\tilde{r}(x, t)_\alpha^2 + \nabla_\alpha \tilde{r}) \quad (36)$$

\mathbf{x}, \mathbf{p} are position and momentum vectors with dimensionality of $3N$, N is the number of particles.

Instead of applying linear basis, cubic basis $(1, x, x^2, x^3)$ is used to approximate non-classical momentum r , as well as classical momentum p . By doing this, we kind of add some freedom to the formula of quantum force but constraint to the motion of trajectories. The new equations of motion with fitted terms in Lagrangian frame of reference, \tilde{p}, \tilde{r} will be

$$\dot{x}_\alpha = \frac{\tilde{p}_\alpha}{m_\alpha} \quad (37)$$

$$\dot{p}_\alpha = -\nabla_\alpha (V(\mathbf{x}) + \tilde{U}(\mathbf{x}, t) - \gamma p_\alpha) \quad (38)$$

$$\dot{r}_\alpha = -\left(\sum_\beta \frac{\nabla_\alpha \tilde{p}_\beta}{m_\beta} \tilde{r}_\beta + \sum_\beta \frac{\nabla_\alpha \nabla_\beta \tilde{p}_\beta}{2m_\beta} \right) \quad (39)$$

A. One dimensional model

Consider an harmonic oscillator with an anharmonic quatic term

$$V(x) = \frac{1}{2}(x^2 + x^4) \quad (40)$$

Choose initial wavefunction as a gaussian

$$\psi(x, 0) = \sqrt[4]{\frac{2\alpha}{\pi}} \exp(-\alpha(x - x_0)^2 + ip(x - x_0)) \quad (41)$$

Parameters are chosen as $x_0 = 0, p = 0$.

B. Two step fitting algorithm

Fitting with larger basis can cause a dramatic increase in computational cost. The size of the basis $x_i x_j$ will be $1 + 3N_{atom} + \frac{3N_{atom}(3N_{atom}-1)}{2}$ if we want to include cubic basis for each DoF and

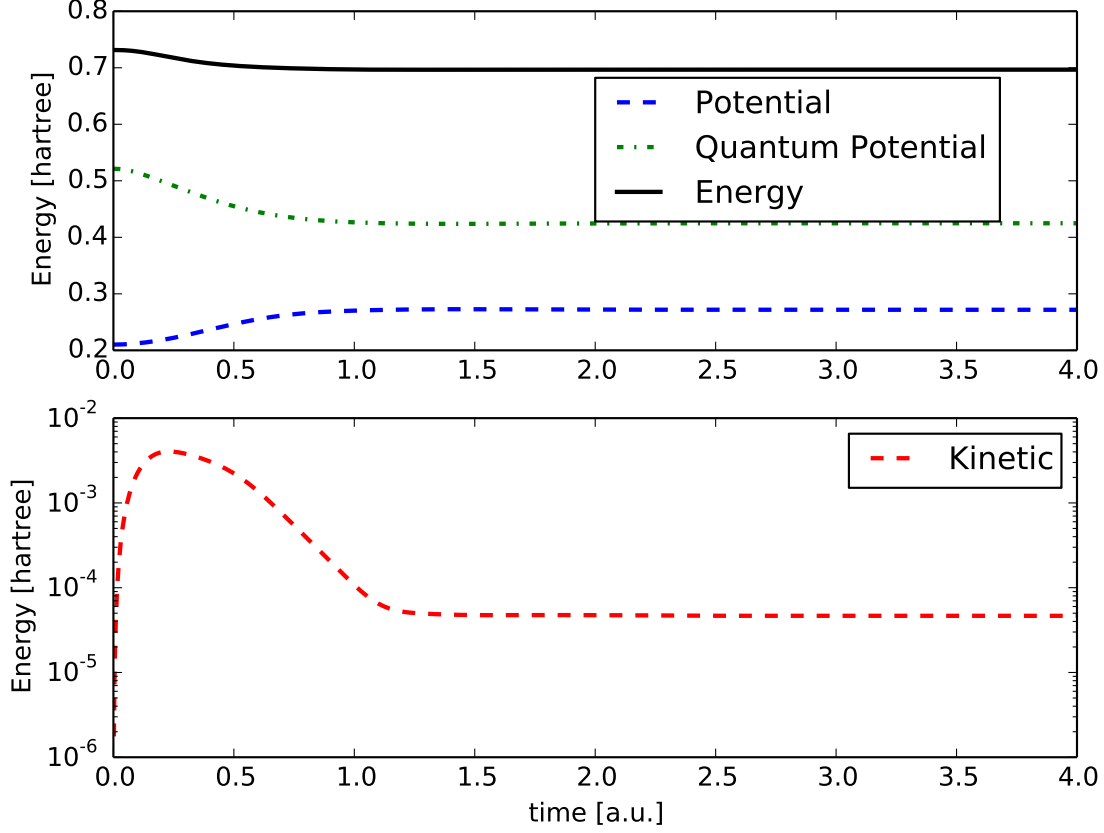


FIG. 1: Energy components with $\gamma = 6$

all the linear coupling terms. To save computational efforts, the least-square fitting procedure is decomposed into two steps after we realize for each DoF, there are some terms that are of little contribution to the fitting, which means the coefficients before these terms remains a small number close to 0.

- 1 The first step is to apply a linear basis $(1, x, y, \dots)$ to do least-square fitting of (\mathbf{p}, \mathbf{r}) to minimize $\sum_{\alpha} \|(r_{\alpha}(x, t) - \tilde{r})_{\alpha}(x, t)\|_2$ and $\sum_{\alpha} \|(p_{\alpha}(x, t) - \tilde{p})_{\alpha}(x, t)\|_2$, the fitted terms can be expressed by
- 2 The second step is to fit the remainder with a cubic basis for each degree of freedom, $(1, x_{\alpha}, x_{\alpha}^2, x_{\alpha}^3)$. The other terms in the basis include linear terms of other DoFs, $(x_{\beta}, \beta = 1..N_c)$, and linear coupling terms $(x_{\alpha}x_{\beta})$. N_c is the number of the coupling DoFs that will be included.

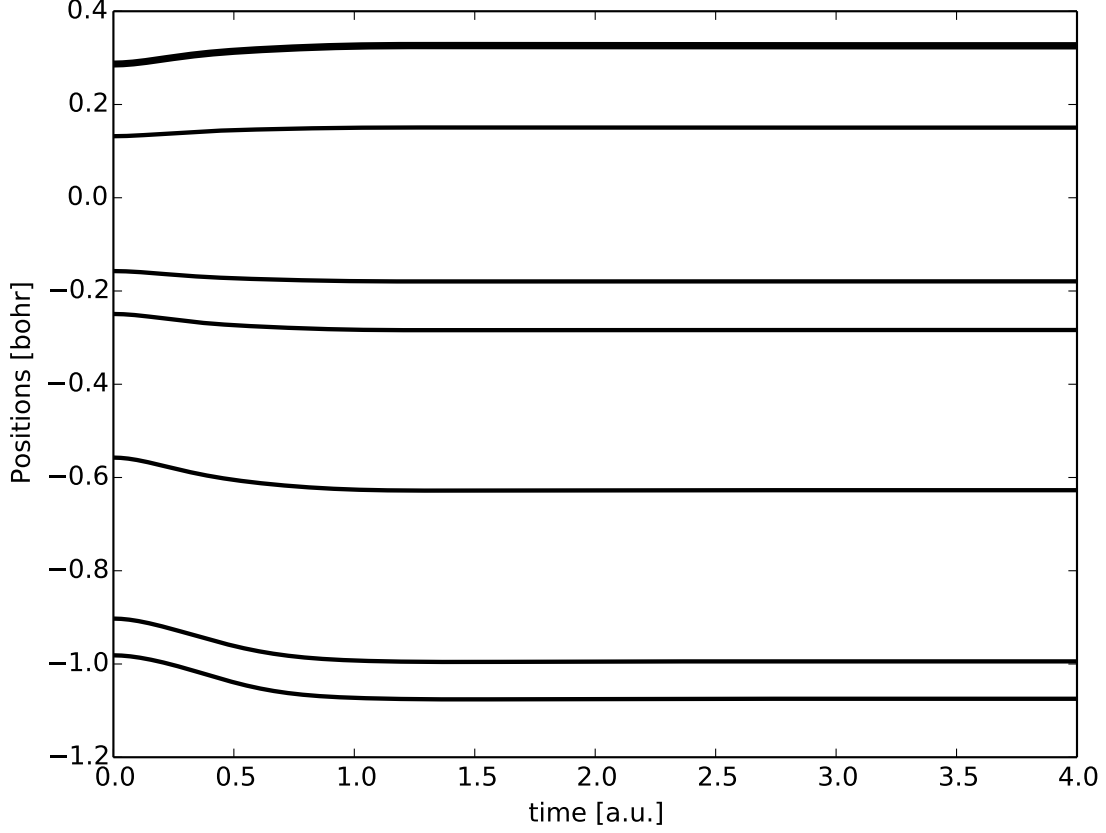


FIG. 2: Propagation of trajectories with $\gamma = 6$

C. Two dimensional model

We want to include coupling between two vibrational mode.

$$V(x) = \frac{1}{2}(x^2 + x^4) + \frac{1}{2}(y^2 + y^4) + \epsilon xy \quad (42)$$

ϵ is a parameter that can be used to control the coupling between two degrees of freedom.

VII. SCALING OF COMPUTATIONAL TIME

The implemented code is parallellised by *Message Passing Interface* (MPI), Fig [?] shows the scaling of the computational cost for different number of processors. [red]Polynomial time algorithm must diverge at certain situations from exact quantum mechanics.

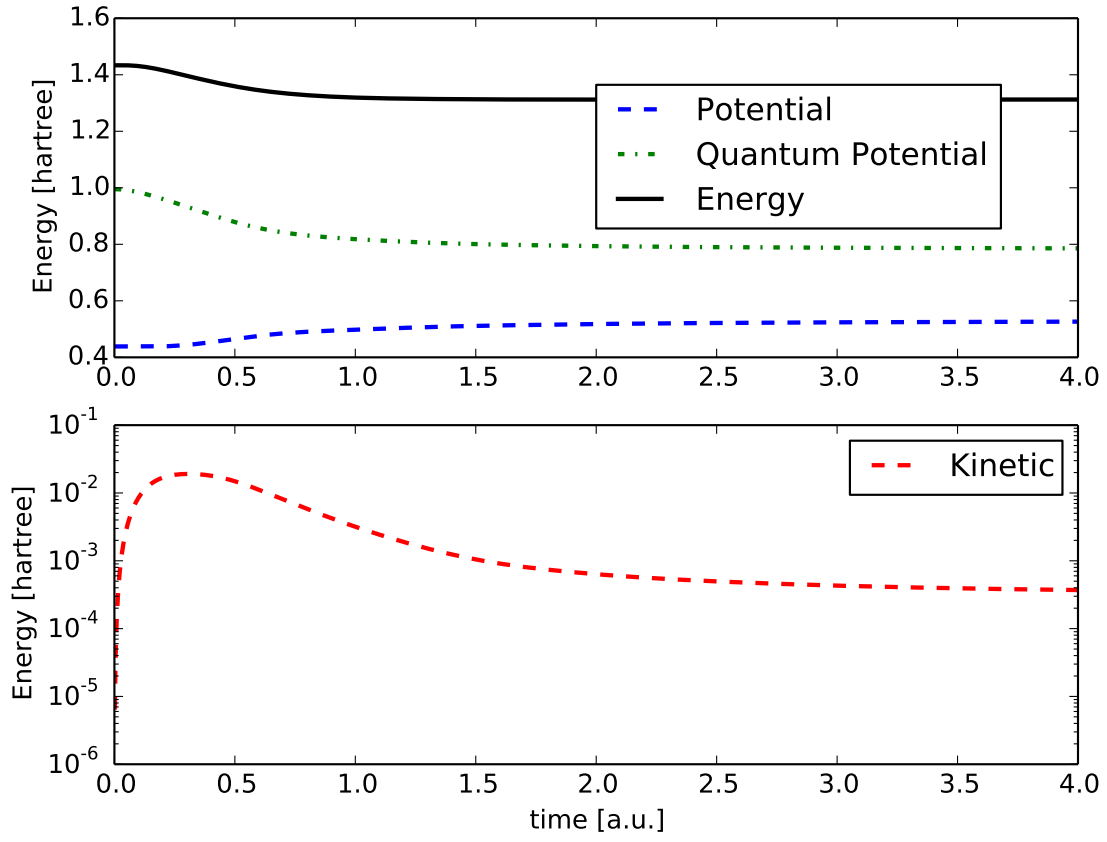


FIG. 3: Energy components with $\gamma = 6$