A modified numerical integrator of ring polymer Hamiltonian dynamics with constraints

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Abstract: In this paper, a symplectic and time-reversible integrator is proposed of simulating the Hamiltonian dynamics with constraints in path integral molecular dynamics. The constraints are tackled by Matrix Inverted Linearized Constraint algorithm (MILC), while a slight modification is requested under normal mode representation, and the slow force is mollified by Equilibrium method (Equilibrium MOLLY) to ameliorate the numerical resonance. It is demonstrated that the slow force impulse can be evaluated only at the centroid of beads, instead of being evaluated at the positions of each bead independently. Therefore, it not only allows longer time step but also reduces the complexity of computation. The numerical experiment is performed using SPC/E model in 298K with eight beads. Further discussion will involve the application of Equilibrium MOLLY in flexible bond model.

Keywords: Path integral molecular dynamics; Ring-polymer molecular dynamics; Equilibrium mollified impulse method; SHAKE; RATTLE; Matrix Inverted Linearized Constraints.

1 Introduction

Molecular dynamics simulations and Ab initio calculations are powerful and important tools in modern computational chemistry [1]. Classical MD simulations can deal with a wide range of experimental dynamics properties, whereas several quantum effects, like zero-point energy, are neglected. Ab initio calculations may provide a more precise description of quantized particles, while solving the quantum dynamics of many-body systems remains one of the most challenging problems to the unfavorable computer scaling with system size and time scale of numerically exact methods [2].

Meanwhile, the computation of the static equilibrium properties of a quantum mechanical is comparatively easy by investigating the path integral, including the primitive path integral molecular dynamics (PIMD), centroid molecular dynamics (CMD) [3] and ring polymer molecular dynamics (RPMD) [4]. These methods make use of the imaginary-time path integral formalism and exploit the exact equilibrium mapping between a quantum-mechanical particle and a classical ring polymer. It is reported that these methods can be employed to calculate properties of a quantum mechanical system composed of thousands of atoms with reasonable accuracy.

As various of techniques of MD simulations can be implemented in PIMD simulation directly [2,3], one of the most important mathematical problems is to find a simple and stable numerical integrator of the ring...
polymer Hamiltonian dynamics. Another problem is to find an effective way of drawing canonical samples from the Boltzmann distribution, but it can be resolved by combining the sampling with the time evolution of the Hamiltonian dynamics plus thermostating. Therefore, the latter problem can be partially incorporated into the former one.

The real problem in numerical integration of Hamiltonian dynamics is that the stiff harmonic springs and the (fast) bonded force restrict the time step, while the computation of the (slow) non-bonded force accounts for most of the computational time [6]. The development of multiple time stepping schemes (MTS) have allowed longer time steps and boosted the computational efficiency dramatically. However, it is also known that the numerical resonance in MTS scheme may lead to an accuracy reduction when the frequency of slow force impulse coincides with a natural frequency of the system [7]. To ameliorate the numerical resonance and overcome MTS stability barrier, the slow force can be replaced by the mollified force, termed mollified impulse method. This method has proved to be efficient in classical molecular dynamics [8].

Another problem in path integral molecular dynamics is that the Hamiltonian system is chaotic, that means one cannot expect to obtain accurate trajectories for more than a short time interval. Therefore, it’s more important to generate the trajectories that satisfy correct statistical properties, like the almost-conservation of the Hamiltonian and preservation of the wedge product, which can be achieved by a symplectic integrator.

In addition, in some rigid-bond models, several constraints are imposed on the Hamiltonian dynamics, which should be satisfied in numerical integration. Traditionally, these constraints can be tackled by SHAKE [9] and RATTLE [10]. For the system composed of small molecules, Matrix Inverted Linearized Constraint (MILC) method seems more efficient [11]. The author will discuss the application of MILC in ring polymer Hamiltonian dynamics, with a slight modification of MILC method under normal mode representation.

In this paper, a composition method is proposed to resolve the above problems. The force is split into two parts, and the slow part is mollified by projecting the sampling points $x$ onto the rest positions of harmonic springs and constraint manifold, using the idea of Equilibrium MOLLY [8]. It is demonstrated that we can split the projection operator $P$ into $P = P_2 \circ P_1$, where $P_1$ projects $x$ onto the centroid of beads and $P_2$ projects the centroid of $x$ onto the rest positions of constraint manifold. Thus the slow force can be evaluated only at the centroid, thereby achieving the overcoming of stability barriers and reduction of computational complexity simultaneously.

This paper is organized as follows. Section 2 begins by reviewing the theory of PIMD briefly. Section 3 presents the modification of MILC under normal mode representation and the choice of projection operator when applying the Equilibrium MOLLY in PIMD. Section 4 presents the numerical results and Section 5 presents the conclusions.
2 Background

In this section we briefly review the methodology of PIMD [12]. The Hamiltonian of a quantum system with \( n \) degrees of freedom

\[
\hat{H}(p_1, ..., p_n, x_1, ..., x_n) = \sum_{i=1}^{n} \frac{p_i^2}{2m} + V(x_1, ..., x_n) .
\]

We denote the inverse thermal energy \( \beta = 1/k_B T \) and the quantum canonical partition function

\[
Z = \text{tr}[e^{-\beta \hat{H}}].
\]

By exploiting the classical isomorphism between path integral representation of quantum mechanical partition function and classical partition function of a ring polymer [13], Eq. (2) can be approximated by the discrete path integral representation as \( Z = \lim_{N \to \infty} Z_N \),

\[
Z_N = \frac{1}{(2\pi\hbar)^N} \int dp \int dx e^{-\beta \hat{H}(p,x)},
\]

where \( \beta_n = \beta/n \) and

\[
H_n(p,x) = \sum_{j=1}^{n} \sum_{k=1}^{N} \left[ \frac{m_j p_j^{(k)}^2}{2m_j} + \frac{m_j}{2\beta_n^2 \hbar^2} \left( x_j^{(k)} - x_{j-1}^{(k)} \right)^2 \right] + \sum_{k=1}^{N} V(x_1^{(k)}, ..., x_n^{(k)}),
\]

subject to the cyclic boundary condition \( x_j^{(0)} = x_j^{(m)} \). We denote \( N \) the Trotter number, indicating the number of the fictitious ring polymer beads. The latent assumption is that the error term \( O(1/N^2) \) is well behaved.

The implementation of PIMD, CMD and RPMD involves obtaining \( x_j^{(k)}(t) \) from the time evolution of the ring polymer Hamiltonian (4)

\[
\dot{p} = -\frac{\partial H_n(p,x)}{\partial x}, \quad \dot{x} = \frac{\partial H_n(p,x)}{\partial p}.
\]

The corresponding equations of motion (EOMs) are

\[
p_j^{(k)} = -\frac{m_j}{\beta_n^2 \hbar^2} \left[ 2x_j^{(k)} - x_{j-1}^{(k)} - x_{j+1}^{(k)} \right] - \frac{\partial V(x_1^{(k)}, ..., x_n^{(k)})}{\partial x_j^{(k)}},
\]

and the equivalent second order ODE

\[
\ddot{x}_j^{(k)} = -\frac{1}{\beta_n^2 \hbar^2} \left[ 2x_j^{(k)} - x_{j-1}^{(k)} - x_{j+1}^{(k)} \right] - \frac{1}{m_j} \frac{\partial V(x_1^{(k)}, ..., x_n^{(k)})}{\partial x_j^{(k)}}.
\]

The potential \( V(x) \) can be chosen as a semi-empirical one. In general, the potential function can be decomposed into three parts, \( V = V_{\text{bond}} + V_{\text{Lennard–Jones}} + V_{\text{electrostatic}} \). The length and angle of bonds can be chosen fixed, like SPC/E water model [14], while several constraints are imposed on the ring polymer Hamiltonian dynamics. The main objective of this paper is to discuss the numerical method of the rigid bond problem, but it will be illustrated in Section 5 that the idea of Equilibrium MOLLY can be employed in flexible bond model.
3 Ring polymer time evolution

We mainly discuss the numerical integration of EOMs (6) with holonomic constraints

\[ g(x) = 0, \]  

\[ g : \mathbb{R}^n \rightarrow \mathbb{R}^m \] and hidden velocity constraints

\[ G(x) \nabla_p H(p, x) = 0, \]  

where \( G(x) = g_x(x) \in \mathbb{R}^{m \times n} \). Therefore, the constraints manifold can be expressed as

\[ \mathcal{M} = \left\{ g(x) = 0, G(x) \nabla_p H(p, x) = 0 \right\}. \]  

A convenient way to derive the corresponding equations of motion is to add a potential that grows large when the system deviates from the locus of the constraints. The modified Hamiltonian \( H_c \) is

\[ H_c(p, x) = H_n(p, x) + \epsilon \cdot g(x)^T g(x), \]  

where \( \epsilon \gg 1 \). The corresponding EOMs are

\[ \dot{p}_j^{(k)} = -\frac{m_j}{\rho_j^2} \left[ 2x_j^{(k)} - x_j^{(k-1)} - x_j^{(k+1)} \right] - g_x \left( x_1^{(k)}, \ldots, x_n^{(k)} \right) \cdot A^{(k)} \left( \frac{\partial V(x_1^{(k)}, \ldots, x_n^{(k)})}{\partial x_j} \right), \]  

\[ x_j^{(k)} = \frac{p_j^{(k)}}{m_j}. \]  

The force term in (12) can be divided into several parts according to their natural frequencies. A wise strategy is to integrate the EOMs (12) by composition method, which is based on the splitting of the Hamiltonian \( H_c \).

\[ H_c(p, x) = T(p) + V^{\text{beads}}(x) + V^{\text{constraints}}(x) + V^{\text{nonbond}}(x), \]  

and \( V^{\text{nonbond}} \) can be split into fast and slow parts,

\[ V^{\text{nonbond}} = V^{\text{nonbond, fast}} + V^{\text{nonbond, slow}}. \]

Denote by \( \varphi_{h}^T \) the flow of the system with Hamiltonian \( H(p, x) \), then by the Trotter formula, the flow \( \varphi_{h}^T \) can be approximated by composition of subflows,

\[ \varphi_{h}^T \approx \varphi_{h/2}^{V^{\text{nonbond, slow}}} \circ \varphi_{h/2}^{V^{\text{nonbond, fast}}} \circ \varphi_{h/2}^{V^{\text{constraints}}} \circ \varphi_{h/2}^{T + V^{\text{beads}}} \circ \varphi_{h/2}^{V^{\text{constraints}}} \circ \varphi_{h/2}^{V^{\text{nonbond, fast}}} \circ \varphi_{h/2}^{V^{\text{nonbond, slow}}}, \]

where \( \varphi_{h}^{T + V^{\text{beads}}} \) can be solved analytically owing to normal mode representation.

Since every flow mapping is symplectic and composition of symplectic mapping is symplectic, the right hand side of (15) is also a symplectic mapping. By choosing appropriate \( \Lambda^{(k)} \), the constraint manifold (10) can be satisfied. As integration of fast force always needs a smaller time step, a slight modification of numerical scheme (15) is

\[ \varphi_{h}^T \approx \varphi_{h/2}^{V^{\text{nonbond, slow}}} \circ \left[ \varphi_{h/2}^{V^{\text{nonbond, fast}}} \circ \varphi_{h/2}^{V^{\text{constraints}}} \circ \varphi_{h}^{T + V^{\text{beads}}} \circ \varphi_{h/2}^{V^{\text{constraints}}} \circ \varphi_{h/2}^{V^{\text{nonbond, fast}}} \circ \varphi_{h/2}^{V^{\text{nonbond, slow}}} \right] \circ \varphi_{h/2}^{V^{\text{nonbond, slow}}}. \]
where $h = n\delta h$. The scheme (16) is also symplectic and satisfies the constraint manifold. The inner loop can be replaced by Verlet algorithm, known as Verlet-IF-REPSA scheme. Although longer time step in outer loop is allowed, it is reported that numerical resonance may contaminate the stability of scheme (16). Therefore, a comparatively small time step is inevitably needed in keeping the integrator stable.

Various of methods have been proposed in order to overcome this stability barrier, including mollified impulse method [16–18], adiabatic separation [19] and normal mode theories [4]. In adiabatic path integral molecular dynamics method, adiabaticity parameters are introduced to select the mass, thereby making the frequency of all the modes identical and increasing the sampling efficiency, although the Hamiltonian is different from the primitive one. It is also known that numerical resonance is less severe in thermostatting, including Langevin dynamics and Nosé-Hoover thermostating [8]. Recent development, like extended isokinetic Nosé-Hoover chain orientational motion multiple time step algorithm, has even achieved giant time steps up to $5\text{ps}$ [20].

The author focuses on mollified impulse methods, especially the Equilibrium version, under normal mode representation. The motivation of the mollified potential stems from the fact that the original impulse method can be expressed as

$$
M \frac{d^2 x}{dt^2} = F_{\text{beads}}(x) + \sum_{m=-\infty}^{\infty} \delta h \cdot \delta (t - m\delta h) F_{\text{fast}}(x) + \sum_{n=-\infty}^{\infty} \delta h \cdot \delta (t - nh) F_{\text{slow}}(x).
$$

The $\delta$-function seems abrupt as it is non-smooth, therefore can be replaced by a smooth mollifier $\psi$. Also the sampling points in impulse should be chosen according the natural frequencies of fastest force, thus an averaging position $\phi(x)$ should be introduced.

There are several choices of $\psi$ and $\phi$, see [16]. The effectiveness of these filter function is related to the extensiveness of time averaging. Another kind of filter function, termed Equilibrium [8], is proposed to take $\phi(x) = P(x)$ as a projection of $x$ to the manifold $\nabla F_{\text{fastest}}(x) = 0$. The latent assumption is that all the non-zero eigenfrequencies of $\nabla^2 V_{\text{fastest}}(x)$ are much large than those of $\nabla^2 V_{\text{slow}}(x)$.

Now replace the slow potential $V_{\text{slow}}(x)$ by $V_{\text{slow}}(P(x))$, with corresponding force term $-(P_x)^T \nabla V_{\text{slow}}(P(x))$. The mollified scheme can be expressed as

\begin{algorithm}
\textbf{Algorithm 3.1 Mollified Impulse method with RATTLE}

1. outer loop:
   \begin{align*}
   p_j^{(k)} &\leftarrow p_j^{(k)} - \frac{\delta h}{2} (P_x)^T \nabla V_{\text{nonbond,slow}}(P(x_1^{(k)}, \ldots, x_n^{(k)}))
   \end{align*}

2. inner loop:
   \begin{enumerate}
   \item $p_j^{(k)} \leftarrow p_j^{(k)} - \frac{\delta h}{2} \nabla V_{\text{nonbond,fast}}(x_1^{(k)}, \ldots, x_n^{(k)})$.
   \item $p_j^{(k)} \leftarrow p_j^{(k)} - \frac{\delta h}{2} \nabla (x_1^{(k)}, \ldots, x_n^{(k)}) \cdot \Lambda_{C}^{(k)}$.
   \item $p_j^{(k)} \leftarrow \psi(\delta h) \nabla (x_1^{(k)}, \ldots, x_n^{(k)})$.
   \item $p_j^{(k)} \leftarrow p_j^{(k)} - \frac{\delta h}{2} \nabla V_{\text{nonbond,fast}}(x_1^{(k)}, \ldots, x_n^{(k)})$.
   \item $p_j^{(k)} \leftarrow p_j^{(k)} - \frac{\delta h}{2} \nabla V_{\text{nonbond,fast}}(x_1^{(k)}, \ldots, x_n^{(k)})$.
   \end{enumerate}

3. outer loop:
\end{algorithm}
\[
p_{j}^{(k)} \leftarrow p_{j}^{(k)} - \frac{k}{\beta} (P_{x})^{T} \nabla_{\text{nonbond,slow}} \left( P_{x}^{(k)} \right) ,
\]
with \( \Lambda_{C}^{(k)} \) chosen such that
\[
g \left( x \right) = 0
\] (18)
and \( \Lambda_{CV}^{(k)} \) chosen such that
\[
G \left( x \right) \nabla_{p} H \left( p, x \right) = 0 .
\] (19)

\( \psi \) is the exact flow mapping of reduced equation generated by the Hamiltonian \( T \left( p \right) + V_{\text{beads}} \left( x \right) \).

It can be verified that the above integrator is symplectic and time-reversible. Detailed discussion will be divided into two parts, including a slight modification of MILC method and application of Equilibrium MOLLY.

A. Matrix Inverted Linearized Constraint SHAKE (MILC)

Traditionally, numerical methods tackling the constraints in Hamiltonian dynamics are SHAKE and its velocity version RATTLE. Both methods preserve the wedge product, while SHAKE is not rigorously symplectic due to its deviation from the constraint manifold. Although it is quite successful in dealing with rigid bonds in large molecules, the SHAKE algorithm also suffers from non-convergence when the distortion is sufficiently large. For small molecules with linear chains or ring topology, matrix inverted linearized constraint method (MILC) is an alternative [11].

In ring polymer Hamiltonian dynamics, however, the MILC should be employed under normal mode representation. Therefore, it is necessary to briefly review the normal mode theory and variation-of-constants formula.

The reduced equations are defined by the flow \( \varphi_{T+N_{\text{beads}}}^{\tau} \).
\[
\dot{p}_{j}^{(k)} = -\frac{m_{j}}{\beta \hbar^{2}} \left[ 2x_{j}^{(k)} - x_{j}^{(k-1)} - x_{j}^{(k+1)} \right] ,
\]
\[
\dot{x}_{j}^{(k)} = \frac{p_{j}^{(k)}}{m_{j}} .
\] (20)
or in matrix formalism,
\[
\begin{bmatrix}
\dot{p} \\
\dot{x}
\end{bmatrix} =
\begin{pmatrix}
0 & K_{1} \\
K_{2} & 0
\end{pmatrix}
\begin{bmatrix}
p \\
x
\end{bmatrix},
\] (21)
where \( K_{1} = \frac{m_{j}}{\beta \hbar^{2}} \begin{pmatrix} \frac{1}{2} & 1 & \cdots & 1 \\ 1 & \frac{1}{2} & \cdots & 1 \\ \vdots & \ddots & \ddots & \vdots \\ 1 & \cdots & 1 & \frac{1}{2} \end{pmatrix} \) and \( K_{2} = \frac{1}{m_{j}} I \).

\( K_{1} \) can be diagonalized by trigonometric functions, namely, there exists a unitary eigenvector matrix \( U \), such that
\[
U^{T} K_{1} U = D ,
\] (22)
where the eigenvalues of diagonal matrix \( D \) is \( \left\{ 0, -4 \alpha^{2} \sin^{2} \frac{\pi}{N}, \cdots, -4 \alpha^{2} \sin^{2} \frac{(N-1) \pi}{N} \right\} \), where \( \alpha = \frac{n}{\beta \hbar} \). Denote by \( \omega_{k} = 2 \alpha \sin \frac{k}{N} \) (\( k = 0, 1, \cdots, N - 1 \)).
Using the variation-of-constants formula, the analytical solution of (20) can be expressed as

\[
\begin{pmatrix}
 x_j^{(1)}(t) \\
 x_j^{(2)}(t) \\
 \vdots \\
 x_j^{(N)}(t)
\end{pmatrix}
= UA(t) U^T \begin{pmatrix}
 x_j^{(1)}(0) \\
 x_j^{(2)}(0) \\
 \vdots \\
 x_j^{(N)}(0)
\end{pmatrix}
+ \frac{1}{m_j} UB(t) U^T \begin{pmatrix}
 p_j^{(1)}(0) \\
 p_j^{(2)}(0) \\
 \vdots \\
 p_j^{(N)}(0)
\end{pmatrix},
\]

(23)

\[
\begin{pmatrix}
 p_j^{(1)}(t) \\
 p_j^{(2)}(t) \\
 \vdots \\
 p_j^{(N)}(t)
\end{pmatrix}
= m_j UC(t) U^T \begin{pmatrix}
 x_j^{(1)}(0) \\
 x_j^{(2)}(0) \\
 \vdots \\
 x_j^{(N)}(0)
\end{pmatrix}
+ UA(t) U^T \begin{pmatrix}
 p_j^{(1)}(0) \\
 p_j^{(2)}(0) \\
 \vdots \\
 p_j^{(N)}(0)
\end{pmatrix},
\]

(24)

where

\[
A(t) = \begin{pmatrix}
 1 & \cos(\omega_1 t) & \cdots & \cos(\omega_{N-1} t) \\
 \vdots & \ddots & \ddots & \vdots \\
 0 & \cdots & \cos(\omega_{N-1} t) & \cos(\omega_N t)
\end{pmatrix},
B(t) = \begin{pmatrix}
 \frac{1}{\omega_1} & \frac{\sin(\omega_1 t)}{\omega_1} & \cdots & \frac{\sin(\omega_{N-1} t)}{\omega_{N-1}} \\
 \vdots & \ddots & \ddots & \vdots \\
 0 & \cdots & \frac{\sin(\omega_{N-1} t)}{\omega_{N-1}} & \frac{\sin(\omega_N t)}{\omega_N}
\end{pmatrix},
C(t) = \begin{pmatrix}
 0 & -\omega_1 \sin(\omega_1 t) & \cdots & -\omega_{N-1} \sin(\omega_{N-1} t)
\end{pmatrix}.
\]

Assume that the linear constraint force can be derived from

\[
v_{\text{constraints}}(x^{(k)}) = \sum_{i=p}^{N} \lambda_{ip}^{(k)} \sigma \left( \left( x_{ij}^{(k)} \right) \right),
\]

(25)

where the summation is over all sites, indexed by \( p \), connected to site \( i \), and \( k \) is the index of bead. \( \lambda^{(k)} \) is undetermined Lagrangian multiplier, which can be solved by iteration.

It remains to add the impulse force into (23)

\[
\begin{pmatrix}
 x_j^{(1)}(h) \\
 x_j^{(2)}(h) \\
 \vdots \\
 x_j^{(N)}(h)
\end{pmatrix}
= \begin{pmatrix}
 x_j^{(1)}(h) \\
 x_j^{(2)}(h) \\
 \vdots \\
 x_j^{(N)}(h)
\end{pmatrix}
- \frac{h}{m_j} UB(h) U^T \begin{pmatrix}
 \sum_{i=p}^{N} \lambda_{ip}^{(1)} x_{ip}^{(1)} \\
 \sum_{i=p}^{N} \lambda_{ip}^{(2)} x_{ip}^{(2)} \\
 \vdots \\
 \sum_{i=p}^{N} \lambda_{ip}^{(N)} x_{ip}^{(N)}
\end{pmatrix},
\]

(26)

where \( h \) is time step and \( x_j^{(k)} \) are the initial guesses by taking \( \lambda_{ip}^{(k)} = 0 \). The difference between (26) and standard SHAKE is the operator \( UBU^T \), which represents the interaction within beads.

The remaining procedure is just similar to standard SHAKE. Write down the expression of \( x_{ij}^{(h)}(h) = x_{ij}^{(k)}(h) - x_j^{(k)}(h) \), and solve the equation with respect to \( \lambda^{(h)} \) to make all the \( x_{ij}^{(k)}(h) \) satisfy the position constraints. Since the equation is nonlinear, it is convenient to omit the nonlinear term and apply iteration until all the position constraints are satisfied.
The standard RATTLE (or MILC-RATTLE) can be directly applied to adjust the velocity, since

\[
\begin{pmatrix}
\dot{p}_{j}^{(1)}(h) \\
\dot{p}_{j}^{(2)}(h) \\
\vdots \\
\dot{p}_{j}^{(N)}(h)
\end{pmatrix} = \begin{pmatrix}
\ddot{p}_{j}^{(1)}(h) \\
\ddot{p}_{j}^{(2)}(h) \\
\vdots \\
\ddot{p}_{j}^{(N)}(h)
\end{pmatrix} - h \begin{pmatrix}
\sum_{i=p}^{\lambda_{ip}^{(1)}} \\
\sum_{i=p}^{\lambda_{ip}^{(2)}} \\
\vdots \\
\sum_{i=p}^{\lambda_{ip}^{(N)}}
\end{pmatrix},
\]

(27)

where \(\ddot{p}_{j}^{k}(h)\) are the initial guesses by choosing \(\lambda_{ip}^{(k)} = 0\). It is noticed that \(\lambda_{ip}^{(k)}\) can be solved without any iteration through MILC-RATTLE.

A simple water model is used to clarify this idea. The notation \(x_{i,s}^{(k)}\) represents the \(sth\) degree of freedom of atom \(x_{i}\) with \(kth\) bead. Since every atom has three degrees of freedom in position, the value of \(s\) can be chosen 1, 2, 3. We assume \(x_{1}\) represents oxygen atom, \(x_{2}, x_{3}\) hydrogen. The bond vector is \((x_{ij,1}^{(k)}, x_{ij,2}^{(k)}, x_{ij,3}^{(k)})\), where \(x_{ij,s}^{(k)} = x_{i,s}^{(k)} - x_{j,s}^{(k)}\).

Now pick up O-H bond constraints

\[
\sum_{s=1}^{3} (x_{12,s}^{(k)})^{2} = \rho_{12}^{2} (k = 1, ..., N),
\]

(28)

and the equation of \(x_{12,s}^{(k)}\)

\[
\begin{pmatrix}
\dot{x}_{12,s}^{(1)} \\
\dot{x}_{12,s}^{(2)} \\
\vdots \\
\dot{x}_{12,s}^{(N)}
\end{pmatrix} = -h U B(h) U^{T} \begin{pmatrix}
\frac{1}{m_{1}} + \frac{1}{m_{2}} \\
\frac{1}{m_{1}} \\
\vdots \\
\frac{1}{m_{2}}
\end{pmatrix} \begin{pmatrix}
\dot{x}_{12,s}^{(1)} \dot{x}_{12,s}^{(2)} \\
\dot{x}_{12,s}^{(2)} \dot{x}_{12,s}^{(3)} \\
\vdots \\
\dot{x}_{12,s}^{(N)} \dot{x}_{12,s}^{(N)}
\end{pmatrix} - \frac{1}{m_{1}} \begin{pmatrix}
\lambda_{12,s}^{(1)} \lambda_{12,s}^{(1)} \\
\lambda_{12,s}^{(2)} \lambda_{12,s}^{(2)} \\
\vdots \\
\lambda_{12,s}^{(N)} \lambda_{12,s}^{(N)}
\end{pmatrix},
\]

(29)

Substitute (29) into (28), we arrive at the system of equations we need to solve (the nonlinear terms are omitted)

\[
\begin{pmatrix}
\sum_{s=1}^{3} (x_{12,s}^{(1)})^{2} - \rho_{12}^{2} \\
\sum_{s=1}^{3} (x_{12,s}^{(2)})^{2} - \rho_{12}^{2} \\
\vdots \\
\sum_{s=1}^{3} (x_{12,s}^{(N)})^{2} - \rho_{12}^{2}
\end{pmatrix} = \sum_{s=1}^{3} 2 \left( \frac{1}{m_{1}} + \frac{1}{m_{2}} \right) \begin{pmatrix}
\dot{x}_{12,s}^{(1)} \\
\dot{x}_{12,s}^{(2)} \\
\vdots \\
\dot{x}_{12,s}^{(N)}
\end{pmatrix} \begin{pmatrix}
\dot{x}_{12,s}^{(1)} \\
\dot{x}_{12,s}^{(2)} \\
\vdots \\
\dot{x}_{12,s}^{(N)}
\end{pmatrix} - \frac{1}{m_{1}} \begin{pmatrix}
\lambda_{12,s}^{(1)} \lambda_{12,s}^{(1)} \\
\lambda_{12,s}^{(2)} \lambda_{12,s}^{(2)} \\
\vdots \\
\lambda_{12,s}^{(N)} \lambda_{12,s}^{(N)}
\end{pmatrix},
\]

(30)
Eq.(30) seems quite cumbersome. But actually, it is only a modified version of MILC-SHAKE under normal mode representation, since the lower diagonal, diagonal, and upper diagonal elements in original MILC-SHAKE have been replaced by block matrices,

\[ J_{i,j-1} = -\frac{2}{m_i} \sum_{s=1}^{3} \begin{pmatrix} x^{(1)}_{i,j,s} \\ \vdots \\ x^{(N)}_{i,j,s} \end{pmatrix} UB(h) U^T \begin{pmatrix} x^{(1)}_{i-1,j,s} \\ \vdots \\ x^{(N)}_{i-1,j,s} \end{pmatrix}, \]

\[ J_{i,j} = 2 \left( \frac{1}{m_i} + \frac{1}{m_{i+1}} \right) \sum_{s=1}^{3} \begin{pmatrix} x^{(1)}_{i,j,s} \\ \vdots \\ x^{(N)}_{i,j,s} \end{pmatrix} UB(h) U^T \begin{pmatrix} x^{(1)}_{i,j+1,s} \\ \vdots \\ x^{(N)}_{i,j+1,s} \end{pmatrix}, \]

\[ J_{i,j+1} = -\frac{2}{m_{i+1}} \sum_{s=1}^{3} \begin{pmatrix} x^{(1)}_{i,j+1,s} \\ \vdots \\ x^{(N)}_{i,j+1,s} \end{pmatrix} UB(h) U^T \begin{pmatrix} x^{(1)}_{i+j+1,s} \\ \vdots \\ x^{(N)}_{i+j+1,s} \end{pmatrix}. \]

For the molecules with ring topology, like H$_2$O, index $i$ is replaced by $i \ (mod \ 3)$. If the interaction between normal modes is omitted, namely, $B(h) \equiv I_{N_xN}$, it reduces to the original SHAKE and MILC-SHAKE.

The update of $\lambda^{(k)}_{ij}$ is obtained by solving the linear equation

\[
\begin{pmatrix} \sum_{s=1}^{3} (\tilde{x}_{12,s}^{(1)})^2 - \tilde{l}_{12}^2 \\ \vdots \\ \sum_{s=1}^{3} (\tilde{x}_{23,s}^{(1)})^2 - \tilde{l}_{23}^2 \\ \vdots \\ \sum_{s=1}^{3} (\tilde{x}_{31,s}^{(1)})^2 - \tilde{l}_{31}^2 \end{pmatrix} = \begin{pmatrix} J_{11} & J_{12} & J_{13} \\ J_{21} & J_{22} & J_{23} \\ J_{31} & J_{32} & J_{33} \end{pmatrix} \begin{pmatrix} h\tilde{X}_{12}^{(1)} \\ \vdots \\ h\tilde{X}_{31}^{(1)} \end{pmatrix} \]

For water molecules with $N$ beads, the size of coefficient matrix in (30) is $3N \times 3N$, therefore its inverse can be achieved efficiently by modern computers. And the iteration in MILC also converges rapidly in numerical simulation.

**B. Equilibrium Mollified Impulse method**

We begin to discuss the choice of mollification and averaging filters, that are proposed to ameliorate the numerical resonance in MTS scheme. The mollified impulse methods have been used in classical molecular dynamics, though their application in path integral molecular dynamics is rarely discussed. It will be shown that one special kind of filter, termed Equilibrium, can also be applied in PIMD and have some new fascinating mathematical properties.
In the Equilibrium MOLLY, the sampling points in impulse are proposed to choose as a projection to the manifold $\nabla V^{\text{fastest}} = 0$, thereby eliminating the contributions of the slow force in the directions that excite the fastest force in the system [8]. The numerical simulation has validated that it is superior to the averaging mollified impulse method, while the numerical resonance cannot be completely eliminated due to the existence of nonlinear fast force (the electrostatic force and Lennard-Jones interaction).

The ring polymer Hamiltonian system, however, seems more complicated than its classical counterpart. Considering a flexible bond model, the fastest forces involve the interaction within beads and bonded force. Although several degrees of freedom can be eliminated in rigid bond model, the penalty terms in SHAKE should be also regarded as the fastest forces. Therefore, to apply the Equilibrium MOLLY in PIMD, one should choose the sampling points as a projection onto the manifold $\nabla (V^{\text{beads}} + V^{\text{constraints}}) = 0$.

The choice of projection operator, in fact, is not unique. A special choice can be made by observing the fact that $V^{\text{beads}}$ only represents the interaction within beads and $V^{\text{constraints}}$ represents the interaction between atoms with the same bead index. Therefore, instead of projecting $x$ onto $\nabla (V^{\text{beads}} + V^{\text{constraints}})(x) = 0$ directly, it is better to make the first projection onto the manifold $\nabla V^{\text{beads}}(x) = 0$, then the second onto $\nabla V^{\text{constraints}}(x) = 0$, namely, we can split the projection operator $P = P_2 \circ P_1$.

Now the question becomes: how to choose $P_1(x)$ so that $\nabla V^{\text{beads}}(P_1(x)) = 0$? A straightforward answer is: it projects all the $x_j^{(k)}$ to the centroid of beads, namely, for every $k$, $P_1x_j^{(k)} = \bar{x}_j = \frac{1}{N} \sum_{k=1}^{N} x_j^{(k)}$. Then the second operator $P_2$ can be determined by the centroid $\bar{x}_j$ using primitive Equilibrium MOLLY. The idea of splitting projection operator is also valid in tackling some simple flexible bond models, like SPC/tw model [21].

This projection operator is quite convenient because the slow force $-\nabla x V^{\text{nonbond,slow}}(x)$ can be replaced by $-P_2 \nabla x V^{\text{nonbond,slow}}(P(x))$, that means, we only need to evaluate the slow force at the centroid of beads, instead of treating beads independently. As the calculation of slow force (for instance, to calculate long range electrostatic forces by Ewald summation [22]) accounts for most of time in simulation, the Equilibrium MOLLY can also reduce the complexity of calculating slow force, which is nearly independent of the Trotter number $N$.

Since the calculation of $P_1$ and $P_2$ seems a little tedious, details are illustrated in Appendix. Now the discussion ends with a final remark. It is reported that the stability of Equilibrium MOLLY is strongly related to the smoothness of slow force function [8]. Therefore, the slow force should be truncated smoothly, which can be achieved by adding a smooth switch function [23]. And only the slow force can be mollified, otherwise a severe instability will occur. These have been validated by numerical simulations.

### 4 Evaluation of methods

The numerical results are presented by making comparisons of Verlet-$t^r$-RESPA algorithm, Impulse method under normal mode representation (Impulse-NM) and Mollified Impulse method under normal mode representation (MOLLY-NM). The constraints are satisfied via original MILC-RATTLE in Verlet-$t^r$-RESPA and MILC-RALLTTE under normal mode representation in Impulse-NM and MOLLY-NM, respectively. Since the stiff harmonic springs occupy most of energy, Impulse-NM and MOLLY-NM clearly conserve the Hamiltonian better than Verlet-$t^r$-RESPA.
Table 1: Parameters in SPC/E water potential.

| Parameter         | Value            |
|-------------------|------------------|
| \( r(\text{OH}) \) (Å) | 1.0              |
| \( \angle(\text{HOH})(\text{deg}) \) | 109.47           |
| \( A(\text{kJmol}^{-1}) \) | 2.633 \( \times 10^6 \) |
| \( B(\text{kJmol}^{-1}) \) | 2.617 \( \times 10^3 \) |
| \( Q_O (|e|) \) | -0.8476          |
| \( Q_H (|e|) \) | 0.4238           |

A. Test problem

The simulations were performed using SPC/E model at 298\( K \) with a density of 0.998 \( cm^{-1} \), which had been used in simulating quantum diffusion in liquid water [6]. The interactions between molecular pairs are

\[
V_{ij} = \sum_{k \in i} \sum_{k' \in j} \frac{Q_k Q_{k'}}{R_{kk'}} + \frac{A}{R_{OO}^{12}} - \frac{B}{R_{OO}^6},
\]

involving a Coulomb contribution and a Lennard-Jones interaction between oxygen atoms. The oxygen-hydrogen bond length and angle are fixed. Parameters are listed in Table 1.

To split the electrostatic potential and Lennard potential into fast and slow parts smoothly, a switching function \( S(r_{ij}) \) should be introduced, so that

\[
U_{\text{nonbond, fast}} = \left( U_{\text{electrostatic}} + U_{\text{Lennard–Jones}} \right) S(r_{ij}),
\]

\[
U_{\text{nonbond, slow}} = \left( U_{\text{electrostatic}} + U_{\text{Lennard–Jones}} \right) \left( 1 - S(r_{ij}) \right),
\]

where \( r_{ij} = \| \vec{x}_j - \vec{x}_i \| \).

The switching function \( S(r) \) is given by [23]

\[
S(r) = \begin{cases} 
1, & (r < r_c - \Delta r) \\
1 + R^2(2R - 3), & (r_c - \Delta r \leq r \leq r_c) \\
0, & (r_c < r)
\end{cases}
\]

where \( R = [r - (r_c - \Delta r)] / \Delta r, r \) is the interatomic distance, \( r_c \) is the short-range cutoff and \( \Delta r \) is the healing length.

B. Performance metrics

Since a good integrator should generate the trajectories with correct statistical properties, one class of performance metrics can be chosen according to the drift of energy.

In each simulation, the history of trajectories and all the components of energy was recorded. Several quantities were used to measure the conservation of the ring polymer Hamiltonian with different numerical methods. All the metrics can be found in [8] and [23].
The pseudoenergy, defined by replacing the $U_{slow}(x)$ with $U_{slow}(A(x))$, was used to monitor the instability since it is the quantity that the integrator is trying to conserve. The precent relative drift is given by $D = d/k$, where $K$ is the average kinetic energy and $d$ is the linear regression coefficient of the absolute pseudoenergy drift. Noise refers to the variation of linear regression model. It has been reported that $D$ is a robust metric of drift in classical molecular dynamics simulation.

The absolute and relative variation in the true energy, $\Delta E$ and $\Delta E_r$, is given by

$$\Delta E = \frac{1}{J} \sum_{i=1}^{J} |E(i) - E_{initial}|, \quad \Delta E_r = \frac{1}{KJ} \sum_{i=1}^{J} |E(i) - E_{initial}|,$$

(35)

where $E_{initial}$ is initial total energy, $E(i)$ is instantaneous total energy, and $J$ is the simulation length. $\Delta E_r$ can measure the distance between the true energy surface in phase space and a modified energy surface arising from the use of finite time step $\Delta t$.

The time length of all the simulations were taken 250, with time step $0.02 \sim 0.125$. The mass of oxygen and hydrogen atom were chosen 15.999 and 1.008, respectively, while the reduced $\hbar$ and Boltzmann constant $\beta$ were both chosen 1. The simulation cell contained eight water molecules with eight beads (192 atoms). The long-range forces were truncated at 6.5Å, with healing distance $\Delta r$ 2.5Å or 4.5Å. All the simulations were performed in MATLAB.

C. Numerical results

All the numerical results are summarized in Table 2. It is shown that both Equilibrium mollified impulse method and impulse method are superior to Verlet-I/r-RESPA scheme, since the interactions between beads are tackled analytically. When the time step $h$ grows longer, the drift of energy in Verlet-I/r-RESPA becomes more severe, while those in MOLLY-NM and Impulse-NM stay at a relatively small level with some fluctuations.

Figure 1 shows the relation between time step and precent relative drift of energy (in logarithm scale), and Figure 2 shows the relations between time step and percent relative error in energy (in logarithm scale). In this case, impulse method under normal mode representation is more stable than Equilibrium MOLLY, while the Equilibrium requires less computation time. Both methods have shown certain degree of stability under longer time steps.

Equilibrium MOLLY may become severely unstable when fast non-bond force is mollified. This phenomenon has been observed in numerical simulations, when the time step is chosen 0.05 and all the non-bond force is mollified. The comparison in Figure 3(a) shows that Equilibrium MOLLY has a severe energy drift, which is not induced by time step.

In Figure 3(b), the instability of Equilibrium MOLLY without smooth truncation function has been observed, where force $V_{nonbond}$ is split into

$$V_{nonbond} = V_{nonbond}^{[r > r_c]} + V_{nonbond}^{[r \leq r_c]},$$

(36)

and $V_{nonbond}^{[r > r_c]}$ is treated as fast force. The indicator function $I_{[r > r_c]}$ is clearly not smooth.

It is shown that when the slow force is defined by a direct truncation, the energy cannot be conserved in a proper way. Actually, the trajectories will be incorrect after a short time interval.
Table 2: Results for simulations of ring-polymer Hamiltonian system with SPC/E potential at 298K. A cell contained 8 molecules with 8 beads. Electrostatic potential and Lennard-Jones potential are truncated at 6.5 Å.

| $h$ (outer) | Method                | $\delta h$ (inner) | $\Delta r$ (Å) | Drift    | Noise    | $\Delta E$ (kJ mol$^{-1}$ K$^{-1}$) | $\Delta E_r$ |
|------------|-----------------------|--------------------|----------------|----------|----------|--------------------------------------|--------------|
| 0.02       | Verlet-I/r-RESPA       | 0.004              | -              | -0.0766% | 7.9759%  | 300.31                               | 0.0766%      |
| 0.02       | Impulse-NM            | 0.02               | -              | 0.0015%  | 0.0149%  | 7.7355                               | 0.0020%      |
| 0.02       | MOLLY-NM              | 0.02 4.5           | 0.0012%        | 0.0193%  | 8.8414   | 0.0023%                              |
| 0.02       | MOLLY-NM              | 0.02 2.5           | 0.0037%        | 0.0268%  | 27.6917  | 0.0071%                              |
| 0.04       | Verlet-I/r-RESPA       | 0.004              | -              | -0.0764% | 7.9800%  | 299.60                               | 0.0764%      |
| 0.04       | Impulse-NM            | 0.04               | -              | 0.0015%  | 0.0162%  | 7.7253                               | 0.0020%      |
| 0.04       | MOLLY-NM              | 0.04 4.5           | 0.0022%        | 0.0148%  | 17.6843  | 0.0045%                              |
| 0.04       | MOLLY-NM              | 0.04 2.5           | 0.0034%        | 0.0203%  | 20.6763  | 0.0053%                              |
| 0.05       | Verlet-I/r-RESPA       | 0.005              | -              | -0.1204% | 19.4579% | 472.06                               | 0.1204%      |
| 0.05       | Impulse-NM            | 0.05               | -              | 0.0013%  | 0.0172%  | 8.4632                               | 0.0022%      |
| 0.05       | MOLLY-NM              | 0.05 4.5           | 0.0025%        | 0.0148%  | 17.5901  | 0.0045%                              |
| 0.05       | MOLLY-NM              | 0.05 2.5           | 0.0037%        | 0.0243%  | 21.1027  | 0.0054%                              |
| 0.0625     | Verlet-I/r-RESPA       | 0.00625            | -              | -0.1891% | 47.5403% | 741.39                               | 0.1893%      |
| 0.0625     | Impulse-NM            | 0.0625             | -              | 0.0015%  | 0.0170%  | 8.2726                               | 0.0021%      |
| 0.0625     | MOLLY-NM              | 0.0625 4.5         | 0.0011%        | 0.0134%  | 11.4564  | 0.0029%                              |
| 0.0625     | MOLLY-NM              | 0.0625 2.5         | 0.0037%        | 0.0215%  | 14.2679  | 0.0036%                              |
| 0.08       | Impulse-NM            | 0.08               | -              | 0.0024%  | 0.0251%  | 7.7223                               | 0.0031%      |
| 0.08       | MOLLY-NM              | 0.08 2.5           | 0.0038%        | 0.0128%  | 12.4829  | 0.0032%                              |
| 0.125      | Impulse-NM            | 0.125              | -              | 0.0013%  | 0.0125%  | 7.4248                               | 0.0019%      |
| 0.125      | MOLLY-NM              | 0.125 2.5          | 0.0040%        | 0.0263%  | 20.8267  | 0.0053%                              |
5 Conclusion and Discussion

In this paper we discuss a symplectic and time-reversible numerical integrator of ring polymer Hamiltonian system with constraints. Constraints are tackled via a modified version of MILC method under normal mode representation, and slow force is mollified by Equilibrium method, thereby improving the numerical stability and reducing computational complexity.

As it is devised for the ring polymer Hamiltonian system, the numerical integrator is expected to be compatible with other techniques. For instance, the time averaging MOLLY can be incorporated in the scheme by mollifying the fast non-bonded force. And Langevin thermostating and Nosé-Hoover-like thermostating can also be performed combining with this integrator, since in thermostating

\[
e^{-\Delta L} \approx e^{-L_{L_{H}}} e^{-L_{H}} e^{-(\Delta t)/2} L_{NHC},
\]

\[
e^{-\Delta L} \approx e^{-L_{L_{H}} L_{NHC}} e^{-(\Delta t)/2} L_{NHC},
\]

(37)
where $L_R$, $L_{NHC}$ and $L_H$ are the Liouvillian of Fokker-Planck equation, Nosé-Hoover chain and ring polymer Hamiltonian system, respectively [24]. The operator $e^{-\Delta t L_H}$ can be replaced by the numerical integrator discussed in this paper.

Although we mainly discuss the rigid bond model, the numerical scheme can be directly applied in the flexible bond model, just as the primitive Equilibrium MOLLY. The corresponding projection operator $P$ can be split into $P = P_2 \circ P_1$, where $P_1$ projects $x$ to their centroid. Then $P_2$ can be determined by the centroid of all beads, using the primitive Equilibrium MOLLY, and the Jacobian matrix $P_\lambda$ can be calculated in the same way as in Appendix.

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**Appendix**

The calculations of $P_1$ and $P_2$ and corresponding Jacobian matrices will be illustrated in this part. The definition of projection operator can be found in [8].

The first operator $P_1$ is defined as

$$P_1\left(x^{(k)}_j\right) = x_j^{(k)} + \frac{1}{m_j} \frac{\partial}{\partial x_j^{(k)}} g\left(x_j^{(1)}, \ldots, x_j^{(N)}\right) \cdot \lambda,$$

where $\lambda$ is chosen so that

$$g\left(P_1x_j\right) = \sum_{k=1}^N \left(P_1x_j^{(k)} - P_1x_j^{(k-1)}\right)^2 = 0,$$

and $x_j^{(0)} = x_j^{(N)}$.

Omit the index $j$ and $m_j$ (which can be incorporated into $\lambda$), then rewrite (37) in matrix form,

$$P_1\left(x\right) = \begin{bmatrix} x^{(1)} + 2\lambda_1 \left(x^{(1)} - x^{(2)}\right) - 2\lambda_N \left(x^{(N)} - x^{(1)}\right) \\ x^{(2)} + 2\lambda_2 \left(x^{(2)} - x^{(3)}\right) - 2\lambda_1 \left(x^{(1)} - x^{(2)}\right) \\ \vdots \\ x^{(N)} + 2\lambda_N \left(x^{(N)} - x^{(1)}\right) - 2\lambda_{N-1} \left(x^{(N-1)} - x^{(N)}\right) \end{bmatrix},$$

(40)

Substitute (40) into (39), we arrive at the linear equation of $\lambda$

$$\begin{bmatrix} 4 \left(x^{(1)} - x^{(2)}\right) & -2 \left(x^{(2)} - x^{(3)}\right) & \cdots & -2 \left(x^{(N)} - x^{(1)}\right) \\ -2 \left(x^{(1)} - x^{(2)}\right) & 4 \left(x^{(2)} - x^{(3)}\right) & \cdots & -2 \left(x^{(3)} - x^{(4)}\right) \\ \vdots & \vdots & \ddots & \vdots \\ -2 \left(x^{(1)} - x^{(2)}\right) & \cdots & -2 \left(x^{(N)} - x^{(N)}\right) & 4 \left(x^{(N)} - x^{(1)}\right) \end{bmatrix} \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \vdots \\ \lambda_N \end{bmatrix} = \begin{bmatrix} x^{(1)} - x^{(2)} \\ x^{(2)} - x^{(3)} \\ \vdots \\ x^{(N)} - x^{(1)} \end{bmatrix}$$

(41)

It is observed that the coefficient matrix in (40) is singular, therefore its solution is not unique. It only remains to find a special solution.
Assume $x^{(k)} - x^{(k+1)} \neq 0$, (otherwise this row can be deleted). Let $\lambda_N = 0$, then $(\lambda_1, \cdots, \lambda_{N-1})$ have a unique solution

$$\lambda_k = \frac{k \bar{x} - \sum_{i=1}^{k} x^{(i)}}{2 (x^{(k)} - x^{(k+1)})},$$

(42)

where $\bar{x} = \frac{x^{(1)} + \cdots + x^{(N)}}{N}$ is the centroid position. In this case, $P_1 \left( x^{(k)}_j \right) = \bar{x}_j$ for all $j$.

The second operator $P_2$ is to project the centroid $(\bar{x}_1, \ldots, \bar{x}_n)$ onto $\nabla_x \nabla V = 0$ (In flexible model, a projection is made so that the projected positions satisfy the reference bond length and angle). The calculation is similar to the constraining in SHAKE algorithm.

$$P_2 (\bar{x}) = \bar{x} + M^{-1} g_\bar{x} (\bar{x})^T \mu,$$

(43)

$\mu$ is chosen by solving a nonlinear equation $g (P_2 (\bar{x})) = 0$ with Newton method. One can refer to [8] for details.

It remains to calculate the Jacobian matrix $P_x$.

$$P (x) = P_1 x + M^{-1} g_\bar{x} (P_1 x)^T \mu,$$

(44)

Differentiating Eq. (44),

$$P_x (x) = P_1 + M^{-1} \sum_{ij} \mu^{ij} (P_1)^T o_i^{ij} (P_1 (x)) + M^{-1} g_\bar{x} (P_1 (x))^T \mu,$$

(45)

where $\mu_x$ can be solved

$$\mu_x = -\left( g_\bar{x} (P (x))^T M^{-1} g_\bar{x} (P_1 (x)) \right)^{-1} g_\bar{x} (P (x))^T \left( P_1 + M^{-1} \mu^{ij} (P_1)^T o^{ij} (P_1 (x)) \right)$$

(46)

since $g_\bar{x} (P (x))^T P_x (x) = 0$ from differentiating $g (P (x)) = 0$.

Therefore, we have got an explicit expression of $P_x$.

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