

Path Integral Monte Carlo Simulations of Flexible Water Clusters with Normal-Mode Sampling in Jacobi Coordinates

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

The primary focus of this thesis is on developing the normal-mode sampling algorithm, an importance sampling method specifically designed for path-integral quantum Monte Carlo simulations of flexible molecular systems. This work is motivated by the desire to include vibrational degrees of freedom in numerical studies of confined molecular lattices. Describing the dynamics of a molecular system using its normal modes naturally allows for the inclusion of molecular rotations, translations, and even vibrations.

We first introduce a novel density matrix factorization that arises from decomposing our system Hamiltonian into its harmonic and anharmonic terms. The normal-mode sampling algorithm is then constructed using this factorization. We also integrate Jacobi coordinates with our normal-mode sampling algorithm to allow for separability between translational and ro-vibrational degrees of freedom.

Finally, we validate our normal-mode sampling algorithm in the context of path-integral quantum Monte Carlo simulations of several flexible molecular systems, namely the water monomer, dimer, hexamer cage, and hexamer prism. For each of these systems, we calculate the ground-state energy and various structural properties, benchmarking our results against exact diagonalization, path integral molecular dynamics, and diffusion Monte Carlo studies from the literature.

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List of Abbreviations

1D one-dimensional [1](#), [2](#), [47](#), [63](#)

CNT carbon nanotube [1](#)

CoM center of mass [22–24](#), [27](#), [29](#), [45](#), [55](#), [64](#)

DMC Diffusion Monte Carlo [29](#), [35](#), [41](#), [45](#), [48](#), [53](#), [55](#), [60](#)

DMRG Density Matrix Renormalization Group [2](#), [64](#)

DoF degrees of freedom [1](#), [2](#), [12](#), [14](#), [21](#), [24](#), [46](#), [47](#), [63](#), [64](#)

DVR Discrete Variable Representation [37](#), [47](#), [48](#)

ED Exact Diagonalization [2](#), [29](#), [36](#), [39](#), [47](#)

HO harmonic oscillator [11](#), [12](#), [15](#), [16](#), [19](#), [64](#)

MC Monte Carlo [6](#), [7](#), [9](#), [10](#), [17](#), [18](#), [20](#), [21](#), [30](#), [34](#), [45](#), [52](#), [55](#)

MH Metropolis-Hastings [6](#), [8](#), [9](#), [13](#), [15](#), [18](#), [24](#), [29–32](#), [41–43](#), [45](#)

PES potential energy surface [2](#), [47](#)

PIGS Path Integral Ground State [6–10](#), [12](#), [14](#), [21](#), [22](#), [24](#), [26](#), [28–30](#), [32](#), [35](#), [37](#), [39](#),
[41–45](#), [47](#), [49](#), [52](#), [53](#), [55](#), [56](#), [60](#), [62](#), [63](#)

PIMC Path Integral Monte Carlo [6](#), [27](#)

PIMD Path Integral Molecular Dynamics [27](#), [29](#), [35](#), [41](#), [45](#), [48](#), [64](#)

QMC Quantum Monte Carlo [2](#), [6](#), [12](#), [28](#), [60](#), [62](#)

Chapter 1

Introduction

Phase transitions in quantum spin models have been widely studied for more than 50 years, but there has also been significant interest over the past several years in discovering critical phenomena in systems of interacting confined molecules [1, 2]. In fact, recent studies have found that such molecular systems can undergo a quantum phase transition characterized by the ordering of electric dipoles, and even remain quantum critical at experimentally accessible temperatures [3–6]. This phenomenon can be physically realized in a [one-dimensional \(1D\)](#) lattice of water molecules interacting through dipole forces. One way of constructing such a molecular chain is using endohedral fullerenes, where a single water molecule is confined inside a buckminsterfullerene (C_{60}) cage [7]. These bodies of $H_2O@C_{60}$ can then be encapsulated within a [carbon nanotube \(CNT\)](#) to form an endofullerene peapod nanomolecular assembly, essentially a chain of dipole-interacting water molecules [8–11]. It is also possible to trap water molecules directly in [CNTs](#) and form a single-file water chain that is capable of dipole-ordering [12]. Other ferroelectric water chains can be constructed in supramolecular architectures, or in minerals such as beryl and cordierite [13–17].

Numerically simulating such molecular lattices is much more challenging compared to spin systems because a molecule has many more [degrees of freedom \(DoF\)](#) to take into

account. These include the electronic and nuclear coordinates, as well as the spins associated with each quantum particle. The full quantum-mechanical treatment of a molecule such as water often employs the Born-Oppenheimer approximation to separate the electronic and nuclear motions based on their difference in timescales [18]. Since electrons are much lighter than nuclei, the nuclear kinetic energy can be neglected when solving the Schrödinger equation for the electronic DoF. The fact that the ground-state electronic energy is parameterized by the fixed positions of the nuclei leads to the concept of a [potential energy surface \(PES\)](#), which determines the quantum dynamics of the nuclei [18]. This thesis is focused on studying the nuclear motion in collections of interacting water molecules.

The quantum dynamics of a single water molecule inside a C_{60} cage can be calculated using [Exact Diagonalization \(ED\)](#), but even with basis truncation methods, [ED](#) is not feasible for systems larger than 10 rotating water molecules due to its exponential scaling with system size [10]. Beyond [ED](#), the [Density Matrix Renormalization Group \(DMRG\)](#) technique has been used to simulate larger chains of water molecules and even study quantum phase transitions [5, 6, 19, 20]. However, [DMRG](#) is restricted to [1D](#) systems and thus far has only treated molecular rotations and translations, but not vibrations. Therefore, alternative approaches like [Quantum Monte Carlo \(QMC\)](#), which do not suffer from the same limitations as [ED](#) and [DMRG](#), are needed. The objective of this thesis is to develop a [QMC](#) simulation framework that is capable of simulating such molecular systems while accounting for rotational, translational, *and* vibrational dynamics.

The remainder of this chapter is organized as follows. In [Section 1.1](#), we develop the formalism for studying the statistical mechanics of quantum systems using imaginary-time path integrals. [Section 1.2](#) presents two [QMC](#) methods that are built upon this path-integral formalism. Finally, [Section 1.3](#) introduces the idea of the *normal modes* of a molecular system, which will play a key role in emphasizing the inclusion of vibrational DoF in our simulations.

1.1 Path Integral Theory

This section introduces the theory behind path integrals and their application to quantum statistical mechanics. Subsection 1.1.1 applies the path-integral formalism to quantum systems in thermal equilibrium, or at finite temperatures. Subsection 1.1.2 deals with the special case of quantum systems at zero temperature and demonstrates how path integrals can be used to represent the quantum-mechanical ground state.

1.1.1 Finite-Temperature Formalism

In the finite-temperature representation of path integrals, we deal with a quantum system of N particles in thermal equilibrium with a heat bath at temperature T . As such, we consider the canonical partition function and resolve its trace in the position basis $\{|\mathbf{q}\rangle\}$:

$$Z = \text{Tr}(e^{-\beta\hat{H}}) = \int d\mathbf{q} \langle \mathbf{q} | e^{-\beta\hat{H}} | \mathbf{q} \rangle, \quad (1.1)$$

where $\hat{H}$ is the Hamiltonian of our system, $\beta = 1/k_{\text{B}}T$ is the reciprocal thermodynamic temperature, and $\mathbf{q} = \{(x_1, y_1, z_1), (x_2, y_2, z_2), \dots, (x_N, y_N, z_N)\}$ denotes the collection of all positional coordinates in our system [21]. To develop the path-integral formulation of quantum statistical mechanics, we introduce the imaginary-time step $\tau = \beta/P$, where P is a large positive integer, and separate the low-temperature thermal density operator into P factors: $e^{-\beta\hat{H}} = (e^{-\tau\hat{H}})^P$ [22]. Substituting this result into Eq. (1.1) and inserting a resolution of the identity in the position basis between each factor of $e^{-\tau\hat{H}}$, we obtain

$$\begin{aligned} Z &= \int d\mathbf{q}_1 \cdots \int d\mathbf{q}_P \langle \mathbf{q}_1 | e^{-\tau\hat{H}} | \mathbf{q}_2 \rangle \langle \mathbf{q}_2 | e^{-\tau\hat{H}} | \mathbf{q}_3 \rangle \cdots \langle \mathbf{q}_{P-1} | e^{-\tau\hat{H}} | \mathbf{q}_P \rangle \langle \mathbf{q}_P | e^{-\tau\hat{H}} | \mathbf{q}_1 \rangle \\ &= \prod_{i=1}^P \int d\mathbf{q}_i \prod_{j=1}^P \rho(\mathbf{q}_j, \mathbf{q}_{j+1}; \tau), \end{aligned} \quad (1.2)$$

where $\mathbf{q}_{P+1} = \mathbf{q}_1$, as is necessary for computing the trace, and we have defined the imaginary-time propagator as the matrix elements of the high-temperature thermal density operator [21, 22]:

$$\rho(\mathbf{q}_i, \mathbf{q}_j; \tau) = \langle \mathbf{q}_i | e^{-\tau\hat{H}} | \mathbf{q}_j \rangle. \quad (1.3)$$

To perform practical path-integral calculations, we require a means of evaluating these density matrix elements, which is typically achieved using approximations. One such common approximation is the second-order symmetric Trotter factorization with respect to our Hamiltonian's kinetic and potential energy components $\hat{H} = \hat{T} + \hat{V}$:

$$\begin{aligned}\rho(\mathbf{q}_i, \mathbf{q}_j; \tau) &= \langle \mathbf{q}_i | e^{-\tau(\hat{T} + \hat{V})} | \mathbf{q}_j \rangle = \langle \mathbf{q}_i | e^{-\tau\hat{V}/2} e^{-\tau\hat{T}} e^{-\tau\hat{V}/2} | \mathbf{q}_j \rangle + \mathcal{O}(\tau^3) \\ &= e^{-\tau V(\mathbf{q}_i)/2} \rho_0(\mathbf{q}_i, \mathbf{q}_j; \tau) e^{-\tau V(\mathbf{q}_j)/2} + \mathcal{O}(\tau^3),\end{aligned}\quad (1.4)$$

where the leading-order error is $\mathcal{O}(\tau^3)$, arising from the non-zero commutator between the kinetic and potential energy operators $[\hat{T}, \hat{V}] \neq 0$ [23, 24]. However, this Trotter error systematically vanishes in the limit as $P \rightarrow \infty$.

Furthermore, the matrix elements of the kinetic thermal density operator, also called the *free-particle* propagator, can be computed exactly by a clever insertion of the resolution of the identity in the momentum basis $\{|\mathbf{p}\rangle\}$:

$$\rho_0(\mathbf{q}_i, \mathbf{q}_j; \tau) = \langle \mathbf{q}_i | e^{-\tau\hat{T}} | \mathbf{q}_j \rangle = \prod_{k=1}^N \left(\frac{m_k}{2\pi\hbar^2\tau} \right)^{3/2} \exp \left(-\frac{m_k}{2\hbar^2\tau} \|\mathbf{r}_k^i - \mathbf{r}_k^j\|^2 \right), \quad (1.5)$$

where m_k and $\mathbf{r}_k^i = (x_k, y_k, z_k)^i$ are the mass and position vector of particle k at imaginary-time slice i , respectively [23]. Substituting Eqs. (1.4) and (1.5) into Eq. (1.2), the final expression for our path integral becomes

$$Z \approx \int \mathcal{D}\vec{\mathbf{q}} \exp \left(-\tau \sum_{i=1}^P \left[V(\mathbf{q}_i) + \sum_{j=1}^N \frac{m_j}{2\hbar^2\tau^2} \|\mathbf{r}_j^i - \mathbf{r}_j^{i+1}\|^2 \right] \right), \quad (1.6)$$

where we have defined the integration measure to absorb any constants that do not affect the physics of our system:

$$\mathcal{D}\vec{\mathbf{q}} = \prod_{j=1}^N \left(\frac{m_j}{2\pi\hbar^2\tau} \right)^{3P/2} \prod_{i=1}^P d\mathbf{q}_i. \quad (1.7)$$

1.1.2 Zero-Temperature Formalism

In the zero-temperature representation of path integrals, we would like to calculate the ground-state properties of an N -particle quantum system, so we assume that the tem-

perature T is small enough such that the only thermally accessible state is the quantum-mechanical ground state of our system. To this end, we consider a trial state $|\psi_T\rangle$, which ideally serves as a good approximation to the true ground state $|\psi_0\rangle$, and define a thermally projected state [25]:

$$|\psi_\beta\rangle = e^{-\beta\hat{H}/2} |\psi_T\rangle. \quad (1.8)$$

The fundamental principle underlying this projective scheme is that, irrespective of our choice in the trial state, $|\psi_\beta\rangle$ always converges to the true ground state in the limit as $\beta \rightarrow \infty$ ¹. Since we are only interested in one quantum state now, namely the ground state, we introduce the *pseudo*-partition function that solely counts this projected state [25]:

$$Z_0 = \langle\psi_\beta|\psi_\beta\rangle = \langle\psi_T|e^{-\beta\hat{H}}|\psi_T\rangle. \quad (1.9)$$

The construction of the ground-state path integral is analogous to that of the finite-temperature formalism: define the imaginary-time step $\tau = \beta/(P-1)$, factorize the thermal density operator $e^{-\beta\hat{H}} = (e^{-\tau\hat{H}})^{P-1}$, and insert a resolution of the identity in the position basis between each factor of $e^{-\tau\hat{H}}$. Applying this process to Eq. (1.9), and inserting additional resolutions of the identity adjacent to $\langle\psi_T|$ and $|\psi_T\rangle$, we obtain

$$\begin{aligned} Z_0 &= \int d\mathbf{q}_1 \cdots \int d\mathbf{q}_P \langle\psi_T|\mathbf{q}_1\rangle \langle\mathbf{q}_1|e^{-\tau\hat{H}}|\mathbf{q}_2\rangle \cdots \langle\mathbf{q}_{P-1}|e^{-\tau\hat{H}}|\mathbf{q}_P\rangle \langle\mathbf{q}_P|\psi_T\rangle \\ &= \prod_{i=1}^P \int d\mathbf{q}_i \psi_T(\mathbf{q}_1) \prod_{j=1}^{P-1} \rho(\mathbf{q}_j, \mathbf{q}_{j+1}; \tau) \psi_T(\mathbf{q}_P), \end{aligned} \quad (1.10)$$

where we have recalled Eq. (1.3). Further recalling Eqs. (1.4) and (1.5) yields the final expression for our ground-state path integral:

$$Z_0 \approx \int \mathcal{D}\vec{q} \psi_T(\mathbf{q}_1) \exp \left(-\tau \left[\sum_{i=2}^{P-1} V(\mathbf{q}_i) + \frac{V(\mathbf{q}_1) + V(\mathbf{q}_P)}{2} + \sum_{i=1}^{P-1} \sum_{j=1}^N \frac{m_j}{2\hbar^2\tau^2} \|\mathbf{r}_j^i - \mathbf{r}_j^{i+1}\|^2 \right] \right) \psi_T(\mathbf{q}_P), \quad (1.11)$$

where the integration measure here differs ever so slightly from Eq. (1.7) only in the constants being absorbed into it:

$$\mathcal{D}\vec{q} = \prod_{j=1}^N \left(\frac{m_j}{2\pi\hbar^2\tau} \right)^{3(P-1)/2} \prod_{i=1}^P d\mathbf{q}_i. \quad (1.12)$$

¹See Appendix A.1 for the proof.

1.2 Quantum Monte Carlo Methods

In this section, we introduce two [QMC](#) methods that are based on the path-integral representation of quantum systems, namely the finite-temperature approach [Path Integral Monte Carlo \(PIMC\)](#) (Subsection 1.2.1) and its zero-temperature counterpart [Path Integral Ground State \(PIGS\)](#) (Subsection 1.2.2). This thesis only makes use of [PIGS](#) as we are primarily concerned with computing the *ground-state* properties of molecular systems. However, we present both schemes here for the sake of clarity and completeness. Subsection 1.2.3 also introduces the naive [Metropolis-Hastings \(MH\)](#) algorithm that is traditionally used for importance sampling in [QMC](#) simulations, which we will compare to after developing our normal-mode sampling algorithm in Chapter 2.

1.2.1 Path Integral Monte Carlo

In [PIMC](#), we want to calculate expectation values with respect to the probability distribution given by the integrand of our path integral:

$$\pi(\vec{q}) \propto \rho(\mathbf{q}_1, \mathbf{q}_2; \tau) \rho(\mathbf{q}_2, \mathbf{q}_3; \tau) \cdots \rho(\mathbf{q}_{P-1}, \mathbf{q}_P; \tau) \rho(\mathbf{q}_P, \mathbf{q}_1; \tau), \quad (1.13)$$

where $\vec{q} = (\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_P)$ is the imaginary-time *path* configuration [23]. It is also helpful to consider the probability distribution associated with a given imaginary-time slice, or bead:

$$\pi(\mathbf{q}_i) \propto \rho_0(\mathbf{q}_{i-1}, \mathbf{q}_i; \tau) e^{-\tau V(\mathbf{q}_i)} \rho_0(\mathbf{q}_i, \mathbf{q}_{i+1}; \tau), \quad (1.14)$$

which follows from Eq. (1.4). The objective of [PIMC](#) is to use [Monte Carlo \(MC\) importance sampling](#) algorithms to sample M path configurations from $\pi(\vec{q})$ so that we can estimate the expectation value of any physical observable $\hat{O}$ as

$$\langle O \rangle = \frac{\text{Tr}(\hat{O} e^{-\beta \hat{H}})}{Z} \approx \frac{1}{M} \sum_{t=1}^M o(\vec{q}_t), \quad (1.15)$$

where the partition function is given by Eq. (1.1) and $o(\vec{q}_t)$ is an estimator for the observable $\hat{O}$ computed using the t^{th} sampled path configuration [23].

1.2.2 Path Integral Ground State

The probability distribution we consider in [PIGS](#) differs slightly from Eq. (1.13) due to the fact that we are no longer resolving a trace, but rather an expectation value with respect to some trial state $|\psi_T\rangle$ [\[23\]](#):

$$\pi(\vec{q}) \propto \psi_T(\mathbf{q}_1) \prod_{i=1}^{P-1} \rho(\mathbf{q}_i, \mathbf{q}_{i+1}; \tau) \psi_T(\mathbf{q}_P). \quad (1.16)$$

In this case, the probability distribution associated with the *middle beads* $i = 2, \dots, P-1$ is still given by Eq. (1.14). However, the probability distributions associated with the *end beads* $i = 1, P$ are now

$$\pi(\mathbf{q}_1) \propto \psi_T(\mathbf{q}_1) e^{-\tau V(\mathbf{q}_1)/2} \rho_0(\mathbf{q}_1, \mathbf{q}_2; \tau), \quad \pi(\mathbf{q}_P) \propto \rho_0(\mathbf{q}_{P-1}, \mathbf{q}_P; \tau) e^{-\tau V(\mathbf{q}_P)/2} \psi_T(\mathbf{q}_P). \quad (1.17)$$

Similarly to Eq. (1.15), our goal is to produce M samples from $\pi(\vec{q})$ using [MC](#) importance sampling in order to estimate the expectation value of any observable $\hat{O}$:

$$\langle O \rangle = \frac{\langle \psi_\beta | \hat{O} | \psi_\beta \rangle}{Z_0} \approx \frac{1}{M} \sum_{t=1}^M o(\vec{q}_t), \quad (1.18)$$

where the thermally projected state and pseudo-partition function are given by Eqs. (1.8) and (1.9), respectively [\[23\]](#).

To evaluate Eq. (1.18), we need to consider the form of the estimator $o(\vec{q})$ for different physical observables of interest $\hat{O}$. In Chapter 3, we will mainly be interested in calculating the total energy of our system (i.e. the ground-state energy in the case of [PIGS](#)) and some of its structural properties, such as positional distribution functions and pair correlation functions [\[23, 24\]](#). Since the total energy operator, or Hamiltonian $\hat{H}$, commutes with the thermal density operator $e^{-\tau \hat{H}}$, in the path-integral formulation we find that the ground-state energy is given by the expectation value of the potential energy at either of the end beads:

$$E_0 = \langle H \rangle = \langle V(\mathbf{q}_1) \rangle = \langle V(\mathbf{q}_P) \rangle, \quad (1.19)$$

where we have also asserted that this thesis purely uses a *constant* trial state $\psi_T(\mathbf{q}) \propto 1$ for simplicity, whose kinetic energy is zero² [26, 27]. Therefore, in practice we use the estimator $o(\vec{q}) = [V(\mathbf{q}_1) + V(\mathbf{q}_P)]/2$ when $\hat{O} = \hat{H}$. Since structural properties are represented by operators $\hat{O}$ that are *diagonal* in the position basis, we find that only the bead exactly in the middle of the path contributes to their expectation values:

$$\langle O \rangle = \langle O(\mathbf{q}_{\frac{P+1}{2}}) \rangle, \quad (1.20)$$

which is why an odd number of beads is recommended for PIGS simulations³ [26, 27]. Thus, when $\hat{O}$ represents a structural property, we use the estimator $o(\vec{q}) = O(\mathbf{q}_{\frac{P+1}{2}})$.

1.2.3 Metropolis-Hastings Sampling

The MH algorithm allows us to sample the probability distribution of interest $\pi(\vec{q})$ by separating it into a proposal distribution $\mathcal{P}(\vec{q})$ and an acceptance distribution $\mathcal{A}(\vec{q})$:

$$\pi(\vec{q}) = \mathcal{P}(\vec{q})\mathcal{A}(\vec{q}), \quad (1.21)$$

where ideally the proposal distribution is amenable to direct sampling and the acceptance distribution is straightforward to evaluate [24]. This factorization effectively breaks down the importance sampling procedure into two steps: (1) propose a new configuration and (2) decide whether to accept or reject it. As implied by their names, the proposal distribution facilitates the first step and the acceptance distribution the second.

Typical forms of proposal distributions include uniform and Gaussian distributions because they are easy to directly sample using software libraries such as `numpy.random` in Python and `Distributions` in Julia [28–31]. We now present the simplest version of the MH algorithm that naively proposes moves from a uniform distribution $\mathcal{P}(\vec{q}) = 1$ and accepts them according to $\mathcal{A}(\vec{q}) = \pi(\vec{q})$. The following steps specify how the naive MH algorithm is carried out:

²See Appendix A.2 for the derivation of Eq. (1.19).

³See Appendix A.3 for the derivation of Eq. (1.20).

1. First, the imaginary-time path is initialized either randomly or in some equilibrium configuration (if one is known for the quantum system of interest) [32].
2. Then, for each MC time step, we randomly sweep through all beads $i = 1, \dots, P$ and all particles $j = 1, \dots, N$. This picks out a specific position vector $\mathbf{r}_j^i$ to be updated. In each iteration of this i, j loop, a new position for this vector is proposed according to $\tilde{\mathbf{r}}_j^i = \mathbf{r}_j^i + \delta\mathbf{r}$, where $\delta\mathbf{r}$ is uniformly sampled from the interval $[-\Delta\mathbf{r}/2, +\Delta\mathbf{r}/2]$ [23].
3. Now, we evaluate the probability distribution of bead i at its current configuration $\pi_{\text{old}} = \pi(\mathbf{q}_i^{\text{old}})$ and its proposed configuration $\pi_{\text{new}} = \pi(\mathbf{q}_i^{\text{new}})$, where

$$\mathbf{q}_i^{\text{old}} = \{\mathbf{r}_1^i, \dots, \mathbf{r}_{j-1}^i, \mathbf{r}_j^i, \mathbf{r}_{j+1}^i, \dots, \mathbf{r}_N^i\}, \quad \mathbf{q}_i^{\text{new}} = \{\mathbf{r}_1^i, \dots, \mathbf{r}_{j-1}^i, \tilde{\mathbf{r}}_j^i, \mathbf{r}_{j+1}^i, \dots, \mathbf{r}_N^i\}.$$

Since we are discussing MH sampling in the context of a PIGS simulation, this probability distribution is evaluated using Eq. (1.14) for the middle beads and Eq. (1.17) for the end beads.

4. Finally, we accept the proposed configuration with probability $\min(1, \pi_{\text{new}}/\pi_{\text{old}})$ [23, 24]. In practice, this is accomplished by first computing the ratio $\pi_{\text{new}}/\pi_{\text{old}}$ and generating a uniformly distributed random number u from the interval $[0, 1]$. If $\pi_{\text{new}}/\pi_{\text{old}} \geq u$, then we accept the proposed configuration and update the position vector $\mathbf{r}_j^i = \tilde{\mathbf{r}}_j^i$. Otherwise, we reject the proposed configuration and leave the position vector as is $\mathbf{r}_j^i = \mathbf{r}_j^i$ for the next MC time step.

The algorithm detailed above generates a sequence of path configurations called a *Markov chain*, where each subsequent configuration is “linked” to the preceding one via a transition probability [23, 24, 32]. Since the proposal distribution of step 2 depends on the current state of the position vector $\mathbf{r}_j^i$, this introduces an inherent correlation between consecutive configurations in the Markov chain. We can quantify this correlation using the autocorrelation function for any observable $\hat{O}$ that is monitored during the MC simulation:

$$C_O(l) = \frac{\sum_{t=1}^M (O_t - \langle O \rangle)(O_{t+l} - \langle O \rangle)}{\sum_{t=1}^M (O_t - \langle O \rangle)^2}, \quad (1.22)$$

where $\{O_1, O_2, \dots, O_M\}$ is the series of measurements obtained by evaluating the observable’s estimator $O_t = o(\vec{q}_t)$ and $\langle O \rangle$ is given by the MC average as in Eqs. (1.15) and (1.18) [23]. In order to overcome this autocorrelation and produce approximately independent samples, rather than evaluating the estimator after every MC step, we do so only after every $N_{\text{skip}}^{\text{th}}$ step instead, so $N_{\text{skip}} - 1$ configurations are discarded between every observable measurement. The optimal N_{skip} chosen in practice usually depends on the autocorrelation time t_{corr} , defined as the lag l (in units of MC time steps) at which Eq. (1.22) decays to $1/e$ [32].

Another important property to keep track of is the acceptance rate, which is the fraction of proposed moves that are accepted throughout the course of the MC simulation. A high acceptance rate implies that there is not much variation between new and old configurations, whereas a low acceptance rate means that there are many identical configurations in the sampled Markov chain [23]. Both of these cases, however, lead to the configuration space being explored slowly, so we typically desire an acceptance rate between 30 % and 50 % to avoid this [23]. One way to achieve a desired acceptance rate is to tune the target interval size that controls the range of the uniform proposal distribution (i.e. update $\Delta \mathbf{r}$ at the end of every MC time step) [32]. Lastly, we note that before any observable measurements are taken, we require a certain number of MC steps to be run without any estimator evaluations to allow the sampled Markov chain to “forget” any initial-state bias (from step 1) and converge to the target distribution $\pi(\vec{q})$ [24]. This duration of N_{therm} steps is referred to as the thermal equilibration period.

1.3 Normal Modes from Hessian Diagonalization

The next chapter will introduce a novel importance sampling technique that enhances the performance of PIGS simulations for quantum systems dominated by the *harmonic* (quadratic) part of its potential energy [33, 34]. In this section, we present the theoretical foundation of this sampling approach by outlining how the normal modes of a molecular system are calculated.

We begin by considering the *classical* Hamiltonian for a molecular system of N atoms:

$$H = \sum_{i=1}^N \frac{m_i}{2} \left[\left(\frac{dx_i}{dt} \right)^2 + \left(\frac{dy_i}{dt} \right)^2 + \left(\frac{dz_i}{dt} \right)^2 \right] + V(\{x_i, y_i, z_i\}), \quad (1.23)$$

where m_i is the mass of atom i and V is the potential energy function that, in general, depends on the coordinates of all N atoms. In our specific case of flexible water clusters, V is described by the q-TIP4P/F quantum water model to be presented in Chapter 3 [35]. Let us now denote our system's equilibrium configuration (i.e. where the potential energy is minimized) by $\{a_i, b_i, c_i\}$ and then define a new set of coordinates $\{q_i\}$ [34]:

$$q_1 = \sqrt{m_1}(x_1 - a_1), q_2 = \sqrt{m_1}(y_1 - b_1), q_3 = \sqrt{m_1}(z_1 - c_1), q_4 = \sqrt{m_2}(x_2 - a_2), \dots \quad (1.24)$$

This definition makes it clear that in equilibrium, we have $q_i = 0$ for all $i = 1, 2, \dots, 3N$. In terms of these new coordinates, we can rewrite our Hamiltonian as

$$H = \frac{1}{2} \sum_{i=1}^{3N} \left(\frac{dq_i}{dt} \right)^2 + V_0 + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial q_i} \right)_0 q_i + \frac{1}{2} \sum_{i,j=1}^{3N} q_i \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_j + \dots, \quad (1.25)$$

where the subscript 0 instructs us to evaluate the relevant quantity at the equilibrium configuration, so we have Taylor-expanded the potential energy about its minimum V_0 . To obtain the normal modes of our system, we need to diagonalize the quadratic component of its potential energy, or the mass-weighted Hessian matrix:

$$V_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0, \quad (1.26)$$

whose eigenvalues $\{\omega_k^2\}$ give us the frequency (squared) of each normal mode k and eigenvectors $\{Q_k\}$ give us the corresponding normal coordinate, defined as a linear combination of the $\{q_i\}$ coordinates [34]. In other words, the coordinate Q_k behaves like a **harmonic oscillator (HO)** vibrating at frequency ω_k . In terms of these normal modes, the *quantum* Hamiltonian for our system can be written as

$$\hat{H} = \underbrace{\sum_{k=1}^{3N} \frac{1}{2} \left(\hat{P}_k^2 + \omega_k^2 \hat{Q}_k^2 \right)}_{\hat{H}_{\text{HO}}} + \Delta \hat{V}, \quad (1.27)$$

where $\hat{P}_k = -i\hbar \frac{\partial}{\partial Q_k}$ is the conjugate momentum of normal mode k and the *anharmonic* part of the potential energy is computed by the simple subtraction:

$$\Delta\hat{V} = \hat{V} - \underbrace{\frac{1}{2} \sum_{k=1}^{3N} \omega_k^2 \hat{Q}_k^2}_{\hat{V}_{\text{HO}}}. \quad (1.28)$$

In practice, the k summation over normal modes in Eqs. (1.27) and (1.28) is often truncated from $3N$ to $3N - 6$, neglecting the six *zero-frequency* modes corresponding to the three global translations and three global rotations of our system as a whole [33]. Lastly, we note that in the *harmonic approximation*, we can use the normal-mode frequencies of our system to estimate its ground-state energy as

$$E_0^{\text{HO}} = V_0 + \sum_{k=1}^{3N-6} \frac{\hbar\omega_k}{2}, \quad (1.29)$$

where we have recalled that the zero-point energy for a single HO of frequency ω is simply $\hbar\omega/2$ [33].

1.4 Thesis Outline

The remainder of this thesis is organized as follows. Chapter 2 contains our main theoretical contributions, where we present a novel factorization of the thermal density matrix based on the normal-mode Hamiltonian decomposition from Section 1.3. Using this density matrix factorization, we develop the normal-mode sampling algorithm (and several variants of it) and show how it can be used to sample path integrals in the context of PIGS QMC simulations. We also introduce a unique coordinate system called Jacobi coordinates, which allows us to treat translational DoF separately from rotations and vibrations in molecular systems.

In Chapter 3, we demonstrate our new path-integral sampling algorithms by presenting our simulation results for the H₂O monomer and other flexible water clusters. We also

compare our normal-mode sampling algorithms to the naive [MH](#) algorithm from Subsection [1.2.3](#). In Chapter [4](#), we end with some concluding remarks and discuss future research directions, which include performance improvements to the methods developed here and extending them to study larger molecular systems.

Chapter 2

Sampling Path Integrals using Normal Modes

This chapter builds off of the background presented in Chapter 1 to develop a novel importance sampling algorithm for PIGS simulations that is based on the normal modes of the quantum system. Sections 2.1 and 2.2 introduce two variants of this normal-mode sampling algorithm, one that samples one imaginary-time slice at a time and another that samples the whole imaginary-time path at once. Section 2.3 discusses Jacobi coordinates and how this coordinate system can be used to sample only specific DoF while leaving others fixed. Lastly, Section 2.4 suggests a modification to our normal-mode sampling algorithms to make them rejection-free in the hopes of reducing computational resources.

2.1 Single-Slice Normal-Mode Sampling

In the context of PIGS, the Hamiltonian decomposition introduced in Eq. (1.27) leads to an alternative Trotter factorization for evaluating the imaginary-time propagators in Eq. (1.10). Rather than “Trotterizing” with respect to our Hamiltonian’s kinetic and

potential energy terms, we Trotterize with respect to its harmonic and anharmonic components instead $\hat{H} = \hat{H}_{\text{HO}} + \Delta\hat{V}$:

$$\begin{aligned}\rho(\mathbf{q}_i, \mathbf{q}_j; \tau) &= \langle \mathbf{q}_i | e^{-\tau(\hat{H}_{\text{HO}} + \Delta\hat{V})} | \mathbf{q}_j \rangle = \langle \mathbf{q}_i | e^{-\tau\Delta\hat{V}/2} e^{-\tau\hat{H}_{\text{HO}}} e^{-\tau\Delta\hat{V}/2} | \mathbf{q}_j \rangle + \mathcal{O}(\tau^3) \\ &\approx e^{-\tau\Delta V(\mathbf{q}_i)/2} \langle \mathbf{q}_i | e^{-\tau\sum_k \hat{H}_k} | \mathbf{q}_j \rangle e^{-\tau\Delta V(\mathbf{q}_j)/2} = e^{-\tau[\Delta V(\mathbf{q}_i) + \Delta V(\mathbf{q}_j)]/2} \prod_{k=1}^{3N} \rho_{\text{HO}}(Q_k^i, Q_k^j; \tau),\end{aligned}\tag{2.1}$$

where we have made an implicit transformation from the coordinates introduced in Eq. (1.24) to our normal coordinates $\mathbf{q} = \{q_1, q_2, \dots, q_{3N}\} \mapsto \{Q_1, Q_2, \dots, Q_{3N}\}$ and defined the independent HO Hamiltonian for a given normal mode:

$$\hat{H}_k = \frac{1}{2} \left(\hat{P}_k^2 + \omega_k^2 \hat{Q}_k^2 \right).\tag{2.2}$$

Similarly to the kinetic thermal density matrix, the matrix elements of the HO's thermal density operator can also be computed exactly, yielding the well-known result [33]:

$$\rho_{\text{HO}}(Q_k^i, Q_k^j; \tau) \propto \exp \left[-\frac{\omega_k}{2\hbar \sinh(\tau\hbar\omega_k)} \left([(Q_k^i)^2 + (Q_k^j)^2] \cosh(\tau\hbar\omega_k) - 2Q_k^i Q_k^j \right) \right].\tag{2.3}$$

By inspection of the integrand in Eq. (1.10) and the Trotter factorization in Eq. (2.1), the probability distribution associated with the middle beads becomes

$$\pi(\mathbf{q}_i) \propto e^{-\tau\Delta V(\mathbf{q}_i)} \prod_{k=1}^{3N} \rho_{\text{HO}}(Q_k^{i-1}, Q_k^i; \tau) \rho_{\text{HO}}(Q_k^i, Q_k^{i+1}; \tau)\tag{2.4}$$

and the probability distributions associated with the end beads are now

$$\pi(\mathbf{q}_1) \propto e^{-\tau\Delta V(\mathbf{q}_1)/2} \prod_{k=1}^{3N} \rho_{\text{HO}}(Q_k^{(1)}, Q_k^{(2)}; \tau), \quad \pi(\mathbf{q}_P) \propto e^{-\tau\Delta V(\mathbf{q}_P)/2} \prod_{k=1}^{3N} \rho_{\text{HO}}(Q_k^{(P-1)}, Q_k^{(P)}; \tau),\tag{2.5}$$

where we have recalled that this thesis only makes use of a constant trial state $\psi_{\text{T}}(\mathbf{q}) \propto 1$.

In contrast to the naive MH algorithm presented in Subsection 1.2.3, rather than using a uniform proposal distribution, this normal-mode sampling strategy instead proposes

moves according to the Gaussian described by the product of HO density matrix elements in Eqs. (2.4) and (2.5) [24]. Referring to Eq. (2.3), we define two intermediate parameters:

$$A_k = \frac{\omega_k}{2\hbar \tanh(\tau\hbar\omega_k)}, \quad B_k = \frac{\omega_k}{\hbar \sinh(\tau\hbar\omega_k)}, \quad (2.6)$$

and reveal the Gaussian nature of the middle beads' proposal distribution:

$$\begin{aligned} \mathcal{P}(\mathbf{q}_i) &= \prod_{k=1}^{3N} \rho_{\text{HO}}(Q_k^{i-1}, Q_k^i; \tau) \rho_{\text{HO}}(Q_k^i, Q_k^{i+1}; \tau) \\ &\propto \prod_{k=1}^{3N} \exp(-A_k [(Q_k^{i-1})^2 + (Q_k^i)^2] + B_k Q_k^{i-1} Q_k^i) \exp(-A_k [(Q_k^i)^2 + (Q_k^{i+1})^2] + B_k Q_k^i Q_k^{i+1}) \\ &= \prod_{k=1}^{3N} \exp(-A_k [(Q_k^{i-1})^2 + 2(Q_k^i)^2 + (Q_k^{i+1})^2] + B_k [Q_k^{i-1} Q_k^i + Q_k^i Q_k^{i+1}]) \\ &= \prod_{k=1}^{3N} \exp\left(-2A_k \left[Q_k^i - \frac{B_k (Q_k^{i-1} + Q_k^{i+1})}{4A_k}\right]^2 - A_k [(Q_k^{i-1})^2 + (Q_k^{i+1})^2] + \frac{B_k^2 [Q_k^{i-1} + Q_k^{i+1}]^2}{8A_k}\right) \\ &\propto \prod_{k=1}^{3N} \exp\left(-2A_k \left[Q_k^i - \frac{B_k (Q_k^{i-1} + Q_k^{i+1})}{4A_k}\right]^2\right) = \prod_{k=1}^{3N} \underbrace{\exp\left[-\frac{(Q_k^i - \mu_k^i)^2}{2(\sigma_k^i)^2}\right]}_{\text{Gaussian}}, \end{aligned} \quad (2.7)$$

where we have “completed the square” and neglected any constant factors not involving the independent variables contained in $\mathbf{q}_i$. It follows from Eq. (2.7) that for $i = 2, \dots, P-1$, new values for each normal coordinate Q_k^i are proposed according to a Gaussian specified by the following mean and standard deviation:

$$\mu_k^i = \frac{B_k (Q_k^{i-1} + Q_k^{i+1})}{4A_k} = \frac{Q_k^{i-1} + Q_k^{i+1}}{2 \cosh(\tau\hbar\omega_k)}, \quad \sigma_k^i = \sqrt{\frac{1}{4A_k}} = \sqrt{\frac{\hbar \tanh(\tau\hbar\omega_k)}{2\omega_k}}. \quad (2.8)$$

Analyzing Eq. (2.5) in an analogous manner reveals the proposal distributions for the end beads to also be Gaussian, but with means and standard deviations of

$$\mu_k^{(1)} = \frac{B_k Q_k^{(2)}}{2A_k} = \frac{Q_k^{(2)}}{\cosh(\tau\hbar\omega_k)}, \quad \sigma_k^{(1)} = \sqrt{\frac{1}{2A_k}} = \sqrt{\frac{\hbar \tanh(\tau\hbar\omega_k)}{\omega_k}} \quad (2.9)$$

for the first bead and

$$\mu_k^{(P)} = \frac{B_k Q_k^{(P-1)}}{2A_k} = \frac{Q_k^{(P-1)}}{\cosh(\tau \hbar \omega_k)}, \quad \sigma_k^{(P)} = \sqrt{\frac{1}{2A_k}} = \sqrt{\frac{\hbar \tanh(\tau \hbar \omega_k)}{\omega_k}} \quad (2.10)$$

for the last bead. Additionally, Eqs. (2.4) and (2.5) allow us to read off the acceptance distributions as $\mathcal{A}(\mathbf{q}_i) \propto e^{-\tau \Delta V(\mathbf{q}_i)}$ for the middle beads and $\mathcal{A}(\mathbf{q}_i) \propto e^{-\tau \Delta V(\mathbf{q}_i)/2}$ for the end beads, respectively. We also note that for the six zero-frequency modes associated with global translations and rotations of our system, the standard deviation expressions in Eqs. (2.8) to (2.10) are undefined *at* $\omega_k = 0$, so rather we take the *limit* as $\omega_k \rightarrow 0$ to get

$$\sigma_k^i = \lim_{\omega_k \rightarrow 0} \sqrt{\frac{\hbar \tanh(\tau \hbar \omega_k)}{2\omega_k}} = \sqrt{\frac{\tau \hbar^2}{2}}, \quad \sigma_k^j = \lim_{\omega_k \rightarrow 0} \sqrt{\frac{\hbar \tanh(\tau \hbar \omega_k)}{\omega_k}} = \sqrt{\tau \hbar^2}, \quad (2.11)$$

for $i = 2, \dots, P-1$ and $j = 1, P$. We now present the steps for performing the single-slice normal-mode sampling algorithm:

1. First, all beads in the imaginary-time path are initialized in some equilibrium configuration (i.e. potential minimum) for the quantum system of interest (recall from Section 1.3 that an equilibrium configuration must be known in order to calculate our system's normal modes) [34].
2. Then, for each MC time step, we randomly sweep through all beads $i = 1, \dots, P$, which picks out a specific bead $\mathbf{q}_i$ to be updated. In each iteration of this i loop, we use the eigenvector matrix obtained from the Hessian diagonalization of Section 1.3 to convert bead i 's current configuration to its normal-coordinate representation:

$$\mathbf{q}_i^{\text{old}} = \{Q_1^i, Q_2^i, \dots, Q_{3N}^i\}.$$

After this, we propose new values for each normal mode $k = 1, \dots, 3N$ by sampling $\tilde{Q}_k^i$ from a Gaussian described by mean μ_k^i and standard deviation σ_k^i . This gives us the proposed configuration for bead i also in its normal-coordinate representation:

$$\mathbf{q}_i^{\text{new}} = \{\tilde{Q}_1^i, \tilde{Q}_2^i, \dots, \tilde{Q}_{3N}^i\}.$$

3. Now, converting both $\mathbf{q}_i^{\text{old}}$ and $\mathbf{q}_i^{\text{new}}$ back to Cartesian coordinates $\{q_j\}$ allows us to evaluate bead i 's acceptance distribution at its current configuration $\mathcal{A}_{\text{old}} = \mathcal{A}(\mathbf{q}_i^{\text{old}})$ and its proposed configuration $\mathcal{A}_{\text{new}} = \mathcal{A}(\mathbf{q}_i^{\text{new}})$.
4. Finally, we accept the proposed configuration with probability $\min(1, \mathcal{A}_{\text{new}}/\mathcal{A}_{\text{old}})$ [23, 24]. This step is almost identical to the last step in Subsection 1.2.3. We first compute the ratio $\mathcal{A}_{\text{new}}/\mathcal{A}_{\text{old}}$ and produce a uniformly distributed random number u from the interval $[0, 1]$. Then if $\mathcal{A}_{\text{new}}/\mathcal{A}_{\text{old}} \geq u$, we accept the proposed moves and update the bead configuration $\mathbf{q}_i = \mathbf{q}_i^{\text{new}}$. Otherwise, we reject the proposed moves and leave the bead configuration as is $\mathbf{q}_i = \mathbf{q}_i^{\text{old}}$ for the next MC time step.

Compared to the naive MH algorithm of Subsection 1.2.3, we expect the normal-mode sampling technique above to result in a shorter autocorrelation time. The intuition behind this follows from Eqs. (2.8) to (2.10), where we see that bead i 's Gaussian proposal distribution does not depend on the current configuration of $\mathbf{q}_i$ itself, so there should be fewer similarities between $\mathbf{q}_i^{\text{old}}$ and $\mathbf{q}_i^{\text{new}}$. However, there still is *some* correlation that arises from μ_k^i 's dependence on the neighbouring beads $Q_k^{i\pm 1}$ and from the rejection step (step 4) as well. Moreover, whereas the naive MH algorithm allowed for control of the acceptance rate by updating the width of the uniform proposal distribution $\Delta\mathbf{r}$, no such fine-tuning is possible now. The analogous widths here would be the normal-mode Gaussians' standard deviations $\{\sigma_k^i\}$ that depend on the imaginary-time step τ , the reduced Planck constant $\hbar$, and the normal-mode frequencies $\{\omega_k\}$, all of which are *fixed* simulation and physical parameters. We also expect the acceptance rate to depend on how much of the potential energy is dominated by its quadratic component $\hat{V}_{\text{HO}}$: predicting a high acceptance rate for more harmonic systems and a low acceptance rate in the presence of large anharmonicity.

2.2 Whole-Path Normal-Mode Sampling

The importance sampling strategy presented in the previous section is called *single-slice* normal-mode sampling as it only updates the configuration of each bead, or imaginary-time slice, one at a time. In this section, we develop an alternative sampling method

that instead uses our system's normal modes to sample new configurations for the *whole* imaginary-time path at once.

Let us start by rewriting our ground-state path integral in terms of our system's normal modes. Substituting Eqs. (2.1) and (2.3) into Eq. (1.10), we can expand our pseudo-partition function as follows:

$$\begin{aligned}
Z_0 &\propto \prod_{i=1}^P \int d\mathbf{q}_i \prod_{j=1}^{P-1} \rho(\mathbf{q}_j, \mathbf{q}_{j+1}; \tau) \approx \prod_{i=1}^P \int d\mathbf{q}_i \prod_{j=1}^{P-1} e^{-\tau[\Delta V(\mathbf{q}_j) + \Delta V(\mathbf{q}_{j+1})]/2} \prod_{k=1}^{3N} \rho_{\text{HO}}(Q_k^j, Q_k^{j+1}; \tau) \\
&\propto \prod_{i=1}^P \int d\mathbf{q}_i \prod_{j=1}^{P-1} e^{-\tau[\Delta V(\mathbf{q}_j) + \Delta V(\mathbf{q}_{j+1})]/2} \prod_{k=1}^{3N} e^{-A_k[(Q_k^i)^2 + (Q_k^{i+1})^2] + B_k Q_k^i Q_k^{i+1}} \propto \int \mathcal{D}\vec{\mathbf{q}} e^{-S_1[\vec{\mathbf{q}}]} e^{-S_0[\vec{\mathbf{q}}]},
\end{aligned} \tag{2.12}$$

where the integration measure $\mathcal{D}\vec{\mathbf{q}} \propto \prod_i d\mathbf{q}_i$ absorbs any proportionality constants arising from the HO density matrix elements and normalizing our constant trial state $\psi_{\text{T}}(\mathbf{q}) \propto 1$. We have also defined two “pseudo-actions”, one corresponding to the anharmonic part of our Hamiltonian:

$$S_1[\vec{\mathbf{q}}] = \frac{\tau}{2} \sum_{i=1}^{P-1} [\Delta V(\mathbf{q}_i) + \Delta V(\mathbf{q}_{i+1})] = \tau \left[\sum_{i=2}^{P-1} \Delta V(\mathbf{q}_i) + \frac{\Delta V(\mathbf{q}_1) + \Delta V(\mathbf{q}_P)}{2} \right] \tag{2.13}$$

and another corresponding to its harmonic part:

$$\begin{aligned}
S_0[\vec{\mathbf{q}}] &= \sum_{i=1}^{P-1} \sum_{k=1}^{3N} (A_k [(Q_k^i)^2 + (Q_k^{i+1})^2] - B_k Q_k^i Q_k^{i+1}) \\
&= \sum_{k=1}^{3N} \sum_{i=1}^P \left[A_k c_i (Q_k^i)^2 - \frac{B_k}{2} (d_{i,1} Q_k^{i-1} Q_k^i + d_{i,P} Q_k^i Q_k^{i+1}) \right] \\
&= \sum_{k=1}^{3N} \sum_{i,j=1}^P Q_k^i \left[A_k c_i \delta_{i,j} - \frac{B_k}{2} (d_{i,1} \delta_{i-1,j} + d_{i,P} \delta_{i+1,j}) \right] Q_k^j \\
&= \frac{1}{2} \sum_{k=1}^{3N} \vec{Q}_k^T \Sigma_k^{-1} \vec{Q}_k,
\end{aligned} \tag{2.14}$$

where

$$c_i = \begin{cases} 1 & \text{if } i = 1, P \\ 2 & \text{otherwise} \end{cases}, \quad d_{i,j} = \begin{cases} 0 & \text{if } i = j \\ 1 & \text{otherwise} \end{cases}, \quad (2.15)$$

and $\vec{Q}_k = [Q_k^{(1)}, Q_k^{(2)}, \dots, Q_k^{(P)}]^T$ is a length- P vector representing the whole-path configuration of normal mode k . Furthermore, Σ_k^{-1} is the $P \times P$ precision matrix (inverse of the covariance matrix) associated with the multivariate Gaussian we will sample proposed $\vec{Q}_k$ configurations from:

$$(\Sigma_k^{-1})_{i,j} = 2A_k c_i \delta_{i,j} - B_k (d_{i,1} \delta_{i-1,j} + d_{i,P} \delta_{i+1,j}), \quad (2.16)$$

so this whole-path sampling scheme is characterized by proposal and acceptance distributions of $\mathcal{P}(\vec{q}) \propto e^{-S_0[\vec{q}]}$ and $\mathcal{A}(\vec{q}) \propto e^{-S_1[\vec{q}]}$, respectively. The following steps specify how to carry out the whole-path normal-mode sampling algorithm:

1. First, all beads in the imaginary-time path are initialized in an equilibrium configuration that minimizes our system's potential energy (identical to the first step in Section 2.1) [34].
2. Then, for each MC time step, we use our Hessian's eigenvector matrix to convert the current configurations of all beads $i = 1, \dots, P$ to their normal-coordinate representation:

$$\vec{q}_{\text{old}} = (\mathbf{q}_1^{\text{old}}, \mathbf{q}_2^{\text{old}}, \dots, \mathbf{q}_P^{\text{old}}); \quad \mathbf{q}_i^{\text{old}} = \{Q_1^i, Q_2^i, \dots, Q_{3N}^i\}.$$

After this, we sample the multivariate Gaussian described by a zero mean vector and covariance matrix Σ_k in order to propose a new whole-path configuration $\vec{Q}_k^{\text{new}} = [\tilde{Q}_k^{(1)}, \tilde{Q}_k^{(2)}, \dots, \tilde{Q}_k^{(P)}]^T$ for each normal mode $k = 1, \dots, 3N$. This yields the proposed configuration for the whole imaginary-time path also in its normal-coordinate representation:

$$\vec{q}_{\text{new}} = (\mathbf{q}_1^{\text{new}}, \mathbf{q}_2^{\text{new}}, \dots, \mathbf{q}_P^{\text{new}}); \quad \mathbf{q}_i^{\text{new}} = \{\tilde{Q}_1^i, \tilde{Q}_2^i, \dots, \tilde{Q}_{3N}^i\}.$$

3. Now, we convert all beads in both $\vec{q}_{\text{old}}$ and $\vec{q}_{\text{new}}$ back to Cartesian coordinates $\{q_i\}$ so that we can evaluate the acceptance distribution of the whole path at its current configuration $\mathcal{A}_{\text{old}} = \mathcal{A}(\vec{q}_{\text{old}})$ and its proposed configuration $\mathcal{A}_{\text{new}} = \mathcal{A}(\vec{q}_{\text{new}})$.

4. Finally, we accept the proposed configuration with probability $\min(1, \mathcal{A}_{\text{new}}/\mathcal{A}_{\text{old}})$ [23, 24]. Once again, we compute the ratio $\mathcal{A}_{\text{new}}/\mathcal{A}_{\text{old}}$ and generate a uniformly distributed random number u from the interval $[0, 1]$. If $\mathcal{A}_{\text{new}}/\mathcal{A}_{\text{old}} \geq u$, we accept the proposed moves and update the path configuration $\vec{q} = \vec{q}_{\text{new}}$. Otherwise, we reject the proposed moves and leave the path configuration as is $\vec{q} = \vec{q}_{\text{old}}$ for the next MC time step.

Compared to the single-slice normal-mode sampling algorithm from the previous section, we expect the whole-path variant to result in an *even* shorter autocorrelation time. This is due to the fact that our proposal distribution now has no “memory” of any prior path configurations as the multivariate Gaussians are all characterized by zero mean vectors and covariance matrices that only depend on fixed parameters, just like the standard deviations from Section 2.1. However, we also expect the acceptance rate to be lower in this case because more variables are being moved before each rejection step takes place. In contrast to the single-slice version where we were only updating one *bead* at a time, here we update the entire *path* all in one go.

2.3 Freezing Out Translational Degrees of Freedom

In Chapter 3, we will apply the normal-mode sampling methodology detailed in the preceding sections to PIGS simulations of various water clusters, namely the H₂O monomer, dimer, and two equilibrium geometries of the hexamer. We are particularly interested in separating distinct DoF (i.e. rotations, vibrations, and translations) from each other so that we can examine their individual contributions to the ground-state properties of these molecular systems. As such, this section first presents a convenient coordinate system for achieving said separability (Subsection 2.3.1). Then, we discuss how these coordinates allow us to fix translational DoF while calculating the normal modes only corresponding to molecular vibrations and rotations (Subsection 2.3.2).

2.3.1 Jacobi Coordinates

In our PIGS simulations, each water molecule is described by three Jacobi vectors: $\vec{R}_{\text{CoM}}$ (position of the molecule's center of mass (CoM) relative to the origin), $\vec{R}_{\text{OH}}$ (position of the oxygen atom relative to the two hydrogen atoms' CoM), and $\vec{R}_{\text{HH}}$ (position of one hydrogen atom relative to the other):

$$\vec{R}_{\text{CoM}} = \frac{m_{\text{H}}(\vec{r}_{\text{H1}} + \vec{r}_{\text{H2}}) + m_{\text{O}}\vec{r}_{\text{O}}}{M_{\text{H}_2\text{O}}}, \quad \vec{R}_{\text{OH}} = \vec{r}_{\text{O}} - \frac{(\vec{r}_{\text{H1}} + \vec{r}_{\text{H2}})}{2}, \quad \vec{R}_{\text{HH}} = \vec{r}_{\text{H2}} - \vec{r}_{\text{H1}}, \quad (2.17)$$

where m_{H} is the atomic mass of hydrogen, m_{O} is the atomic mass of oxygen, $M_{\text{H}_2\text{O}} = 2m_{\text{H}} + m_{\text{O}}$ is the molecular mass of water, $\vec{r}_{\text{H1}}$ and $\vec{r}_{\text{H2}}$ are the positions of the two H atoms, and $\vec{r}_{\text{O}}$ is the position of the O atom [36, 37]. These Jacobi vectors are depicted in Fig. 2.1 for a system of three water molecules.

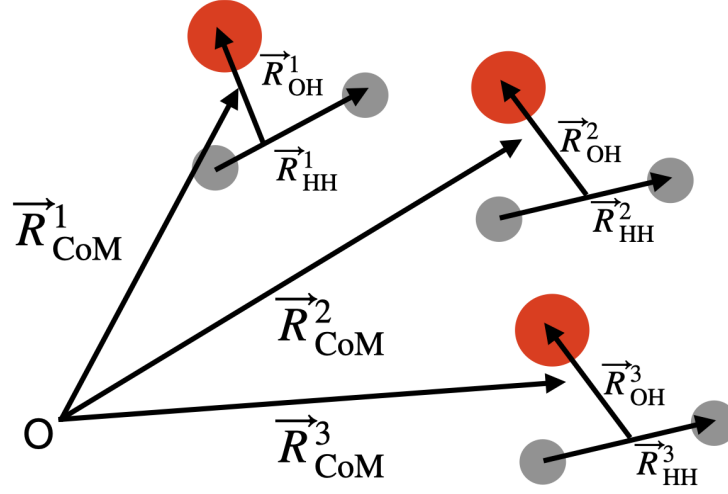


Figure 2.1: A system of three H_2O molecules represented in Jacobi coordinates.

Looking at Fig. 2.1, this definition makes it clear that $\vec{R}_{\text{CoM}}^i$ is purely responsible for molecule i 's translational motion, whereas $\vec{R}_{\text{OH}}^i$ and $\vec{R}_{\text{HH}}^i$ are jointly responsible for molecule i 's ro-vibrational (rotational and vibrational) motion. In order to capture our molecular

system's kinetic energy in this coordinate system, we also need to define the reduced masses assigned to these Jacobi vectors:

$$\mu_{\text{CoM}} = M_{\text{H}_2\text{O}}, \quad \mu_{\text{OH}} = \frac{2m_{\text{H}}m_{\text{O}}}{M_{\text{H}_2\text{O}}}, \quad \mu_{\text{HH}} = \frac{m_{\text{H}}}{2}, \quad (2.18)$$

where the μ subscripts indicate which reduced mass corresponds to which Jacobi vector [36, 37].

2.3.2 Pinned Normal Modes

In Section 1.3, we dealt with the Hamiltonian for a molecular system written in terms of its atomistic coordinates $\{x_i, y_i, z_i\}$, where i indexes different atoms in the system. Here, we instead consider the Hamiltonian for a system of N water molecules expressed as a function of Jacobi coordinates:

$$H = \sum_{i=1}^N \frac{1}{2} \left[\mu_{\text{CoM}} \left(\frac{d\vec{R}_{\text{CoM}}^i}{dt} \right)^2 + \mu_{\text{OH}} \left(\frac{d\vec{R}_{\text{OH}}^i}{dt} \right)^2 + \mu_{\text{HH}} \left(\frac{d\vec{R}_{\text{HH}}^i}{dt} \right)^2 \right] + V(\{\vec{R}_{\text{CoM}}^i, \vec{R}_{\text{OH}}^i, \vec{R}_{\text{HH}}^i\}), \quad (2.19)$$

where i now indexes different water molecules in the system. The normal modes obtained by applying the process described in Section 1.3 to Eq. (2.19) we refer to as the “*full* normal modes” because they involve all $9N$ coordinates in our system, including the **CoM** positions $\{\vec{R}_{\text{CoM}}^i\}$.

Suppose we would like to study a constrained version of our water cluster, where the **CoM** positions of each H_2O molecule are fixed at certain user-specified values, but the intramolecular coordinates $\{\vec{R}_{\text{OH}}^i, \vec{R}_{\text{HH}}^i\}$ are allowed to vary. In this case, the Hamiltonian of such a constrained system becomes

$$H = \sum_{i=1}^N \frac{1}{2} \left[\mu_{\text{OH}} \left(\frac{d\vec{R}_{\text{OH}}^i}{dt} \right)^2 + \mu_{\text{HH}} \left(\frac{d\vec{R}_{\text{HH}}^i}{dt} \right)^2 \right] + V(\{\vec{R}_{\text{OH}}^i, \vec{R}_{\text{HH}}^i\}; \{\vec{R}_{\text{CoM}}^i\}), \quad (2.20)$$

where the translational kinetic energy terms have vanished and the potential energy V , now only a function of the intramolecular coordinates $\{\vec{R}_{\text{OH}}^i, \vec{R}_{\text{HH}}^i\}$, is parameterized by the

fixed CoM positions $\{\vec{R}_{\text{CoM}}^i\}$. Applying the procedure detailed in Section 1.3 to Eq. (2.20) then yields what we call our system’s “*pinned* normal modes” as they only pertain to the $6N$ intramolecular coordinates $\{\vec{R}_{\text{OH}}^i, \vec{R}_{\text{HH}}^i\}$ and they leave the remaining $3N$ coordinates $\{\vec{R}_{\text{CoM}}^i\}$ pinned. Therefore, if we want to freeze out translational DoF and study pure ro-vibrational dynamics, we can do so by performing PIGS simulations that sample according to either of the approaches described in the previous two sections, but using our system’s pinned normal modes rather than its full normal modes.

2.4 Rejection-Free Normal-Mode Sampling with Configuration Reweighting

Sections 2.1 and 2.2 introduced two different MH-based (i.e. includes a rejection step) schemes for normal-mode sampling. Here, we present an alternative sampling technique that accepts 100% of the proposed moves and opts for reweighting these sampled configurations in lieu of a rejection step. The single-slice variant of this rejection-free sampling is almost identical to the steps of Section 2.1, except that we neglect step 4 (the rejection step) and modify step 3 to only evaluate $\mathcal{A}_{\text{new}} = \mathcal{A}(\mathbf{q}_i^{\text{new}})$, which we save as our configuration weight ($\mathcal{A}_{\text{old}} = \mathcal{A}(\mathbf{q}_i^{\text{old}})$ is not necessary anymore as there is no longer a rejection step). Similarly, the whole-path version of this rejection-free sampling follows the steps of Section 2.2, but we once again neglect step 4 and modify step 3 to only evaluate the configuration weight $\mathcal{A}_{\text{new}} = \mathcal{A}(\vec{\mathbf{q}}_{\text{new}})$.

Recalling Eqs. (2.12) to (2.14), we can now express the expectation value of any observable $\hat{O}$ as

$$\langle O \rangle = \frac{\int \mathcal{D}\vec{\mathbf{q}} o(\vec{\mathbf{q}}) e^{-S_1[\vec{\mathbf{q}}]} e^{-S_0[\vec{\mathbf{q}}]}}{\int \mathcal{D}\vec{\mathbf{q}} e^{-S_1[\vec{\mathbf{q}}]} e^{-S_0[\vec{\mathbf{q}}]}} = \frac{\langle O e^{-S_1} \rangle_0}{\langle e^{-S_1} \rangle_0} \approx \frac{\sum_{t=1}^M o(\vec{\mathbf{q}}_t) e^{-S_1[\vec{\mathbf{q}}_t]}}{\sum_{t=1}^M e^{-S_1[\vec{\mathbf{q}}_t]}}, \quad (2.21)$$

where the subscript 0 indicates that we are computing an expectation value with respect to the Gaussian proposal distribution $\mathcal{P}(\vec{\mathbf{q}}) \propto e^{-S_0[\vec{\mathbf{q}}]}$. In order to effectively calculate expectation values with respect to the true distribution of interest $\pi(\vec{\mathbf{q}}) = \mathcal{P}(\vec{\mathbf{q}})\mathcal{A}(\vec{\mathbf{q}})$,

Eq. (2.21) also reweights each observable estimator sample $o(\vec{q}_t)$ according to the weight of the t^{th} sampled path configuration $\mathcal{A}(\vec{q}_t) \propto e^{-S_1[\vec{q}_t]}$.

The motivation behind this rejection-free approach is two-fold: (1) increase computational efficiency and (2) decrease autocorrelation time. We expect the first benefit on account of essentially cutting the number of potential energy function calls in half by only requiring $\mathcal{A}_{\text{new}}$ to be evaluated and not $\mathcal{A}_{\text{old}}$. The second benefit is expected because we now always accept the configurations that are sampled from the proposal distribution $\mathcal{P}$, which lessens the probability of successive sampled configurations being identical. However, the results presented in the next chapter will show whether this actually turns out to be the case.

Chapter 3

Application to Flexible Water Clusters

In this chapter, we apply the normal-mode sampling methodology developed in Chapter 2 to PIGS simulations of several flexible water clusters, namely the H₂O monomer ($N = 1$), dimer ($N = 2$), and two low-energy hexamer ($N = 6$) isomers: the cage and prism [38]. To this end, Section 3.1 introduces the potential energy model used in our simulations and Section 3.2 discusses some computational details about the simulation codes, while Sections 3.3, 3.4, and 3.5 present our results for the monomer, dimer, and hexamer, respectively.

We note that although the theory behind the whole-path normal-mode sampling algorithm was developed in the preceding chapter, its implementation and testing are outside the scope of this thesis. Thus, for the sake of brevity, the remainder of this chapter will refer to the single-slice normal-mode sampling algorithm as just the normal-mode sampling algorithm.

3.1 q-TIP4P/F Potential Energy Model

Since we are interested in the quantum-mechanical treatment of *flexible* water clusters, the potential energy function in our simulations is given by q-TIP4P/F, an empirical water model specifically designed for path-integral (i.e. quantum) simulations, such as [PIMC](#) and [Path Integral Molecular Dynamics \(PIMD\)](#), which allows for molecular flexibility instead of treating each water molecule as *rigid* [\[35\]](#).

For a system of N water molecules, the intermolecular interactions in this model are described by a pairwise-additive potential:

$$V_{\text{inter}} = \sum_{i=1}^N \sum_{j=i+1}^N \left\{ 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \sum_{m \in i} \sum_{n \in j} \frac{q_m q_n}{r_{mn}} \right\}, \quad (3.1)$$

where r_{ij} is the distance between O atoms in molecules i and j and r_{mn} is the distance between partial charge sites m and n [\[35\]](#). Each molecule contains three partial charges, two positive charges of $+q_M/2$ on the two H atoms and a negative charge of $-q_M$ at the point M lying a fraction γ along the vector pointing from the H atoms' [CoM](#) to the O atom:

$$\vec{r}_M = \frac{(\vec{r}_{\text{H1}} + \vec{r}_{\text{H2}})}{2} + \gamma \vec{R}_{\text{OH}}, \quad (3.2)$$

where we recall that $\vec{r}_{\text{H1}}$ and $\vec{r}_{\text{H2}}$ are the positions of the two H atoms and $\vec{R}_{\text{OH}}$ is one of the Jacobi vectors defined in Subsection [2.3.1](#) [\[35\]](#). The intramolecular flexibility in this model comes from a harmonic treatment of the bond angles and a quartic anharmonicity in the O-H bonds:

$$V_{\text{intra}} = \sum_{i=1}^N \left[V_{\text{OH}}(r_{i1}) + V_{\text{OH}}(r_{i2}) + \frac{k_\theta}{2} (\theta_i - \theta_{\text{eq}})^2 \right], \quad (3.3)$$

where

$$V_{\text{OH}}(r) = D_r \left[\alpha_r^2 (r - r_{\text{eq}})^2 - \alpha_r^3 (r - r_{\text{eq}})^3 + \frac{7}{12} \alpha_r^4 (r - r_{\text{eq}})^4 \right] \quad (3.4)$$

and r_{i1} , r_{i2} , and θ_i are the O-H bond lengths and H-O-H bond angle, respectively, in molecule i [\[35\]](#). The parameter values used in q-TIP4P/F are summarized in Table [3.1](#).

Table 3.1: Parameters in the q-TIP4P/F quantum water model [35].

Parameter	Value
ε [kcal/mol]	0.1852
σ [Å]	3.1589
q_M [$ e $]	1.1128
γ	0.73612
D_r [kcal/mol]	116.09
α_r [Å ⁻¹]	2.287
r_{eq} [Å]	0.9419
k_θ [kcal/mol/rad ²]	87.85
θ_{eq} [deg]	107.4

It is important to acknowledge that more rigorous quantum potentials do exist, such as MB-pol, an *ab initio* water model that includes *many-body* interactions beyond pairwise (two-body) contributions and accounts for *polarization* effects [39]. However, MB-pol is also several orders of magnitude more computationally expensive and q-TIP4P/F captures enough of the correct physics to be used at the stage of method development, which is the scope of this thesis. For example, when studying the quantum criticality of water chains in Refs. [5, 6, 20], Serwatka *et al.* initially used q-TIP4P/F to establish their methodology and then used MB-pol to yield more accurate results.

3.2 Computational Details

Before presenting our simulation results in the following sections, we would like to discuss some details about how our PIGS QMC simulations were implemented in code. Firstly, all of the code for our simulations was written in-house using the scientific-computing programming language Julia, making use of various libraries for linear algebra, file I/O, statistics, and plotting [30]. We also recall from Section 1.3 that to calculate the normal

modes of our system, we need to have an equilibrium configuration (i.e. potential minimum) to Taylor-expand about. For the water monomer, the equilibrium geometry was straightforward to construct according to the q-TIP4P/F model parameters r_{eq} and θ_{eq} from the previous section. For the water dimer, we obtained a guess for the equilibrium geometry as a `.pdb` file from an initial energy minimization in Python’s molecular dynamics package `OpenMM` [28, 40]. This initial guess was then optimized further by integrating Julia’s forward-mode automatic differentiation package `ForwardDiff` with its optimization package `Optim` to minimize the potential energy function from q-TIP4P/F [30, 41, 42]. The final geometry resulting from this minimization was used as the equilibrium geometry in our dimer simulations. For the water hexamer, several low-energy geometries are known, but here we focus on the cage and prism isomers [38]. In a similar manner, initial guesses for the cage and prism were obtained as `.xyz` files from the supplementary information of Ref. [43], which are once again optimized further using `Optim` and `ForwardDiff` in Julia [30, 41, 42]. Lastly, we note that `ForwardDiff` in Julia was also used to exactly compute (up to floating-point numerical precision) the second derivatives in Eq. (1.26) for constructing the mass-weighted Hessian matrix.

3.3 Monomer Results

In this section, we present the results from our `PIGS` simulations of the water monomer. Subsection 3.3.1 compares two of our normal-mode sampling algorithms (`MH`-based and rejection-free) to the naive `MH` algorithm, characterizing each importance sampling scheme according to their autocorrelation time and simulation runtime. In Subsection 3.3.2, we use `PIGS` and the harmonic approximation to calculate the monomer’s ground-state energy and compare to prior `PIMD` and `Diffusion Monte Carlo (DMC)` studies. The focus of Subsection 3.3.3 is on computing structural properties of the monomer, primarily in the form of probability density functions. Some of these distributions are also benchmarked against `ED` results.

We also note that for a single water molecule, its `CoM` Jacobi vector $\vec{R}_{\text{CoM}}$ plays no role in the physics, so whether we use the monomer’s pinned normal modes or full normal

modes does not matter. In either case, we end up with only three non-zero normal-mode frequencies, corresponding to the monomer’s bending, symmetric stretching, and asymmetric stretching modes [25, 44]. By default, our importance sampling methods do not sample the other zero-frequency modes anyway.

3.3.1 Comparison of Sampling Algorithms

As mentioned in Section 2.1, one advantage we predicted our normal-mode sampling algorithm to have was that it would decorrelate sampled configurations in the Markov chain faster than the naive MH algorithm. To investigate this, we run three PIGS simulations, each differing only in their importance sampling technique: (1) the naive MH algorithm, (2) the MH-based normal-mode sampling algorithm, and (3) the rejection-free normal-mode sampling algorithm. All other parameters are common between the three simulations: $N = 1$ water molecules, $P = 251$ beads, $\beta = 0.005 \text{ K}^{-1}$, $M = 1000000$ observable measurements, $N_{\text{skip}} = 1$ MC steps between each estimator evaluation, and $N_{\text{therm}} = 10000$ MC steps in the thermal equilibration period. For the purposes of this autocorrelation analysis, the only observable we measure is the ground-state energy, using the estimator given by Eq. (1.19). We then use Eq. (1.22) to calculate the autocorrelation function from the resulting series of energy measurements $\{E_1, E_2, \dots, E_M\}$. The autocorrelation functions from the three simulations are plotted in Fig. 3.1 and their respective autocorrelation times are displayed in Table 3.2, along with the simulation runtimes.

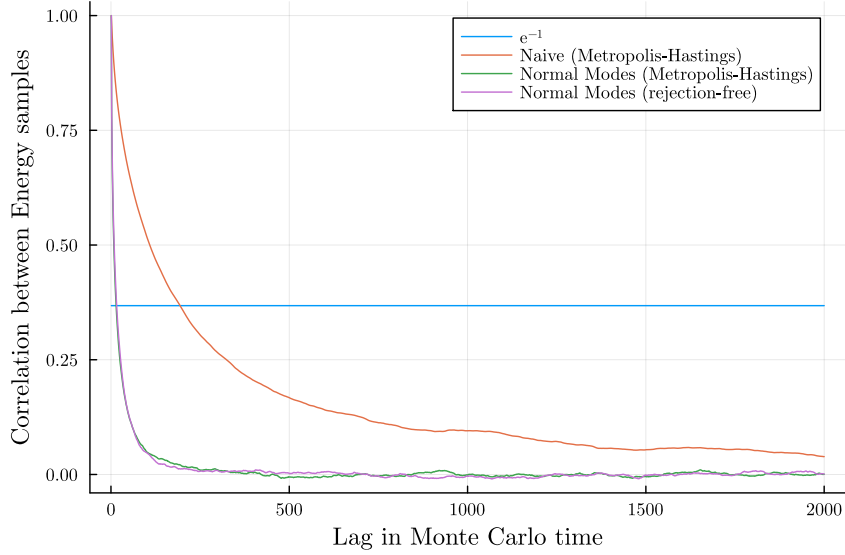


Figure 3.1: Autocorrelation in the H_2O monomer’s ground-state energy as a function of lag in MC time.

From Fig. 3.1 and Table 3.2, we indeed find that both normal-mode sampling algorithms result in autocorrelation times that are an order of magnitude shorter than that of the naive MH algorithm. However, between the two normal-mode sampling algorithms, we find that the rejection-free algorithm’s autocorrelation time is slightly longer than its MH-based counterpart, which is inconsistent with our expectation from Section 2.4 that it would decorrelate samples faster.

Table 3.2: Comparison of autocorrelation times and simulation runtimes from different sampling algorithms used in PIGS simulations of the H_2O monomer.

Sampling algorithm	t_{corr} [MC steps]	Runtime [hh:mm:ss]
Naive MH	194	00:27:59
Normal Modes (MH)	15	00:17:13
Normal Modes (rejection-free)	16	00:13:07

In terms of simulation runtime though, the results in Table 3.2 are promising, with

the MH-based normal-mode sampling algorithm outperforming the naive MH algorithm by a factor of ~ 1.63 . The rejection-free normal-mode sampling algorithm also surpasses its MH-based counterpart, but the speed-up is not as impressive as we expected.

3.3.2 Energetic Properties

Having found the MH-based normal-mode sampling algorithm to be superior with respect to autocorrelation, we move forward with this importance sampling approach in our PIGS simulations of the water monomer. First, we study energetic properties, namely the ground-state energy. In order to obtain an *exact* value that is free from any Trotter error, we want to run several PIGS simulations, each with a different number of beads (and hence a different imaginary-time step) and use the ground-state energies reported from these simulations to perform an extrapolation to $\tau = 0$. Such a process is called a “ τ convergence”.

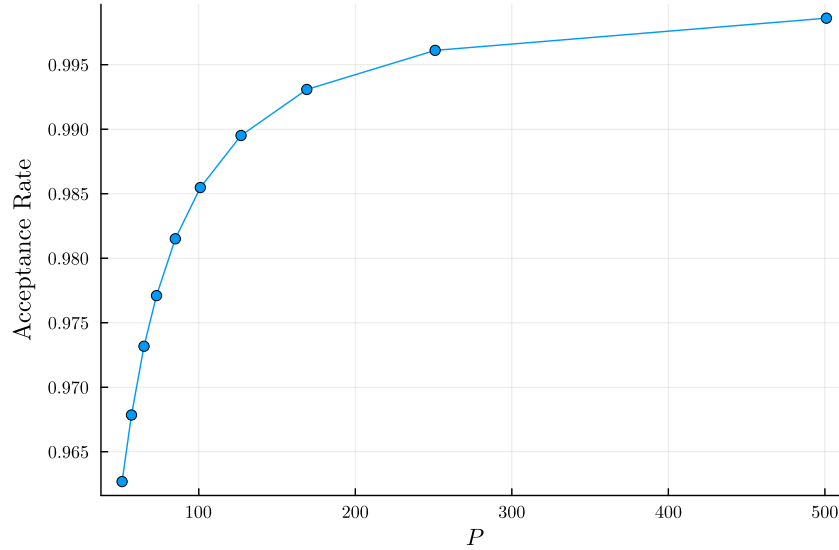


Figure 3.2: Acceptance rate as a function of the number of beads in a PIGS simulation of the H_2O monomer.

We begin with an initial sweep over $P = 51, 57, 65, 73, 85, 101, 127, 169, 251, 501$, where

all other parameters are fixed as in the previous subsection: $N = 1$, $\beta = 0.005 \text{ K}^{-1}$, $M = 1000000$, $N_{\text{skip}} = 1$, and $N_{\text{therm}} = 10000$. After each of these simulations, we record the acceptance rate and calculate the autocorrelation time, both of which are plotted in Figs. 3.2 and 3.3.

From Fig. 3.2, we see a trend of increasing acceptance rate with increasing P , which is expected if we recall from Section 2.1 that the widths of the Gaussian proposal distributions have a dependence on the imaginary-time step τ . We also observe that all acceptance rates shown in Fig. 3.2 are greater than 96 %, which tells us that our normal-mode proposal distribution captures *most* of the target distribution in the case of the monomer. This is explained by referring back to the q-TIP4P/F potential energy model, which for $N = 1$ is almost purely harmonic besides the cubic and quartic terms in the O-H bonds [35]. These high acceptance rates reassure us that our simulation results from all values of P are reliable.

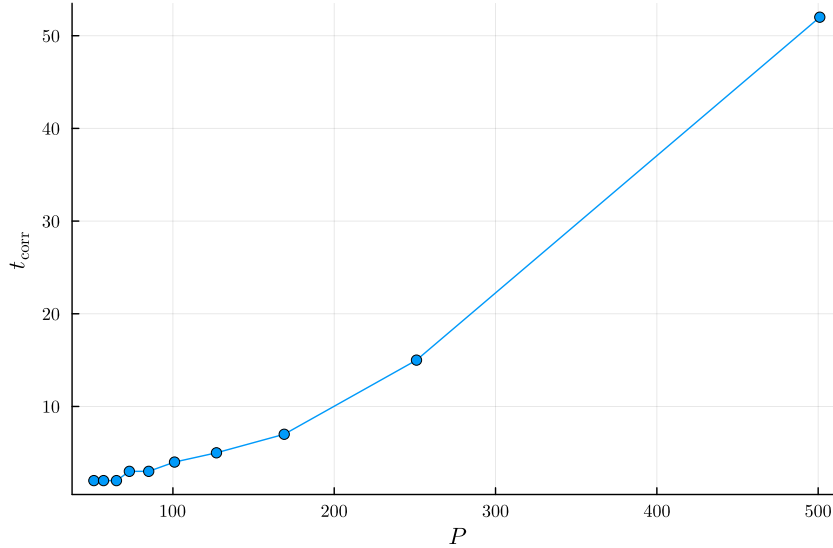


Figure 3.3: Autocorrelation time as a function of the number of beads in a PIGS simulation of the H_2O monomer.

Fig. 3.3 tells us that the largest autocorrelation time we find across all values of P is

$t_{\text{corr}} = 52$ MC steps. As such, we set $N_{\text{skip}} = 100$ for all simulations involved in our τ convergence, which is almost double this maximum autocorrelation time and ensures that our observable measurements are approximately independent samples.

We carry out another sweep over the same values of P , this time with the common parameters being $N = 1$, $\beta = 0.005 \text{ K}^{-1}$, $M = 100000$, $N_{\text{skip}} = 100$, and $N_{\text{therm}} = 100000$. After each of these simulations, we compute the average ground-state energy and its associated standard error from the resulting series of energy measurements. Since these sampled estimator evaluations are only *approximately* independent, we cannot calculate standard error in the usual way and must account for correlations in our data to avoid underestimating the error. To do so, we use the binning method of error analysis, where adjacent measurements are binned into blocks of size b , using these block averages as our new data points determining the standard error, and making b larger until the standard error plateaus as a function of bin size [23, 32, 45].

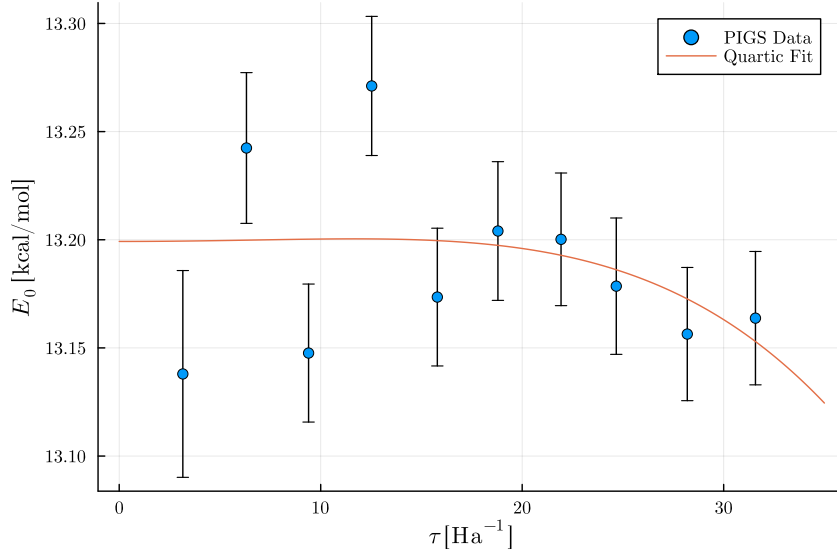


Figure 3.4: τ convergence for the H_2O monomer’s ground-state energy with a quartic-fit extrapolation to $\tau = 0$.

In order to determine the functional form of our curve fit and extrapolate to $\tau = 0$,

we recall that our symmetric Trotterization of the imaginary-time propagator leads to an $\mathcal{O}(\tau^3)$ error in both Z and Z_0 . This translates to an $\mathcal{O}(\tau^2)$ error in the average energy because it is often derived by differentiating the partition function with respect to β [23, 33]. Therefore, we expect $E(\tau)$ to be a quadratic function for small enough τ . However, we also add a quartic term, corresponding to the next order in Trotter error, to account for the possibility that some of our τ values might not fall into this “quadratic region” [26]:

$$E(\tau) = E_0 + c_2\tau^2 + c_4\tau^4. \quad (3.5)$$

The ground-state energies and their associated standard errors from our P -sweep of PIGS simulations are plotted as a function of τ in Fig. 3.4 with a fit to Eq. (3.5) superimposed. In Table 3.3, we present our τ -converged ground-state energy as the fitted E_0 parameter from Eq. (3.5). We compare our ground-state energy from PIGS to prior PIMD and DMC simulation results, as well as the harmonic approximation given by Eq. (1.29) [26, 46].

Table 3.3: Ground-state energy obtained from the curve fit in Fig. 3.4, benchmarked against the harmonic approximation, PIMD, and DMC results [26, 46].

Simulation method	E_0
PIGS	(13.20 ± 0.02) kcal/mol
PIMD	(13.20 ± 0.02) kcal/mol
DMC	13.16 kcal/mol
Harmonic	13.37 kcal/mol

3.3.3 Structural Properties

In addition to the ground-state energy, we would like to compute structural properties as well, specifically the probability density functions for the bond angle and various interatomic distances. Of particular interest are the distribution functions for the so-called Pakeris coordinates [47]. This coordinates system is well-suited for characterizing structural properties in three-body systems such as the water molecule [48, 49]. The Pakeris

coordinates are defined as the radii of mutually tangent circles that are centered at the three atomic positions, as depicted in Fig. 3.5. The three coordinates can be expressed in terms of interatomic distances as

$$r_1 = \frac{1}{2}(R_{12} + R_{31} - R_{23}), \quad r_2 = \frac{1}{2}(R_{12} + R_{23} - R_{31}), \quad r_3 = \frac{1}{2}(R_{23} + R_{31} - R_{12}), \quad (3.6)$$

where R_{ij} is the distance between atoms i and j [47, 50]. For the water monomer, the two H atoms are treated on equal footing, so we define $r_2 = r_3 = r_H$ and $r_1 = r_O$.

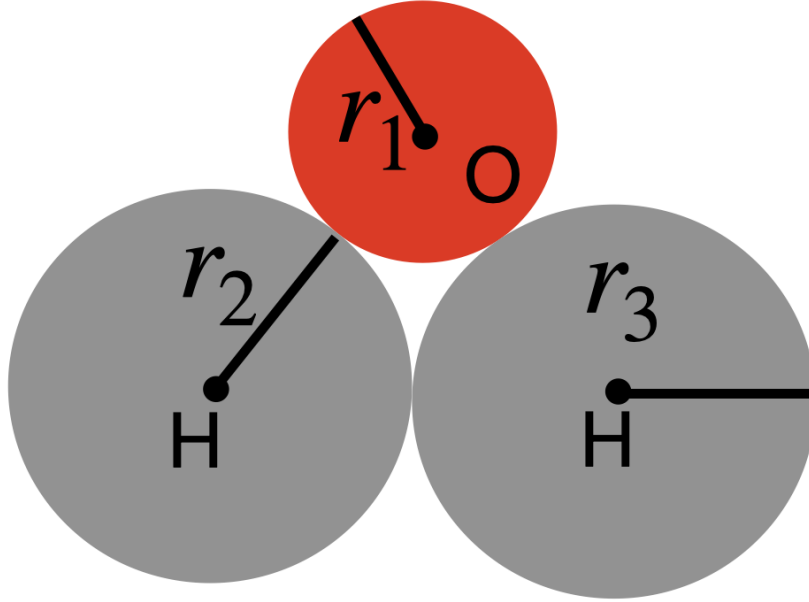


Figure 3.5: Illustration of the Pekeris coordinate system defined in Eq. (3.6) for the H_2O molecule.

Since the monomer is only a three-body system, ED results are tractable [48, 49]. The Pekeris coordinates provide a convenient coordinate system for constructing the Hamiltonian matrix and diagonalizing it. For a triatomic molecule described by Pekeris coordinates $\{r_i\}$ and respective masses $\{m_i\}$, the vibrational Hamiltonian (i.e. the molecular system is assumed to be in its rotational ground state with $J = 0$) in atomic units (where $\hbar = 1$)

takes the following form [50]:

$$H = -\frac{1}{2} \sum_{j,k=1}^3 \frac{\partial}{\partial r_j} G_{jk} \frac{\partial}{\partial r_k} + V_a + V, \quad (3.7)$$

where

$$G_{ii} = r_i \left[\frac{r_i + r_j + r_k}{m_i R_{ij} R_{ik}} + \frac{r_j}{m_k R_{ki} R_{kj}} + \frac{r_k}{m_j R_{jk} R_{ji}} \right] \quad (3.8)$$

and

$$G_{ij} = G_{ji} = -\frac{r_i r_j}{m_k R_{ki} R_{kj}}. \quad (3.9)$$

Note that the indices $i, j, k = 1, 2, 3$ obey cyclic permutations in Eqs. (3.8), (3.9) and

$$V_a = \frac{1}{8(R_{12}R_{23}R_{31})^2} \left[\frac{R_{23}^4}{m_1} + \frac{R_{31}^4}{m_2} + \frac{R_{12}^4}{m_3} \right] \quad (3.10)$$

is analogous to the Watson term in Watson’s nuclear motion Hamiltonian [50, 51]. The final term V is simply given by the q-TIP4P/F potential detailed in Section 3.1.

Following Ref. [50], the matrix elements of Eq. (3.7) are evaluated in a [Discrete Variable Representation \(DVR\)](#) based on Jacobi polynomial basis functions [52, 53]. Using the same [DVR](#) and basis function parameters as in Ref. [26], the Hamiltonian matrix is diagonalized with a sparse symmetry-adapted Lanczos eigensolver [48, 49, 54]. The smallest eigenvalue from this Hamiltonian diagonalization yields a ground-state energy of $E_0 = 13.1778$ kcal/mol, which is in good agreement with the values presented in Table 3.3. Moreover, the eigenvector associated with this eigenvalue is the ground-state wavefunction, which can be squared and then marginalized to give us probability density functions for the Pekeris coordinates r_O and r_H .

These probability density functions can be obtained from [PIGS](#) as well, using the middle bead of the imaginary-time path according to the structural estimator in Eq. (1.20). From the P -sweep of the preceding subsection, we use the [PIGS](#) simulation corresponding to $P = 73$ because its reported ground-state energy was closest to the $\tau = 0$ extrapolated value and also had the smallest standard error. The probability density functions for the Pekeris coordinates r_O and r_H are plotted in Figs. 3.6 and 3.7, respectively.

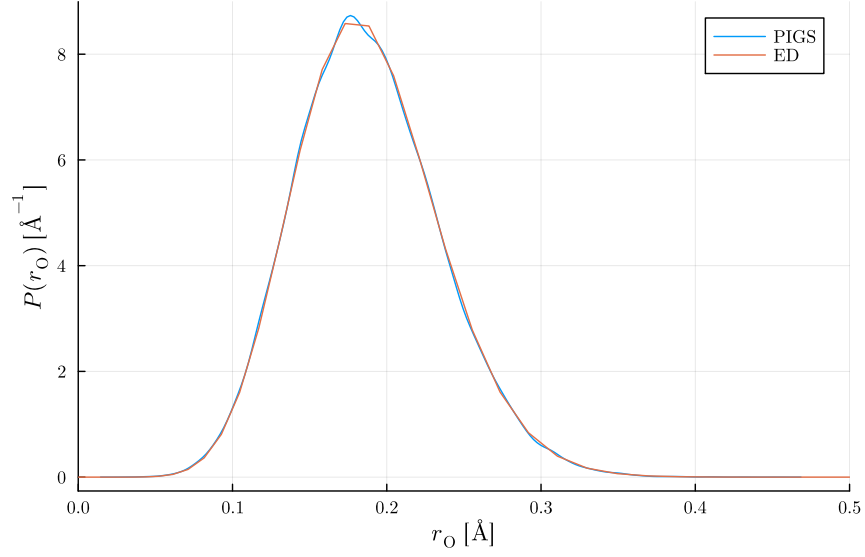


Figure 3.6: Probability density function for the r_O Pekeris coordinate from a PIGS simulation of the H_2O monomer, benchmarked against ED results.

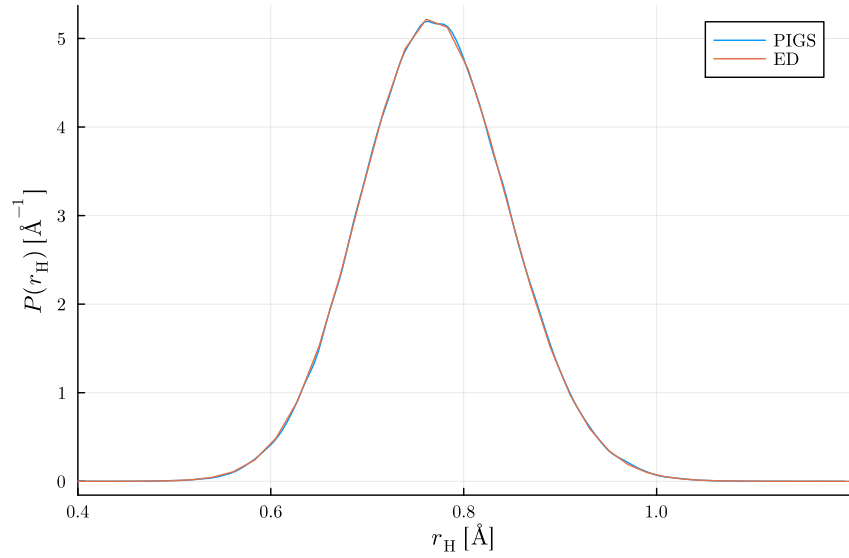


Figure 3.7: Probability density function for the r_H Pekeris coordinate from a PIGS simulation of the H_2O monomer, benchmarked against ED results.

From Figs. 3.6 and 3.7, we observe that the distributions from our PIGS simulations are in excellent agreement with those from ED. Other structural properties of interest are the probability density functions for the O-H bond lengths, H-H distance, and H-O-H bond angle, which are plotted in Figs. 3.8, 3.9, and 3.10, respectively.

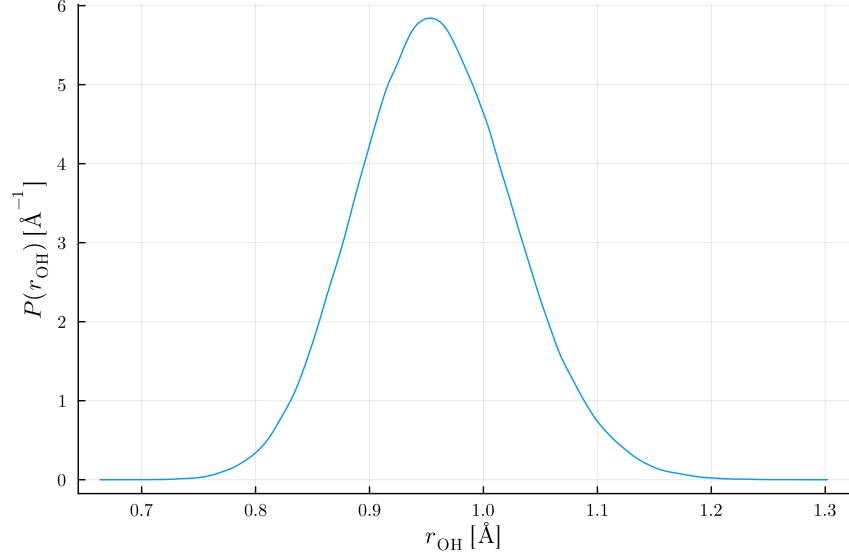


Figure 3.8: Probability density function for the O-H bond lengths from a PIGS simulation of the H₂O monomer.

It is worth mentioning that the distributions shown in Figs. 3.8, 3.9, and 3.10 are in qualitative agreement with those seen in Ref. [26]. More quantitatively, Table 3.4 tells us that the average O-H bond length, H-H distance, and H-O-H bond angle are also in excellent agreement with those calculated in Ref. [26].

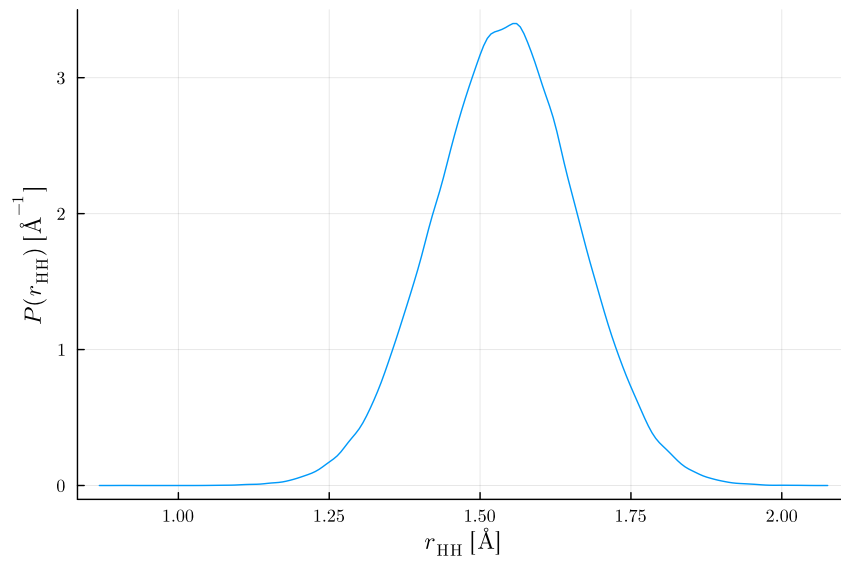


Figure 3.9: Probability density function for the H-H distance from a PIGS simulation of the H_2O monomer.

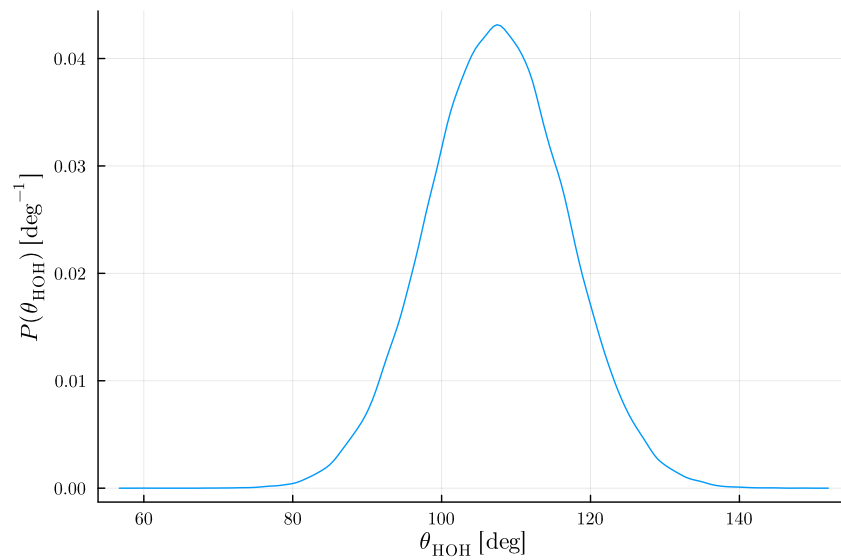


Figure 3.10: Probability density function for the H-O-H bond angle from a PIGS simulation of the H_2O monomer.

Table 3.4: Average ground-state structural properties from a PIGS simulation of the H₂O monomer, benchmarked against PIMD results [26].

	PIGS	PIMD
$\langle r_{\text{HH}} \rangle$	$(1.5409 \pm 0.0004) \text{ \AA}$	$(1.5408 \pm 0.0004) \text{ \AA}$
$\langle r_{\text{OH}} \rangle$	$(0.9583 \pm 0.0002) \text{ \AA}$	$(0.9582 \pm 0.0002) \text{ \AA}$
$\langle \theta_{\text{HOH}} \rangle$	$(107.42 \pm 0.04) \text{ deg}$	$(107.42 \pm 0.03) \text{ deg}$

3.4 Dimer Results

In this section, we present the results from our PIGS simulations of the water dimer, whose equilibrium geometry is illustrated in Fig. 3.11. Subsection 3.4.1 compares two of our normal-mode sampling algorithms (MH-based and rejection-free) to the naive MH algorithm, characterizing each importance sampling approach according to their autocorrelation time and simulation runtime. In Subsection 3.4.2, we first use PIGS and the harmonic approximation to calculate the ground-state energy of the full dimer and compare to prior PIMD and DMC studies. Then, we do the same for the ground-state energy of the pinned dimer, but go one step further and use the dimer’s pinned normal modes to provide a “semi-harmonic” treatment of the full dimer’s quantum dynamics. The focus of Subsection 3.4.3 is on computing structural properties of the dimer, primarily in the form of probability density functions.

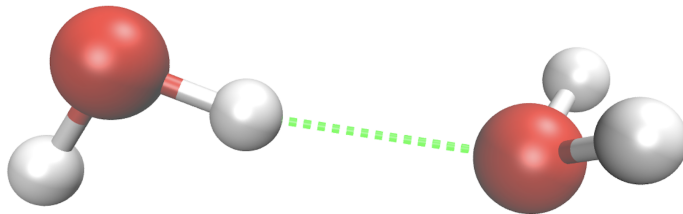


Figure 3.11: Equilibrium geometry of the H₂O dimer.

3.4.1 Comparison of Sampling Algorithms

Analogously to Subsection 3.3.1, we start off by running three PIGS simulations of the full (i.e. not pinned) water dimer, each differing only in their importance sampling technique: (1) the naive MH algorithm, (2) the MH-based normal-mode sampling algorithm, and (3) the rejection-free normal-mode sampling algorithm. All other parameters are still common between the three simulations: $N = 2$, $P = 501$, $\beta = 0.01 \text{ K}^{-1}$, $M = 1000000$, $N_{\text{skip}} = 1$, and $N_{\text{therm}} = 10000$. Again, we collect a series of energy measurements using Eq. (1.19) and calculate the autocorrelation function using Eq. (1.22). The autocorrelation functions from the three simulations are plotted in Fig. 3.12 and their respective autocorrelation times are displayed in Table 3.5, along with the simulation runtimes.

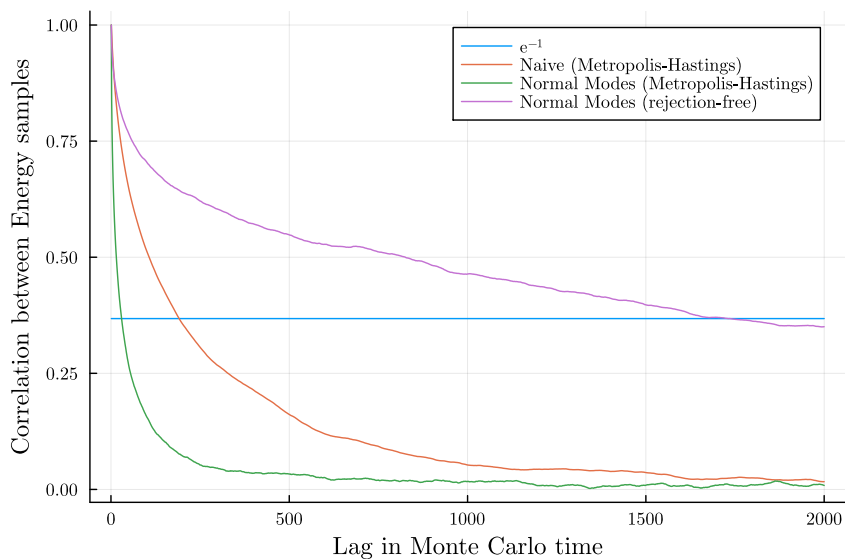


Figure 3.12: Autocorrelation in the H_2O dimer’s ground-state energy as a function of lag in MC time.

From Fig. 3.12 and Table 3.5, we find that the MH-based normal-mode sampling algorithm decorrelates sampled energy measurements almost an order of magnitude faster than the naive MH algorithm, just as it did for the monomer. However, what is shocking

here is that the rejection-free algorithm is *significantly* slower at decorrelating samples compared to the other two importance sampling methods. This hints that maybe the harmonic approximation is not as good at capturing all the physics in the dimer as it was for the monomer.

Table 3.5: Comparison of autocorrelation times and simulation runtimes from different sampling algorithms used in PIGS simulations of the H₂O dimer.

Sampling algorithm	t_{corr} [MC steps]	Runtime [hh:mm:ss]
Naive MH	191	05:17:42
Normal Modes (MH)	30	01:16:59
Normal Modes (rejection-free)	1731	01:03:47

In terms of simulation runtime, we still find that the MH-based normal-mode sampling algorithm outperforms the naive MH algorithm, this time by a factor of ~ 4.13 , which is even more impressive than the speed-up in Table 3.2. This increased speed-up factor is due to the fact that the performance improvement between the naive MH algorithm and the normal-mode sampling algorithms is mostly in the number of calls to the potential energy function, which itself scales as N^2 according to Eq. (3.1). Once again, the rejection-free normal-mode sampling algorithm surpasses its MH-based counterpart with a less pronounced speed-up.

3.4.2 Energetic Properties

As before, we move forward with the MH-based normal-mode sampling algorithm in our PIGS simulations of the water dimer, and attempt to carry out another τ convergence, similarly to Subsection 3.3.2. Since we are using a larger β here compared to the monomer, but still want to sweep over the same τ values, we do so by sweeping through larger P values than before: $P = 101, 113, 127, 145, 169, 201, 251, 335, 501, 1001$. Keeping all other parameters fixed as in the previous subsection: $N = 2$, $\beta = 0.01 \text{ K}^{-1}$, $M = 1000000$, $N_{\text{skip}} = 1$, and $N_{\text{therm}} = 10000$, we record the acceptance rate from each of these simulations, which is plotted in Fig. 3.13.

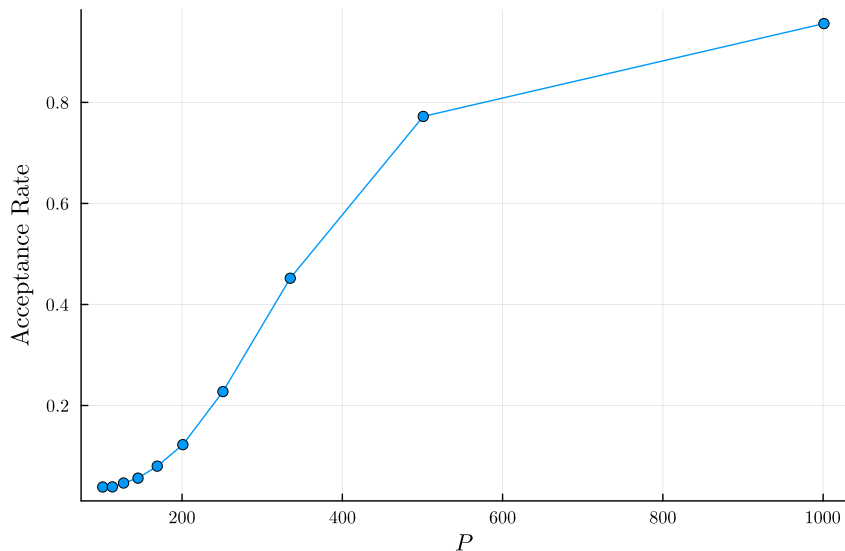


Figure 3.13: Acceptance rate as a function of the number of beads in a PIGS simulation of the H_2O dimer.

From Fig. 3.13, we again see a trend of increasing acceptance rate with increasing P . However, we also observe that not all of the acceptance rates are as high as they were for the monomer. In fact, for some values of P , the acceptance rate is lower than 4%. This is concerning, but it also confirms our earlier suspicion that the normal-mode approximation is not that good for the water dimer, so perhaps the target distribution is actually dominated by the anharmonic acceptance distribution rather than the harmonic proposal distribution. This could be understood by referring back to the q-TIP4P/F potential energy model, where for $N = 2$, more anharmonic terms are introduced by including the Lennard-Jones and Coulomb-like interactions in the intermolecular energy [35]. Unfortunately, a τ convergence is not practical in the case of the dimer as we cannot trust the ground-state energies reported from those PIGS simulations with such low acceptance rates.

Thus, we must pick just one value of τ to run a PIGS simulation at and report our best estimate of the dimer's ground-state energy. Looking at Fig. 3.13, we choose $P = 401$ to

move forward with, in the hopes of yielding an acceptance rate between 30 % and 50 %, as is the rule-of-thumb for traditional MH sampling [23]. We proceed with an autocorrelation analysis for a PIGS simulation with $P = 401$ and find the autocorrelation time to be $t_{\text{corr}} = 30$ MC steps. Then, we run a PIGS simulation with $N = 2$, $P = 401$, $\beta = 0.01 \text{ K}^{-1}$, $M = 100000$, $N_{\text{skip}} = 60$, and $N_{\text{therm}} = 100000$. Again, since N_{skip} is double the autocorrelation time, the resulting series of energy measurements should be approximately independent. The ground-state energy computed from this PIGS simulation, as well as the standard error calculated using the binning method, are displayed in Table 3.6. We still compare our ground-state energy from PIGS to prior PIMD and DMC simulation results, as well as the harmonic approximation given by Eq. (1.29) [26, 46].

Table 3.6: Ground-state energy of the full H₂O dimer obtained from a PIGS simulation with $P = 401$ beads, benchmarked against the harmonic approximation, PIMD, and DMC results [26, 46].

Simulation method	E_0
PIGS	$(21.88 \pm 0.07) \text{ kcal/mol}$
PIMD	$(21.87 \pm 0.02) \text{ kcal/mol}$
DMC	21.80 kcal/mol
Harmonic	22.38 kcal/mol

Now that we are studying the water dimer, where the CoM positions of each molecule do affect the physics, we can take advantage of the normal-mode sampling scheme using our system’s pinned normal modes to investigate the dependence of the pinned dimer’s ground-state energy on its intermolecular distance r_{12} . To this end, we sweep over various intermolecular distances ranging from 2 Å to 10 Å. At each r_{12} value, we run a PIGS simulation of the pinned dimer with fixed CoM positions $\vec{R}_{\text{CoM}}^{(1)} = (0, 0, 0)$, $\vec{R}_{\text{CoM}}^{(2)} = (0, 0, r_{12})$ and the same parameters that produced the ground-state energy in Table 3.6. This r_{12} -sweep allows us to plot the ground-state energy as a function of intermolecular distance, as shown in Fig. 3.14, superimposed with the harmonic ground-state energy from evaluating Eq. (1.29) using the dimer’s pinned normal modes.

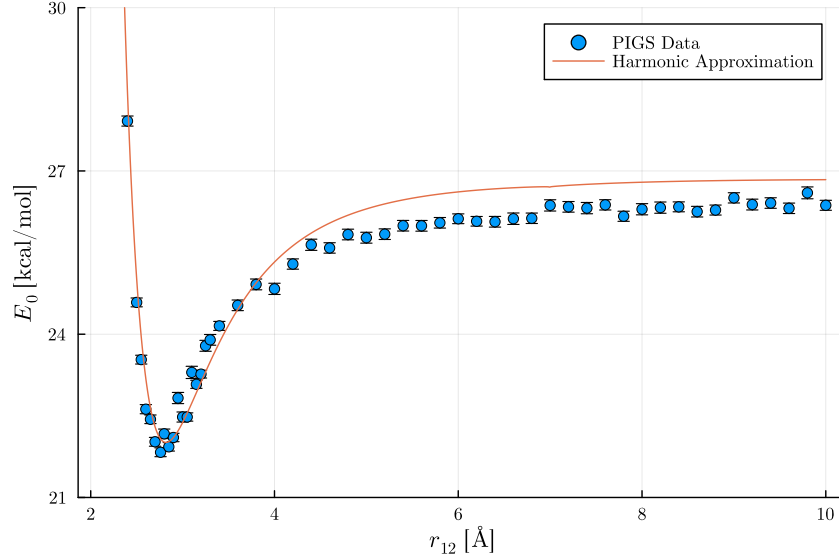


Figure 3.14: Ground-state energy as a function of intermolecular distance from PIGS simulations of the H_2O dimer, overlaid with the harmonic approximation from pinned normal modes.

From Fig. 3.14, we find that the harmonic approximation always overestimates the energy, as we also saw in Tables 3.3 and 3.6. We can then obtain the ground-state energy of the pinned water dimer as the minima of the curves plotted in Fig. 3.14, which are displayed in Table 3.7 along with the locations of these minima.

Table 3.7: Ground-state energy of the pinned H_2O dimer, from PIGS simulations and the harmonic approximation in Fig. 3.14.

Simulation method	$E_0^{\min}$	$r_{12}^{\min}$
PIGS	$(21.83 \pm 0.08) \text{ kcal/mol}$	$2.76 \text{ \AA}$
Harmonic	22.01 kcal/mol	$2.82 \text{ \AA}$

Since the ground-state energy reported in Table 3.6 corresponds to the full dimer (i.e. includes all DoF), but the ground-state energy reported in Table 3.7 corresponds to the

pinned dimer (i.e. excludes translational DoF), we can take the difference of these two values to estimate the translational contribution to the ground-state energy as $E_0^{\text{trans}} \approx 0.05$ kcal/mol.

It is also worth comparing the results of Fig. 3.14 and Table 3.7 to Ref. [27], which performed a similar sweep through intermolecular distances for PIGS simulations of the water dimer. However, their PIGS simulations treated each water molecule as an asymmetric top rotor, not a flexible molecule, so they did not account for molecular vibrations, only rotations. In the case of Ref. [27], their $E_0(r_{12})$ curve’s minimum value and location were $E_0^{\text{min}} = (-4.397 \pm 0.007)$ kcal/mol and $r_{12}^{\text{min}} = 2.9$ Å, respectively. This is in contrast to our PIGS results presented in Table 3.7, which tells us that including vibrational DoF has a substantial impact on both energetic and structural properties.

Additionally, instead of just locating the minimum of the harmonic $E_0(r_{12})$ curve from Fig. 3.14, we can also treat this curve as a PES for the 1D quantum dynamics problem pertaining to the intermolecular coordinate r_{12} . Here, we rely on the timescale difference between the r_{12} motion and the remaining ro-vibrational DoF internal to the water molecules. This adiabatic separation is in the spirit of the Born-Oppenheimer approximation discussed at the beginning of Chapter 1.

This problem is now amenable to ED using the Colbert-Miller DVR [55]. In this DVR for one Cartesian dimension, we discretize r_{12} on a grid with equal spacing Δr [55]. The potential energy matrix is diagonal in this finite basis:

$$V_{\text{eff}}[i, i] = E_0(r_{12}[i]) - E_0(r_{12} \rightarrow \infty), \quad (3.11)$$

where we subtract the “long-distance value” $E_0(r_{12} \rightarrow \infty)$ to remove any intramolecular contributions from the total energy. Since $\vec{r}_{12} = \vec{R}_{\text{CoM}}^{(2)} - \vec{R}_{\text{CoM}}^{(1)}$ is essentially a Jacobi vector connecting two particles of mass $M_{\text{H}_2\text{O}}$, the reduced mass associated with the coordinate $r_{12} = \|\vec{r}_{12}\|$ is $\mu_{12} = M_{\text{H}_2\text{O}}/2$ [36, 37]. Therefore, the kinetic energy matrix in the Colbert-Miller DVR is given by the following [55]:

$$T[i, j] = \frac{\hbar^2}{2\mu_{12}(\Delta r)^2} \begin{cases} \frac{\pi^2}{3} & \text{for } i = j \\ \frac{2(-1)^{i-j}}{(i-j)^2} & \text{for } i \neq j \end{cases}. \quad (3.12)$$

Constructing the Hamiltonian matrix in this DVR using Eqs. (3.11) and (3.12) yields the wavefunctions for the ground state and first three excited states shown in Fig. 3.15. Note that these wavefunctions are scaled and shifted such that their baselines align with their associated eigenenergies, which are also reported in Table 3.8.

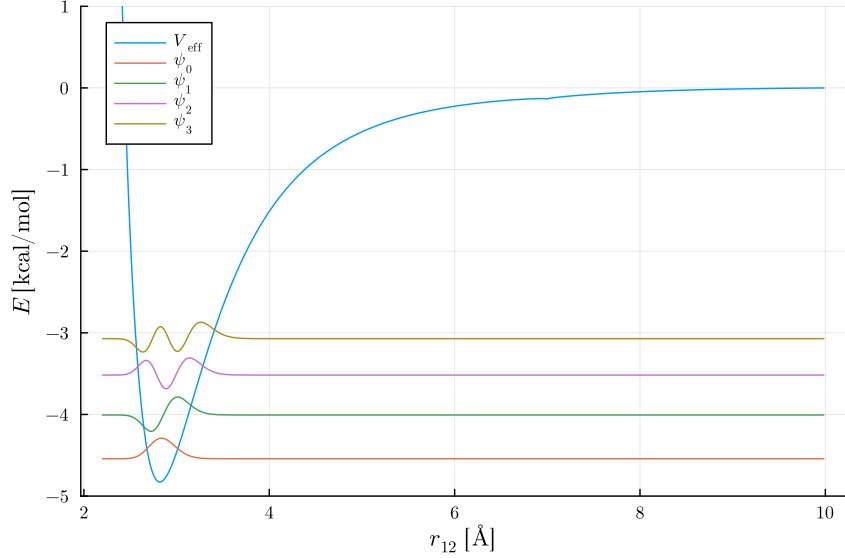


Figure 3.15: Effective potential as a function of intermolecular distance for the H₂O dimer, overlaid with the first four eigenstate wavefunctions.

Since we already removed all monomer contributions to the total energy by subtracting the long-distance value $E_0(r_{12} \rightarrow \infty)$, the smallest eigenvalue displayed in Table 3.8 actually corresponds to the water dimer’s dissociation energy D_0 , which is in excellent agreement with the PIMD result $D_0 = (4.54 \pm 0.04)$ kcal/mol from Ref. [26] and the DMC result $D_0 = 4.53$ kcal/mol from Ref. [46].

Table 3.8: First four eigenenergies from diagonalizing the effective intermolecular Hamiltonian of the H₂O dimer.

	E_n
$n = 0$	-4.54 kcal/mol
$n = 1$	-4.01 kcal/mol
$n = 2$	-3.52 kcal/mol
$n = 3$	-3.07 kcal/mol

3.4.3 Structural Properties

Just as we did for the monomer in Subsection 3.3.3, we would like to calculate structural properties for the water dimer too. We are particularly interested in the probability density functions for the O-H distances, H-H distances, H-O-H bond angles, O-O distance, and intermolecular distance, which we obtain from the middle bead of the full dimer PIGS simulation that produced the result in Table 3.6. These distributions are plotted in Figs. 3.16 to 3.20.

Once again, we find that the distributions shown in Figs. 3.16, 3.17, and 3.19 are in qualitative agreement with those seen in Ref. [26], with peaks of roughly the same location, height, and width. Quantitatively, we report the average H-O-H bond angle, O-O distance, and intermolecular distance in Table 3.9.

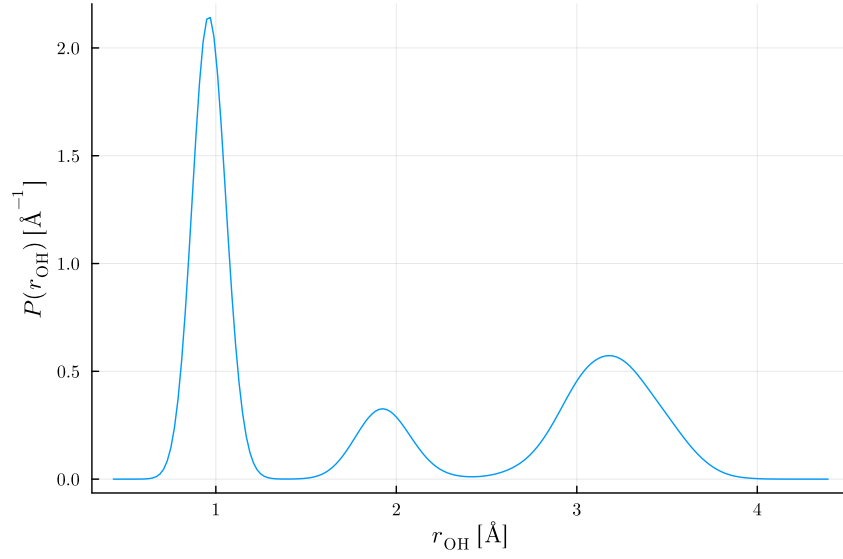


Figure 3.16: Probability density function for the O-H distances from a PIGS simulation of the H₂O dimer.

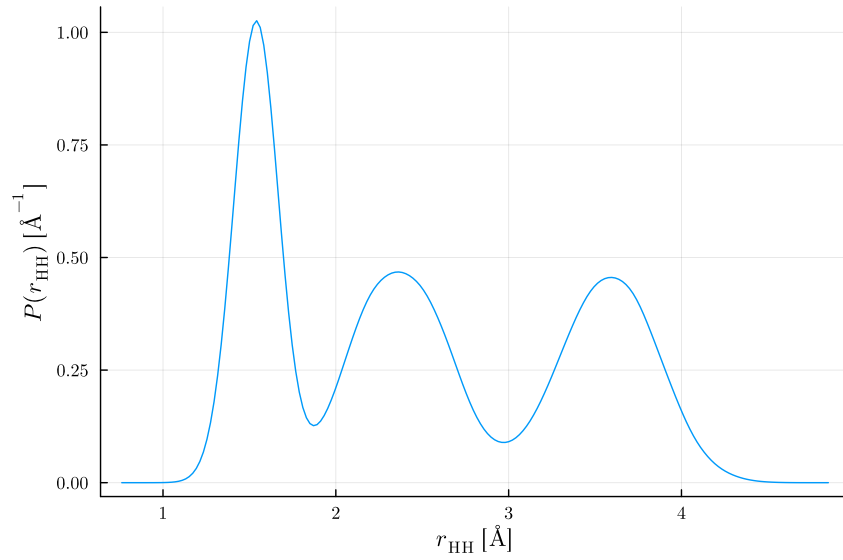


Figure 3.17: Probability density function for the H-H distances from a PIGS simulation of the H₂O dimer.

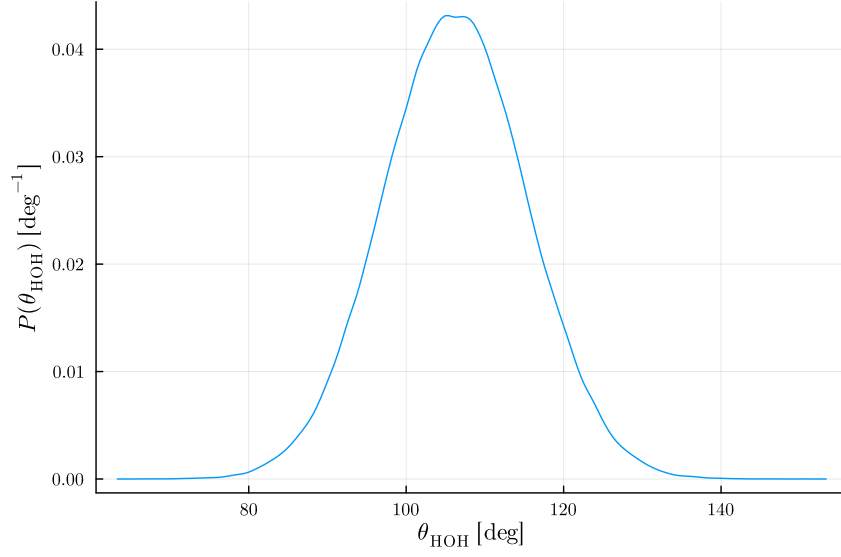


Figure 3.18: Probability density function for the H-O-H bond angles from a PIGS simulation of the H_2O dimer.

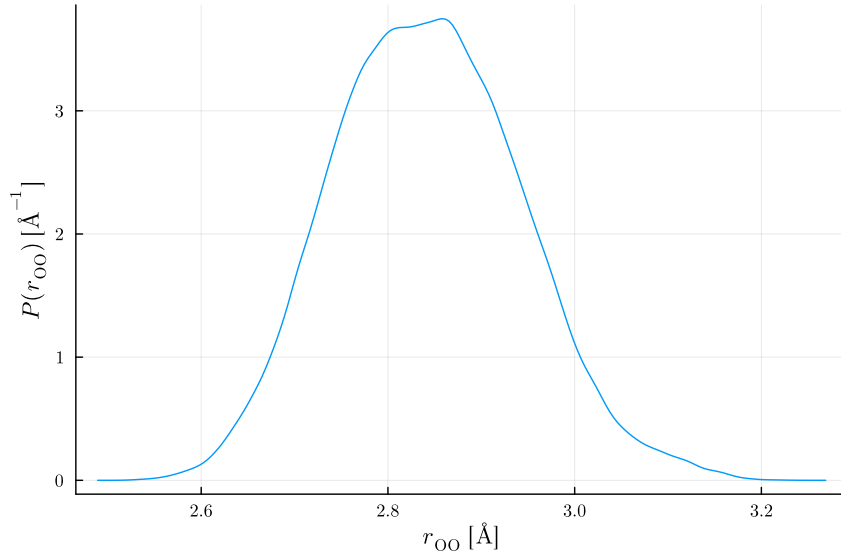


Figure 3.19: Probability density function for the O-O distance from a PIGS simulation of the H_2O dimer.

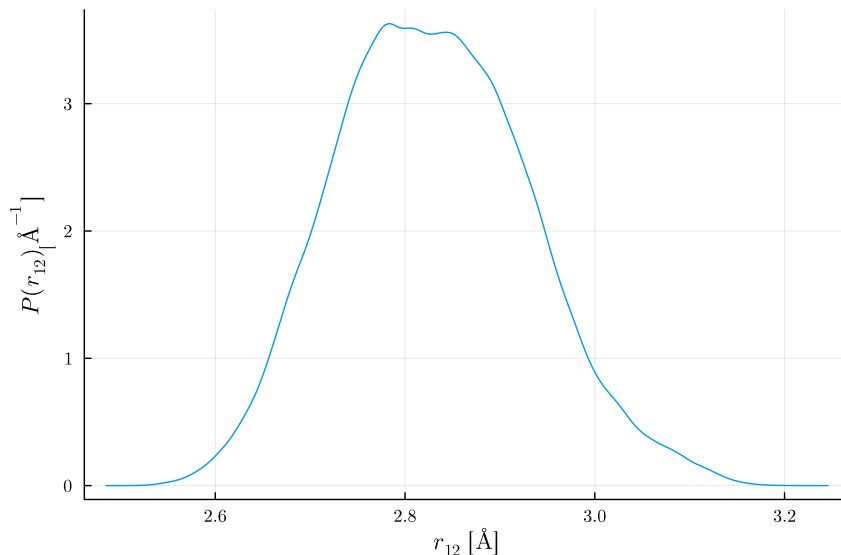


Figure 3.20: Probability density function for the intermolecular distance from a PIGS simulation of the H₂O dimer.

Comparing Tables 3.4 and 3.9, we observe that the interaction between two water molecules does have an effect on the average H-O-H bond angle in the dimer. This could be explained by looking back at the water dimer’s equilibrium geometry in Fig. 3.11, where the O-H bond connecting the two molecules likely has an effect on the stretching and bending of the intramolecular O-H bonds. Furthermore, we can also compare the average r_{12} value here to the PIGS result for $r_{12}^{\min}$ in Table 3.7, which unfortunately do not agree with each other. However, Figs. 3.19 and 3.20 display peaks that are not well-defined and Table 3.9’s error bars are orders of magnitude larger than those in Table 3.4, so it is possible that more MC steps are required to produce sharper peaks and smaller error bars.

Table 3.9: Average ground-state structural properties from a PIGS simulation of the H₂O dimer.

	PIGS
$\langle r_{\text{OO}} \rangle$	$(2.83 \pm 0.03) \text{ \AA}$
$\langle r_{12} \rangle$	$(2.81 \pm 0.03) \text{ \AA}$
$\langle \theta_{\text{HOH}} \rangle$	$(106.0 \pm 0.1) \text{ deg}$

3.5 Hexamer Results

In this section, we present the results from our [PIGS](#) simulations of the cage and prism, two of the many low-energy isomers of the water hexamer. The equilibrium geometries of the cage and prism are illustrated in Figs. [3.21](#) and [3.22](#), respectively. Subsection [3.5.1](#) focuses on calculating the ground-state energy of these hexamer isomers, using both their full and pinned normal modes. The ground-state energies are then benchmarked against a prior [DMC](#) study. In Subsection [3.5.2](#), we move on to computing structural properties of both isomers and plotting the resulting probability density functions, which are again compared to the same [DMC](#) study.

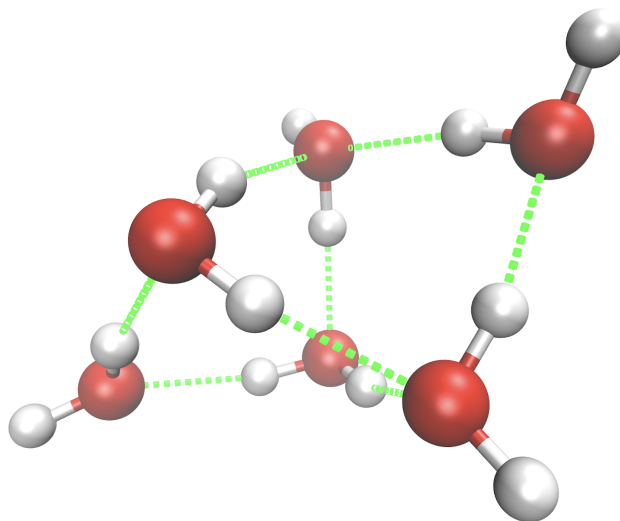


Figure 3.21: Equilibrium geometry for the cage isomer of the H_2O hexamer.

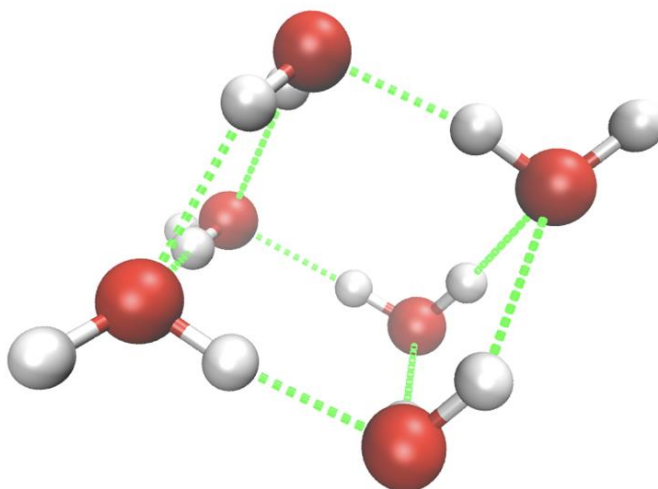


Figure 3.22: Equilibrium geometry for the prism isomer of the H_2O hexamer.

3.5.1 Energetic Properties

Like we did for the dimer, we use a single **PIGS** simulation to report our best estimate of the ground-state energy for both the cage and prism. To get the same value of τ as in Subsection 3.4.2, we choose $\beta = 0.05 \text{ K}^{-1}$ and $P = 2001$ beads to move forward with. We proceed with an autocorrelation analysis for **PIGS** simulations of the full cage and prism isomers, which yields autocorrelation times of 17 and 13 **MC** steps, respectively. As such, we set $N_{\text{skip}} = 20$ in all of the following **PIGS** simulations, which is larger than both autocorrelation times and should generate approximately independent samples. We then run four **PIGS** simulations with $N = 6$, $P = 2001$, $\beta = 0.05 \text{ K}^{-1}$, $M = 100000$, $N_{\text{skip}} = 20$, $N_{\text{therm}} = 100000$: (1) the full cage, (2) the full prism, (3) the pinned cage, and (4) the pinned prism. Although the pinned **PIGS** simulations remove translational contributions to the ground-state energy, pinning the molecules’ **CoM** also prevents the water hexamer from transitioning between different isomer structures, which is a known concern in other numerical studies [38, 43, 46]. The ground-state energies from these **PIGS** simulations, along with both the full and pinned harmonic approximations from Eq. (1.29), are reported in Table 3.10 and compared to prior **DMC** simulation results.

Table 3.10: Ground-state energies of the H_2O hexamer cage and prism isomers obtained from **PIGS** simulations with $P = 2001$ beads and the harmonic approximation, using both their full and pinned normal modes, benchmarked against **DMC** results [46].

Simulation method	E_0^{cage}	E_0^{prism}
PIGS (full)	$(42.1 \pm 0.1) \text{ kcal/mol}$	$(42.2 \pm 0.1) \text{ kcal/mol}$
PIGS (pinned)	$(38.7 \pm 0.1) \text{ kcal/mol}$	$(39.2 \pm 0.1) \text{ kcal/mol}$
DMC	41.09 kcal/mol	41.74 kcal/mol
Harmonic (full)	42.81 kcal/mol	43.43 kcal/mol
Harmonic (pinned)	39.69 kcal/mol	40.40 kcal/mol

Looking at Table 3.10, although our **PIGS** ground-state energies do not necessarily agree with the **DMC** values, we at least see that we yield the correct energy ranking. That is, in all cases (i.e. **PIGS**, harmonic, full, pinned), the cage’s ground-state energy is lower

than the prism's as is expected from the literature [38, 43, 46]. The higher-than-expected ground-state energies from the full PIGS simulations of the cage and prism indicate that β might not be large enough to suppress all unwanted excitations and project onto the true ground state.

3.5.2 Structural Properties

We now move on to calculating the same structural properties as we did for the dimer in Subsection 3.4.3. From the full PIGS simulations of the previous subsection, we use the middle bead to obtain the both the cage and prism's probability density functions for the O-H distances, H-H distances, H-O-H bond angles, and O-O distances. These distributions are plotted in Figs. 3.23 to 3.30.

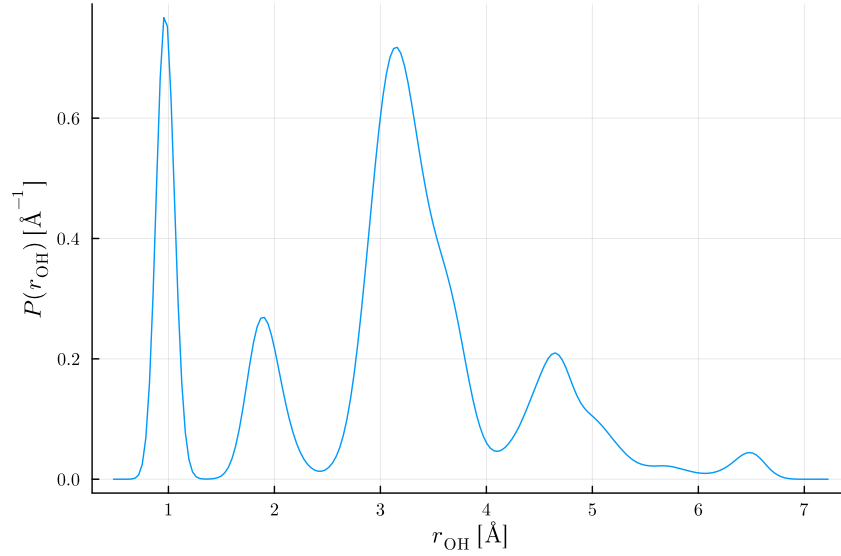


Figure 3.23: Probability density function for the O-H distances from a PIGS simulation of the H₂O hexamer cage.

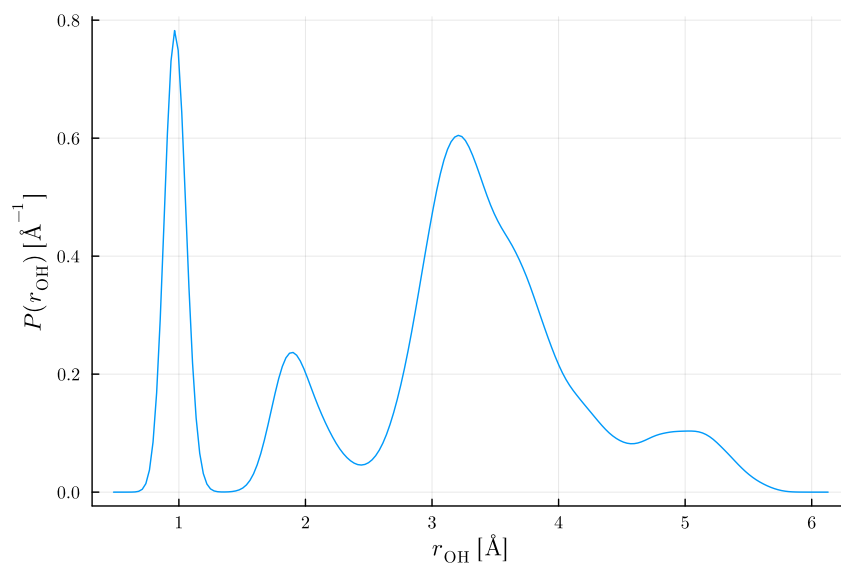


Figure 3.24: Probability density function for the O-H distances from a PIGS simulation of the H₂O hexamer prism.

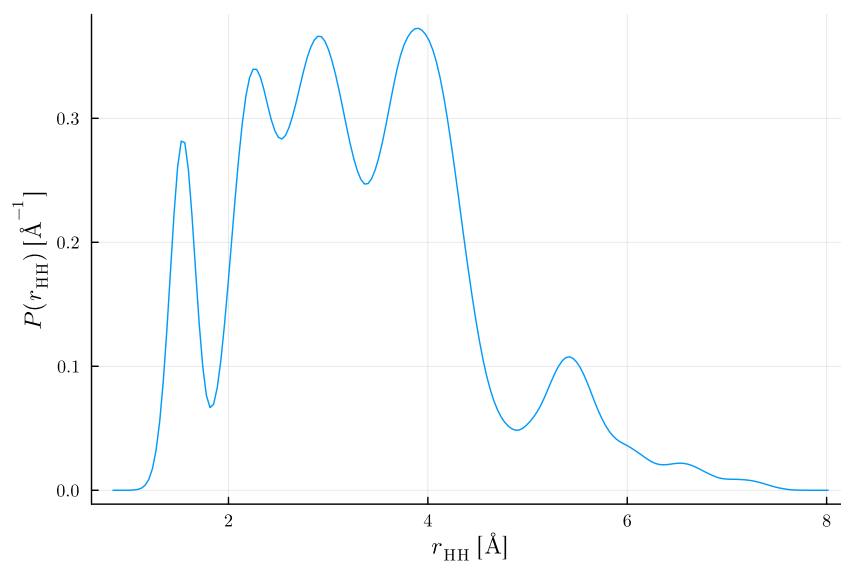


Figure 3.25: Probability density function for the H-H distances from a PIGS simulation of the H₂O hexamer cage.

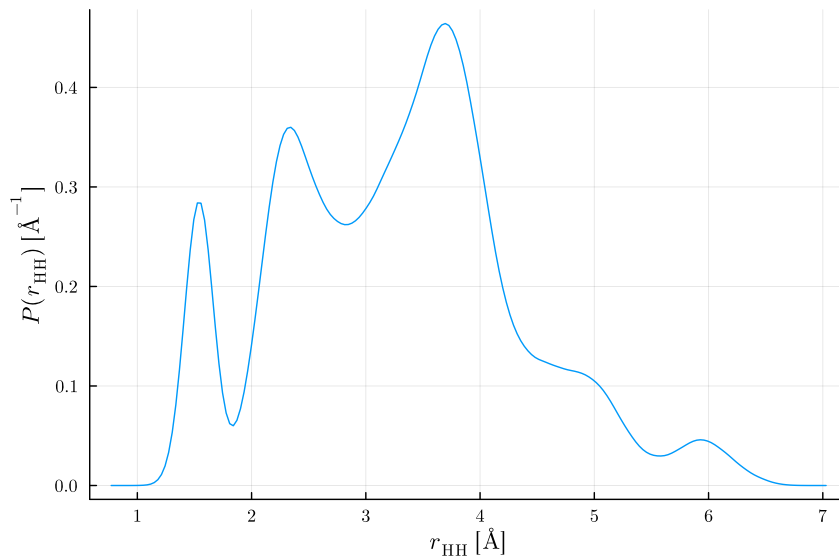


Figure 3.26: Probability density function for the H-H distances from a PIGS simulation of the H₂O hexamer prism.

From Figs. 3.23 to 3.26, we observe a trend that the cage distributions in general have more peaks than the prism distributions. This could be explained by looking back at their equilibrium geometries in Figs. 3.21 and 3.22, where we see that the prism is more symmetric than the cage. Thus, for any given atom, the probability for any two of the other five atoms to be an equal distance away is higher in the prism than in the cage.

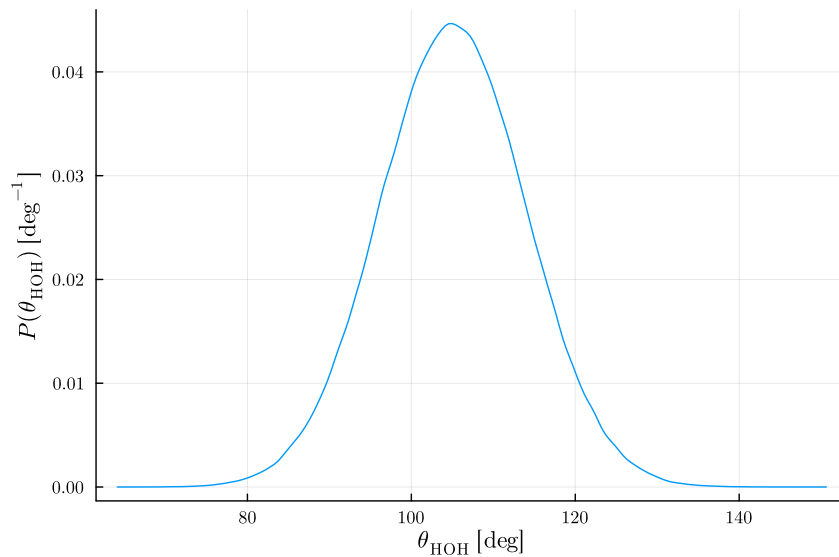


Figure 3.27: Probability density function for the H-O-H bond angles from a PIGS simulation of the H_2O hexamer cage.

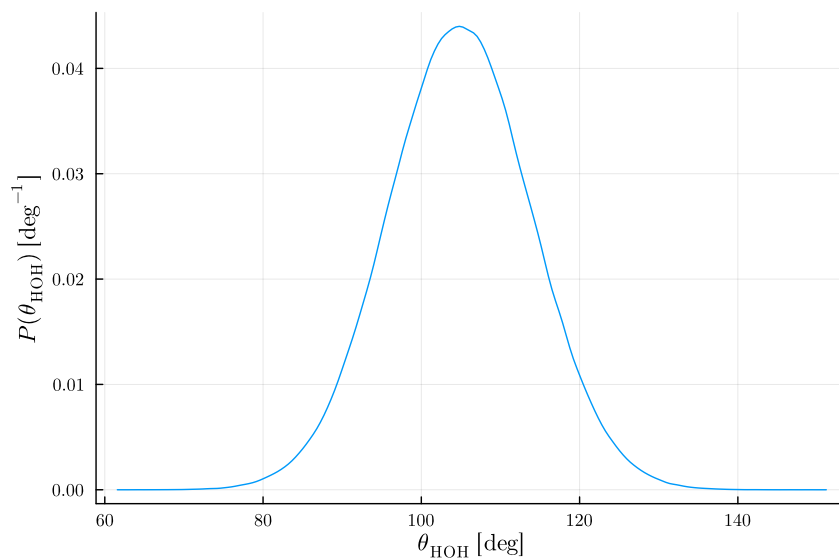


Figure 3.28: Probability density function for the H-O-H bond angles from a PIGS simulation of the H_2O hexamer prism.

We point out that the O-O distributions in Figs. 3.29 and 3.30 are in qualitative agreement with those seen in Ref. [46], but we also notice that our PIGS distributions are more jagged than the smooth DMC distributions of Ref. [46]. However, it is known in the literature that other QMC methods like variational Monte Carlo and DMC cannot calculate *unbiased* structural properties that are independent from the trial state $|\psi_T\rangle$ [23, 56, 57]. This is not an issue for PIGS as we can obtain unbiased structural properties from the middle bead of the imaginary-time path according to Eq. (1.20). Therefore, it is possible that our O-O distributions from PIGS are more accurate than those in Ref. [46].

As a quantitative result, we report the average H-O-H bond angles for both hexamer isomers in Table 3.11, which are approximately equal when taking the standard error into account.

Table 3.11: Average ground-state H-O-H bond angles from PIGS simulations of the H₂O hexamer cage and prism isomers.

Isomer	$\langle\theta_{\text{HOH}}\rangle$
Cage	$(105.04 \pm 0.08) \text{ deg}$
Prism	$(104.91 \pm 0.07) \text{ deg}$

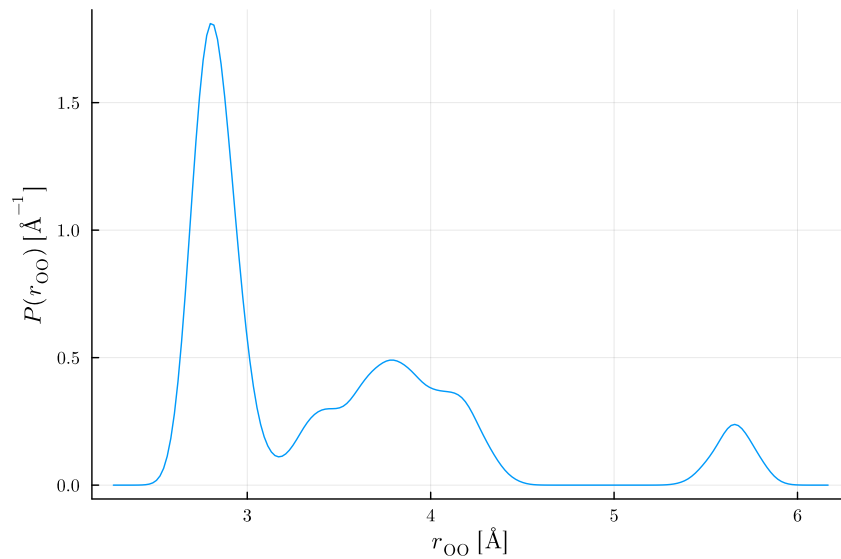


Figure 3.29: Probability density function for the O-O distances from a PIGS simulation of the H₂O hexamer cage.

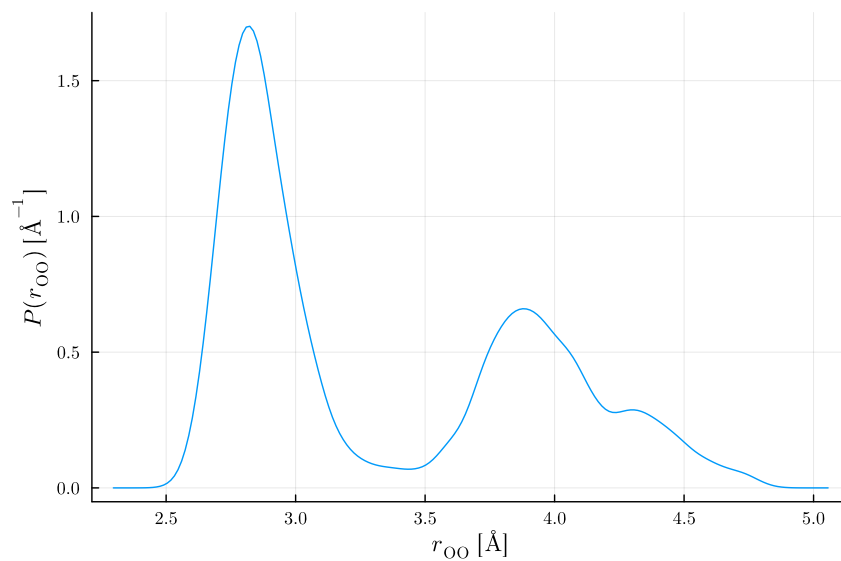


Figure 3.30: Probability density function for the O-O distances from a PIGS simulation of the H₂O hexamer prism.

Chapter 4

Conclusion

In this thesis, we developed the normal-mode sampling algorithm for enhancing the efficiency of [PIGS](#) simulations of flexible molecular systems. Chapter [1](#) introduced the motivation for this work, as well as the background theory needed for path-integral [QMC](#) methods and computing the normal modes of a molecular system.

In Chapter [2](#), we first presented our novel factorization of the thermal density matrix that is based on a normal-mode decomposition of our system Hamiltonian. Then, we used this factorization to construct two variants of normal-mode sampling: a *single-slice* algorithm that samples one imaginary-time slice at a time and a *whole-path* algorithm that samples all beads in the imaginary-time path in one go. We also discussed the potential performance differences between these two algorithms. Finally, we introduced the coordinate system used in our simulations, Jacobi coordinates, and showed how they can be integrated with normal-mode sampling to separate translational motions from ro-vibrational motions using *pinned* normal modes.

The purpose of Chapter [3](#) was to demonstrate a proof-of-concept for our normal-mode sampling algorithm by employing it in [PIGS](#) simulations of the water monomer, dimer, and two low-energy isomers of the hexamer: the cage and prism. We calculated both energetic and structural properties for each of these systems. We also found our results to be most

accurate for the water monomer, as it is the most harmonic system of the four and thus its dynamics are well-described by normal modes. However, the results we obtained for the water dimer and hexamer were still in good agreement with prior numerical studies from the literature. Furthermore, the pinned normal modes allowed for an interesting semi-harmonic treatment of the water dimer, where we adiabatically separated molecular translations from ro-vibrations.

4.1 Future Work

There are several future studies that could build off of the work presented in this thesis. Firstly, we recall from Section 3.4 that in our PIGS simulations of the dimer using single-slice normal-mode sampling, we observed severe changes in the acceptance rate depending on the number of beads in the imaginary-time path. This prevented us from performing a τ convergence to eliminate Trotter error from our best estimate of the dimer’s ground-state energy. An imminent research direction will be to resolve this low acceptance rate issue. A potential avenue for accomplishing this would be to include a scaling factor in each of the standard deviations describing the normal-mode Gaussians. This scaling factor can then be optimized to achieve a desired acceptance rate, say 40 %. However, we must be cautious with this approach and make sure that the acceptance distribution accounts for this scaling factor so that we are still effectively sampling the correct target distribution.

Additionally, we mentioned at the beginning of Chapter 3 that the whole-path normal-mode sampling algorithm had not yet been realized in code. The sampling of this multivariate Gaussian will be beneficial to implement in the near future, as it would allow us to globally sample all DoF in our imaginary-time path at once. We can then compare the performance of this whole-path algorithm to its single-slice counterpart, characterizing each by their computational runtime, autocorrelation time, and acceptance rate.

Moreover, the normal-mode sampling algorithm based on pinned normal modes would require little-to-no modifications to be adapted to PIGS simulations of 1D water chains, or even higher-dimensional confined molecular lattices. To date, such molecular chains have

only been studied in the rigid rotor approximation, but our simulation framework provides a course for investigating the effects of molecular flexibility on the quantum criticality and universal behaviour in the dipole-ordering phase transition [5, 6, 20].

Following our semi-harmonic treatment of the water dimer, we could also develop more sophisticated strategies for this adiabatic separation between the CoM motion of water molecules and their higher frequency intramolecular coordinates. For example, a hybrid approach can be constructed where the high-frequency ro-vibrational DoF are sampled using the current normal-mode sampling scheme, but the slower translations are time-evolved using the Langevin equation path integral ground state method, a ground-state version of PIMD [25, 26].

Finally, the pinned normal modes established here could form a set of HO basis functions, which can be used to represent the matrix product state many-body wavefunction in DMRG calculations of the quantum critical water chain *with* vibrational dynamics. The results of which can be compared to existing DMRG studies that only considered molecular rotations [5, 6].

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APPENDICES

Appendix A

Mathematical Proofs and Derivations

A.1 PIGS Trial State

Let $\hat{H}$ be the Hamiltonian for the system of interest, $\{|\psi_n\rangle\}$ be its complete set of eigenstates, and $\{E_n\}$ be the respective eigenenergies. By the spectral theorem, $\{|\psi_n\rangle\}$ forms an orthonormal basis for the Hilbert space on which $\hat{H}$ acts. Thus, any trial state $|\psi_T\rangle$ can be expressed as

$$|\psi_T\rangle = \sum_n c_n |\psi_n\rangle.$$

Acting on this trial state with the thermal density operator $e^{-\beta\hat{H}/2}$, we get

$$\begin{aligned} |\psi_\beta\rangle &= e^{-\beta\hat{H}/2} |\psi_T\rangle = \sum_n c_n e^{-\beta\hat{H}/2} |\psi_n\rangle = \sum_n c_n e^{-\beta E_n/2} |\psi_n\rangle \\ &= [c_0 e^{-\beta E_0/2} |\psi_0\rangle + c_1 e^{-\beta E_1/2} |\psi_1\rangle + c_2 e^{-\beta E_2/2} |\psi_2\rangle + \dots] \\ &= e^{-\beta E_0/2} [c_0 |\psi_0\rangle + c_1 e^{-\beta(E_1-E_0)/2} |\psi_1\rangle + c_2 e^{-\beta(E_2-E_0)/2} |\psi_2\rangle + \dots]. \end{aligned}$$

Since $E_n > E_0$ for all $n > 0$, all terms in the square brackets vanish in the limit as $\beta \rightarrow \infty$, except for the first one:

$$\lim_{\beta \rightarrow \infty} |\psi_\beta\rangle \propto |\psi_0\rangle.$$

This condition ensures that for large enough β , $|\psi_\beta\rangle$ always projects onto the ground state $|\psi_0\rangle$, regardless of the choice in trial state $|\psi_T\rangle$.

A.2 Energy Estimator

We estimate the ground-state energy as the expectation value of the Hamiltonian $\hat{H}$ with respect to the thermally projected state $|\psi_\beta\rangle = e^{-\beta\hat{H}/2} |\psi_T\rangle$:

$$\langle H \rangle = \frac{\langle \psi_\beta | \hat{H} | \psi_\beta \rangle}{\langle \psi_\beta | \psi_\beta \rangle} = \frac{\langle \psi_T | e^{-\beta\hat{H}/2} \hat{H} e^{-\beta\hat{H}/2} | \psi_T \rangle}{\langle \psi_T | e^{-\beta\hat{H}} | \psi_T \rangle}.$$

Since $\hat{H}$ commutes with $e^{-\beta\hat{H}/2}$, we can move it to the right to get

$$\langle H \rangle = \frac{\langle \psi_T | e^{-\beta\hat{H}} \hat{H} | \psi_T \rangle}{\langle \psi_T | e^{-\beta\hat{H}} | \psi_T \rangle}.$$

Then, we factorize the thermal density operator $e^{-\beta\hat{H}} = (e^{-\tau\hat{H}})^{P-1}$ and insert P resolutions of the identity in the position basis, just as we did to the pseudo-partition function in PIGS:

$$\begin{aligned} \langle H \rangle &= \frac{\int d\mathbf{q}_1 \cdots \int d\mathbf{q}_P \langle \psi_T | \mathbf{q}_1 \rangle \langle \mathbf{q}_1 | e^{-\tau\hat{H}} | \mathbf{q}_2 \rangle \cdots \langle \mathbf{q}_{P-1} | e^{-\tau\hat{H}} | \mathbf{q}_P \rangle \langle \mathbf{q}_P | \hat{H} | \psi_T \rangle}{\langle \psi_T | e^{-\beta\hat{H}} | \psi_T \rangle} \\ &= \frac{\int d\mathbf{q}_1 \cdots \int d\mathbf{q}_P \langle \psi_T | \mathbf{q}_1 \rangle \langle \mathbf{q}_1 | e^{-\tau\hat{H}} | \mathbf{q}_2 \rangle \cdots \langle \mathbf{q}_{P-1} | e^{-\tau\hat{H}} | \mathbf{q}_P \rangle \langle \mathbf{q}_P | \hat{V} | \psi_T \rangle}{\langle \psi_T | e^{-\beta\hat{H}} | \psi_T \rangle}, \end{aligned}$$

where we have asserted that $|\psi_T\rangle \propto 1$, so $\hat{H}|\psi_T\rangle = \cancel{\hat{T}|\psi_T\rangle}^0 + \hat{V}|\psi_T\rangle = \hat{V}|\psi_T\rangle$ because a constant trial state yields zero when acted on by the Laplacian in the kinetic energy

operator. Now, we insert an additional resolution of the identity in the position basis:

$$\begin{aligned}
\langle H \rangle &= \frac{\int d\mathbf{q}_1 \cdots \int d\mathbf{q}_P \langle \psi_T | \mathbf{q}_1 \rangle \langle \mathbf{q}_1 | e^{-\tau \hat{H}} | \mathbf{q}_2 \rangle \cdots \langle \mathbf{q}_{P-1} | e^{-\tau \hat{H}} | \mathbf{q}_P \rangle \int d\mathbf{q}' \langle \mathbf{q}_P | \hat{V} | \mathbf{q}' \rangle \langle \mathbf{q}' | \psi_T \rangle}{\langle \psi_T | e^{-\beta \hat{H}} | \psi_T \rangle} \\
&= \frac{\int d\mathbf{q}_1 \cdots \int d\mathbf{q}_P \langle \psi_T | \mathbf{q}_1 \rangle \langle \mathbf{q}_1 | e^{-\tau \hat{H}} | \mathbf{q}_2 \rangle \cdots \langle \mathbf{q}_{P-1} | e^{-\tau \hat{H}} | \mathbf{q}_P \rangle \int d\mathbf{q}' V(\mathbf{q}') \delta(\mathbf{q}' - \mathbf{q}_P) \langle \mathbf{q}' | \psi_T \rangle}{\langle \psi_T | e^{-\beta \hat{H}} | \psi_T \rangle} \\
&= \frac{\int d\mathbf{q}_1 \cdots \int d\mathbf{q}_P \langle \psi_T | \mathbf{q}_1 \rangle \langle \mathbf{q}_1 | e^{-\tau \hat{H}} | \mathbf{q}_2 \rangle \cdots \langle \mathbf{q}_{P-1} | e^{-\tau \hat{H}} | \mathbf{q}_P \rangle V(\mathbf{q}_P) \langle \mathbf{q}_P | \psi_T \rangle}{\langle \psi_T | e^{-\beta \hat{H}} | \psi_T \rangle} \\
&= \frac{\int \mathcal{D}\vec{q} V(\mathbf{q}_P) \pi(\vec{q})}{\langle \psi_T | e^{-\beta \hat{H}} | \psi_T \rangle} = \langle V(\mathbf{q}_P) \rangle,
\end{aligned}$$

where we have recalled that the potential energy is diagonal in the position basis, integrated out $\mathbf{q}'$, and finally recognized an expectation value with respect to the probability distribution from PIGS $\pi(\vec{q}) \propto \psi_T(\mathbf{q}_1) \prod_{i=1}^{P-1} \langle \mathbf{q}_i | e^{-\tau \hat{H}} | \mathbf{q}_{i+1} \rangle \psi_T(\mathbf{q}_P)$. We could also repeat the above by starting with moving $\hat{H}$ to the left:

$$\langle H \rangle = \frac{\langle \psi_T | \hat{H} e^{-\beta \hat{H}} | \psi_T \rangle}{\langle \psi_T | e^{-\beta \hat{H}} | \psi_T \rangle},$$

which would lead to the end result $\langle H \rangle = \langle V(\mathbf{q}_1) \rangle$.

A.3 Structural Estimator

A structural property is represented by an observable $\hat{O}$ that is diagonal in the position basis. The expectation value of $\hat{O}$ with respect to the thermally projected state $|\psi_\beta\rangle = e^{-\beta \hat{H}/2} |\psi_T\rangle$ is given by

$$\langle O \rangle = \frac{\langle \psi_\beta | \hat{O} | \psi_\beta \rangle}{\langle \psi_\beta | \psi_\beta \rangle} = \frac{\langle \psi_T | e^{-\beta \hat{H}/2} \hat{O} e^{-\beta \hat{H}/2} | \psi_T \rangle}{\langle \psi_T | e^{-\beta \hat{H}} | \psi_T \rangle}.$$

Analogous to the pseudo-partition function in PIGS, we factorize the thermal density operator $e^{-\beta \hat{H}/2} = (e^{-\tau \hat{H}})^{(P-1)/2}$ and insert $(P+1)/2$ resolutions of the identity in the

position basis on either side of $\hat{O}$ (ignoring the denominator to reduce clutter):

$$\begin{aligned}
\langle O \rangle &\propto \int d\mathbf{q}_1 \cdots \int d\mathbf{q}_P \left[\langle \psi_T | \mathbf{q}_1 \rangle \langle \mathbf{q}_1 | e^{-\tau \hat{H}} | \mathbf{q}_2 \rangle \cdots \left\langle \mathbf{q}_{\frac{P-1}{2}} \left| e^{-\tau \hat{H}} \right| \mathbf{q}_{\frac{P+1}{2}} \right\rangle \right. \\
&\quad \times \int d\mathbf{q}' \left\langle \mathbf{q}_{\frac{P+1}{2}} \left| \hat{O} \right| \mathbf{q}' \right\rangle \left\langle \mathbf{q}' \left| e^{-\tau \hat{H}} \right| \mathbf{q}_{\frac{P+3}{2}} \right\rangle \cdots \langle \mathbf{q}_{P-1} | e^{-\tau \hat{H}} | \mathbf{q}_P \rangle \langle \mathbf{q}_P | \psi_T \rangle \left. \right] \\
&= \int d\mathbf{q}_1 \cdots \int d\mathbf{q}_P \left[\langle \psi_T | \mathbf{q}_1 \rangle \langle \mathbf{q}_1 | e^{-\tau \hat{H}} | \mathbf{q}_2 \rangle \cdots \left\langle \mathbf{q}_{\frac{P-1}{2}} \left| e^{-\tau \hat{H}} \right| \mathbf{q}_{\frac{P+1}{2}} \right\rangle \right. \\
&\quad \times \int d\mathbf{q}' O(\mathbf{q}') \delta(\mathbf{q}' - \mathbf{q}_{\frac{P+1}{2}}) \left\langle \mathbf{q}' \left| e^{-\tau \hat{H}} \right| \mathbf{q}_{\frac{P+3}{2}} \right\rangle \cdots \langle \mathbf{q}_{P-1} | e^{-\tau \hat{H}} | \mathbf{q}_P \rangle \langle \mathbf{q}_P | \psi_T \rangle \left. \right] \\
&= \int d\mathbf{q}_1 \cdots \int d\mathbf{q}_P \left[\langle \psi_T | \mathbf{q}_1 \rangle \langle \mathbf{q}_1 | e^{-\tau \hat{H}} | \mathbf{q}_2 \rangle \cdots \left\langle \mathbf{q}_{\frac{P-1}{2}} \left| e^{-\tau \hat{H}} \right| \mathbf{q}_{\frac{P+1}{2}} \right\rangle \right. \\
&\quad \times O(\mathbf{q}_{\frac{P+1}{2}}) \left\langle \mathbf{q}_{\frac{P+1}{2}} \left| e^{-\tau \hat{H}} \right| \mathbf{q}_{\frac{P+3}{2}} \right\rangle \cdots \langle \mathbf{q}_{P-1} | e^{-\tau \hat{H}} | \mathbf{q}_P \rangle \langle \mathbf{q}_P | \psi_T \rangle \left. \right] \\
&= \int \mathcal{D}\vec{q} O(\mathbf{q}_{\frac{P+1}{2}}) \pi(\vec{q}) \propto \left\langle O(\mathbf{q}_{\frac{P+1}{2}}) \right\rangle,
\end{aligned}$$

where we have recalled that $\hat{O}$ is diagonal in the position basis, integrated out $\mathbf{q}'$, and finally recognized an expectation value with respect to the probability distribution from PIGS $\pi(\vec{q}) \propto \psi_T(\mathbf{q}_1) \prod_{i=1}^{P-1} \langle \mathbf{q}_i | e^{-\tau \hat{H}} | \mathbf{q}_{i+1} \rangle \psi_T(\mathbf{q}_P)$.