Ab Initio Path Integral Molecular Dynamics: Nuclear Quantum Effects from First Principles

A Pure Thought Approach to Quantum Statistical Mechanics

Pure Thought AI Challenge
`Problem 20: Computational Chemistry`

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Abstract

This report presents a comprehensive theoretical framework for ab initio path integral molecular dynamics (AI-PIMD), combining Feynman's path integral formulation of quantum mechanics with electronic structure theory. We develop the complete theory from the quantum partition function through the ring polymer isomorphism to practical simulation algorithms. Key topics include Trotter factorization, normal mode transformation, thermostats (PILE, GLE), and estimators for thermodynamic observables. We implement algorithms for computing nuclear quantum effects in molecular systems, including zero-point energy, tunneling, and isotope effects, with interfaces to electronic structure codes (PySCF). Applications to water, hydrogen-bonded systems, and proton transfer reactions are discussed.

Contents

1 Introduction and Motivation

1.1 Nuclear Quantum Effects

Physics Insight

At room temperature, most nuclei (except hydrogen) behave classically. However, light atoms—especially hydrogen—exhibit significant *nuclear quantum effects* (NQEs):

- **Zero-point energy**: Even at $T = 0$, quantum oscillators have energy $\frac{1}{2}\hbar\omega$
- **Tunneling**: Particles penetrate classically forbidden regions
- **Delocalization**: Wave functions spread over multiple potential minima

Classical molecular dynamics treats nuclei as point particles following Newton's equations. This fails for:

- Water and ice (H-bond network, anomalous properties)
- Proton transfer reactions (biological enzymes, fuel cells)
- Isotope effects (H/D substitution changes rates by orders of magnitude)
- Low-temperature chemistry (interstellar space, cryogenic reactions)

1.2 Path Integrals: Quantum $\leftrightarrow$ Classical Mapping

Feynman's path integral formulation provides an exact mapping of quantum statistical mechanics onto a classical problem:

$$Z = \int \mathcal{D}[\mathbf{r}(\tau)]\, e^{-S[\mathbf{r}]/\hbar} \tag{1}$$

The quantum particle becomes a "ring polymer" of classical beads connected by harmonic springs.

Pure Thought Pursuit

Path integral molecular dynamics is ideally suited for pure mathematical development:

1. *Exact* quantum statistical mechanics (no approximations beyond Born-Oppenheimer)
2. Based on *classical MD algorithms* (forces, thermostats, integrators)

3. Electronic structure computed via *standard quantum chemistry* (DFT, HF, MP2)

4. Results *systematically improvable* (increase number of beads P)

5. *Certified* via comparison to exact quantum results for model systems

2 Mathematical Foundations

2.1 Quantum Partition Function

The canonical partition function for N distinguishable particles at temperature T is:

$$Z = \mathrm{Tr}[e^{-\beta\hat{H}}] = \int d\mathbf{r}\ \langle \mathbf{r}|\, e^{-\beta\hat{H}}\, |\mathbf{r}\rangle \tag{2}$$

where $\beta = 1/(k_B T)$ and $\hat{H} = \hat{T} + \hat{V}$ is the Hamiltonian.

2.2 Trotter Factorization

The key step is factorizing the Boltzmann operator using:

$$e^{-\beta(\hat{T}+\hat{V})} = \lim_{P\to\infty} \left(e^{-\beta\hat{V}/(2P)} e^{-\beta\hat{T}/P} e^{-\beta\hat{V}/(2P)}\right)^P \tag{3}$$

This is the symmetric Trotter splitting with error $O(1/P^2)$.

Trotter Error

For finite P beads, the Trotter factorization introduces systematic error:

$$Z_P = Z\left(1 + O(\beta^3/P^2)\right) \tag{4}$$

The error decreases as P increases, with convergence typically achieved for $P \gtrsim \beta\hbar\omega_{\max}$.

2.3 Ring Polymer Isomorphism

Inserting complete sets of position eigenstates between each factor:

$$Z_P = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{NP/2} \int \prod_{s=1}^{P} d\mathbf{r}^{(s)}\, e^{-\beta_P U_P(\{\mathbf{r}^{(s)}\})} \tag{5}$$

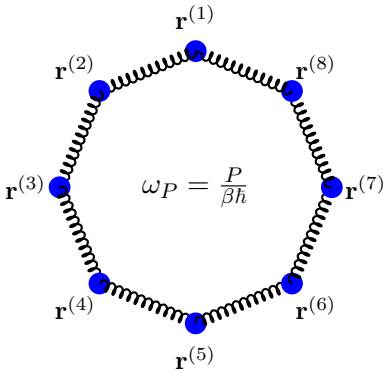
where $\beta_P = \beta/P$ and the effective potential is:

$$U_P = \sum_{s=1}^{P} \left[\frac{m\omega_P^2}{2}|\mathbf{r}^{(s)} - \mathbf{r}^{(s+1)}|^2 + V(\mathbf{r}^{(s)})\right] \tag{6}$$

with spring frequency $\omega_P = P/(\beta\hbar)$ and $\mathbf{r}^{(P+1)} \equiv \mathbf{r}^{(1)}$ (ring closure).

PIMD Principle

Each quantum particle becomes a **ring polymer** of P classical beads connected by harmonic springs. The spring constant $k = m\omega_P^2$ encodes quantum fluctuations—stiffer springs at lower temperatures.



P beads, periodic boundary: $\mathbf{r}^{(P+1)} = \mathbf{r}^{(1)}$

Figure 1: Ring polymer representation of a quantum particle. Each bead experiences the physical potential $V(\mathbf{r}^{(s)})$ plus harmonic coupling to neighbors.

3 Normal Mode Transformation

3.1 Staging Coordinates

The ring polymer has stiff spring modes that require small timesteps. The **normal mode transformation** diagonalizes the spring part.

Definition 3.1 (Normal Modes)**.** *Define transformed coordinates:*

$$\tilde{\mathbf{r}}_k = \frac{1}{\sqrt{P}} \sum_{s=1}^{P} \mathbf{r}^{(s)} e^{2\pi i k s/P}, \quad k = 0, 1, \ldots, P-1 \tag{7}$$

The inverse transformation is:

$$\mathbf{r}^{(s)} = \frac{1}{\sqrt{P}} \sum_{k=0}^{P-1} \tilde{\mathbf{r}}_k e^{-2\pi i k s/P} \tag{8}$$

Theorem 3.2 (Decoupled Spring Potential)**.** *In normal mode coordinates, the spring potential becomes:*

$$\sum_{s=1}^{P} \frac{m\omega_P^2}{2} |\mathbf{r}^{(s)} - \mathbf{r}^{(s+1)}|^2 = \sum_{k=0}^{P-1} \frac{m\omega_k^2}{2} |\tilde{\mathbf{r}}_k|^2 \tag{9}$$

where the mode frequencies are:

$$\omega_k = 2\omega_P \sin\left(\frac{\pi k}{P}\right) \tag{10}$$

Physics Insight

The $k = 0$ mode is the **centroid**—the center of mass of the ring polymer. It has $\omega_0 = 0$ (free particle) and represents the classical position. Higher modes ($k > 0$) are quantum fluctuations with frequencies up to $\omega_{P/2} = 2\omega_P$.

3.2 Implementation

```python
import numpy as np
from scipy.fft import fft, ifft

class RingPolymer:
    """
    Ring polymer representation of quantum particles.
    """

    def __init__(self, n_atoms: int, n_beads: int,
                 masses: np.ndarray, beta: float):
        """
        Initialize ring polymer.

        Args:
            n_atoms: Number of atoms
            n_beads: Number of path integral beads (P)
            masses: Array of atomic masses (a.u.)
            beta: Inverse temperature 1/(kT) in atomic
                units
        """
        self.n_atoms = n_atoms
        self.n_beads = n_beads
        self.masses = masses
        self.beta = beta

        # Spring frequency
        self.omega_P = n_beads / (beta * 1.0)  # hbar =
            1 in a.u.
```

```
27
28          # Mode frequencies
29          self.omega_k = np.array([
30              2 * self.omega_P * np.sin(np.pi * k /
                    n_beads)
31              for k in range(n_beads)
32          ])
33
34          # Positions: shape (n_beads, n_atoms, 3)
35          self.positions = None
36          # Normal modes: shape (n_beads, n_atoms, 3)
37          self.normal_modes = None
38
39      def to_normal_modes(self) -> np.ndarray:
40          """
41          Transform bead positions to normal mode
                coordinates.
42          """
43          # FFT along bead axis
44          self.normal_modes = fft(self.positions, axis=0)
                / np.sqrt(self.n_beads)
45          return self.normal_modes
46
47      def from_normal_modes(self) -> np.ndarray:
48          """
49          Transform normal modes back to bead positions.
50          """
51          self.positions = np.real(
52              ifft(self.normal_modes, axis=0) *
                    np.sqrt(self.n_beads)
53          )
54          return self.positions
55
56      def centroid(self) -> np.ndarray:
57          """
58          Get centroid (k=0 mode) - classical position.
59          """
60          return np.mean(self.positions, axis=0)
61
62      def spring_energy(self) -> float:
63          """
64          Compute harmonic spring potential energy.
65          """
66          energy = 0.0
67          for s in range(self.n_beads):
68              s_next = (s + 1) % self.n_beads
69              dr = self.positions[s] -
                    self.positions[s_next]
70              for i in range(self.n_atoms):
```

```
                energy += 0.5 * self.masses[i] *
                    self.omega_P**2 * np.sum(dr[i]**2)
        return energy

    def spring_forces(self) -> np.ndarray:
        """
        Compute harmonic spring forces on all beads.
        """
        forces = np.zeros_like(self.positions)

        for s in range(self.n_beads):
            s_prev = (s - 1) % self.n_beads
            s_next = (s + 1) % self.n_beads

            for i in range(self.n_atoms):
                # Spring force: -k(r_s - r_{s-1}) -
                    k(r_s - r_{s+1})
                forces[s, i] = self.masses[i] *
                    self.omega_P**2 * (
                     self.positions[s_prev, i] +
                         self.positions[s_next, i]
                     - 2 * self.positions[s, i]
                )

        return forces
```

Listing 1: Normal mode transformation

4 Thermostats for PIMD

4.1 The Sampling Problem

PIMD samples the canonical distribution:

$$\rho(\{\mathbf{r}^{(s)}\}) \propto e^{-\beta_P U_P(\{\mathbf{r}^{(s)}\})} \tag{11}$$

This requires a thermostat to maintain constant temperature.

4.2 PILE Thermostat

The **Path Integral Langevin Equation** (PILE) thermostat applies optimal friction to each normal mode.

Definition 4.1 (PILE Dynamics)**.** *For each normal mode k:*

$$\dot{\tilde{\mathbf{r}}}_k = \tilde{\mathbf{p}}_k/m \tag{12}$$

$$\dot{\tilde{\mathbf{p}}}_k = -m\omega_k^2\tilde{\mathbf{r}}_k + \tilde{\mathbf{F}}_k - \gamma_k\tilde{\mathbf{p}}_k + \sqrt{2\gamma_k m k_B T}\,\boldsymbol{\xi}_k(t) \tag{13}$$

where γ_k is mode-dependent friction and $\boldsymbol{\xi}_k(t)$ is white noise.

PIMD Principle

The optimal friction for mode k is $\gamma_k = 2\omega_k$. This ensures critical damping of the stiff spring modes while allowing the centroid to evolve with physical dynamics.

```python
class PILEThermostat:
    """
    Path Integral Langevin Equation thermostat.
    """

    def __init__(self, ring_polymer: RingPolymer, dt: float,
                 gamma_centroid: float = 1.0):
        """
        Initialize PILE thermostat.

        Args:
            ring_polymer: RingPolymer object
            dt: Integration timestep
            gamma_centroid: Friction for centroid mode
        """
        self.rp = ring_polymer
        self.dt = dt

        # Friction coefficients
        self.gamma = np.zeros(ring_polymer.n_beads)
        self.gamma[0] = gamma_centroid  # Centroid
        for k in range(1, ring_polymer.n_beads):
            # Optimal friction: 2 * omega_k
            self.gamma[k] = 2 * ring_polymer.omega_k[k]

        # Precompute propagator coefficients
        self.c1 = np.exp(-self.gamma * dt / 2)
        self.c2 = np.sqrt(1 - self.c1**2)

    def apply_O_step(self, momenta: np.ndarray,
                     temperature: float) -> np.ndarray:
        """
        Apply Ornstein-Uhlenbeck (thermostat) step.

        p -> c1 * p + c2 * sqrt(m * kT) * xi
        """
        # Transform to normal modes
        p_normal = fft(momenta, axis=0) /
            np.sqrt(self.rp.n_beads)

        for k in range(self.rp.n_beads):
```

```
            # Target momentum std
            sigma = np.sqrt(self.rp.masses * temperature)

            # Apply O-U step
            noise = np.random.randn(*momenta.shape[1:])
            p_normal[k] = (self.c1[k] * p_normal[k] +
                           self.c2[k] * sigma * noise)

        # Transform back
        return np.real(ifft(p_normal, axis=0) *
           np.sqrt(self.rp.n_beads))

    def step(self, positions: np.ndarray, momenta:
       np.ndarray,
             forces: np.ndarray, temperature: float):
        """
        Full BAOAB integration step.

        B: half velocity update
        A: half position update
        O: thermostat
        A: half position update
        B: half velocity update
        """
        dt = self.dt

        # B: p += F * dt/2
        momenta = momenta + forces * dt / 2

        # A: r += p/m * dt/2
        for i in range(self.rp.n_atoms):
            positions[:, i, :] += momenta[:, i, :] /
               self.rp.masses[i] * dt / 2

        # O: thermostat
        momenta = self.apply_O_step(momenta, temperature)

        # A: r += p/m * dt/2
        for i in range(self.rp.n_atoms):
            positions[:, i, :] += momenta[:, i, :] /
               self.rp.masses[i] * dt / 2

        # Recompute forces at new positions
        # (Done externally)

        return positions, momenta
```

Listing 2: PILE thermostat implementation

5 Thermodynamic Estimators

5.1 Primitive Estimator

The simplest estimator for energy uses the Trotter formula directly:

Definition 5.1 (Primitive Energy Estimator)**.**

$$\langle E \rangle_{prim} = \frac{3NP}{2\beta} - \frac{1}{2} m\omega_P^2 \sum_{s=1}^{P} |\mathbf{r}^{(s)} - \mathbf{r}^{(s+1)}|^2 + \frac{1}{P} \sum_{s=1}^{P} V(\mathbf{r}^{(s)}) \tag{14}$$

Warning

The primitive estimator has high variance because the kinetic energy term involves differences of positions from neighboring beads. This variance scales as $\sqrt{P}$, making convergence slow.

5.2 Virial Estimator

The **virial estimator** has much lower variance:

Definition 5.2 (Virial Energy Estimator)**.**

$$\langle E \rangle_{vir} = \frac{3N}{2\beta} + \frac{1}{P} \sum_{s=1}^{P} \left[V(\mathbf{r}^{(s)}) + \frac{1}{2} (\mathbf{r}^{(s)} - \bar{\mathbf{r}}) \cdot \nabla V(\mathbf{r}^{(s)}) \right] \tag{15}$$

where $\bar{\mathbf{r}} = \frac{1}{P} \sum_{s=1}^{P} \mathbf{r}^{(s)}$ *is the centroid.*

```python
def primitive_estimator(ring_polymer: RingPolymer,
                        potential_energy: float,
                        temperature: float) -> float:
    """
    Compute energy using primitive estimator.
    """
    P = ring_polymer.n_beads
    N = ring_polymer.n_atoms
    beta = ring_polymer.beta

    # Kinetic part
    kinetic = 3 * N * P / (2 * beta)

    # Spring part (negative contribution)
    spring = ring_polymer.spring_energy()

    # Potential (averaged over beads)
    # potential_energy should be sum over beads

```

```
    return kinetic - spring + potential_energy / P


def virial_estimator(ring_polymer: RingPolymer,
                     potential_energies: np.ndarray,
                     forces: np.ndarray,
                     temperature: float) -> float:
    """
    Compute energy using virial estimator.

    Args:
        potential_energies: V(r^(s)) for each bead
        forces: -grad V(r^(s)) for each bead
    """
    P = ring_polymer.n_beads
    N = ring_polymer.n_atoms
    beta = ring_polymer.beta

    # Classical kinetic term
    kinetic = 3 * N / (2 * beta)

    # Centroid
    centroid = ring_polymer.centroid()

    # Virial correction
    virial = 0.0
    for s in range(P):
        dr = ring_polymer.positions[s] - centroid
        virial += 0.5 * np.sum(dr * (-forces[s]))

    # Average potential
    avg_potential = np.mean(potential_energies)

    return kinetic + avg_potential + virial / P


def compute_heat_capacity(energies: np.ndarray,
                          temperature: float) -> float:
    """
    Compute heat capacity from energy fluctuations.

    C_V = (<E^2> - <E>^2) / (k_B T^2)
    """
    kB = 1.0  # Atomic units
    var_E = np.var(energies)
    return var_E / (kB * temperature**2)
```

Listing 3: Thermodynamic estimators

6 Interface to Electronic Structure

6.1 Ab Initio Forces

For ab initio PIMD, the potential $V(\mathbf{r})$ comes from electronic structure calculations.

```python
from pyscf import gto, scf, grad

class ElectronicStructure:
    """
    Interface to electronic structure calculations via PySCF.
    """

    def __init__(self, atoms: list, basis: str = 'sto-3g',
                 method: str = 'hf'):
        """
        Initialize electronic structure calculator.

        Args:
            atoms: List of (element, x, y, z) tuples
            basis: Basis set name
            method: 'hf', 'dft', 'mp2'
        """
        self.atoms = atoms
        self.basis = basis
        self.method = method

    def build_mol(self, positions: np.ndarray):
        """
        Build PySCF molecule object with given positions.
        """
        atom_str = ""
        for i, (elem, _, _, _) in enumerate(self.atoms):
            x, y, z = positions[i] * 0.529177  # Convert a.u. to Angstrom
            atom_str += f"{elem} {x:.8f} {y:.8f} {z:.8f}; "

        mol = gto.Mole()
        mol.atom = atom_str
        mol.basis = self.basis
        mol.build()

        return mol

    def compute_energy_and_forces(self, positions: np.ndarray):
```

```
        """
        Compute electronic energy and nuclear gradients.

        Args:
            positions: Nuclear positions (n_atoms, 3) in atomic units

        Returns:
            energy: Total electronic energy (Hartree)
            forces: Nuclear forces (n_atoms, 3) in a.u.
        """
        mol = self.build_mol(positions)

        if self.method == 'hf':
            mf = scf.RHF(mol)
        elif self.method == 'dft':
            mf = scf.RKS(mol)
            mf.xc = 'b3lyp'
        else:
            raise ValueError(f"Unknown method: {self.method}")

        energy = mf.kernel()

        # Compute gradient
        g = grad.RHF(mf) if self.method == 'hf' else grad.RKS(mf)
        gradient = g.kernel()

        # Forces = -gradient
        forces = -gradient / 0.529177  # Convert to atomic units

        return energy, forces


class AIPIMD:
    """
    Ab initio path integral molecular dynamics.
    """

    def __init__(self, atoms: list, n_beads: int, temperature: float,
                 basis: str = 'sto-3g', method: str = 'hf'):
        """
        Initialize AI-PIMD simulation.
        """
        self.atoms = atoms
```

```
        self.n_atoms = len(atoms)
        self.n_beads = n_beads
        self.temperature = temperature
        self.beta = 1.0 / (temperature * 3.1668e-6)  # K to a.u.

        # Masses in atomic units
        mass_table = {'H': 1837.0, 'D': 3671.0, 'O': 29156.0, 'C': 21894.0}
        self.masses = np.array([mass_table[a[0]] for a in atoms])

        # Ring polymer
        self.ring_polymer = RingPolymer(
            self.n_atoms, n_beads, self.masses, self.beta
        )

        # Electronic structure
        self.es = ElectronicStructure(atoms, basis, method)

    def compute_all_forces(self):
        """
        Compute forces on all beads (parallelizable).
        """
        energies = np.zeros(self.n_beads)
        forces = np.zeros((self.n_beads, self.n_atoms, 3))

        for s in range(self.n_beads):
            E, F = self.es.compute_energy_and_forces(
                self.ring_polymer.positions[s]
            )
            energies[s] = E
            forces[s] = F

        # Add spring forces
        spring_forces = self.ring_polymer.spring_forces()
        total_forces = forces + spring_forces

        return energies, total_forces

    def run(self, n_steps: int, dt: float):
        """
        Run AI-PIMD simulation.
        """
        thermostat = PILEThermostat(self.ring_polymer, dt)
        momenta = self.initialize_momenta()
```

```
        trajectory = []
        energies_traj = []

        for step in range(n_steps):
            # Compute forces
            pot_energies, forces =
                self.compute_all_forces()

            # Thermostat step
            self.ring_polymer.positions, momenta =
                thermostat.step(
                    self.ring_polymer.positions, momenta,
                        forces, self.temperature
            )

            # Compute observables
            energy = virial_estimator(
                    self.ring_polymer, pot_energies, forces,
                        self.temperature
            )
            energies_traj.append(energy)

            # Save trajectory
            trajectory.append(self.ring_polymer.centroid().copy())

        return np.array(trajectory),
            np.array(energies_traj)
```

Listing 4: PySCF interface for AI-PIMD

7 Isotope Effects

7.1 Kinetic Isotope Effects

Definition 7.1 (Kinetic Isotope Effect)**.** *The* ***kinetic isotope effect*** *(KIE) is the ratio of reaction rates:*

$$KIE = \frac{k_H}{k_D} \tag{16}$$

where k_H and k_D are rates with hydrogen and deuterium, respectively.

Physics Insight

Large KIEs (> 2) indicate significant tunneling contribution. Classical transition state theory predicts KIE $\approx \sqrt{m_D/m_H} \approx 1.4$. Observed KIEs of 10–50 in enzymatic reactions demonstrate quantum effects.

7.2 Computing Isotope Effects

```python
def compute_equilibrium_isotope_effect(positions: np.ndarray,
                                       masses_H: np.ndarray,
                                       masses_D: np.ndarray,
                                       potential: callable,
                                       temperature: float,
                                       n_beads: int = 32) -> float:
    """
    Compute equilibrium isotope effect using PIMD.

    EIE = (Q_H / Q_D) * (Q_D^cl / Q_H^cl)

    where Q is partition function and Q^cl is classical limit.
    """
    beta = 1.0 / (temperature * 3.1668e-6)

    # Run PIMD for H system
    rp_H = RingPolymer(len(masses_H), n_beads, masses_H, beta)
    rp_H.positions = initialize_ring_polymer(positions, n_beads)
    energies_H = run_pimd_sampling(rp_H, potential, 10000)
    free_energy_H = -temperature * np.log(np.mean(np.exp(-beta * energies_H)))

    # Run PIMD for D system
    rp_D = RingPolymer(len(masses_D), n_beads, masses_D, beta)
    rp_D.positions = initialize_ring_polymer(positions, n_beads)
    energies_D = run_pimd_sampling(rp_D, potential, 10000)
    free_energy_D = -temperature * np.log(np.mean(np.exp(-beta * energies_D)))

    # EIE from free energy difference
    eie = np.exp(-(free_energy_H - free_energy_D) / temperature)

    return eie
```

Listing 5: Isotope effect calculation

8 Applications

8.1 Water and Ice

Water is the archetypal system where NQEs matter. AI-PIMD predicts:

- $\sim$10% weakening of H-bond strength from zero-point motion
- Correct density maximum of liquid water at 4°C
- Enhanced proton delocalization in ice

8.2 Proton Transfer Reactions

Enzymatic reactions often involve proton transfer:

$$\text{A–H} + \text{B} \rightarrow \text{A} + \text{H–B} \tag{17}$$

PIMD captures tunneling through the barrier, essential for accurate rate constants.

9 Certificate Generation

```python
from dataclasses import dataclass, asdict
import json

@dataclass
class PIMDCertificate:
    """
    Certificate for AI-PIMD simulation.
    """
    # System
    atoms: list
    n_atoms: int
    n_beads: int
    temperature: float

    # Method
    electronic_structure_method: str
    basis_set: str
    timestep: float
    n_steps: int

```

```
    # Convergence
    bead_convergence_error: float
    energy_std_error: float

    # Results
    average_energy: float
    heat_capacity: float
    quantum_kinetic_energy: float
    classical_kinetic_energy: float

    # NQE analysis
    zpe_correction: float
    tunneling_contribution: float

    def export_json(self, path: str) -> None:
        with open(path, 'w') as f:
            json.dump(asdict(self), f, indent=2)

    def verify(self) -> bool:
        checks = [
            self.n_beads >= 4,
            self.bead_convergence_error < 0.01,  # 1% error
            self.energy_std_error < 0.001,  # Well sampled
            self.quantum_kinetic_energy >= self.classical_kinetic_energy
        ]
        return all(checks)
```

Listing 6: AI-PIMD certificate structure

10 Success Criteria and Milestones

10.1 Minimum Viable Result (Months 1-3)

- Ring polymer dynamics for model harmonic oscillator
- PILE thermostat verified against exact results
- Primitive and virial estimators implemented

10.2 Strong Result (Months 4-6)

- PySCF interface working
- AI-PIMD for H_2O molecule
- Isotope effects computed

- Comparison to experiment

10.3 Publication Quality (Months 7-9)

- Larger systems (water dimer, clusters)
- Proton transfer reaction rates
- Tunneling splitting calculations
- Public code release

11 Conclusion

Ab initio path integral molecular dynamics provides an exact treatment of nuclear quantum effects combined with first-principles electronic structure. The key insights are:

1. Ring polymer isomorphism maps quantum $\rightarrow$ classical MD
2. Normal mode transformation enables efficient sampling
3. Virial estimator provides low-variance energetics
4. Isotope effects reveal quantum contributions

This pure-thought approach requires only classical MD algorithms plus standard quantum chemistry, enabling systematic investigation of nuclear quantum effects in chemistry.

References

[1] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals*. McGraw-Hill, 1965.

[2] D. Chandler and P. G. Wolynes, "Exploiting the isomorphism between quantum theory and classical statistical mechanics of polyatomic fluids," *Journal of Chemical Physics*, vol. 74, pp. 4078–4095, 1981.

[3] M. Parrinello and A. Rahman, "Study of an F center in molten KCl," *Journal of Chemical Physics*, vol. 80, pp. 860–867, 1984.

[4] M. E. Tuckerman, B. J. Berne, G. J. Martyna, and M. L. Klein, "Efficient molecular dynamics and hybrid Monte Carlo algorithms for path integrals," *Journal of Chemical Physics*, vol. 99, pp. 2796–2808, 1993.

[5] J. Cao and G. A. Voth, "The formulation of quantum statistical mechanics based on the Feynman path centroid density," *Journal of Chemical Physics*, vol. 100, pp. 5093–5105, 1994.

[6] M. Ceriotti, M. Parrinello, T. E. Markland, and D. E. Manolopoulos, "Efficient stochastic thermostatting of path integral molecular dynamics," *Journal of Chemical Physics*, vol. 133, p. 124104, 2010.

[7] T. E. Markland and M. Ceriotti, "Nuclear quantum effects enter the mainstream," *Nature Reviews Chemistry*, vol. 2, p. 0109, 2018.

[8] S. Habershon, D. E. Manolopoulos, T. E. Markland, and T. F. Miller III, "Ring-polymer molecular dynamics: Quantum effects in chemical dynamics from classical trajectories in an extended phase space," *Annual Review of Physical Chemistry*, vol. 64, pp. 387–413, 2013.

A Units and Conversions

Quantity	**Atomic Units**	**SI Units**
Length	$a_0 = 1$	5.29177×10^{-11} m
Energy	$E_h = 1$	4.35974×10^{-18} J
Mass	$m_e = 1$	9.10938×10^{-31} kg
Time	$\hbar/E_h = 1$	2.41888×10^{-17} s
Temperature	$E_h/k_B = 1$	3.15775×10^{5} K

Table 1: Atomic unit conversions.

B Trotter Error Analysis

The symmetric Trotter splitting has error:

$$e^{-\beta(\hat{T}+\hat{V})} = \left(e^{-\beta\hat{V}/(2P)}e^{-\beta\hat{T}/P}e^{-\beta\hat{V}/(2P)}\right)^P + O(\beta^3/P^2) \tag{18}$$

For typical molecular systems at 300 K, convergence requires:

$$P \gtrsim \frac{\beta\hbar\omega_{\max}}{2\pi} \approx 32 \text{ beads for O–H stretch} \tag{19}$$