Virial Coefficients Of Hydrogen And Nitrogen Including Quantum Effects Using Path Integral Monte Carlo (PIMC) Method

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Overview

1 Introduction to Path Integrals
   - Background & History
   - Conceptual development
   - Mathematical development

2 Partition function - evaluation
   - Statistical Mechanics
   - The density matrix
   - Partition function

3 Orientational Sampling
   - Introduction
   - Existing algorithm
   - New algorithm

4 Future Work

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Probability in quantum mechanics

- Light and electrons → sometimes they behave as waves and sometimes, as particles
- Completely resolved in 1926 – 1927 with the advent of quantum mechanics
- Experiments whose outcome is fundamentally unpredictable → probability of various outcomes
- Classical probability of Laplace = \( \lim_{\text{size of objects in experiments} \to \infty} \) quantum mechanical laws of probability
- It is not the concept/definition of probability which is altered but how we calculate it for objects of very small sizes
Experiment #1

Aim: Calculate the probability as a function of $x$, the distance from the center of the screen

- Observed $P \rightarrow$ intensity pattern of two waves starting at the source
- Associate a (complex) amplitude with probability, $\phi(x)$
Experiment #2

Aim: Unambiguously determine the hole through which the electron passed

- Place a light source behind the screen containing the holes
- Light will be scattered either behind hole 1 or behind hole 2 and never behind both
- Combine both the experiments and the observed $P$ is:
Amplitude for any event $\equiv$ sum of the amplitudes for the various alternative ways that the event can occur

$$P = |\phi(x)|^2, \phi(x) = \phi_1(x) + \phi_2(x) + \ldots$$

Two holes represent two kinds of alternatives:-

- **Interfering alternatives:** if both of them are open and no attempt is made to determine through which hole the electron passed, i.e. $\phi = \phi_1 + \phi_2$

- **Exclusive alternatives:** if only one of them is open or if an attempt is made to determine through which hole the electron passed, i.e. $\phi = \phi_i, i = 1, 2$

Amplitude → can be analyzed in many ways. For most detailed analysis → associate amplitude with the path (position vs. time) of the particle
Amplitude and Kernel

- Path \( \rightarrow x(y) \rightarrow 1D \) motion, 'time' \( \rightarrow x(t) \)
- Existence of an amplitude contribution for each trajectory of the particle
  \[ K[b, a] = \sum_{all \ paths} \text{contribution of each path, to the overall amplitude} \]
- Classical trajectory (path) \( \rightarrow \) path with least action contributes the most,
  \[ S = \int_{t_a}^{t_b} L(\dot{x}, x, t) dt, \text{ where } L(\dot{x}, x, t) = \frac{m\dot{x}^2}{2} - V(x, t) \]
- Quantum trajectory (path) \( \rightarrow \) all paths contribute equally to the amplitude but do so at different phases
- Phase contribution from each path \( \propto S[x(t)] \)
  \[ \phi(x, t) = \text{const.} e^{iS[x(t)]/\hbar} \Rightarrow K[b, a] = \sum_{all \ paths} \phi[x(t)] \]
- \( P(b, a) = |K[b, a]|^2 \)
Constructing the Path Integral

- Analogous to the Riemann integral → construct the path integral
- Divide the independent variable 't' into steps of width '$\epsilon$'
- At each $t_i$, select some special point $x_i$ and join consecutive $x_i$ by a straight line to form a path
  
  $\sum_{\text{all paths}} \phi[x(t)] = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \phi[x(t)] \, dx_1 \, dx_2 \ldots \, dx_{N-1}$

where,

$N\epsilon = t_b - t_a$

$\epsilon = t_{i+1} - t_i$

$t_0 = t_a; \, x_0 = x_a$

$t_N = t_b; \, x_N = x_b$

Note: In the above formula $\lim_{\epsilon \to 0}$ does not exist. Need a normalizing factor
Kernel as a path integral

- For a particle of mass \( m \) travelling in a potential \( V(x, t) \),
  \[ L(\dot{x}, x, t) = \frac{m\dot{x}^2}{2} - V(x, t) \]

- Normalizing factor is \( A^{-N} \) where
  \[ A = \left( \frac{2\pi i \hbar \epsilon}{m} \right)^{\frac{1}{2}} \]

- Therefore
  \[ K[b, a] = \lim_{\epsilon \to 0} \frac{1}{A} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{\frac{iS[b,a]}{\hbar}} \frac{dx_1}{A} \frac{dx_2}{A} \cdots \frac{dx_{N-1}}{A} \]

  \( where \), \( S[b, a] = \int_{t_a}^{t_b} L(\dot{x}, x, t) \ dt \)

- New notation for the path integral: \( K[b, a] = \int_a^b e^{\frac{iS[b,a]}{\hbar}} Dx(t) \)
Properties of the Kernel

Consider another point $x_c$ at an intermediate time $t_c$ such that $t_a < t_c < t_b$

\[ S[b, a] = S[c, a] + S[b, c] \]
\[ K[b, a] = \int_{-\infty}^{\infty} K[c, a] K[b, c] \, dx_c \]

Extend it to $N$ time intervals

\[ K[b, a] = \int_{x_{N-1}}^{x_N} \cdots \int_{x_2}^{x_3} \int_{x_1}^{x_2} K[b, N-1] K[N-1, N-2] \cdots K[i + 1, i] \cdots K[1, a] \, dx_1 \, dx_2 \cdots dx_{N-1} \]

Alternative definition of the Kernel for two points separated by a very small time interval $\epsilon$ (correct upto first order in $\epsilon$):

\[ K[i + 1, i] = \frac{1}{A} \exp \left\{ \frac{i \epsilon}{\hbar} L \left( \frac{x_{i+1} - x_i}{\epsilon}, \frac{x_{i+1} + x_i}{2}, \frac{t_{i+1} + t_i}{2} \right) \right\} \]
The wavefunction and the Kernel

- Let the amplitude to arrive at any point \((x, t)\) irrespective of its past, be \(\psi(x, t) = K[x, t; \text{any } x, \text{any } t]\)
- \(\psi(x, t)\) also has the same probability characteristics of the Kernel \(K[b, a]\) i.e.,
  \[
P = |\psi(x, t)|^2,
\]
  \(\psi(x, t)\) is called the wavefunction

\[
\psi(x_b, t_b) = \int_{-\infty}^{\infty} K[x_b, t_b; x_c, t_c] \psi(x_c, t_c) \, dx_c
\]
- If we know \(\psi(x, t)\) we can calculate \(\psi(x', t')\) where \(t' > t\)
- All of history’s effect upon the future of the universe could be obtained from **one gigantic wavefunction**
Schrödinger’s equation $\rightarrow$ Kernel

- In operator form, $\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} \mathcal{H} \psi$
- Special case of time-independent Hamiltonian, let $\psi(x, t) = \phi(x)f(t)$
- Separation of variables:
  \[ \psi(x, t) = \phi(x)e^{(-i/\hbar)Et}, \text{ where } \phi(x) \text{ satisfies} \]
  \[ \mathcal{H}\phi(x) = E\phi(x) \]

- Using orthonormal basis functions to represent $\psi(x, t)$:

  \[ K[x_b, t_b; x_a, t_a] = \begin{cases} 
  \sum_{n=1}^{\infty} \phi_n(x_b)\phi_n(x_a)^*e^{(-i/\hbar)E_n(t_b-t_a)} & \text{if } t_b > t_a \\
  0 & \text{if } t_b < t_a 
  \end{cases} \]

$K[x_b, t_b; x_a, t_a]$ also satisfies the Schrödinger equation!
Review

- At thermal equilibrium, the probability that a system exists in a state with energy \( E \propto e^{-E/kT} \).

- Assuming non-degenerate states, the normalized probability distribution is

\[
p_n = \frac{1}{Z} e^{-\beta E_n}, \text{ where}
\]

\[
Z = \sum_n e^{-\beta E_n}
\]

- Suppose 'A' is some property of interest and its mean value in the \( n^{th} \) energy state is:

\[
A_n = \int \phi_n^* A \phi_n \, d\Gamma
\]

- The statistical average for A for the whole system is

\[
\bar{A} = \sum_n p_n A_n = \frac{1}{Z} \sum_n A_n e^{-\beta E_n}
\]
Probability of a state

For a system in a state ’x’ in configuration space, what is the probability of observing ’x’?

- If the system exists in a single state defined by the wavefunction $\phi_n(x)$

$$p(x) = |\phi_n^*(x) \phi_n(x)|^2 \Rightarrow \text{average over all states} \Rightarrow$$

$$P(x) = \sum_n \phi_n^*(x) \phi_n(x) e^{-\beta E_n}$$

- For any desired quantity $A$, the expected value is:

$$\bar{A} = \frac{1}{Z} \sum_n A_n e^{-\beta E_n} = \frac{1}{Z} \sum_n \int \phi_n^*(x) A \phi_n(x) e^{-\beta E_n} dx$$
Definition

We can calculate the expected value of any quantity $A$ if we know the function:

$$\rho(x', x) = \sum_n \phi_n(x')\phi_n^*(x)e^{-\beta E_n}$$

Given $P(x) = \sum_n \phi_n^*(x)\phi_n(x)e^{-\beta E_n}$ and by definition of $\rho(x', x)$

$$P(x) = \frac{1}{Z}\rho(x, x),$$

$$Z = \int \rho(x, x)dx \equiv \text{trace}\{\rho\}$$

where $\rho(x', x)$ is called the statistical thermal density matrix at temperature $T$. 
Comparison to the kernel

- Compare the expressions for the kernel and the density matrix:

\[ K[x_b, t_b; x_a, t_a] = \sum_n \phi_n(x_b)\phi_n^*(x_a) e^{-(i/\hbar)E_n(t_b-t_a)} \]

\[ \rho(x', x) = \sum_n \phi_n(x')\phi_n^*(x) e^{-\beta E_n} \]

- Replace \( t_b - t_a \) by \(-i/\beta \hbar\) and both expressions are identical
- If \( x_b = x', x_a = x, u_b = -\beta \hbar, u_a = 0 \)
- Can be shown that:

\[ \rho(x_b, x_a; \tau) = \int \exp \left\{ -\frac{1}{\hbar} \int_0^\tau \left[ \frac{m}{2} \dot{x}(u)^2 + V(x(u)) \right] du \right\} Dx(u) \]

where \( \tau = \beta \hbar \) and has units of time
Properties

- **Exact property of the density matrix (similar to the kernel):**

\[ \rho(x_b, x_a; \tau) = \int_{-\infty}^{\infty} \rho(x_b, x_c; \tau_1) \rho(x_c, x_a; \tau_2) \, dx_c \]

where \( \tau = \tau_1 + \tau_2 \)

- **Expression for the density matrix when the time interval is divided into M equal slices \([1,2]\):**

\[
\rho(x_b, x_a; \beta) = \int_{x_{M-1}}^{x_1} \cdots \int_{x_2}^{x_1} \rho(x_b, x_{M-1}; \tau) \rho(x_{M-1}, x_{M-2}; \tau) \cdots \rho(x_1, x_a; \tau) \, dx_1 \, dx_2 \cdots \, dx_{M-1}
\]

where \( \tau \equiv \frac{\beta}{M} \)
Expression for the kernel when the time interval is divided into $N$ equal steps

$$K[b, a] = \int_{x_{N-1}} K[b, N-1] K[N-1, N-2] \ldots$$

$$K[i + 1, i] \ldots K[1, a] \, dx_1 \, dx_2 \ldots \, dx_{N-1}$$

Expression for the density matrix when the time interval is divided into $M$ equal slices $[1, 2]$:

$$\rho(x_b, x_a; \beta) = \int_{x_{M-1}} \ldots \int_{x_2} \int_{x_1} \rho(x_b, x_{M-1}; \tau) \rho(x_{M-1}, x_{M-2}; \tau) \ldots$$

$$\rho(x_1, x_a; \tau) \, dx_1 \, dx_2 \ldots \, dx_{M-1}$$

where $\tau \equiv \frac{\beta}{M}$
Properties

- **Expression for the kernel when the time interval is divided into N equal steps**

\[
K[b, a] = \int_{x_{N-1}}^{x_N} \cdots \int_{x_2}^{x_1} K[b, N - 1] K[N - 1, N - 2] \cdots K[i + 1, i] \ldots K[1, a] \, dx_1 \, dx_2 \ldots \, dx_{N-1}
\]

- **Expression for the density matrix when the time interval is divided into M equal slices [1, 2]**:

\[
\rho(x_b, x_a; \beta) = \int_{x_{M-1}}^{x_M} \cdots \int_{x_2}^{x_1} \rho(x_b, x_{M-1}; \tau) \rho(x_{M-1}, x_{M-2}; \tau) \cdots \rho(x_1, x_a; \tau) \, dx_1 \, dx_2 \ldots \, dx_{M-1}
\]

where \( \tau \equiv \frac{\beta}{M} \)
Evaluation

- In operator form,

\[ \rho(x, x'; \beta) = \langle x | e^{-\beta \hat{H}} | x' \rangle \]

- Since \( Z = \int \rho(x, x) \, dx \),

\[
Z_N = \Lambda_m^{3N} \sum_k \sum_{\pi} \langle k | \exp \left( -\beta \hat{H}_N \right) \hat{P}_\pi | k \rangle
\]

where, \( \hat{H}_N \) is the N-body Hamiltonian operator, \( |k\rangle \) denotes a complete set of N-particle states and \( \hat{P}_\pi \) is a permutation operator, with the proper sign to take into account for bosonic or fermionic nature of the particles [3]
Mathematical background

- The exact operator identity is [1]:

\[ e^{-\tau(T+V)} + \frac{\tau^2}{2} [T,V] = e^{-\tau T} e^{-\tau V} \]

\[ \tau \to 0 \Rightarrow e^{-\tau(T+V)} \approx e^{-\tau T} e^{-\tau V} \]

- This is called the *primitive approximation*.

- Trotter formula:

\[ e^{-\beta(T+V)} = \lim_{M \to \infty} [e^{-\tau T} e^{-\tau V}]^M \]

ensures there is no error as \( M \to \infty \).

- Using the operator form of \( \rho \) and the primitive approximation [2]:

\[ \rho(x,x';\tau) \approx \int dx'' \langle x | e^{-\tau T} | x'' \rangle \langle x'' | e^{-\tau V} | x' \rangle \]
Rigid rotor approximation

Assuming quantum rigid rotors, the kinetic operator of the form,

\[ T = -\frac{\hbar^2}{2m} \sum_{i}^{N} \nabla R_i^2 + \frac{\hbar^2}{2I} \sum_{i}^{N} L_i^2 \]

\[ \langle x | e^{-\tau T} | x' \rangle = \left( \frac{2\pi \hbar^2 \tau}{m} \right)^{-3N/2} \exp \left[ -\frac{m|\mathbf{R} - \mathbf{R}'|^2}{4 \hbar^2 \tau} \right] \]

\[ \sum_{j=0}^{j_{\text{max}}} \frac{2j + 1}{4\pi} \exp[-B \tau j(j + 1)] P_j(\cos \theta) \]

\[ \langle x | e^{-\tau V} | x' \rangle = e^{-\tau V(x)} \delta(x - x') \]

where, \( L_i \) is the angular momentum of the \( i^{th} \) molecule, \( B = \frac{\hbar^2}{2I} \), \( \mathbf{R}, \mathbf{R}' \) are the center of mass position vector of the \( i^{th} \) molecule, \( \theta \) is the polar angle between \( \Omega \) and \( \Omega' \), \( P_j(\cos \theta) \) is the legendre polynomial of order \( j \), \( j \) is the angular/azimuthal quantum number.
A rigid diatomic molecule

- Consider a sphere 'S' with diameter equal to the bond length of the molecule ($r = 0.5 \times$ bond length)
- Sampling points on the surface $\Rightarrow$ Sampling orientations of the molecule
- For PIMC, adjacent beads $\rightarrow$ harmonic bonds
- Only constraint for orientational sampling (of a rigid molecule) $\rightarrow$ harmonic energy of the total system
- Note: There will be two rings, one for each atom.
Mathematical formulation

- Consider one ring of a molecule with only 2 beads on the surface of 'S'
- Consider 2 points with spherical coordinates \(A(r, 0, 0)\) and \(B(r, 0, \phi_1)\) (where \(\phi\) is measured from the positive Z axis)
- Un-normalized probability for the 2 points to be harmonically connected is:

\[
P_{01}(\phi_1) = 2\pi \sin\phi_1 \ast \exp\{-k_h[4 \ast (1 - \cos\phi_1)]\}
\]

where, \(k_h = \frac{\pi P}{\Lambda^2}\)

- Extend it to 3 beads → \(A(r, 0, 0), B(r, \theta_1, \phi_1), C(r, \theta_2, \phi_2)\)

\[
P_{02}(\phi_2) = \int_{\theta_1=0}^{2\pi} \int_{\theta_2=0}^{2\pi} \int_{\phi_1=0}^{\pi} \sin\phi_2 \ast \exp\{-k_{\text{harmonic}}[4 \ast (1 - \cos\gamma)]\}
\]

where, \(\cos(\gamma) = \cos\phi_1 \cos\phi_2 + \sin\phi_1 \sin\phi_2 \cos(\theta_2 - \theta_1)\)

\(\gamma\) is the angle between the position vectors of B, C
It was found that:

\[ P_{0n}(\phi_n)a = P_{01}(k_{\text{eff}}^n, \gamma) \text{, where} \]

\[ k_{\text{eff}}^n \propto \frac{k_h \cos(\gamma/2)}{P} \]

Normalized universal probability distribution function:

\[ P_{0n}(\gamma) = \frac{e^{2k_{\text{eff}}^n} - e^{k_{\text{eff}}^n}(1+\cos\gamma)}{e^{2k_{\text{eff}}^n} - 1} \]

Simple, analytic and can be computed on the fly
Comparison between the algorithms

\[ P_{01}(\gamma) = \exp\{-4k_h r^2 (1 - \cos \gamma)\}, \quad P_{\text{even/odd}}(\gamma) = \frac{\sum_{j=\text{even/odd}}^{50} \frac{2j + 1}{4\pi} \exp\{-B\tau j(j + 1)\} P_j(\cos \gamma)}{C} \]
- Working on a bond length change move → flexible potentials
- Extend the algorithm for other complicated molecules such as water
