Path Integrals

The path integral formulation, here from the statistical mechanical point of view, is an elegant method by which quantum mechanical contributions can be incorporated within a classical simulation using Feynman path integrals (see the additional reading section). Such simulations are particularly applicable to light atoms and molecules such as hydrogen, helium, neon and argon, as well as quantum rotators such as methane and hydrogen-bonded systems such as water. From a more idealized point of view path integrals are often used to study quantum hard spheres.

Principles

In the path integral formulation the canonical partition function (in one dimension) is written as \( Q(\beta, V) = \int \int \int \int \int Dx(\tau) e^{-S(x(\tau))} \) where \( S(x(\tau)) \) is the Euclidean action, given by

\[ S(x(\tau)) = \int_0^\beta \hbar H(x(\tau)) ~ d\tau \]

when \( x(\tau) \) is the path in time \( \tau \) and \( H \) is the Hamiltonian. This leads to

\[ Q_P = \left( \frac{mP}{2\pi^2 \beta \hbar^2} \right)^{P/2} \int \cdots \int Dx_1 \cdots Dx_P e^{-\beta \Phi_P(x_1 \cdots x_P; \beta)} \]

where \( \beta \) is the Trotter number. In the Trotter limit, where \( \beta \to \infty \) these equations become exact. In the case where \( P=1 \) these equations revert to a classical simulation. It has long been recognised that there is an isomorphism between this discretised quantum mechanical description, and the classical statistical mechanics of polyatomic fluids, in particular flexible ring molecules, due to the periodic boundary conditions in imaginary time. It can be seen from the first term of the above equation that each particle \( x_t \) interacts with its neighbours \( x_{t-1} \) and \( x_{t+1} \) via a harmonic spring. The second term provides the internal potential energy.

The following is a schematic for the interaction between atom \( i \) (green) and atom \( j \) (orange). Here we show the atoms having five Trotter slices \( P=5 \), forming what can be thought of as a "ring polymer molecule". The harmonic springs between Trotter slices are in yellow, and white/blue bonds represent the classical intermolecular pair potential.
In three dimensions one has the density operator
\[
\hat{\rho}(\beta) = \exp\left[-\beta \hat{H}\right]
\]
which thanks to the Trotter formula we can tease out \(\exp\left[-\beta(U_{\text{spring}} + U_{\text{internal}}}\right]\), where
\[
U_{\text{spring}} = \frac{mP}{2\beta^2 \hbar^2} \sum_{t=1}^P |\mathbf{r}_t - \mathbf{r}_{t+1}|^2
\]
\[
U_{\text{internal}} = \frac{1}{P} \sum_{t=1}^P V(\mathbf{r}_t)
\]
The internal energy is given by
\[
\langle U \rangle = \frac{3NP}{2\beta} - \langle U_{\text{spring}} \rangle + \langle U_{\text{internal}} \rangle
\]
The average kinetic energy is known as the primitive estimator, i.e.
\[
\langle K_P \rangle = \frac{3NP}{2\beta} - \langle U_{\text{spring}} \rangle
\]

**Harmonic oscillator**

The density matrix for a harmonic oscillator is given by (Eq. 10-44)
\[\rho(x',x) = \sqrt{\frac{m \omega}{2 \pi \hbar \sinh \omega \beta \hbar}} \exp \left( - \frac{m \omega}{2 \hbar (\sinh \omega \beta \hbar)^2} \left( (x^2 + x'^2) \cosh \omega \beta \hbar - 2xx'\right)\right)\]

See also refs [4] [5]

**Wick rotation and imaginary time**

Wick rotation [6]. One can identify the inverse temperature, \(\beta\) with an imaginary time \(i(\beta/\hbar)\) (see [7] § 2.4).

**Rotational degrees of freedom**

In the case of systems having \((d)\) rotational degrees of freedom the Hamiltonian can be written in the form ([8] Eq. 2.1):
\[\hat{H} = \hat{T}^{\text{translational}} + \hat{T}^{\text{rotational}} + \hat{V}\]
where the rotational part of the kinetic energy operator is given by ([8] Eq. 2.2)
\[\hat{T}^{\text{rotational}} = \sum_{i=1}^{d^{\text{rotational}}} \frac{\hat{L}_i^2}{2 \Theta_{ii}}\]
where \(\hat{L}_i\) are the components of the angular momentum operator, and \(\Theta_{ii}\) are the moments of inertia.

**Computer simulation techniques**

The following are a number of commonly used computer simulation techniques that make use of the path integral formulation applied to phases of condensed matter.

**References**


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Additional reading
- P. A. M. Dirac "The Lagrangian in Quantum Mechanics", Physikalische Zeitschrift der Sowjetunion 3 pp. 64-72 (1933)
- F. W. Wiegel "Path integral methods in statistical mechanics", Physics Reports 16 pp. 57-114 (1975)
- J. A. Barker "A quantum-statistical Monte Carlo method; path integrals with boundary conditions", Journal of Chemical Physics 70 pp. 2914-2918 (1979)
- Charusita Chakravarty "Path integral simulations of atomic and molecular systems", International Reviews in Physical Chemistry 16 pp. 421-444 (1997)
External links

- Density matrices and path integrals computer code on SMAC-wiki.
- A simple implementation of PIMD integrator (C++)

Contributors

- SklogWiki