Research Note
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RPMD Hamiltonian in Normal Mode Representation

For ring polymer with P beads, where it will be assumed to be an even integer for convenience, one can write the single particle partition function as

$$Z \cong \frac{1}{(2\pi\hbar)^P} \int \int d\boldsymbol{p} d\boldsymbol{q}\, exp(-\beta_P H_P) \tag{1}$$

using the Trotter discretization of the trace and have $\beta_P = \frac{\beta}{P}$ and H_P is the classical Hamiltonian where

$$\sum_{k=1}^{P} \left(\frac{{p_k}^2}{2m} + \frac{m{\omega_P}^2}{2} (x_{k+1} - x_k)^2 + U(x_k) \right) \tag{2}$$

with position and momentum of the kth bead x_k and p_k, $\omega_P = \frac{1}{\beta_P \hbar}$, periodic boundary condition such that $x_{P+1} = x_1$, and external potential $U(x_k)$.

Using the vector and matrix notation, the RPMD Hamiltonian can be written more compactly. Let $\boldsymbol{x}, \boldsymbol{p}$ be a P dimensional column vector with x_k, p_k as its k th element. Then, the Hamiltonian becomes

$$H_{RPMD}(\boldsymbol{x}, \boldsymbol{p}) = \frac{1}{2m} \boldsymbol{p}^T \boldsymbol{p} + \frac{m{\omega_P}^2}{2} \boldsymbol{x}^T \boldsymbol{A} \boldsymbol{x} + \sum_{k=1}^{P} U(x_k) \tag{3}$$

where the characteristic spring matrix $\boldsymbol{A}$ is the P by P characteristic matrix for the harmonic nearest neighbor coupling with elements

$$\boldsymbol{A}_{ij} = 2\delta_{i,j} - \delta_{i,j+1} - \delta_{i,j-1}$$

also with cyclic boundary condition of $P + 1 \to 1$.

For ease of calculation, we diagonalize the characteristic matrix $\boldsymbol{A}$ with orthogonal matrix $\boldsymbol{O}$ where

$$\boldsymbol{O}_{ij} = \begin{cases} \sqrt{1/P}, i = 1 \\ \sqrt{2/P}\, cos\left(\frac{2\pi(i-1)j}{P}\right), i = 2, \dots, \frac{P}{2} \\ (-1)^j \sqrt{1/P}, i = \frac{P}{2} + 1 \\ \sqrt{2/P}\, sin\left(\frac{2\pi(i-1)j}{P}\right), i = \frac{P}{2} + 2, \dots, P \end{cases} \tag{4}$$

Then, using the property of orthogonal matrix, we can rewrite the spring coupling term in the Hamiltonian as

$$\boldsymbol{x}^T \boldsymbol{A} \boldsymbol{x} = \boldsymbol{x}^T \boldsymbol{O}^T \boldsymbol{O} \boldsymbol{A} \boldsymbol{O}^T \boldsymbol{O} \boldsymbol{x} = (\boldsymbol{x}^T \boldsymbol{O}^T)(\boldsymbol{O} \boldsymbol{A} \boldsymbol{O}^T)(\boldsymbol{O} \boldsymbol{x}) \tag{5}$$

which conveniently defines a coordinate change from the bead representation to normal mode representation. The normal mode position and momentum vectors $\boldsymbol{u}$ and $\boldsymbol{\gamma}$ are defined by

$$\begin{gathered} \boldsymbol{u} = \boldsymbol{O} \boldsymbol{x} \\ \boldsymbol{x} = \boldsymbol{O}^T \boldsymbol{u} \end{gathered} \qquad \begin{gathered} \boldsymbol{\gamma} = \boldsymbol{O} \boldsymbol{p} \\ \boldsymbol{p} = \boldsymbol{O}^T \boldsymbol{\gamma} \end{gathered} \tag{6}$$

and a diagonal matrix $\boldsymbol{\Lambda}$ such that

$$\boldsymbol{\Lambda} = \boldsymbol{O} \boldsymbol{A} \boldsymbol{O}^T \tag{7}$$

with *k* th eigenvalues defined by

$$\lambda_k = 4 sin^2 \left(\frac{(k-1)\pi}{P}\right). \tag{8}$$

The Hamiltonian then can be written using the normal mode coordinate as

$$H_{RPMD}(\boldsymbol{u}, \boldsymbol{\gamma}) = \frac{1}{2m} \boldsymbol{\gamma}^T \boldsymbol{\gamma} + \frac{m {\omega_P}^2}{2} \boldsymbol{u}^T \boldsymbol{\Lambda} \boldsymbol{u} + \sum_{k=1}^{P} U\big(x_k(u_1, \dots, u_P)\big). \tag{9}$$

Or, without using the vector notation, have

$$H_{RPMD}(\{u_k\},\{\gamma_k\}) = \sum_{k=1}^{P}\left(\frac{{\gamma_k}^2}{2m} + \frac{m{\alpha_k}^2}{2}{u_k}^2\right) + \sum_{k=1}^{P} U\big(x_k(u_1,\dots,u_P)\big) \tag{10}$$

where α_k is the natural frequency of the normal mode and is defined as

$${\alpha_k}^2 = {\omega_P}^2\lambda_k. \tag{11}$$