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Research paper

Path integral molecular dynamics at zero thermal temperature

Soohaeng Yoo Willow

Department of Micro/Nano-electronics, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, PR China

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A B S T R A C T

Path integral molecular dynamics (PIMD) simulations at the zero thermal temperature still remain inconceivable. Herein, the quantum-mechanical partition function is revised in conjunction with the time-independent Schrödinger equation. The *imaginary* temperature for the quantum–mechanical partition function is introduced as an independent variable and defined under the guidance of the virial theorem. In the end, computational evidences are provided showing that this revised PIMD simulation at the zero thermal temperature reproduces both the zero-point energy and the probability density obtained from the Schrödinger equation for the harmonic oscillator.

1. Introduction

The Born–Oppenheimer molecular dynamics (BOMD) simulations of liquid water have recently been reported using the density functional theory (DFT) [1–4] and the second-order many–body perturbation (MP2) theory [5,6] in the prediction of physical properties and vibrational spectra of liquid water. But, there is a discrepancy between simulated and observed liquid water. A possible explanation for this discrepancy has been discussed by showing the effect of the polarizability and the dispersion attraction on the physical properties of liquid water [7]. A better quantitative agreement with the experimental physical properties can be achieved by systematically raising the level of theories (i.e. random phase approximation (RPA) and coupled-cluster (CC) theories) [8]. Furthermore, the inclusion of the embedded three-body interactions in the embedded many-body expansion method for the calculation of the potential energy [9–13,5] is critical in improving the prediction of the physical properties of liquid water [14–16].

On the other hand, the inclusion of nuclear quantum effect such as zero-point energy (ZPE) into the Born–Oppenheimer potential energy surface plays a judicial role in the description of the thermodynamic properties of ice/liquid water (i.e. anomalous volume isotope effects rendering the number density of D_2O lower than that of H_2O) [17] and the better quantitative agreement with experimental spectra as well [18,19]. A path integral molecular dynamics (PIMD) technique [20–22] has been developed and improved into the ring–polymer molecular dynamics (RPMD) [23–26,17] and centroid molecular dynamics (CMD) [27–29,19] techniques to include the ZPE in the on-the-fly simulations. The applications of PIMD, RPMD, and CMD methods are, however, restricted from their simulations at lower thermal temperature T at which a huge number of replicas (beads) are required according to the following rule:

$$\mathcal{P} > \frac{\hbar\omega_{\max}}{k_B T}. \tag{1}$$

where $\mathcal{P}$, $\hbar$, k_B, and $\omega_{\max}$ are the number of beads per nucleus, the reduced Planck constant, the Boltzmann constant, and the maximum value of the intra-molecular angular frequency, respectively.

In this paper we recall the quantum–mechanical partition function in conjunction with the time–independent vibrational Schrödinger equation and then suggest that the temperature for the quantum–mechanical partition function is an independent variable and determined by the virial theorem of the harmonic oscillator in the statistical mechanics (see Supplementary material). Lastly, computational evidences are provided to reveal that the ZPE is calculated exactly at the zero thermal temperature.

2. Theory

2.1. Time–independent Schrödinger equation for a diatomic molecule

The connection between the time–independent Schrödinger equation and the quantum partition function needs to be briefly reviewed at the beginning. A one-dimensional diatomic molecule is illustrated in Fig. 1, which especially shows the distributions $\varrho(x_Q)$ of quantum particles in addition to classical nuclei at X_Q. $\varrho(x_Q)$ is a Gaussian distribution with a expectation value X_Q. When an internuclear distance of the diatomic molecule is at $X_{AB}^{\min} = X_A - X_B$ where the potential energy surface V is the

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E-mail address: sy7willow@gmail.com

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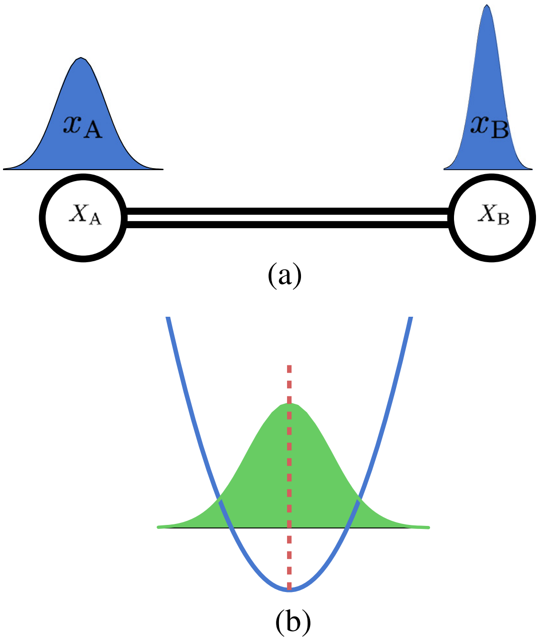

Fig. 1. (a) Schematic plot of a one-dimensional diatomic molecule. X_{Q} and x_{Q} represent the positions of classical and quantum particles for nucleus Q, respectively. Due to Heisenburg's uncertainty principle, the quantum particle for the Qth nucleus has a Gaussian distribution $\varrho(x_{\mathrm{Q}})$ with the expectation value X_{Q} and standard deviation σ_{Q} (see blue shaded areas). (b) Potential energy curve (in blue solid line) of the diatomic molecule with a harmonic vibration. Also shown is its probability density $\rho(x_{\mathrm{AB}}|X_{\mathrm{AB}}^{\mathrm{min}}) = |\Psi_{\mathrm{vib}}^{2}(x_{\mathrm{AB}}|X_{\mathrm{AB}}^{\mathrm{min}})|$ (in green shaded area) at the ground state, where $\Psi_{\mathrm{vib}}(x_{\mathrm{AB}}|X_{\mathrm{AB}}^{\mathrm{min}})$ is a vibrational wave function at the ground state and x_{AB} is an internuclear distance for quantum particles: $x_{\mathrm{AB}} = x_{\mathrm{A}} - x_{\mathrm{B}}$. The internuclear distance at the minimum $X_{\mathrm{AB}}^{\mathrm{min}}$ is highlighted by red dashed line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

minimum, the time-independent Schrödinger equation for the one-dimensional diatomic vibrational motion reads

$$\widehat{H}_{\mathrm{vib}}\Psi_{\mathrm{vib}}(x_{\mathrm{AB}}|X_{\mathrm{AB}}^{\mathrm{min}}) = E_{\mathrm{vib}}\Psi_{\mathrm{vib}}(x_{\mathrm{AB}}|X_{\mathrm{AB}}^{\mathrm{min}}), \tag{2}$$

where $\widehat{H}_{\mathrm{vib}}$ is a Hamiltonian operator for the vibrational motion; E_{vib} and Ψ_{vib} are the eigenvalue and eigenstate of the Hamiltonian operator for the vibration motion, respectively. Here, the eigenstate $\Psi_{\mathrm{vib}}(x_{\mathrm{AB}}|X_{\mathrm{AB}}^{\mathrm{min}})$ depends *explicitly* on the internuclear distance of the quantum particles $x_{\mathrm{AB}} = x_A - x_B$, but *parametrically* on the minimum internuclear distance $X_{\mathrm{AB}}^{\mathrm{min}}$ of the classical nuclei.

The Hamiltonian operator is the sum of the kinetic $\widehat{K}_{\mathrm{vib}}$ and potential $\widehat{V}_{\mathrm{vib}}$ operators [30]:

$$\widehat{K}_{\mathrm{vib}} = \frac{\hat{p}_{\mathrm{A}}^2}{2m_{\mathrm{A}}} + \frac{\hat{p}_{\mathrm{B}}^2}{2m_{\mathrm{B}}}, \tag{3}$$

$$\widehat{V}_{\mathrm{vib}} = V(x_{\mathrm{AB}}) - V(X_{\mathrm{AB}}^{\mathrm{min}}), \tag{4}$$

where $\hat{p}_{\mathrm{Q}}$ and m_{Q} are the momentum operator and the mass of the Qth quantum particle, respectively. The eigenvalue E_{vib} at the ground state becomes the zero-point energy E_{ZPE}. When the diatomic molecule gives an angular frequency ω in the harmonic approximation, the eigenvalue E_{vib} at the ground state reads

$$E_{\mathrm{vib}} = E_{\mathrm{ZPE}} = \frac{1}{2}\hbar\omega. \tag{5}$$

It is only when the system is located at the minimum, i.e., $X_{\mathrm{AB}}^{\mathrm{min}}$ that the time-independent Schrödinger equation for the vibrational motion gives both the eigenvalue E_{vib} and the eigenstate Ψ_{vib}. Hence, regarding $X_{\mathrm{AB}} \neq X_{\mathrm{AB}}^{\mathrm{min}}$, the eigenvalue E_{vib} cannot be calculated analytically, but can be estimated numerically via the PIMD simulation.

2.2. Path integral configuration partition function

Eq. (2) gives a physical interpretation that the distributions $\varrho(x_{\mathrm{Q}})$ of the quantum particles should be obtained in the field of the fixed classical nuclei. Therefore, an *imaginary* temperature $\mathcal{T}$ for the motion of quantum particles is introduced as an independent variable, whereas the thermal temperature T is used for the motion of the classical particles. When the distributions $\varrho(x_{\mathrm{Q}})$ of the quantum particles are obtainable at *imaginary* temperature $\mathcal{T}$ as shown in Fig. 1(a), the quantum–mechanical partition function Z in conjunction with Eq. (2) reads

$$Z = \mathrm{Tr}\left[e^{-\beta\widehat{H}_{\mathrm{vib}}}\right], \tag{6}$$

where $\beta = 1/(k_B\mathcal{T})$ and Tr denotes the trace of the operator.

When β in Eq. (6) is replaced by $\beta = 1/(k_BT)$, one has the conventional definition of the quantum–mechanical partition function in which the distribution of quantum particles depends *explicitly* on the thermal temperature *T*. In the end, the conventional PIMD schemes including RPMD and CMD eventually demand an infinite value of $\mathcal{P}$ near $T = 0$ K thanks to Eq. (1).

If a finite number $\mathcal{P}$ of the beads per nucleus depicts the distribution $\varrho(x_{\mathrm{Q}})$ of the quantum particle (see blue shaded areas in Fig. 1(a)), this Z in Eq. (6) practically approximates the imaginary-time PI configuration partition function $Z_{\mathcal{P}}$ [31]

$$Z \approx Z_{\mathcal{P}} = \frac{1}{\Lambda^{DN\mathcal{P}}}\int \mathrm{d}\boldsymbol{q}_1\cdots\mathrm{d}\boldsymbol{q}_{\mathcal{P}}(\exp[-\beta E_{\mathrm{eff}}]), \tag{7}$$

where D is a dimensionality of the position, N is the number of nuclei ($N = 2$ for the diatomic molecule) and Λ is the de Broglie wavelength of beads,

$$\Lambda = \left[\frac{2\pi\hbar^2\beta}{m\mathcal{P}}\right]^{1/2}. \tag{8}$$

$\boldsymbol{q}_p$ is a set of atomic positions $\boldsymbol{q}_p = \{q_p^1, \ldots, q_p^N\}$ of the pth beads with the constraint of

$$\boldsymbol{q} = \frac{1}{\mathcal{P}}\sum_{p=1}^{\mathcal{P}}\boldsymbol{q}_p, \tag{9}$$

where $\boldsymbol{q}$ is a set of atomic positions of the classical nuclei.

The effective potential E_{eff} in Eq. (7) reads

$$E_{\mathrm{eff}} = \frac{1}{\mathcal{P}}\sum_{p=1}^{\mathcal{P}}V_{\mathrm{vib}}(\boldsymbol{q}_p) + \sum_{p=1}^{\mathcal{P}}\sum_{\mathrm{Q}=1}^{N}\frac{1}{2}m_{\mathrm{Q}}\omega_{\mathcal{P}}^2\left(q_p^{\mathrm{Q}} - q_{p+1}^{\mathrm{Q}}\right)^2, \tag{10}$$

with the periodicity $\boldsymbol{q}_{\mathcal{P}+1} = \boldsymbol{q}_1$ and constant $\omega_{\mathcal{P}} = \sqrt{\mathcal{P}}k_B\mathcal{T}/\hbar$. $V_{\mathrm{vib}}(\boldsymbol{q}_p) = V(\boldsymbol{q}_p) - V(\boldsymbol{q})$ according to Eq. (4). Eventually a practical formula of the expectation value of the Hamiltonian operator is given by

$$\langle\widehat{H}_{\mathrm{vib}}\rangle \approx \frac{1}{Z_{\mathcal{P}}}\frac{1}{\Lambda^{DN\mathcal{P}}}\int \mathrm{d}\boldsymbol{q}_1\cdots\mathrm{d}\boldsymbol{q}_{\mathcal{P}}\left[E_{\mathrm{eff}}e^{-\beta E_{\mathrm{eff}}}\right] = \langle E_{\mathrm{eff}}\rangle. \tag{11}$$

The quantum–mechanical partition function Z and the PI configuration partition function $Z_{\mathcal{P}}$ are introduced to evaluate the E_{ZPE} as the expectation value $\langle E_{\mathrm{eff}}\rangle$ of the Hamiltonian operator. Nevertheless, the value of the *imaginary* temperature $\mathcal{T}$ in Eqs. (6), (7) and (11) has never been defined yet. Determining $\mathcal{T}$ is a crucial step so that the expectation value of the Hamiltonian operator becomes the zero-point energy: $\langle E_{\mathrm{eff}}\rangle = E_{\mathrm{ZPE}}$. Using the virial