Electronic Supplementary Material (ESI) for Chemical Science.

Modeling Quantum Nuclei with Perturbed Path Integral Molecular Dynamics

Igor Poltavsky[1] and Alexandre Tkatchenko[1]

[1] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

HEAT CAPACITY ESTIMATOR

The correction to the standard PI heat capacity estimator is

$$-\frac{4P^3}{\hbar^2\beta^3}C_{\rm q} = \sum_{s=1}^{P}\frac{1}{m}\left\langle \vec{f}_s{}^2\right\rangle + \frac{\beta^2}{3}\sum_{s=1}^{P}\frac{1}{m}\left(\left\langle \vec{f}_s{}^2\right\rangle\langle\epsilon\rangle - \left\langle \vec{f}_s{}^2\epsilon\right\rangle\right)\left(\frac{3}{\beta}+\langle\epsilon\rangle\right) + \frac{\beta^2}{6}\sum_{s=1}^{P}\frac{1}{m}\left(\left\langle \vec{f}_s{}^2\epsilon^2\right\rangle - \left\langle \vec{f}_s{}^2\right\rangle\langle\epsilon^2\rangle\right) + \frac{\beta^2}{3}\sum_{s=1}^{P}\frac{1}{m}\left(\left\langle \vec{f}_s{}^2\right\rangle\langle\kappa\rangle - \left\langle \vec{f}_s{}^2\kappa\right\rangle\right), \tag{1}$$

where κ is the coupling term in the PI effective potential

$$\kappa = \sum_{s=1}^{P}\frac{m\omega_P^2\left(\vec{q}_{i+1}-\vec{q}_i\right)^2}{2}. \tag{2}$$

FIRST-ORDER CUMULANT EXPANSION OF THE TI APPROACH

The partition function within the Takahashi and Imada (TI) approach is

$$Z_{\rm TI} = A\int dq_1\ldots dq_P\, e^{-\beta U_{\rm eff}(\{\vec{q}_s\})}e^{-\beta U_{\rm TI}(\{\vec{q}_s\})}, \tag{3}$$

where

$$U_{\rm TI} = \frac{\hbar^2\beta^2}{24P^3}\sum_{s=1}^{P}\frac{1}{m}\vec{f}_s{}^2. \tag{4}$$

This partition function can be rewritten as

$$Z_{\rm TI} = \frac{Z_{\rm PI}}{Z_{\rm PI}}Z_{\rm TI} = Z_{\rm PI}\left\langle e^{-\beta U_{\rm TI}(\{\vec{q}_s\})}\right\rangle_{\rm PI}, \tag{5}$$

where

$$Z_{\rm PI} = A\int dq_1\ldots dq_P\, e^{-\beta U_{\rm eff}(\{\vec{q}_s\})}, \tag{6}$$

and the average $\langle\ldots\rangle_{\rm PI}$ means the average over the second-order distribution.

Now we replace the average in Eq. (5) with a first-order cumulant expansion, which gives

$$Z_{\rm TI} \simeq Z_{\rm PI}e^{-\beta\langle U_{\rm TI}(\{\vec{q}_s\})\rangle_{\rm PI}}. \tag{7}$$

The right side of Eq. (7) coincides with the $Z_{\rm PPI}$ partition function proposed in this Letter. This fact nevertheless does not answer the question which partition function (3) or (7) describes the properties of the original quantum system more accurately at finite number of beads. As it is shown in this Letter the $Z_{\rm PPI}$ form of the partition function can be also obtained as a quasi-classical correction to the second-order PI partition function. In fact, there is a qualitative difference between the proposed method and the TI approach. Within the TI scheme first the fourth-order decomposition of the exponential of the Hamiltonian is applied to correct the commutation properties of kinetic and potential-energy operators and after that the Trotter expansion is used to diminish the higher order terms which were not included. Within the developed approach we first make the system more classical using the second-order decomposition of the exponential of the Hamiltonian and applying the Trotter expansion. After that we derive a correction to the obtained PI partition function to include higher-order quantum effects.

SECOND-ORDER CUMULANT EXPANSION OF THE TI APPROACH

In the same manner as the first-order cumulant expansion of the TI approach the second-order cumulant expansion (SCE) can be derived. After necessary mathematical manipulations the corresponding correction to the total energy can be written in the form

$$\Delta E_{SCE} = \frac{\hbar^4 \beta^6}{1152 P^6 m^2} \sum_{s,s'} \left[2 \left(\left\langle \vec{f}_s^{\,2} \right\rangle \langle \epsilon \rangle - \left\langle \vec{f}_s^{\,2} \epsilon \right\rangle \right) \left\langle \vec{f}_{s'}^{\,2} \right\rangle - \left(\left\langle \vec{f}_s^{\,2} \vec{f}_{s'}^{\,2} \right\rangle \langle \epsilon \rangle - \left\langle \vec{f}_s^{\,2} \vec{f}_{s'}^{\,2} \epsilon \right\rangle \right) - \frac{6}{\beta} \left(\left\langle \vec{f}_s^{\,2} \vec{f}_{s'}^{\,2} \right\rangle - \left\langle \vec{f}_s^{\,2} \right\rangle \left\langle \vec{f}_{s'}^{\,2} \right\rangle \right) \right].$$

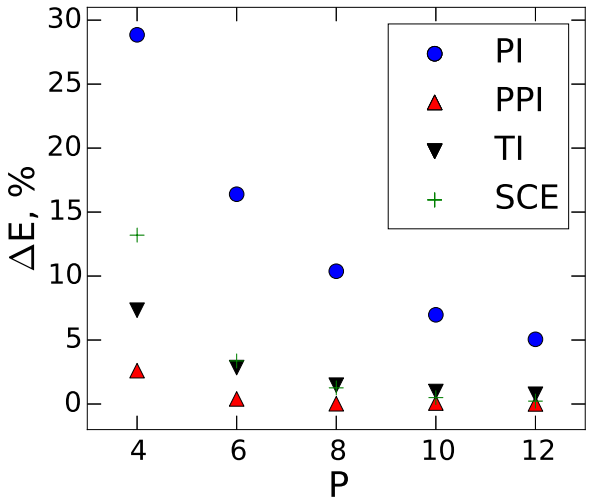

FIG. 1. The relative error in the NQF contribution to the total energy of 1D double-wall potential (DWP) at fixed temperature. The results are shown as a function of the number of beads with respect to the converged value. Blue circles are the results of the conventional PIMD approach (PI), red triangles up correspond to the developed method (PPI), black triangles down are the results of the Takahashi and Imada (TI) [1] Monte Carlo simulations, and green pluses are the results of the second-order cumulant expansion (SCE) of the TI partition function. The parameters of simulations are: $\Delta = 1$, $d = 0.5$, and $T = 1.2$.

Figure 1 shows the performance of the second-order cumulant expansion in comparison with the conventional PI approach, developed PPI method, and Takahashi and Imada (TI) approach. As can be seen SCE does not improve the accuracy as compared to the PPI correction. An interesting observation here is the relatively slow convergence of the cumulant expansion to the results of the original TI scheme. This fact is explained by the increasing power in which forces enter high-order expansion terms. Being large in the systems with pronounced quantum behavior forces significantly slow down the convergence of the cumulant expansion of the TI partition function.

[1] M. Takahashi and M. Imada, *J. Phys. Soc. Japan*, 1984, **53**, 3765–3769.