Molecular quantum dynamics: Exercise series 13

Problem 1: Virial estimator for energy

In the lecture, I derived the path integral representation for the partition function at inverse temperature $\beta = 1/(k_B T)$:

$$Q_{\mathrm{PI}}(\beta, N) = \left(\frac{mN}{2\pi\hbar^2\beta}\right)^{N/2} \int dq_1 \cdots \int dq_N e^{-\beta V_{\mathrm{eff}}(q)},$$

where N is the number of imaginary time slices (or "path integral beads" in the jargon of PIMC or PIMD communities) and

$$V_{\mathrm{eff}}(q) = \frac{mN}{2\hbar^2\beta^2} \sum_{j=1}^{N} (q_j - q_{j-1})^2 + \frac{1}{N} \sum_{j=1}^{N} V(q_j)$$

is the **effective potential**. I also showed you that to evaluate the quantum thermal energy $E(\beta)$, one needs to average a so-called **estimator** $E_{\mathrm{est.}}(\beta, N)$ for energy over different configurations of the ring polymer. I derived the simplest such estimator, called **thermodynamic estimator**,

$$E_{\mathrm{th.\ est.}}(\beta, N) = \frac{N}{2\beta} - \frac{mN}{2\hbar^2\beta^2} \sum_{j=1}^{N} (q_j - q_{j-1})^2 + \frac{1}{N} \sum_{j=1}^{N} V(q_j),$$

which however, suffers from slow convergence due to large statistical errors which grow with N as one approaches the quantum limit $N \to \infty$.

Exercise. Employ the change of variables $x_j := q_j/\sqrt{\beta}$ to express the partition function in terms of x_j instead of q_j, $j = 1, \ldots, N$, and use the new but equivalent form of Q to derive the so-called **virial estimator** $E_{\mathrm{vir.\ est.}}(\beta, N)$ for energy, in which the statistical errors are drastically reduced. *Hint*: Remember that $E(\beta) = -d \ln Q(\beta)/d\beta$. Discuss why $E_{\mathrm{vir.\ est.}}(\beta, N)$ is expected to reduce statistical errors.