Without Compromising Efficiency and Accuracy: Solving the Nuclear Schrödinger Equation using Path Integral Monte Carlo Simulation with Modified Shepard Interpolation

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Feynman's path integral formalism describes nuclei in a quantum system as "ring polymers", which describe the closed quantum paths the system can take. Thermodynamic properties, described in terms of the thermal density matrix, are calculated by sampling all possible paths using Monte Carlo simulation, which are weighted by their action. The convergence of the method, that is, the number of beads for each ring polymer and the number of Monte Carlo steps taken, can be improved by using more accurate description of the action (Symplectic schemes). We compare the convergence efficiency between four current existing action formalisms, primitive approximation (PA), Takahashi-Imada (TI), Suzuki factorisation (SF), and Chin approximation (CA) formalisms. [3] We further numerically optimised the parameters for SF and CA schemes, by doing so, lower order commutators roughly cancel in order to achieve higher order numerical accuracy and improve the computational efficiency. We apply the resulting schemes to three realistic systems, H2O,[1] HCN-HNC, [2] and CH4. The first two systems adopted relatively inexpensive however spectroscopically accurate PESs in order to demonstrate the convergence efficiency between four formalisms. The PES of methane was constructed by using modified Shepard interpolation, [4] that is, as a weighted sum of second order Taylor expansion about a set of PES data points at regions of interest, calculated at a given level of electronic structure theory, the technique for combining modified Shepard interpolation and path integrals formalisms is novel, and we intend to demonstrate that it is efficient and potentially accurate to calculate the total internal energy for systems larger than four atoms.

References

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