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Ab initio hybrid Monte Carlo and *ab initio* path integral hybrid Monte Carlo simulations using an auxiliary potential energy surface

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Efficiencies of the *ab initio* hybrid Monte Carlo and *ab initio* path integral hybrid Monte Carlo methods are enhanced by employing an auxiliary potential energy surface that is used to update the system configuration via molecular dynamics scheme. As a simple illustration of this method, a dual-level approach is introduced where potential energy gradients are evaluated by computationally less expensive *ab initio* electronic structure methods.

Computer simulations via molecular dynamics (MD) and Monte Carlo (MC) methods are widely used in a variety of fields ranging from drug design to materials science.¹ Instead of using empirical force fields, *ab initio* molecular dynamics or *ab initio* Monte Carlo method, which solves the electronic Schrödinger equation for nuclear potential energy (or its derivatives) as needed, is now being widely used to investigate static and also dynamic properties of molecular systems from first principles. The computational cost for such *ab initio* simulations is, however, still highly expensive when combined with statistical simulations where 10^5 - 10^6 simulation steps are usually required, thus limiting their applicability to relatively small system sizes.

Recently, we have proposed an efficient sampling scheme for *ab initio* Monte Carlo calculations by employing an approximate potential constructed by an interpolation method and it has been shown that the computational cost is reduced significantly by almost an order of magnitude.² In this letter, we introduce a simple scheme for *ab initio* hybrid Monte Carlo (HMC) method, which enhances sampling efficiency by utilizing an auxiliary potential for updating the system configuration. This is similar in spirit to the approximate potential method^{3,4} reported previously.

The hybrid Monte Carlo method combines the advantages of both the MD and MC methods, allowing the global update of the system configuration with reasonable acceptance ratio.^{5,6} It is an exact method and does not suffer from the finite step-size errors of MD simulations. In an update process of the system configuration, the time-reversible and area-preserving MD algorithm needs to be used to ensure the detailed balance and the commonly used velocity Verlet algorithm satisfies this requirement. The initial momenta $\mathbf{P}^{(i)}$ are drawn randomly from the Boltzmann distribution at the given inverse temperature β and after a fixed number of MD steps, the final configuration $\mathbf{R}^{(i)}$ is accepted according to the following criterion

$$\min \left[1, \frac{\rho(\mathbf{R}^{(i)}) \exp(-\beta T(\mathbf{P}^{(i)}))}{\rho(\mathbf{R}^{(i)}) \exp(-\beta T(\mathbf{P}^{(i)}))} \right] = \min \left[1, \frac{\exp(-\beta H(\mathbf{P}^{(i)}, \mathbf{R}^{(i)}))}{\exp(-\beta H(\mathbf{P}^{(i)}, \mathbf{R}^{(i)}))} \right] \quad (1)$$

where $\mathbf{P}^{(i)}$ are momenta at the final configuration and ρ is the target distribution. In this study, ρ is given as $\exp(-\beta V)$, therefore the acceptance probability is rewritten as in the right-hand side of eq. (1)

In this letter, we propose a method which employs a computationally inexpensive potential energy surface V_{low} and its gradient for an MD update part, but uses the same acceptance probability given above to ensure that the target distribution is still determined under the potential V . Note that $\mathbf{P}^{(i)}$ are the momenta which evolve under the potential V_{low} from initial phase space variables $\mathbf{P}^{(i)}$ and $\mathbf{R}^{(i)}$. In the context of *ab initio* simulations, one can use energy gradients of less expensive *ab initio* potentials for an MD update part. The numerical evaluation of the energy gradients requires additional computational cost, which could be several times higher than that of the energy calculation, thus there would be a great saving in computational effort if the above approach is utilized. For example, the potential energies are calculated at the level of CCSD(T)/cc-pVTZ, but energy gradients of HF/cc-pVDZ level are used for an MD update. It nevertheless gives the correct distribution determined by CCSD(T)/cc-pVTZ.

As a simple illustration of the present method, we first show the results of *ab initio* HMC calculations on an H₂O molecule at $T = 300$ K. The target level of *ab initio* method is set to MP2/cc-pVDZ. For simplicity, a single step was used for an MD part in one MC cycle and a total of 50,000 MC steps were taken. *Ab initio* MD calculations at a constant temperature of 300 K were also carried out for comparison at the level of MP2/cc-pVDZ using the massive Nosé-Hoover thermostat chains. All *ab initio* calculations were performed using the MOLPRO2006 package.⁷

Figure 1 shows the acceptance ratio as a function of a time step by employing various auxiliary potentials obtained from different (low-level) *ab initio* methods and basis sets. It is seen that good acceptance ratio is obtained even when the time step is increased to 1.5 ~ 2.0 fs. Figure 2 shows the statistical errors of potential energies (σ_V) and OH bond lengths (σ_R) as a function of acceptance ratio. A good convergence is achieved when the acceptance ratio is around 40 ~ 60 %. The statistical errors are reduced in most cases in comparison to *ab initio* MD simulations with $\Delta t = 0.1$ fs. Considering that the CPU time decreases dramatically as a level of *ab initio* calculations is lowered for computing gradients and that the efficiency of the method is proportional to the inverse of the square of statistical errors, a significant computational saving is achieved. Note that increasing a time step of *ab initio* MD calculations will certainly reduce the statistical errors, but will induce large systematic errors due to finite step-size. In *ab initio* MD, the total energy deviates

from its initial value by ~ 1.2 kcal/mol for the entire run when the time step is increased to 0.5 fs.

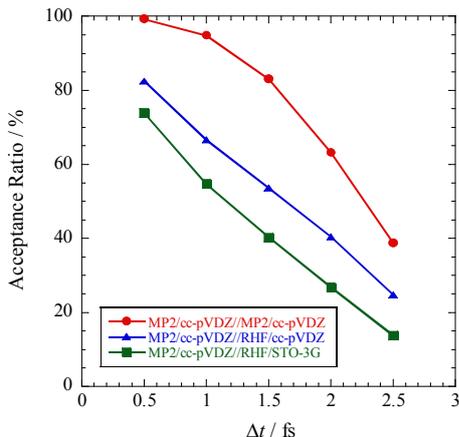


Figure 1. Acceptance ratio as a function of time step in *ab initio* HMC simulation. MP2/cc-pVDZ//RHF/STO-3G indicates that the target distribution is calculated at the level of MP2/cc-pVDZ and the energy gradients are obtained by RHF/STO-3G for an MD update of the configuration.

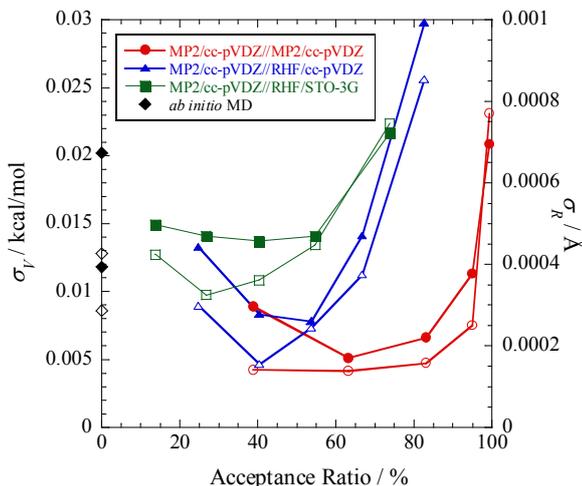


Figure 2. Statistical errors of potential energies (filled symbols) and OH bond lengths (hollow symbols) as a function of acceptance ratio. The errors are estimated by the block averages using 50 blocks in both the *ab initio* HMC and MD simulations. The errors of *ab initio* MD calculations are shown at zero, where the higher (lower) values correspond to simulations with $\Delta t = 0.2$ fs ($\Delta t = 0.1$ fs). The average values of potential energy and OH bond length taken from the run of minimum errors are $\langle V \rangle = 0.906$ kcal/mol and $\langle R \rangle = 0.9678$ Å, respectively.

Ab initio path integral hybrid Monte Carlo calculations, which incorporate quantum effects of nuclei,⁸ were also performed for H₂O and H₃O⁺ molecules with 16 imaginary-time slices and compared with the *ab initio* path integral MD simulations⁹ (MP2/cc-pVDZ) at a constant temperature of 300 K. The normal mode coordinates¹⁰ were used in all calculations and a total of 50,000 steps were taken for both path integral HMC and path integral MD calculations. The results obtained are shown in Table I and the performance is essentially similar to that obtained in *ab initio* HMC simulations. Again, *ab initio* path integral HMC calculations

with auxiliary potentials offered a significant increase in computational efficiency.

It is noted that the similarity of the target and auxiliary potentials is of course a key factor which determines the efficiency of the method. One needs to find a compromise between accuracy of an auxiliary potential and computational cost for evaluating energy gradients. The one of the notable advantages of the present method is again that it does not require energy gradients calculations for target (high-level) *ab initio* potentials. This is particularly useful for simulations with highly correlated electronic structure methods such as CCSD(T), where the evaluation of energy gradients is highly demanding or the module for analytical gradients is not available.

Table I. Acceptance ratio and statistical errors of potential energies (σ_V in units of kcal/mol) and OH bond lengths (σ_R in units of Å) for H₂O and H₃O⁺ molecules in *ab initio* path integral HMC and MD simulations. The average values of potential energy and OH bond length taken from the run of minimum errors are $\langle V \rangle = 6.022$ kcal/mol and $\langle R \rangle = 0.9811$ Å for H₂O, and $\langle V \rangle = 10.013$ kcal/mol and $\langle R \rangle = 1.0019$ Å for H₃O⁺.

H ₂ O	Δt	%	$\sigma_V \times 10^{-2}$	$\sigma_R \times 10^{-4}$
MP2/cc-pVDZ//MP2/cc-pVDZ	1.0	94.4	3.0	3.2
	2.0	58.4	1.8	1.7
MP2/cc-pVDZ//RHF/cc-pVDZ	1.0	67.2	3.8	3.9
	2.0	38.6	2.8	2.5
MP2/cc-pVDZ//RHF/STO-3G	1.0	57.0	4.3	4.3
	2.0	29.5	3.0	3.2
path integral MD	0.1	—	12.5	5.9
	0.2	—	4.6	4.5
H ₃ O ⁺	Δt	%	$\sigma_V \times 10^{-2}$	$\sigma_R \times 10^{-4}$
MP2/cc-pVDZ//MP2/cc-pVDZ	1.0	93.8	4.7	3.3
	2.0	55.8	3.2	2.6
MP2/cc-pVDZ//RHF/cc-pVDZ	1.0	65.5	6.4	6.5
	2.0	35.2	3.7	2.1
MP2/cc-pVDZ//RHF/STO-3G	1.0	73.1	5.6	4.6
	2.0	43.0	3.6	2.7
path integral MD	0.1	—	15.8	5.7
	0.2	—	9.5	4.5

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