Nonlocal pseudopotentials and time-step errors in diffusion Monte Carlo [1]

Tyler A. Anderson and C. J. Umrigar
Laboratory of Atomic and Solid State Physics,
Cornell University, Ithaca, NY
taa65@cornell.edu

Abstract

We introduce an additional Metropolis-Hastings accept-reject step after each T-move, which further reduces the time-step error by sampling $|\Psi_0|^2$ when $\Psi_{\mathrm{T}} \to \Psi_0$.

Introduction

- Nonlocal pseudopotentials lead to an additional sign problem in DMC.
- To avoid this, either the locality approximation (LA) or the T-moves approximation [2, 3] are used.
- T-moves typically has a larger time-step error than LA. We remedy this by adding a Metropolis-Hastings accept-reject step.

Definitions

We describe the usual DMC approach, without any proposed modifications.

- The Green's function is split into parts using local and nonlocal components of the pseudopotential.

$$G(\mathbf{R}^{'},\mathbf{R}) \approx \int d\mathbf{R}^{''} \underbrace{G_L(\mathbf{R}^{'},\mathbf{R}^{''})}_{\text{local}} \underbrace{T(\mathbf{R}^{''},\mathbf{R})}_{\text{nonlocal}}, \tag{1}$$

- Part using local component of pseudopotential has familiar drift-diffusion and reweighting terms:

$$G_L(\mathbf{R}^{'},\mathbf{R}) \approx \underbrace{\frac{1}{(2\pi\tau)^{3/2}} e^{\frac{-(\mathbf{R}^{'}-\mathbf{R}-\bar{\mathbf{V}}(\mathbf{R})\tau)^2}{2\tau}}}_{\text{drift \& diffusion}} \underbrace{e^{\tau_{\mathrm{eff}}(E_T-(\bar{E}_L(R')+\bar{E}_L(R))/2)}}_{\text{reweighting}}, \tag{2}$$

  and is followed by a Metropolis-Hastings accept-reject step.

- Part using nonlocal component of pseudopotential responsible for nonlocal T-moves:

$$T(\mathbf{R}^{'},\mathbf{R}) = \frac{\Psi(\mathbf{R}^{'})}{\Psi(\mathbf{R})}\langle \mathbf{R}^{'}|e^{-\tau\hat{v}_{\mathrm{NL}}}|\mathbf{R}\rangle \;=\; \prod_{i=1}^{N_{\mathrm{elec}}} t(\mathbf{R}_i^{\prime},\mathbf{R}_i,\tau). \tag{3}$$

Improved Reweighting Term

- Near the nodes of Ψ_{T}, $E_L(\mathbf{R}) \propto \frac{1}{d}$ and $\mathbf{V}(\mathbf{R}) \propto \frac{1}{d}$.
- To reduce the time-step error, must average both the local energy and the local velocity over τ [4]. This gives $\bar{E}_L(\mathbf{R})$ and $\bar{\mathbf{V}}(\mathbf{R})$ in previous section.
- Here we use an alternate reweighting/averaging scheme for $E_L(\mathbf{R})$ described in more detail in our paper.

Accept-Reject Step for T-Moves

- The T-moves probability is viewed as a Metropolis-Hastings proposal probabitlity (similar to the drift-diffusion probablity in the usual DMC algorithm), whose acceptance is given by:

$$A(\mathbf{R}_i^{\prime},\mathbf{R}_i) = \min\left\{1, \frac{\Psi_{\mathrm{T}}^2(\mathbf{R}_i^{\prime})}{\Psi_{\mathrm{T}}^2(\mathbf{R}_i)}\frac{P(\mathbf{R}_i,\mathbf{R}_i^{\prime})}{P(\mathbf{R}_i^{\prime},\mathbf{R}_i)}\right\} \;=\; \min\left\{1, \frac{\int d\mathbf{R}_i^{\prime\prime}\, t(\mathbf{R}_i^{\prime\prime},\mathbf{R}_i)}{\int d\mathbf{R}_i^{\prime\prime}\, t(\mathbf{R}_i^{\prime\prime},\mathbf{R}_i^{\prime})}\right\}. \tag{4}$$

- In the $\Psi_T \to \Psi_0$ limit, $|\Psi_0|^2$ is sampled for all τ.

Summary of Improved Algorithm

1. For each electron in the walker, propose T-moves with the probabilities in Eq. 3 and accept them with the probabilities in Eq. 4.
2. For each electron in the walker, perform the drift, diffusion and accept-reject steps as usual.
3. Calculate the local energy at the current position and use this and the saved local energy from the previous Monte Carlo (MC) step to reweight the walker. No additional computation is needed at each step until a T-move is accepted.

Results

- Our modifications to the reweighting term and T-moves consistently reduce the time-step error for multiple systems, especially for operators that do not commute with the Hamiltonian (see Fig. 2), while leaving $\tau = 0$ limit unchanged..
- The improved reweighting term reduces hump near $\tau = 0$ limit in the locality approximation, aiding extrapolation.

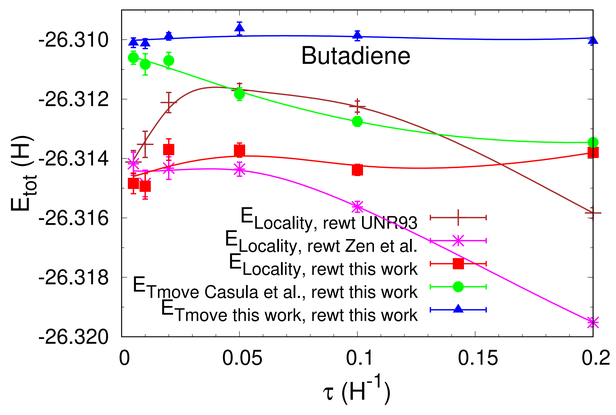

Figure 1: Time-step errors of the total energy. The curves labeled "UNR93" and "Zen et al." employ the reweighting factors of Refs. [4] and [5] respectively. The three locality approximation curves must extrapolate to the same energy at $\tau = 0$, as must the two T-moves approximation curves. Both the reweighting factor and the modified T-moves algorithm proposed in this work contribute to reducing the time-step errors.

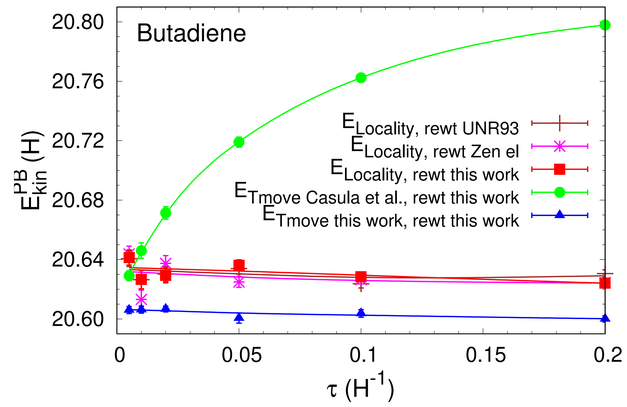

Figure 2: Same as Fig. 1 but for the kinetic energy. Note that the T-moves curves should converge to the same value at $\tau = 0$, though this is to some extent obscured by the statistical errors and the steepness of the kinetic energy curves.

Conclusions

- The proposed modifications greatly reduce the time-step error, and enable one to use much larger τ than in the unmodified algorithm.
- With our modifications, the time-step error of observables not commuting with the Hamiltonian is greatly reduced, especially when using good Ψ_{T}.
- Near $\tau = 0$, the curves obtained using our improvements are nearly linear, aiding extrapolation.
- Efficiency of our improved T-moves is slightly greater than that of the locality approximation, due to decreased autocorrelation time of T-moves.

References

[1] Tyler A. Anderson and C. J. Umrigar. Nonlocal pseudopotentials and time-step errors in diffusion monte carlo. *The Journal of Chemical Physics*, 154(21):214110, 2021.

[2] Michele Casula. Beyond the locality approximation in the standard diffusion monte carlo method. *Phys. Rev. B*, 74:161102, 2006.

[3] Michele Casula, Saverio Moroni, Sandro Sorella, and Claudia Filippi. Size-consistent variational approaches to nonlocal pseudopotentials: Standard and lattice regularized diffusion Monte Carlo methods revisited. *J. Chem. Phys.*, 132(15), 2010.

[4] C. J. Umrigar, M.P. Nightingale, and K.J. Runge. A diffusion monte-carlo algorithm with very small time-step errors. *J. Chem. Phys.*, 99(4):2865–2890, 1993.

[5] Andrea Zen, Sandro Sorella, Michael J. Gillan, Angelos Michaelides, and Dario Alfe. Boosting the accuracy and speed of quantum Monte Carlo: Size consistency and time step. *Phys. Rev. B*, 93(24), 2016.

Acknowledgements

We thank Michele Casula and Claudia Filippi for discussions and comments on the manuscript, and Andrea Zen and Dario Alfe for discussions about size consistency. This work was supported in part by the AFOSR grant FA9550-18-1-0095. Computations on Si_{15} were performed on the Bridges computer at the Pittsburgh Supercomputing Center supported by NSF grant ACI-1445606, as part of the XSEDE program supported by NSF grant ACI-1548562.