Diffusion Quantum Monte Carlo With Gaussian Trial Wave Functions

Calculating Anharmonic Zero Point Energies

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Introduction

- Diffusion quantum Monte Carlo (DQMC) solves the nucelonic Schrödinger equation and gives the quantum-mechanical ground state energy to calculate the zero-point energy (ZPE).
- We use Gaussian guiding wave function to improve the convergence.
- DFTB+ is used for energy calculations.
- The goal is to improve the harmonic approximation for the ZPE

The Unguided DQMC Algorithm

- The stationary solution of the diffusion equation satisfies the imaginary-time Schrödinger equation and has the propagator
  $G(x, y; \Delta\tau) = \frac{1}{\sqrt{2\pi\Delta\tau}} e^{-(x-y)^2/(2\Delta\tau)} e^{-\Delta\tau(V(y)-E_T)}$.
- We simulate a ensemble of walkers to reach this stationary solution and the Schrödinger equation is solved.
- The propagator consists of a diffusion term $\frac{1}{\sqrt{2\pi\Delta\tau}} e^{-(x-y)^2/(2\Delta\tau)}$ and a branching term $e^{-\Delta\tau(V(y)-E_T)}$.
- The diffusion term is simulated by randomly displacing the walker from its previous position according to a Gaussian distribution.
- The branching term updates the weight of a walkers according to which the walker survives, reproduces or dies.
- The trial energy E_T is then adjusted to keep the population of walkers stable.
- With time, the trial energy E_T converges to the solution of the Schrödinger equation.

The Guiding Wave Function

- We use the harmonic approximation of the potential energy surface with the Hessian matrix.
- Gaussian guiding wave functions $\psi_{\mathrm{T}}(\mathrm{x}) = \mathcal{N}\mathrm{e}^{-\mathrm{x}^2/(2\sigma^2)}$ are placed along the normal modes.
- The width of the Gaussian is given by $\sigma^2 = \frac{1}{\omega \mathrm{m}}$, where ω^2 is the corresponding eigenvalue of the Hessian matrix.
- This extends the algorithm with a drift velocity $\mathrm{v}(\mathrm{x}) = \nabla_{\mathrm{x}}\psi_{\mathrm{T}}(\mathrm{x})$ which is added to the pure diffusion and a kinetic energy term in the local energy $\mathrm{E_L}(\mathrm{x}) = (\mathrm{H}\psi_{\mathrm{T}}(\mathrm{x}))/\psi_{\mathrm{T}}(\mathrm{x})$ which replaces the potential energy in the branching step.
- With Gaussian trial wave functions, we can calculate the drift velocity and the local energy analytically.

The Guiding Wave Function

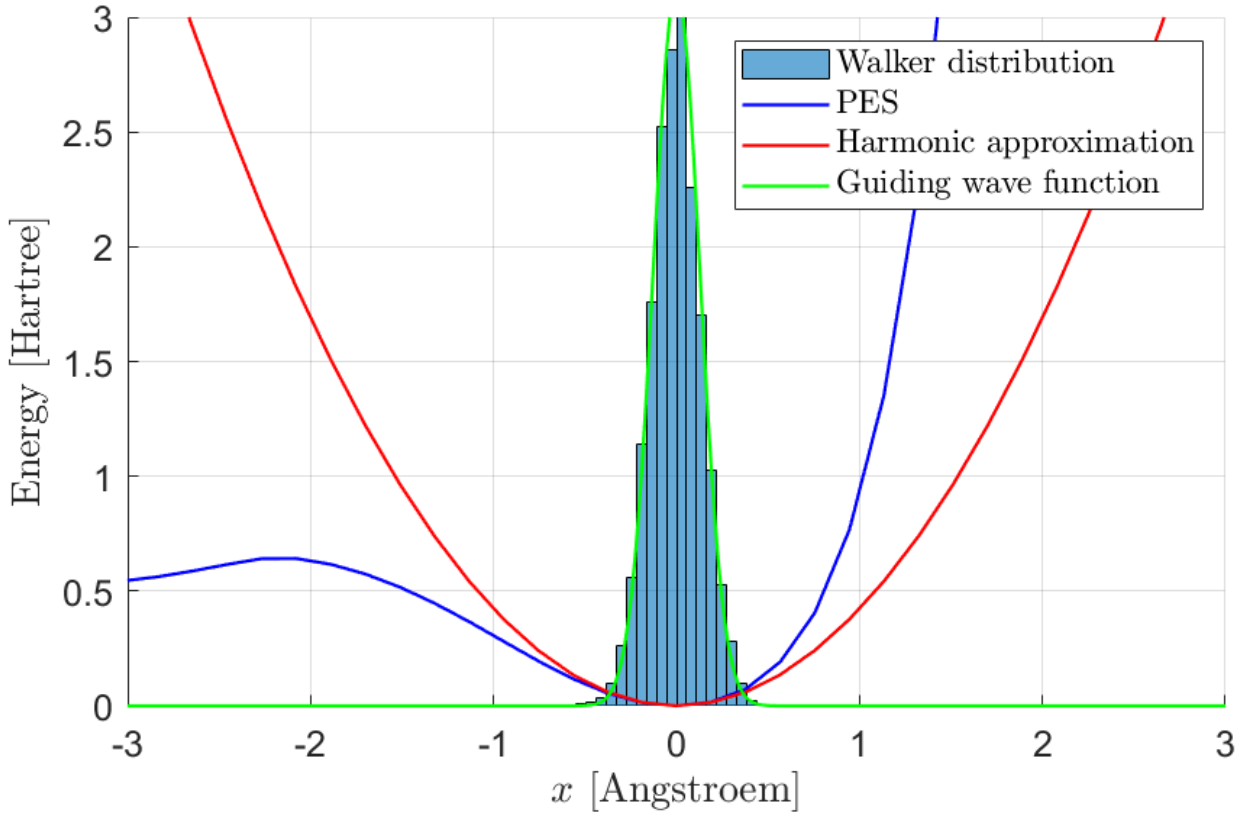

Fig. 1. Typical dimension in the coordinate system of the normal modes.

Input and Output

Input:

- Equilibrium geometry of the atoms (must not be perfect as the geometry will be optimized by DFTB+)
- Masses of the atoms

Output:

- ZPE with a statistical uncertainty
- The walker distribution give a sample of the nucleonic wave function

Results

C_2H_6 (first test case)

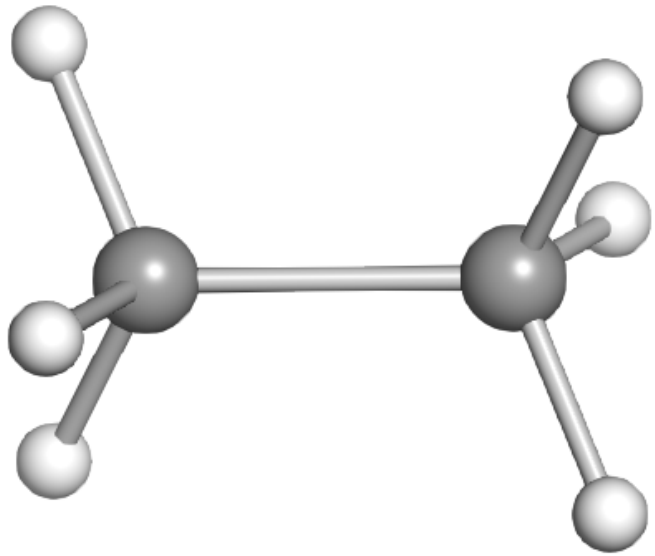

Fig. 2. Input structure of Ethane

First test case to develop the algorithm and check the result with a literature value.

Results

C_2H_6

10 simulations with 1000 walkers for 10000 time steps.

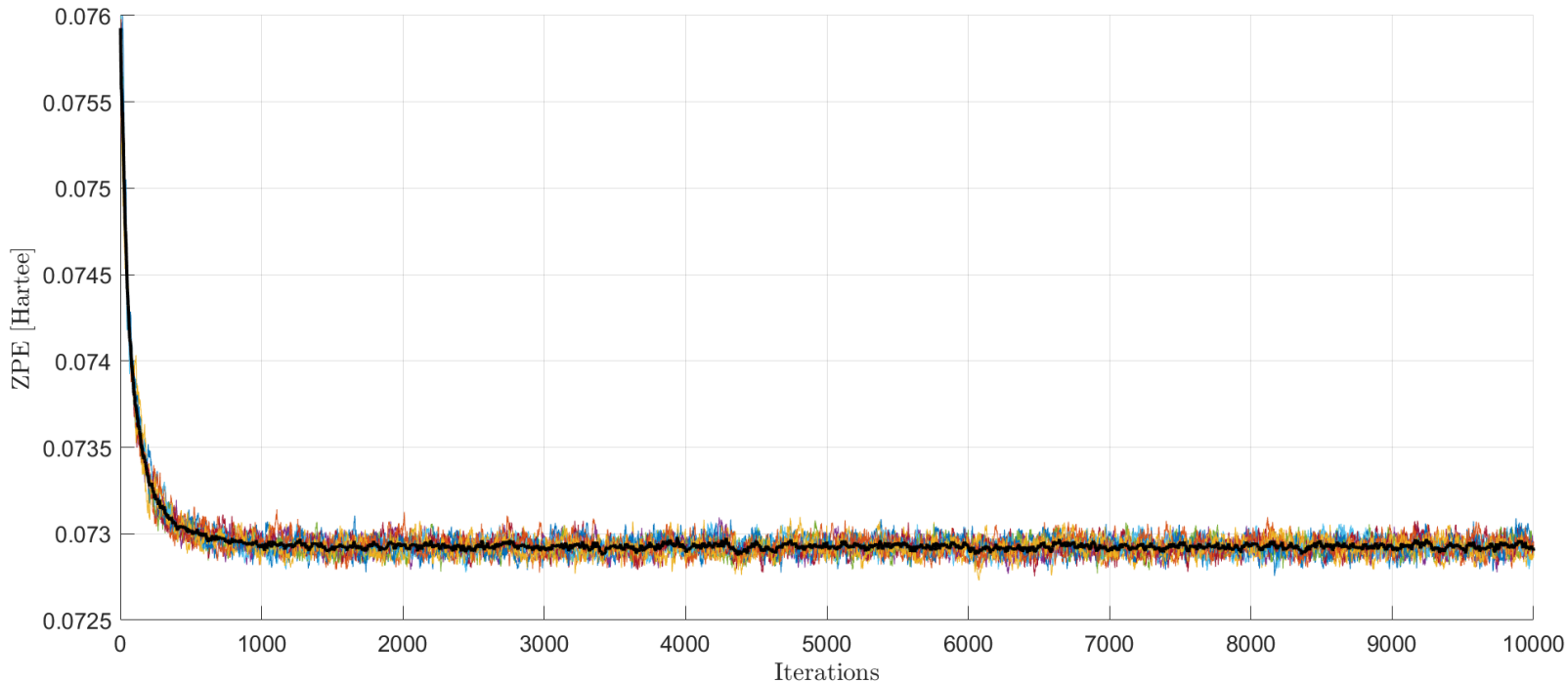

Fig. 3. ZPE convergence for C_2H_6. The black line shows the average over the 10 simulations.

ZPE = 0.07293 Hartree with a standard deviation of 0.02 mHa. The literature value is 0.073927 Hartree [1].

Results

C_2H_6

Simulation with 10000 walkers for 10000 time steps

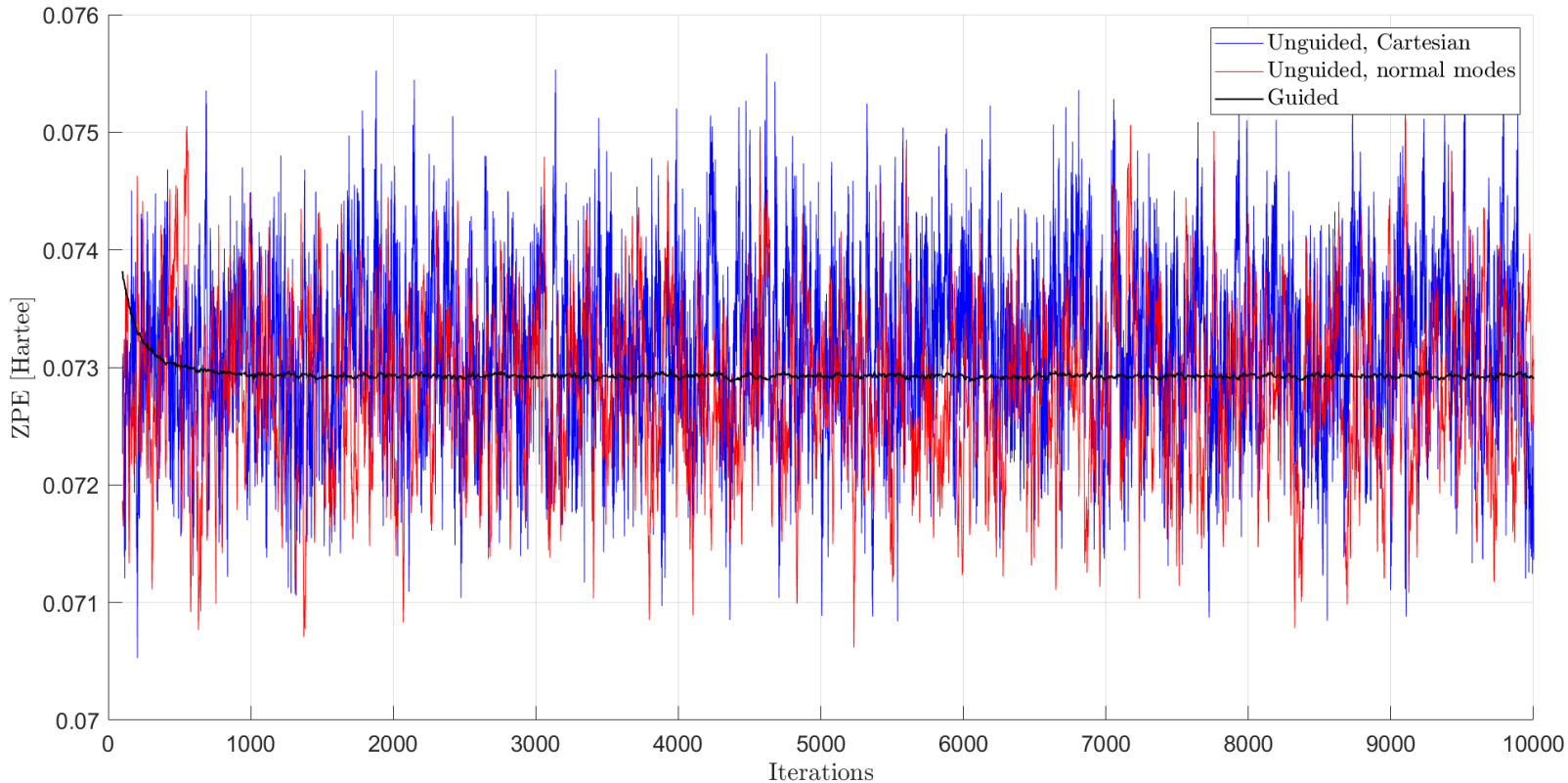

Fig. 4. Comparison between guided and unguided DQMC

The fluctuations for unguided DQMC are about 30 to 40 times larger compared to guided DQMC

Results

C_2H_6

Method	$\overline{\text{ZPE}}$ [Hartree]	ΔZPE [Hartree]
Harmonic approximation	0.07264	
Unguided, Cartesian	0.07322	0.00076
Unguided, normal modes	0.07288	0.00062
Guided	0.07293	0.00002
Ref. [1]	0.07393	
CCCBDB experimental	0.07223	
CCCBDB calculated	$0.07 - 0.08$	

Table 1: Summary of the results and literature values.
The guided DQMC needs about a fifth of the simulation time to get the same statistical uncertainty as the unguided DQMC.

Results

C_{60}

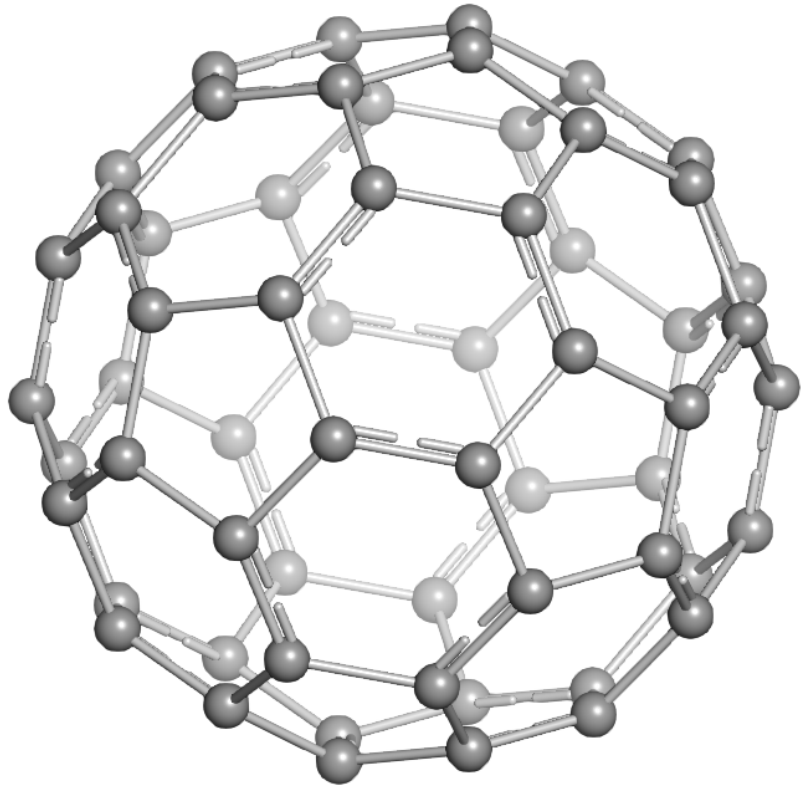

Fig. 5. Input structure of the C_{60} Buckminsterfullerene

A larger molecule to how the scaling of the algorithm with system size.

Results

C_{60}

10 simulations with 1000 walkers for 10000 time steps.

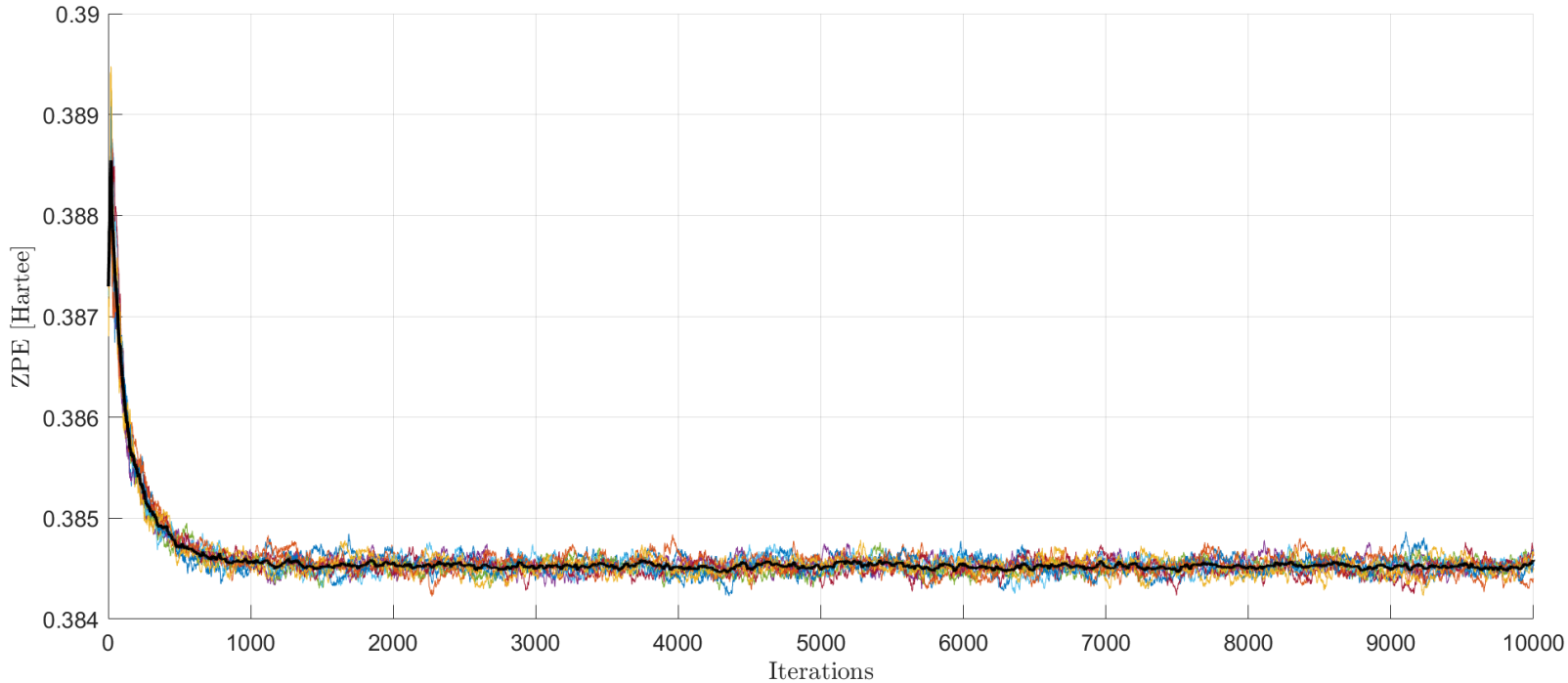

Fig. 6. ZPE convergence for C_2H_6. The black line shows the average over the 10 simulations.

The convergence behavior is similar to C_2H_6. We get a ZPE of 0.38452 Hartree with an uncertainty of 0.01 mHa. The harmonic approximation gives 0.38177 Hartree.

Results

$H_2@C_{60}$

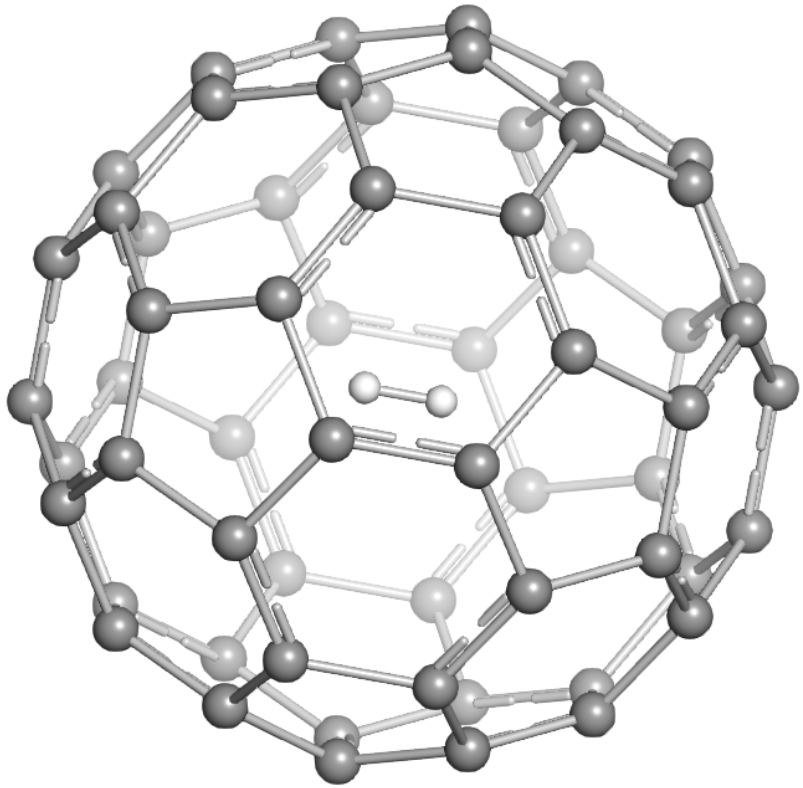

Fig. 7. Input structure of the endohedral hydrogen fullerene

The endohedral hydrogen fullerene shows strong anharmonic effects on the ZPE.

Results

$H_2@C_{60}$

The harmonic approximation fails for $H_2@C_{60}$.

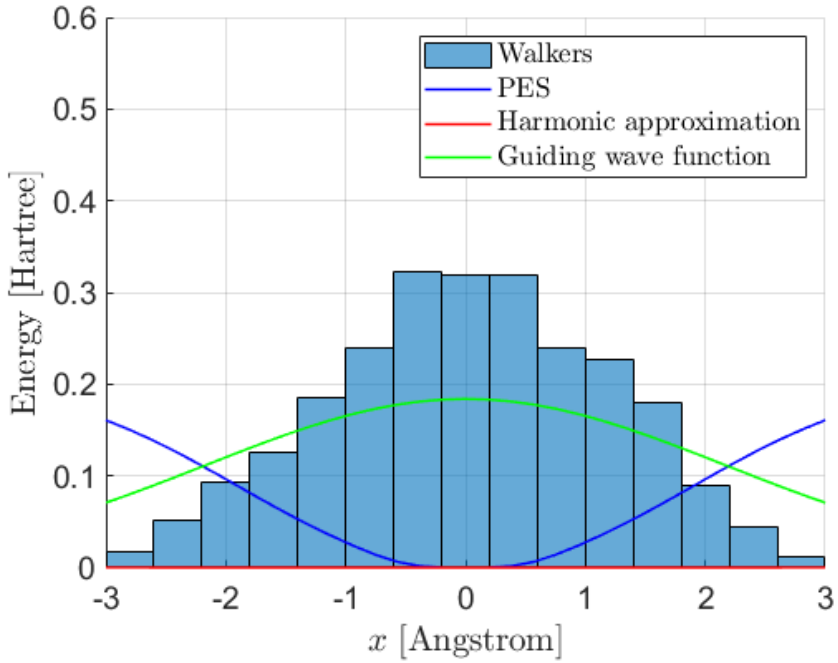

Fig. 8. Softest vibrational mode of $H_2@C_{60}$

Results

$H_2@C_{60}$

Simulation with 1000 walkers for 250000 time steps

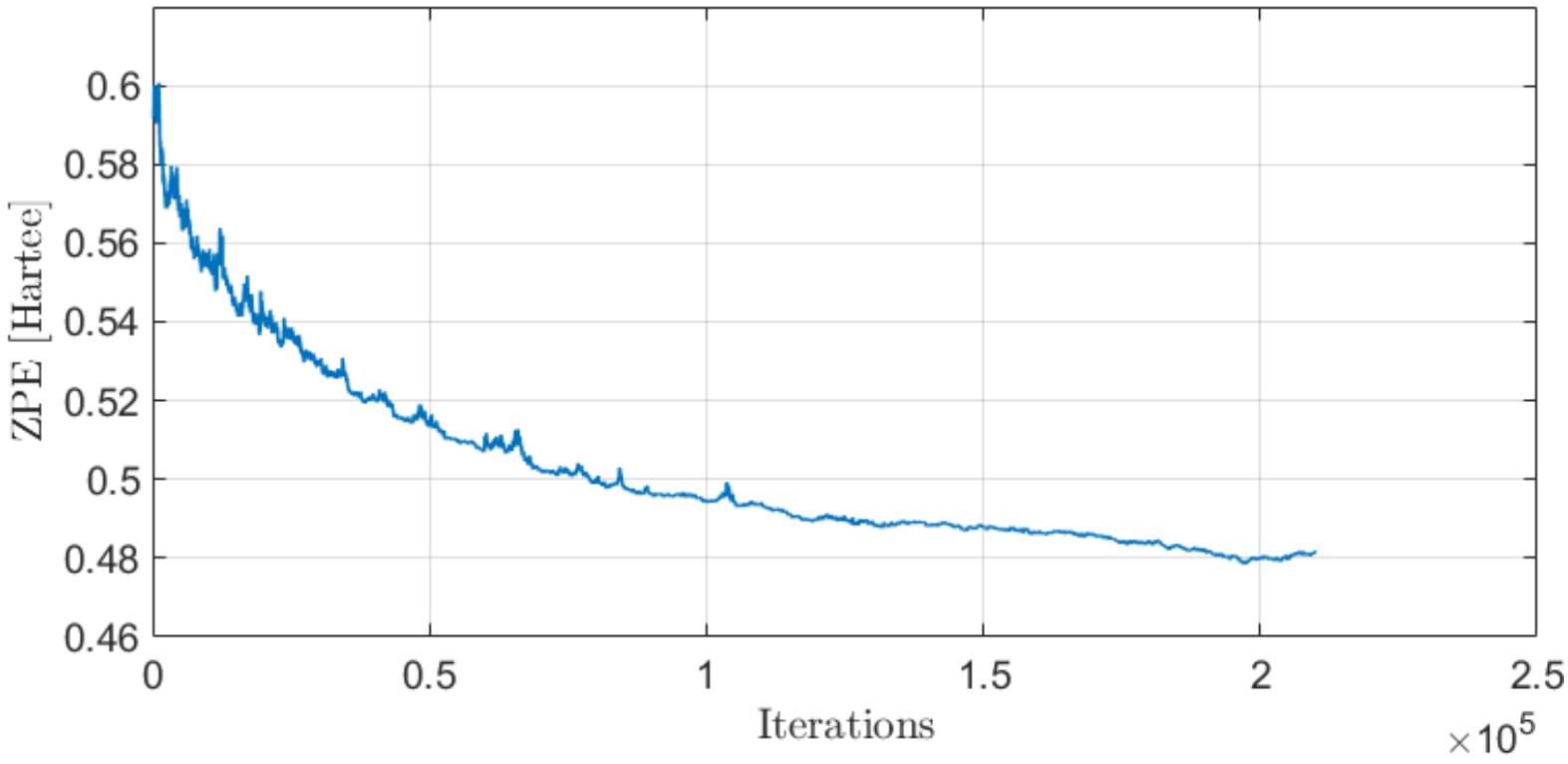

Fig. 9. ZPE convergence of $H_2@C_{60}$ (simulation still running)

ZPE $\approx$ 0.48 Hartree which is about 20% higher than the harmonic approximation of 0.3984 Hartree.

Results

$H_2@C_{60}$

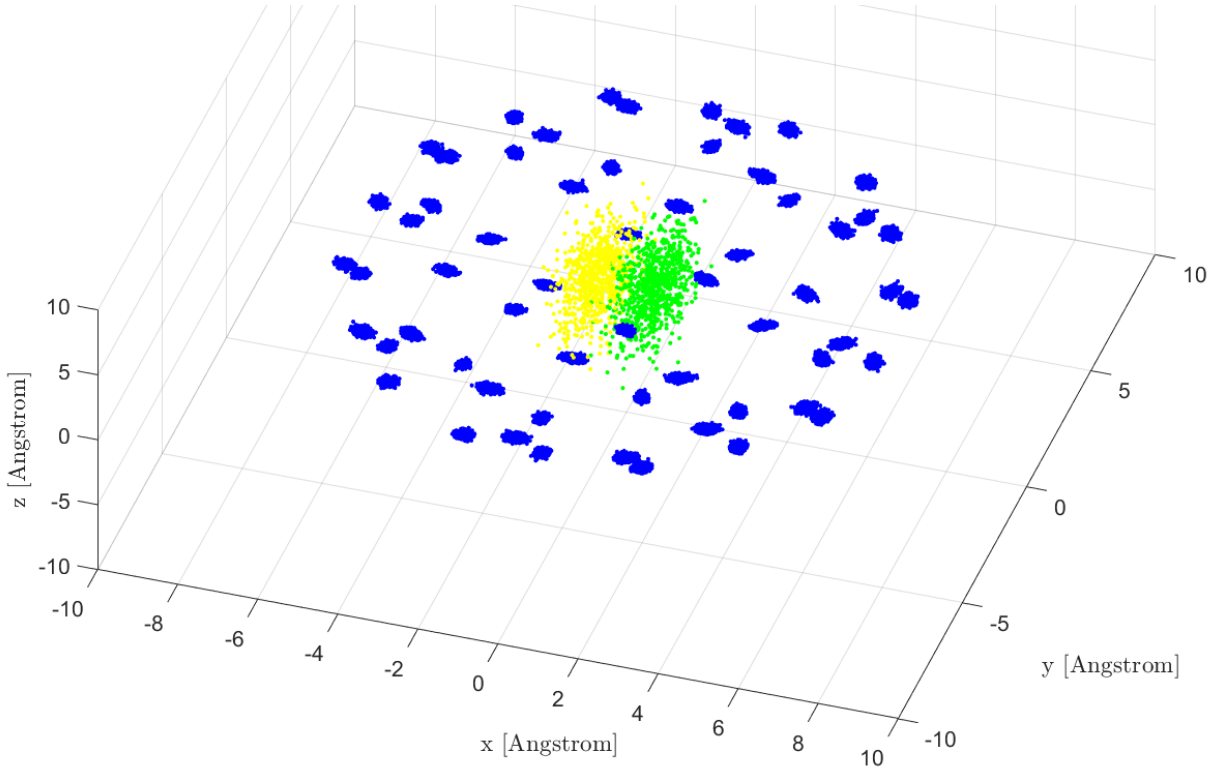

Fig. 10. Final positions of the walkers after the simulation.

Conclusions

- DQMC is a very stable and versatile method to calculate the ZPE.
- The convergence does not depend on the size of the system but on how good the harmonic approximation is.
- For C_2H_6 and C_{60} the harmonic approximation is good and we converge within 2000 steps.
- For $H_2@C_{60}$ the harmonic approximation fails and we need over 200000 steps to converge, but we can get large anharmonic corrections to the ZPE.

Further Research

Marco and the group will continue our work on guided DQMC, adapt the algorithm to periodic structures and compute ZPEs for molecular crystals.

References

Amir Karton, Branko Ruscic, and Jan M.L. Martin.
Benchmark atomization energy of ethane: Importance of accurate zero-point vibrational energies and diagonal born–oppenheimer corrections for a 'simple' organic molecule.
Journal of Molecular Structure: THEOCHEM, 811(1):345–353, 2007.
Computational Organic Chemistry.