Guided Diffuison Quantum Monte Carlo for Calculating Zero Point Energies

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Introduction

- DQMC solves the Schrödinger equation and gives the quantum-mechanical ground state energy to then calculate the zero point energy (ZPE).
- A Gaussian guiding wave function is used to improve the performance.
- DFTB+ is used for calculation the energy.[1]

The Unguided DQMC Algorithm [2]

- The stationary solution of the diffusion equation satisfies the Schrödinger equation and has the propagator $G(x, y; \Delta t) = \frac{1}{\sqrt{2\pi\Delta t}} e^{-(x-y)^2/(2\Delta t)} e^{-\Delta t(V(y)-E_T)}$.
- We simulate a ensemble of walkers to reach this stationary solution and the Schrödinger equation is solved.
- The propagator consists of a diffusion term $\frac{1}{\sqrt{2\pi\Delta t}} e^{-(x-y)^2/(2\Delta t)}$ and a branching term $e^{-\Delta t(V(y)-E_T)}$.
- 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.

The Guiding Wave Function [3]

- Harmonic approximation of the potential energy surface with the Hessian matrix.
- Gaussian guiding wave functions along the normal modes $\psi_{\mathrm{T}}(\mathrm{x}) = \mathcal{N} \mathrm{e}^{-\mathrm{x}^2/(2\sigma^2)}$.
- 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 is incorporated to 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.

The Guiding Wave Function

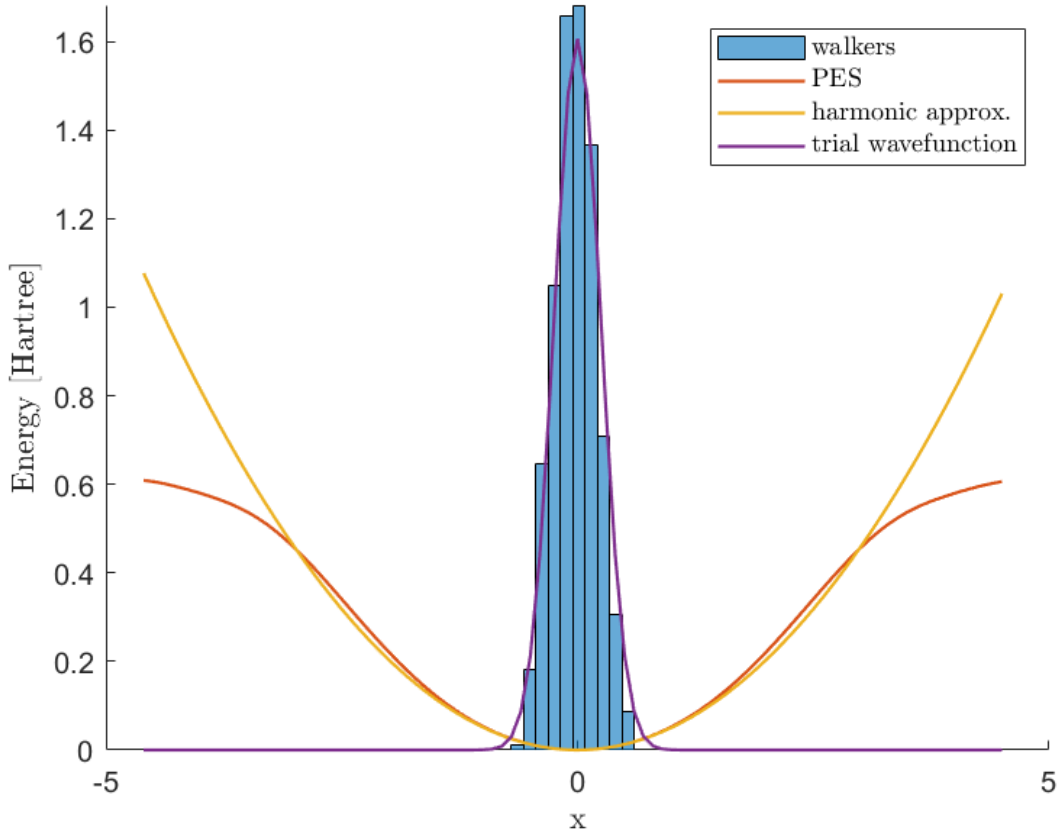

Fig. 1. Typical dimension in the coordinate system of the normal modes.

Input and Output

Input:

- Equilibrium geometry of the atoms (must not be perfectly accurate as geomety will be optimized by DFTB+ in the beginning)
- Masses of the atoms

Output:

- Zero point energy
- Walker positions give a sample of the nucleonic wave function

Results

C_2H_6 (first test case)

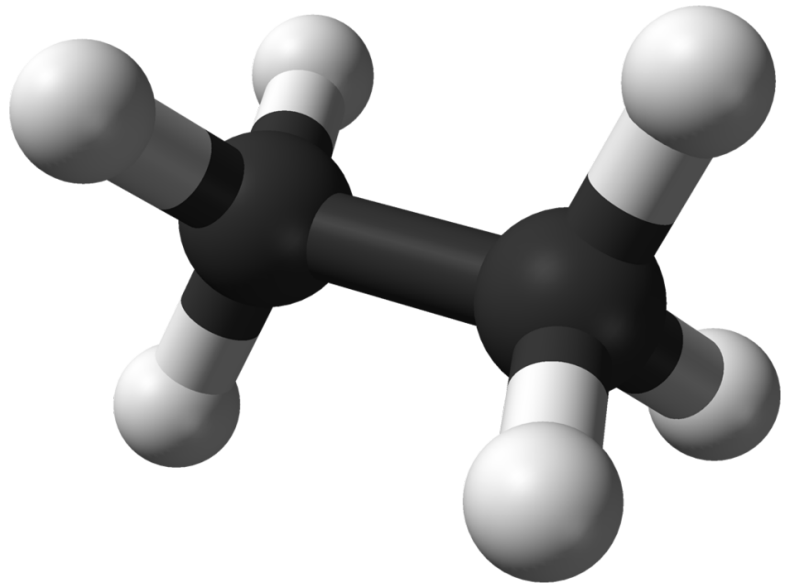

Fig. 2. Input structure of Ethane

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

Results

C_2H_6 (first test case)

Simulation with 1000 walkers for 2000 time steps

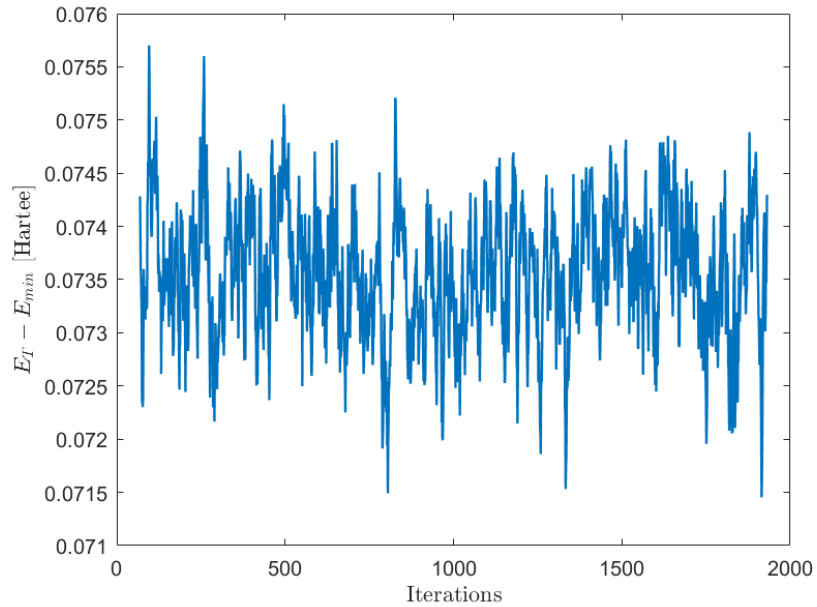

Fig. 3. Fluctuation of the ZPE after equilibration.

ZPE = 0.07356 hartee with a standard deviation of 0.00060 hartee. The literature value is 0.073927 hartree [4].

Results

C_2H_6 (first test case)

Simulation with 1000 walkers for 2000 time steps

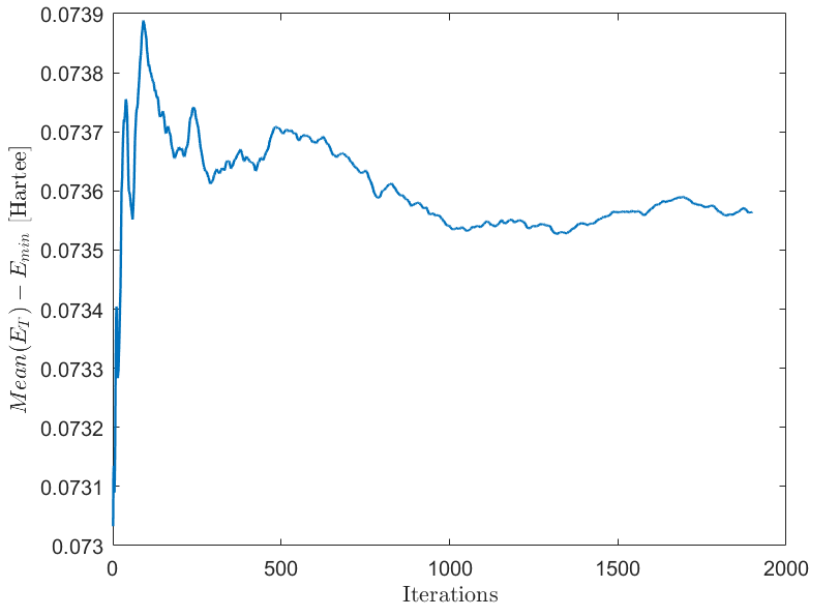

Fig. 4. Convergence of the ZPE after equilibration.

Simulation time: 14 hours. $\approx$ 0.02 seconds per energy calculation.

Results

$C_{12}H_{10}O$

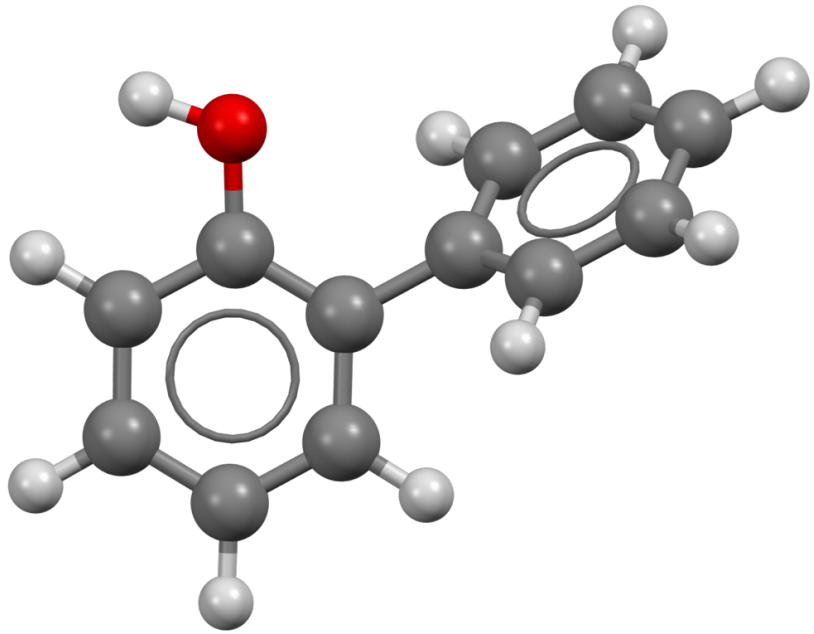

Fig. 5. Input structure of 2-Phenylphenol

Slightly larger molecule to test the performance of the algorithm.

Results

$C_{12}H_{10}O$

Simulation with 1000 walkers for 2000 time steps

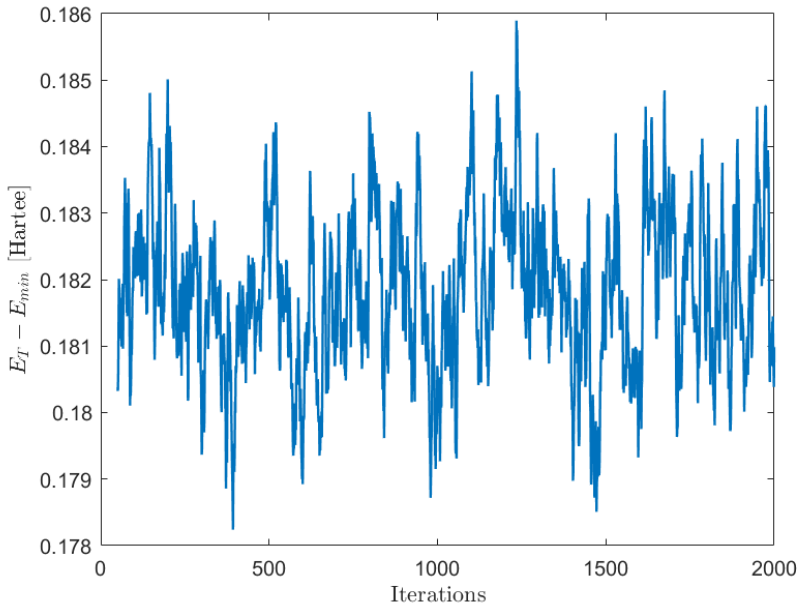

Fig. 6. Fluctuation of the ZPE after equilibration.

ZPE = 0.18184 hartee with a standard deviation of 0.00117 hartee.

Results

$C_{12}H_{10}O$

Simulation with 1000 walkers for 2000 time steps

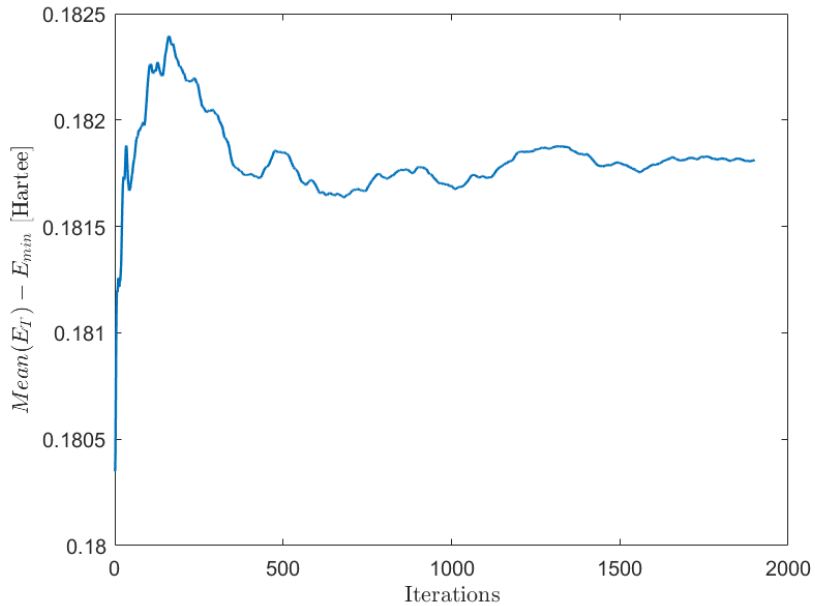

Fig. 7. Convergence of the ZPE after equilibration.

Simulation time: 57 hours. ≈ 0.11 seconds per energy calculation.

Results

$H_2@C_{60}$

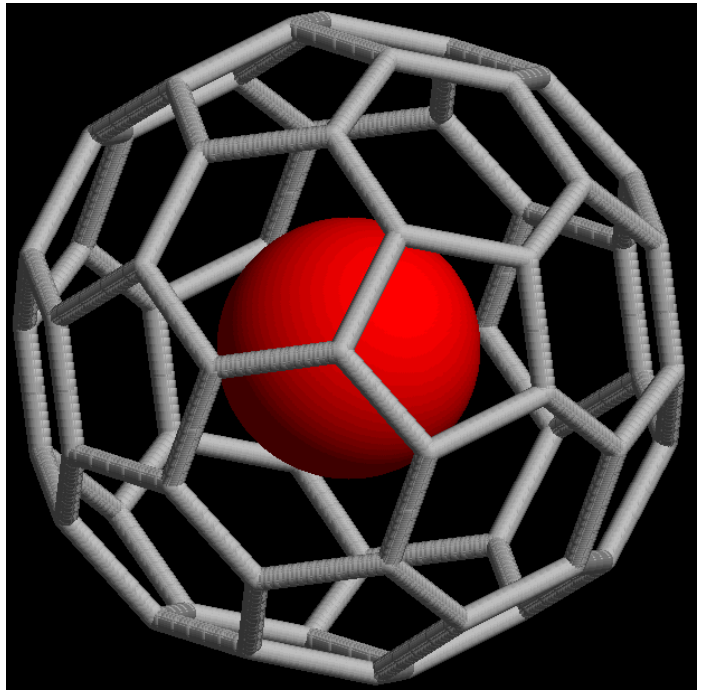

Fig. 8. Input structure of the dihydrogen endofullerene

The dihydrogen endofullerene is expected to show strong anharmonic effects on the zero point energy.

Results

$H_2@C_{60}$

Simulation with 1000 walkers for 2000 time steps

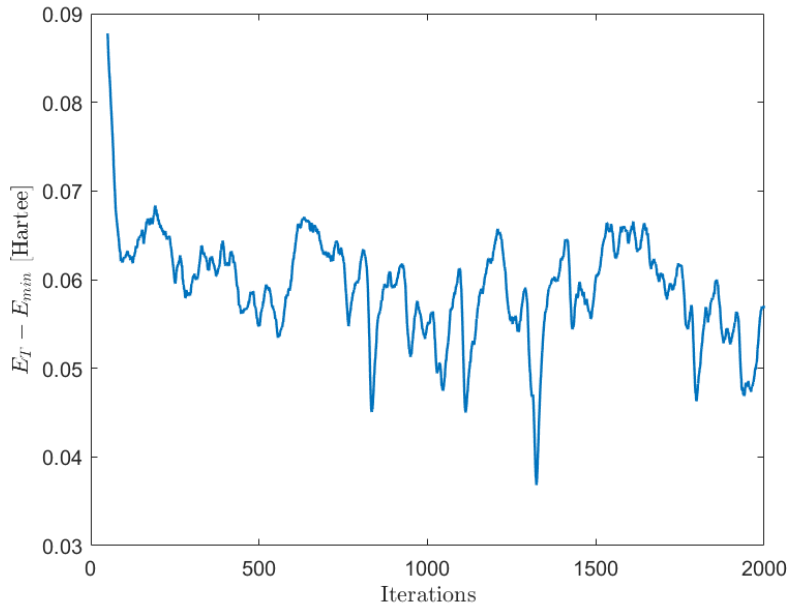

Fig. 9. Fluctuation of the ZPE after equilibration.

ZPE = 0.05914 hartee with a standard deviation of 0.00569 hartee.

Results

$H_2@C_{60}$

Simulation with 1000 walkers for 2000 time steps

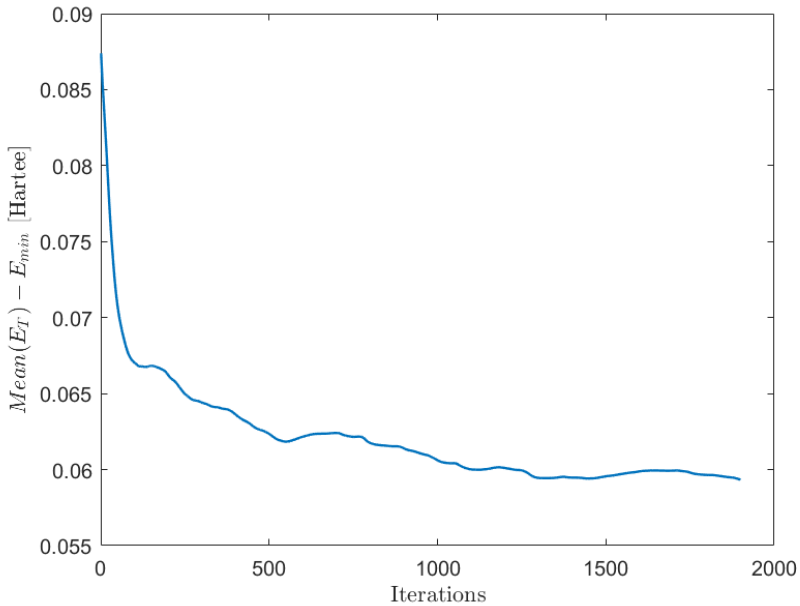

Fig. 10. Convergence of the ZPE after equilibration.

Simulation time: 51 hours. ≈ 0.10 seconds per energy calculation.

Conclusions and Improvements

Conclusions:

- DQMC delivers moderately accurate results for the ZPE in reasonable time.
- DQMC is very versatile and can calculate the ZPE of most molecules.

Improvements:

- Adjustments for periodic structures
- Parallelization
- Making it more user-friendly

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