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Quantum-Monte-Carlo simulations of polyethylene

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Abstract. The diffusion Quantum-Monte-Carlo method of solving the Schrödinger equation is applied to the vibrational ground state of a polyethylene molecule. The results for the ground state energy show good agreement with normal mode analysis. In addition to stretching, bending and torsional interaction van-der-Waals interaction is applied to a single chain showing a decrease of the energy of 5%. The decrease for a polyethylene system of 5 chains with 10 atoms per molecule at the positions of a unit cell is determined to be 4.8% per molecule. Finally first steps towards simulating excited states were performed.

PACS. 03.67.Lx Quantum computation – 36.20.-r Macromolecules and polymer molecules – 83.20.Jp Computer simulation

1 Introduction

One of the most successful algorithms for determining the quantum mechanical properties of molecules is the diffusion Quantum-Monte-Carlo (DQMC) method. Its origins go back to Wigner noting the equivalence of the Schrödinger equation and the diffusion equation [1]. A random walk simulation was first suggested by Metropolis and Ulam in 1949 [2], but the first algorithm which was able to determine the ground state energy of simple electronic systems such as H_3^+ was developed by Anderson in 1975 [3]. During the following years DQMC produced very accurate results for systems with few electrons such as LiH [4], HeH [5] and H_2 [6]. For larger systems such as H_2O [7], CH_4 [8] or HF [9] DQMC still provides the best results available [10].

In 1995 Kreitmeier *et al.* first applied Anderson's DQMC algorithm to a linear, one-dimensional polyatomic molecule [12]. In our paper the method will be extended to describe a polyethylene molecule with stretching, bending, torsional and van-der-Waals interaction using an importance sample algorithm. Section 2 gives a short description of the DQMC method. In Section 3 we describe the simulated system. Section 4 presents the results for the single interactions. Section 5 describes the results for the ground state energy in comparison with normal mode analysis. Section 6 deals with the decrease of the ground state energy by implementing van-der-Waals interaction both in a single molecule and in a polyethylene unit cell with 10 atoms as chain length. Section 7 finally shows first simulation results for excited states.

2 Theory

The general principles of the DQMC method are described in [3,11]. Its application to a linear polyatomic molecule is shown in [12]. Here we only give a short summary.

The Schrödinger equation in a potential V,

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi, \tag{1}$$

can be transformed by the substitution $\tau := \frac{it}{\hbar}$ to

$$\frac{\partial\psi}{\partial\tau} = \frac{\hbar^2}{2\mu}\nabla^2\psi - V\psi \tag{2}$$

with the formal solution

$$\psi(x,\tau) = \sum_n \alpha_n \Phi_n(x)\exp(-E_n\tau). \tag{3}$$

By defining $E_n \geq 0$ without restriction the solutions decay exponentially. Since the excited states decay faster, wave function Φ_0 and energy E_0 of the ground state can be determined for large values of τ. The origin of the method rests in the formal equivalence of the Schrödinger equation and the diffusion equation with a first order rate term $-KC$ serving as a source or sink for particles:

$$\text{Schrödinger: } \frac{\partial\psi}{\partial\tau} = \frac{\hbar^2}{2\mu}\nabla^2\psi - V\psi \tag{4}$$

$$\text{Diffusion: } \frac{\partial C}{\partial t} = D\nabla^2 C - KC. \tag{5}$$

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Therefore the basic idea of the simulation technique is to postulate ψ-particles or "psips" which undergo a diffusion process with the parameters of the Schrödinger equation. The average potential energy of the psips after reaching steady state is equal to the ground state energy E_0.

This "simple sampling" algorithm achieves good results for linear molecules with less than 25 atoms. For larger molecules the results start to differ from the results of normal mode analysis as stated in [12]. Therefore we programmed an "importance sampling" algorithm to gain better results for large molecules [13]. The main idea is to use knowledge or assumptions about ψ in a wave function ψ_{trial} representing the expected final state. Multiplication of the Schrödinger equation with ψ_{trial}

$$\frac{\partial \psi}{\partial \tau}\psi_t = \frac{\hbar^2}{2\mu}\left(\nabla^2\psi\right)\psi_t - V\psi\psi_t \tag{6}$$

leads to the following equation for $f := \psi\psi_t$:

$$\frac{\partial f}{\partial \tau} = \underbrace{\frac{\hbar^2}{2\mu}\nabla^2 f}_{\text{(a)}} - \underbrace{\frac{\hbar^2}{\mu}\nabla(f\nabla\ln\psi_t)}_{\text{(b)}} - \underbrace{\left(\frac{H\psi_t}{\psi_t} - V_{ref}\right)f}_{\text{(c)}}. \tag{7}$$

The right side consists of three parts. Term (a) represents the "free" part of the Schrödinger equation simulated by a Random Walk as in the simple sampling algorithm. Term (c) represents the modified term deciding about multiplication or removal of psips in the system. Term (b) is new. It represents a drift with velocity $\nabla \ln \psi_t$ towards the maxima of ψ_t allowing a faster convergence and more stability of the simulation. In our case of the vibrational ground state of a polyethylene molecule the ψ_{trial} used was a sum over Gaussians located at the equilibrium positions of the atoms:

$$\psi_t = \sum_{i=1}^{N} a e^{-b(x-x_i)^2} \tag{8}$$

with N the number of atoms and x_i the equilibrium position of the ith atom. The parameters a and b were determined by fitting Gaussians on the ψ produced by simple sampling simulations. The fit showed that the standard deviation $\sim b^{-1/2}$ is much smaller than the distance between the atoms: $b^{-1/2} \ll r_{eq}$. Thus the Gaussians can be treated as independent and both the parameter a and the sums in term $(H\psi_t)/\psi_t$ can be reduced producing simple additional terms for importance sampling.

3 Simulated system

In this article both the simple sampling and the importance sampling algorithm are applied to a model of a polyethylene molecule in three stages of approximation. The ground state conformation of polyethylene is sketched in Figure 1 representing a sequence of 4 atoms in the molecule [15]. It already implies usage of the united atom model. The resulting conformation of the carbon atoms shows a zigzag with an equilibrium bending angle of $\theta_{eq} = 111.6°$ defined in the plane of three atoms j, k, l in sequence. The torsional interaction between the atoms of such a chain is described by the angle τ defined as the angle between the planes i, j, k and j, k, l.

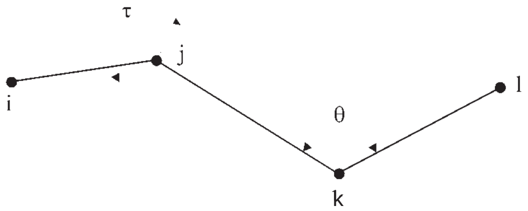

Fig. 1. Conformation of polyethylene sequence.

First we only considered a linear one-dimensional chain of carbon atoms with a harmonic stretching potential

$$V_{str} = \sum_{i=1}^{N-1} \frac{1}{2} D(r_{i,i+1} - r_{eq})^2 \tag{9}$$

where $r_{i,i+1}$ is the absolute distance between atoms i and $i+1$, $r_{eq} = 1.53$ Å their equilibrium distance, N the number of atoms and $D = 2651$ kJ/mol the force constant. This system was already described with simple sampling in [12].

We then expanded this system to a two-dimensional chain with a bending potential of the form

$$V_{bend} = \sum_{i=1}^{N-2} \frac{1}{2} K_\theta(\theta_{i,i+1,i+2} - \theta_{eq})^2 \tag{10}$$

with $K_\theta = 663.1$ kJ/mol as force constant and θ as bending angle.

As a third step torsional interaction was added to the other forces and three dimensional simulations were executed. The form of the torsional potential was taken from [14]:

$$V_{tor} = \sum_{i=1}^{N-3} (a - b\cos\tau_{i,i+1,i+2,i+3} + c\cos^3\tau_{i,i+1,i+2,i+3}) \tag{11}$$

where a, b and c are constants with $a = 8.4$ kJ/mol, $b = 18.4$ kJ/mol and $c = 26.8$ kJ/mol. An angle of $\tau = \pi$ represents the ground state corresponding to the all-trans conformation.

Finally van-der-Waals interaction was implemented. We described the interaction by the Lennard-Jones potential

$$V_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]. \tag{12}$$

The parameters ε and σ were chosen to be $\varepsilon = 0.477$ kJ/mol and $\sigma = 3.98$ Å [17]. Due to the fact that we did not use internal coordinates for describing the system as done in [16] but used Cartesian coordinates instead, implementing the Lennard-Jones potential was possible without problems.

The simulations were performed with 10 000 psips and 50 000 time steps with $\Delta\tau = 0.09$ a.u. for molecules with 10 and 25 atoms and with 5 000 psips and 20 000 time steps for larger molecules.

4 Results for single interactions

First we consider the interaction energies for the individual oscillators, exemplary for chains of 10 atoms. As stated in [12] the stretching energy of the oscillators of a linear chain were not distributed like a single Gaussian, but could be best fitted by overlapping two Gaussians:

$$P(E) = \frac{a}{\sigma_a\sqrt{2\pi}} \exp\left(-\frac{(E-E_a)^2}{2\sigma_a^2}\right) + \frac{b}{\sigma_b\sqrt{2\pi}} \exp\left(-\frac{(E-E_b)^2}{2\sigma_b^2}\right). \qquad (13)$$

The ratio of the parameters a and b was chosen to be 7/2 for a 10 atomic molecule reflecting the ratio of middle and end oscillators for stretching interaction. In the simulation the energy of the single interactions was determined for each oscillator and each MC time step after steady state was reached. The number of hits in a certain energy interval during steady state is plotted. This quantity is proportional to the probability for an oscillator to have this energy at steady state. The histogram, the Gaussians and the resulting fit $P(E)$ are shown for the linear one-dimensional molecule with stretching and the three-dimensional polyethylene molecule with stretching, bending and torsional interaction in Figures 2 and 3. In analogy to the stretching case the ratio of a/b for the distinction of end and center oscillators was chosen to be 6/2 for bending and 5/2 for torsional interaction. The fit parameters of the single interactions are given in Table 1.

In [12] Kreitmeier proposed that the double peak structure was due to a higher energy of the end oscillators. Simulations with periodic boundaries as seen in the insert of Figure 2 proved this assumption since no second Gaussian can be seen in this case. The fact that the peak is lowered about 2% compared with the original case is consistent with the observation that the results show a slight asymptotic decrease of the energy with increasing number of atoms. Periodic boundaries thus serve as the limiting case.

Comparing Figures 2 and 3 with respect to stretching interaction one recognizes that the peaks of the two Gaussians are much closer in the three-dimensional case then in the one-dimensional one. The reason for this behavior is due to the bending angle of 111.6° in the second case. Since this angle is reasonably close to 90° the oscillators' forces are almost perpendicular leading roughly to a coincidence of the Gaussians.

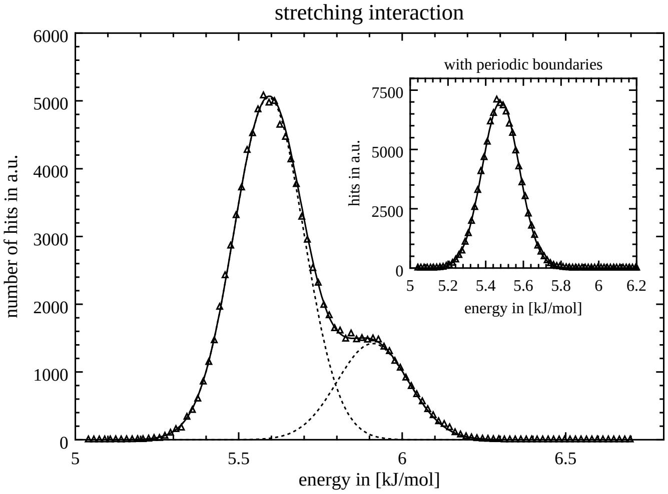

Fig. 2. Distribution of stretching energy for a single oscillator in a linear, one-dimensional molecule *versus* energy. Insert: same simulation using periodic boundary conditions.

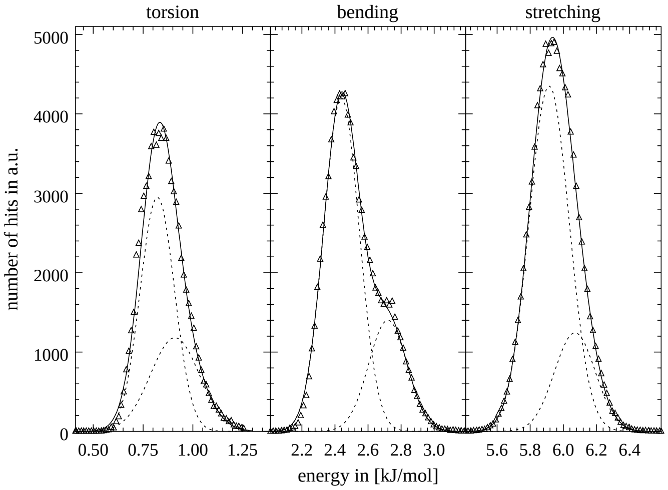

Fig. 3. Distribution of stretching, bending and torsional energy for a single oscillator in a polyethylene molecule *versus* energy. Dotted and solid lines: fits with Gaussians and sum of Gaussians.

5 Results for the ground state energy

Based on the results of [12] we implemented bending and torsional interaction and importance sampling. A histogram for the energy values at steady state was made and fit with a Gaussian with parameters E_0 and σ. They are given in Table 2.

The comparison shows good agreement between simulation and normal mode analysis data for importance sampling simulations. The agreement with simple sampling is limited to short chains (less than about 25 atoms) as pointed out in [12]. Deviations from 2-6% are obtained for simulations with bending and torsional interaction. Their are mainly due to the fact that the torsional potential is nonlinear while normal mode analysis only deals with a harmonic approximation.

Table 1. Parameters for Gaussian fits of the single interactions. All energies in kJ/mol.

Interaction	E_a	σ_a	E_b	σ_b
stretching (linear molecule)	5.59	0.11	5.91	0.11
stretching (polyethylene molecule)	5.91	0.12	6.07	0.12
bending	2.43	0.10	2.69	0.13
torsion	0.81	0.08	0.91	0.12

Table 2. Simulation and normal mode analysis data for the polyethylene molecule with stretching, bending, torsional and van-der-Waals interaction. All energies in kJ/mol. Indices s and i refer to simple and importance sampling.

# of atoms	1 dim		2 dim		3 dim		
					without vdW int.		with vdW int.
	E_0^{sim}	E_0^{mode}	E_0^{sim}	E_0^{mode}	E_0^{sim}	E_0^{mode}	E_0^{sim}
10s	51.03 ± 0.42	51.13	74.51 ± 0.71	73.67	79.83 ± 0.84	80.03	
10i	51.53 ± 0.21	51.13	74.76 ± 0.42	73.67	82.76 ± 0.59	80.03	79.87 ± 0.70
25s	135.4 ± 1.6	134.63	208.5 ± 4.0	198.00	229.4 ± 5.4	216.88	
25i	131.2 ± 0.4	134.63	201.0 ± 1.0	198.00	223.5 ± 1.6	216.88	213.1 ± 1.6
50i	275.4 ± 1.6	273.70	412.3 ± 2.3	404.79	463.8 ± 3.6	444.76	438.3 ± 4.0
75i	416 ± 3	412.76	627 ± 4	611.99	706 ± 5	672.56	669 ± 5
100i	558 ± 4	554.38	842 ± 5	822.16	956 ± 8	900.41	913 ± 8
125i					1197 ± 13	1139.80	1139 ± 14
150i					1453 ± 13	1356.68	1373 ± 13

One also recognizes that in all cases the energy is directly proportional to the number of atoms as expected. This indicates that the importance sampling method is suitable for even larger molecules in contrast to simple sampling.

6 Implementation of van-der-Waals interaction

Next we studied the consequences of implementing van-der-Waals interaction between every atom of the molecule. Table 2 shows the comparison between importance sampling simulations with and without van-der-Waals interaction in addition to stretching, bending and torsional interaction.

Implementing van-der-Waals interaction thus yields a lowering of the ground state energy of approximately 5% more or less independent of the length of the molecule.

Next we expanded our method to a system of two molecules with 10 carbon atoms separated by a distance of $a = 4.9$ Å which is equal to the shortest distance of two molecules in a polyethylene crystal with orthorhombic structure. Comparing with a system of two molecules with only intramolecular van-der-Waals interaction a lowering of the energy of 4.3% per molecule is found.

We finally considered 5 molecules with 10 carbon atoms arranged in the unit cell of the orthorhombic structure with dimensions of $a = 4.9$ Å and $b = 7.4$ Å [17]. No periodic boundary conditions were applied but a single unit cell was studied instead. The intermolecular van-der-Waals force between the atoms of the unit cell leads to a lowering of the ground state energy of 4.8% per molecule.

7 Excited states

Finally we started simulating excited states to demonstrate future possibilities. Due to the fact that a linear polyatomic molecule reduces to a single oscillator in normal coordinates we first dealt with such a system to test the algorithm applying some methods of Anderson for electronic systems [10]. Excited states are characterized by the nodes of ψ. Due to the analogy between amplitude of ψ and concentration of psips *via* equations (4, 5) a sink for psips is installed at the node. The algorithm compares the position of every psip before and after every time step. If a psip crosses a node within the time step it is removed from the system. When trying to describe systems with several nodes we found it necessary to separately simulate all areas divided by nodes. Otherwise the psips of the area with higher average potential energy are continuously removed from the system whereas the psips in the area with lower energy are permanently subject to multiplication until no psip is left in the first area. Reconnection of the areas is done *via* adjusting the slopes of ψ at the nodes. Figure 4 shows the result for the third excited state. Theory and simulation are in excellent agreement.

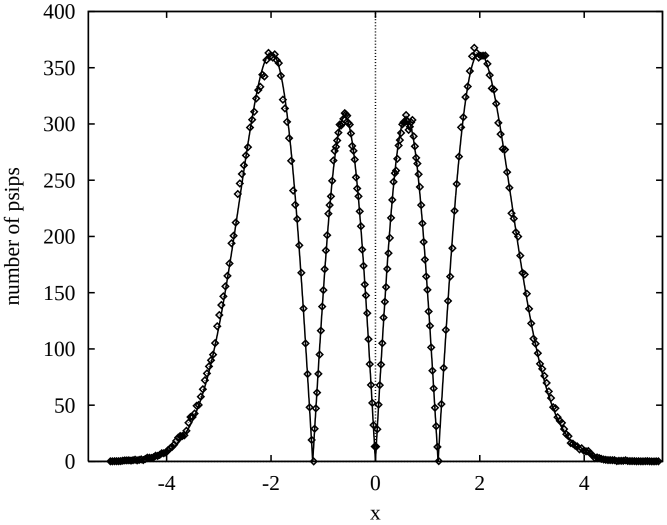

Fig. 4. Third excited state of the harmonic oscillator; points: simulation, line: theory.

8 Conclusion

The aim of our work was to gain information about the vibrational ground state of a polyethylene molecule. We extended Kreitmeier's simulation of a polyatomic linear chain [12] to a polyethylene molecule with all-trans conformation applying stretching, bending, torsional and van-der-Waals interaction. The results for the single interactions showed that a double peak structure of the energy dispersion can not only be found for stretching, but also for bending and torsional interaction. Simulations with periodic boundaries showed that this structure is in fact due to a different energy of middle and end oscillators. A comparison of the results for ground state energy between simulation and normal mode analysis shows good agreement for molecules with up to 150 atoms. By adding van-der-Waals interaction the ground state energy of a chain of arbitrary length was lowered 5%. Next we simulated a polyethylene unit cell with 5 molecules and 10 atoms each, coupled by intermolecular van-der-Waals interaction and found an additional decrease of the ground state energy of 4.8% per molecule. Finally we made first steps towards a description of the excited states. Simulations with the test system of a harmonic oscillator showed that the algorithm can describe excited states very well.

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