ELSEVIER

Polymer 44 (2003) 1765–1770

polymer

www.elsevier.com/locate/polymer

Quantum Monte-Carlo calculation of correlation functions of undistorted, *cis*-distorted and *trans*-distorted polyacene

S. Goumri-Said[a,b,*], H. Aourag[b,c], L. Salomon[a], J.-P. Dufour[a]

[a]*Laboratoire de Physique (LPUB), CNRS UMR 5027, Université de Bourgogne, Groupe d'Optique de Champ Proche,*
Faculté des Sciences Mirande, 9 Avenue Alain Savary BP 47870, 21078 Dijon Cedex, France
[b]*Computational Materials Science Laboratory, Department of Physics, University of Sidi Bel-Abbes, 22 Rue Hoche, Sidi Bel Abbès 22000, Algeria*
[c]*LERMPS, Université de Technologie de Belfort-Montbeliard, Site des Sévenans, 90010 Belfort, France*

Received 22 September 2002; accepted 19 December 2002

Abstract

We have studied polyacene within the Hubbard model to explore the effect of electrons correlations on the bond–bond correlation as well as spin–spin correlation functions. We employ the determinantal quantum Monte-Carlo to resolve the microscopic Hamiltonian of this system which involves a nearest-neighbor electron hopping matrix element t, an on-site Coulomb repulsion U. The objective of this study is to understand the effect of electron–electron (e–e) correlations on the structural instability in polyacene. We find strong similarities between polyacene and polyacetylene. The system shows no tendency to destroy the imposed bond-alternation pattern. The spin–spin correlations show that undistorted polyacene is susceptible to a spin-density wave distortion for large interaction strength (U).

Keywords: Polyacene; Hubbard model; Determinantal quantum Monte-Carlo

1. Introduction

Since the discovery in 1977 that *trans*-polyacetylene can be made electrically conducting by means of doping [1] several conjugated polymers with interesting properties in the conducting and semiconducting phases have been discovered. These materials are of great practical interest due to large number of applications that have been proposed. The conducting polymers are also of interest from theoretical point of view as case of quasi one-dimensional systems, in particular the formation of certain particle-like defect states (solitons), polarons and bipolarons states [2,3].

One of the fascinating phenomena in the field of conjugated polymers, the structural instabilities or the so-called Peierls instability (i.e. pseudo Jahn–Teller distortion) [4], which removes the orbital degeneracy at the Fermi-level by breaking the symmetric geometry of the hypothetical equal bond-lengths polymers chain. This lead to the creation of an alternating sequence of short and long bonds along the chain with a bond alternation of the order δ. Therefore there has been much interest in studying the effect of electron correlations on the Peierls instability in conjugated polymers, in particular polyacetylene [5]. The effect of electron correlations on the ground state of polyacetylene is not obvious, and contradictory results were obtained from different approximate theoretical approaches within the Hubbard and Peierls–Hubbard models [6–11].

In recent years, the determinantal quantum Monte-Carlo (DQMC) method has emerged as a technique which is particularly well suited to study the Hubbard model in higher dimensions. In this paper, we report our DQMC studies on the role of electron correlations on the different correlation functions and instabilities in polyacene. The DQMC method provides a treatment of the Hubbard model that is exact within statistical errors, and makes no assumptions about the structure of the wave function in estimating correlation functions. The technique also allows us to study significantly larger system sizes than have been accessible through other approaches.

A physical picture of the ground state can be obtained by analyzing the various correlation functions. The aim of our

---

* Corresponding author. Tel.: +33-3-80-39-68-99; fax: +33-3-80-39-60-50.

E-mail addresses: sgoumri@u-bourgogne.fr (S. Goumri-Said), hafid.aourag@utbm.fr (H. Aourag).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(03)00010-7

work will concentrate on systems with odd numbers of rings and specially on the system of 11 rings. We focus our attention on the calculation of the bond–bond and spin–spin correlations of these systems, by considering the boundary conditions, undistorted, *cis*- and *trans*-distorted forms of polyacene.

The paper is organized as follows: in Section 2, we present a computational details applied to the Hubbard model. The numerical results will be discussed in Section 3. We end with a summary of our results in Section 4.

2. Model and technique

2.1. The Hubbard model

In most theoretical studies of the strongly systems and conjugated polymers, it has been assumed that the Coulomb repulsion between electrons can be described by a Hubbard model in which this interaction is replaced by a pointlike on-site interaction. Moreover, it has been assumed that the on-site Hubbard parameter U is an order of magnitude larger than the nearest-neighbor electron hopping energy scale t. This picture is based on the Fermi-liquid theory notion of screening of the effective electron–electron interaction. The Hamiltonian for polyacene is given by [12]

$$H = \sum_{\langle ij\rangle} \sum_{\sigma} t_{ij}(c_{i\sigma}^{+} c_{j\sigma} + \mathrm{H.c}) + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow} \tag{1}$$

where $c_{i\sigma}^{+}(c_{i\sigma})$ is the creation (annihilation) operator for an electron with spin σ in the Wannier orbital at the ith site, and the summation $\langle ij\rangle$ runs over bonded atom pairs, and $n_i = n_{i\uparrow} + n_{i\downarrow}$. t is the hopping parameter matrix, which is introduced from the Hückel theory representing the degree to which the π-orbitals on adjacent atoms in a chain overlap.

2.2. DQMC technique

We present numerical studies of the described model using a particular type of quantum Monte-Carlo (QMC) method, the temperature dependent QMC formulation in the grand canonical ensemble [8]. We emphasize that the QMC approach has the potential to treat these types of strongly correlated systems, allowing us to go far beyond certain approximative methods. Unlike most standard analytical techniques, our method provides an approximation-free, numerically exact ansatz and yields information about systems much larger than those accessible by exact diagonalization algorithms.

The partition function, using Trotter approximation [13] in separating the one-particle and two-particle terms and dividing the imaginary time interval $[0, \beta]$ into L subintervals of width $\Delta\tau = \beta/L$, may be written as:

$$Z = \mathrm{Tr}(\mathrm{e}^{-\beta\hat{H}}) = \mathrm{Tr}\prod_{l=1}^{L} \mathrm{e}^{-\Delta\tau\hat{H}} \approx \mathrm{Tr}\prod_{l=1}^{L} \mathrm{e}^{-\Delta\tau\hat{H}_0}\,\mathrm{e}^{-\Delta\tau\hat{H}_1} \tag{2}$$

To eliminate the two-body interaction term, we use the discrete Hubbard–Stratonovich transformation [14] using the identity

$$\mathrm{Tr}\,\exp(-c_i^{+} A_{ij} c_j)\exp(-c_i^{+} B_{ij} c_j) = \det(1 + \mathrm{e}^{-A}\,\mathrm{e}^{-B}) \tag{3}$$

for arbitrary matrices A and B and taking the trace over fermions [15], one obtains

$$Z = \mathrm{Tr}_{\sigma} \prod_{\alpha=\pm 1} \prod_{l=1}^{L} [1 + B_L(\alpha) B_{L-1}(L) \cdots B_1(\alpha)] \tag{4}$$

$$Z = \mathrm{Tr}_{\sigma} \det O_{\uparrow} \det O_{\downarrow} \tag{5}$$

where O_{σ} is an $NL \times NL$ matrix

$$O_{\sigma} = 1 + \prod_{l=1}^{L} B_l^{\sigma}(\alpha) \tag{6}$$

$$B_l(\alpha) = \exp[-\Delta\tau K]\exp[V^{\alpha}(l)] \tag{7}$$

$$K_{i,j} = -t(>0) \quad \text{for } i,j \text{ nearest neighbour,}$$

$$= 0 \ \text{ otherwise}$$

$$V_{ij}^{\alpha}(l) = \delta_{ij}\left[\lambda\alpha\sigma_i(l) + \Delta\tau(\mu - \frac{U}{2})\right] \tag{8}$$

$$\lambda = \cosh^{-1}\left(\Delta\tau\frac{U}{2}\right) \tag{9}$$

To perform the Monte-Carlo simulation, we can take the determinant in Eq. (5) as the Boltzmann weight. For the case of half-filled band, the product in Eq. (4) is positive for arbitrary σ configurations [15].

The heat-bath algorithm is used to perform the sum over Ising spins. Suppose, R_{α} is the ratio of new to old determinant for fermion spin α on flipping a given Ising spin, the flipping probability for this, is given by:

$$P = \frac{R_{\uparrow} R_{\downarrow}}{1 + R_{\uparrow} R_{\downarrow}} \tag{10}$$

R_{α} can be computed by using the procedure introduced by Blakenbecler, Scalapino and Sugar [16,17], which involves updating the Green's function exactly when a move is accepted. This allows us to perform reliable and stable calculations of correlation functions.

3. Numerical results

Before proceeding to the details of our results we must recall here that all the physical observables are calculated for a 11 rings, with periodic boundary conditions. All that the measurements are taken only every other full Monte-Carlo sweeps through the (1 + 1)-dimensional lattice. We have performed our calculations for the following auxiliary data: 400 warm-ups sweep and the number of time slices (L) is taken equal to 30. We must notice that this set of values is selected with a purely 'computational criterion' [8,15].

3.1. Polyacene

Ladder polymers are conjugated polymers with at least two conduction paths in parallel. They share many of the properties with the polymers with a single conjugation path. In particular, many of the ladder polymers support polarons and bipolarons [18]. Polyacene is the simplest ladder polymer. The polyacene chain, with two identical backbones in parallel, can be viewed as two strongly interacting chains of *trans*-polyacetylene (see Fig. 1(a)). Polyacene is yet to be synthesized as a polymer with a large number of monomer unit [19]. We have considered the undistorted and *cis*- and *trans*-distorted (about the cross-links) forms shown in Fig. 1.

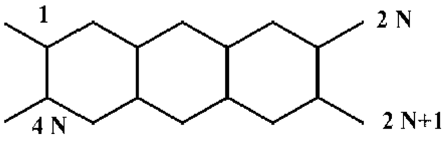
We must keep in mind, that the comparisons with other works are to provide a context and qualitative arguments and are not quantitative comparisons, because the Hamiltonians used are not identical.

3.2. Bond–bond correlation function

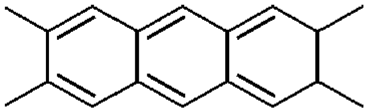
The existence of the bond order wave (BOW) in these systems, is investigated through the bond–bond correlation function, which is defined by:

$$\langle b_i b_j \rangle = \left\langle \sum_{\sigma} (c^{+}_{i,\sigma} c_{i+1,\sigma} + \mathrm{H.c.})(c^{+}_{j,\sigma} c_{j+1,\sigma} + \mathrm{H.c}) \right\rangle \tag{11}$$

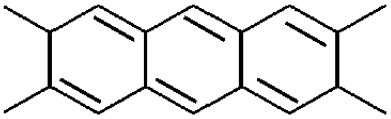
We notice here, that the bond–bond correlation function can describe relative distortions of bond in the system. Moreover, its Fourier transform would give the amplitudes for various kinds of BOW distortions. Our system has five bonds per unit cell, and hence there are 15 possible bond–bond correlation functions. We do not consider all these 15 correlation functions but instead consider only those correlation functions that correspond to the distortions shown in Fig. 1(b) and (c). With the exception of the bonds labeled $2N$ and $4N$, which connect sites 1 with $2N$ and $4N$ with $2N+1$, the bond which connects sites i and $i+1$ is labeled i.



(a) Undistored polyacene



(b) cis-distored polyacene



(c) trans-distored polyacene

Fig. 1. Structure of (a) undistorted, (b) *cis*-distorted, and (c) *trans*-distorted polyacene.

In Fig. 2(a) and (c) we present the bond–bond correlations $\langle b_1 b_j \rangle$ for $U/t = 2.0$ for undistorted, ($\delta = 0.1$)

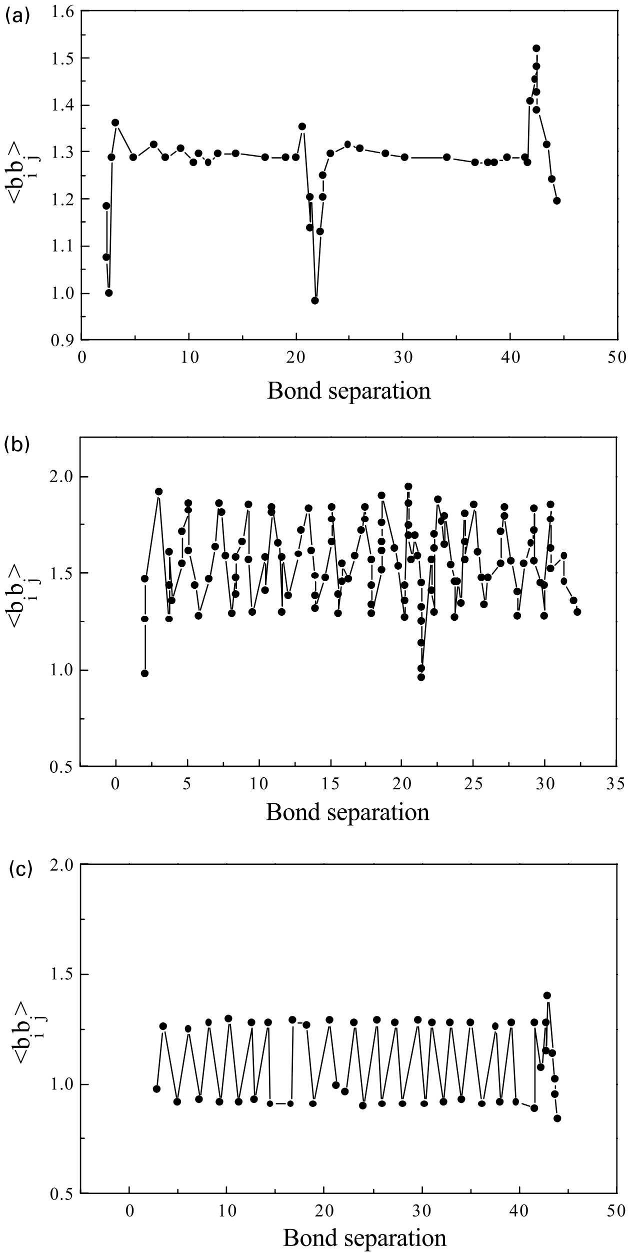


Fig. 2. Bond–bond correlations versus bond separation for (a) undistorted, (b) *cis*-distorted ($\delta = 0.1$), and (c) *trans*-distorted polyacene ($\delta = 0.1$) for $U/t = 2.0$.

cis- and *trans*-distorted forms of polyacene (11 rings), respectively. From Fig. 2(b) and (c), we see that the bond–bond correlation function reflects the *cis* and *trans* bond alternation. We have calculated the bond–bond correlation function for $U/t = 4.0$, shown in Fig. 3(a) and (c). It is evident, by comparing theses figures with Fig. 2(a) and (c), to see that increasing correlation strength does not bring about any qualitative changes in this observable. However, the amplitude for the *cis* distortion is larger than that for the *trans* distortion for the same imposed bond alternation δ. It is also seen that on going from $U/t = 2.0$ to 4.0, the amplitude of the *cis* distortion increases slightly, while that of the *trans* distortion decreases. The bond–bond correlation functions indicate a larger susceptibility to distortion of the *cis* type, although energetically, the *cis* and *trans* distortions are favored almost equally [12].

3.3. Spin–spin correlation function

In Figs. 4(a)–(c), and 5(a) and (b) we report the spin–spin correlations, for $U/t = 2.0$ and $U/t = 4.0$, respectively, given by the following formula

$$\langle S_iS_j\rangle = \langle (n_{i\uparrow} - n_{i\downarrow})(n_{j\uparrow} - n_{j\downarrow})\rangle \tag{12}$$

where $j = 2, \ldots, 4N$, for the numbering shown in Fig. 1(a).

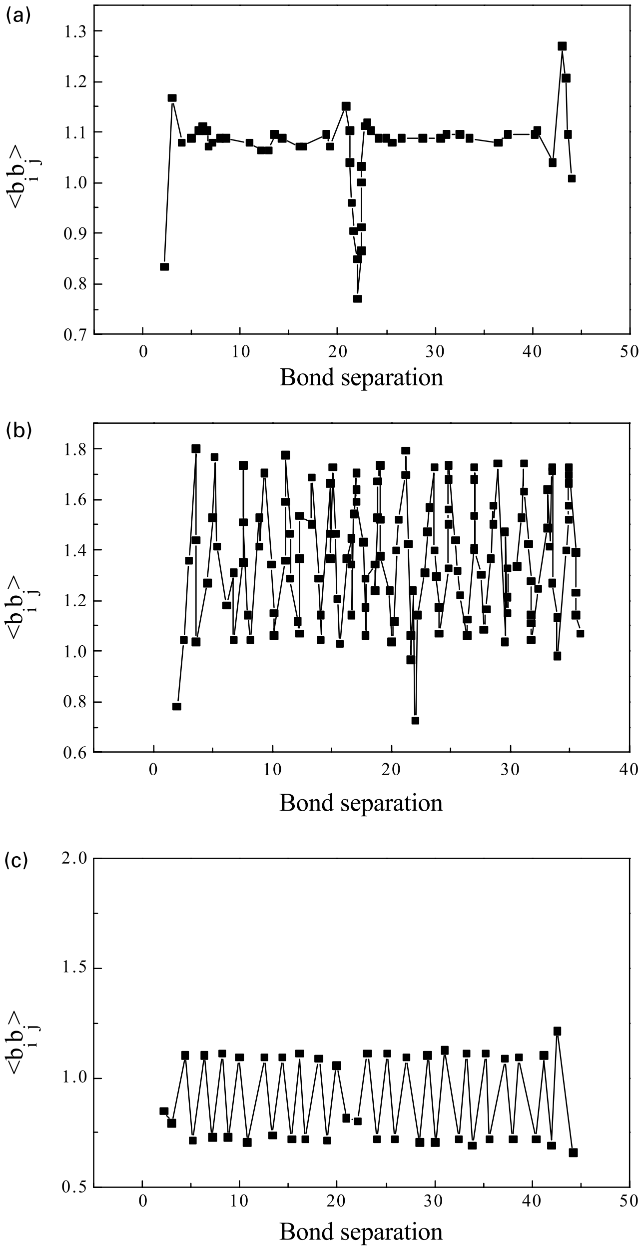


Fig. 3. Bond–bond correlations versus bond separation for (a) undistorted, (b) *cis*-distorted ($\delta = 0.1$), and (c) *trans*-distorted polyacene ($\delta = 0.1$) for $U/t = 4.0$.

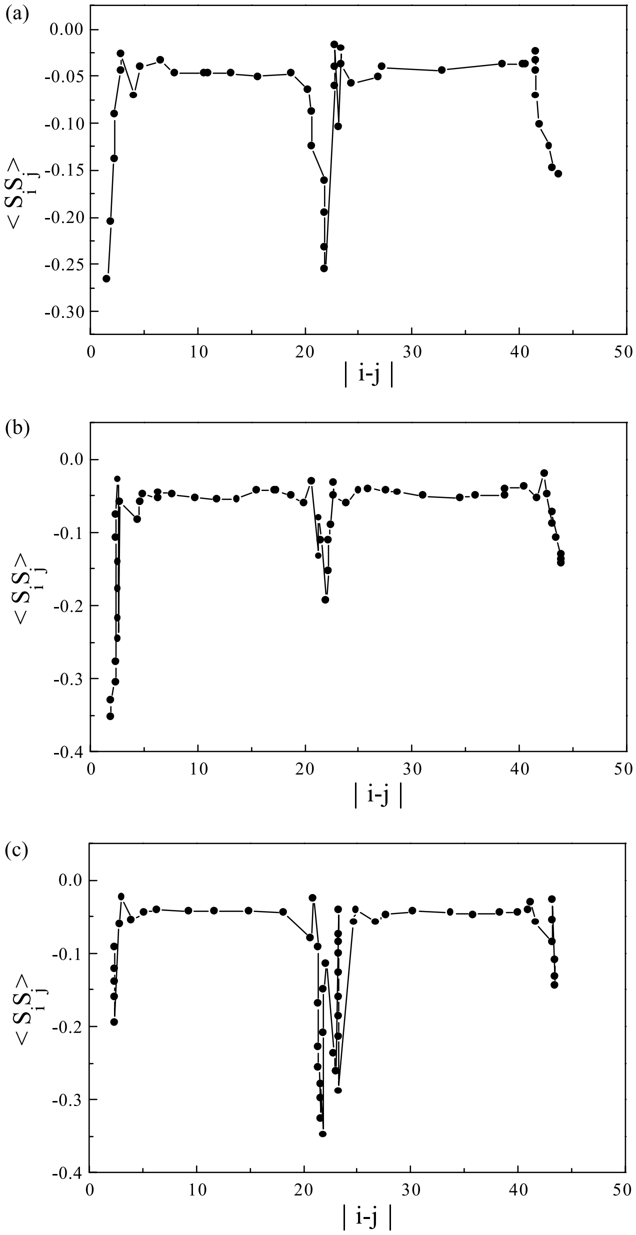


Fig. 4. Spin–spin correlations versus intersite separation for (a) undistorted, (b) *cis*-distorted ($\delta = 0.1$), and (c) *trans*-distorted polyacene ($\delta = 0.1$), for $U/t = 2.0$.

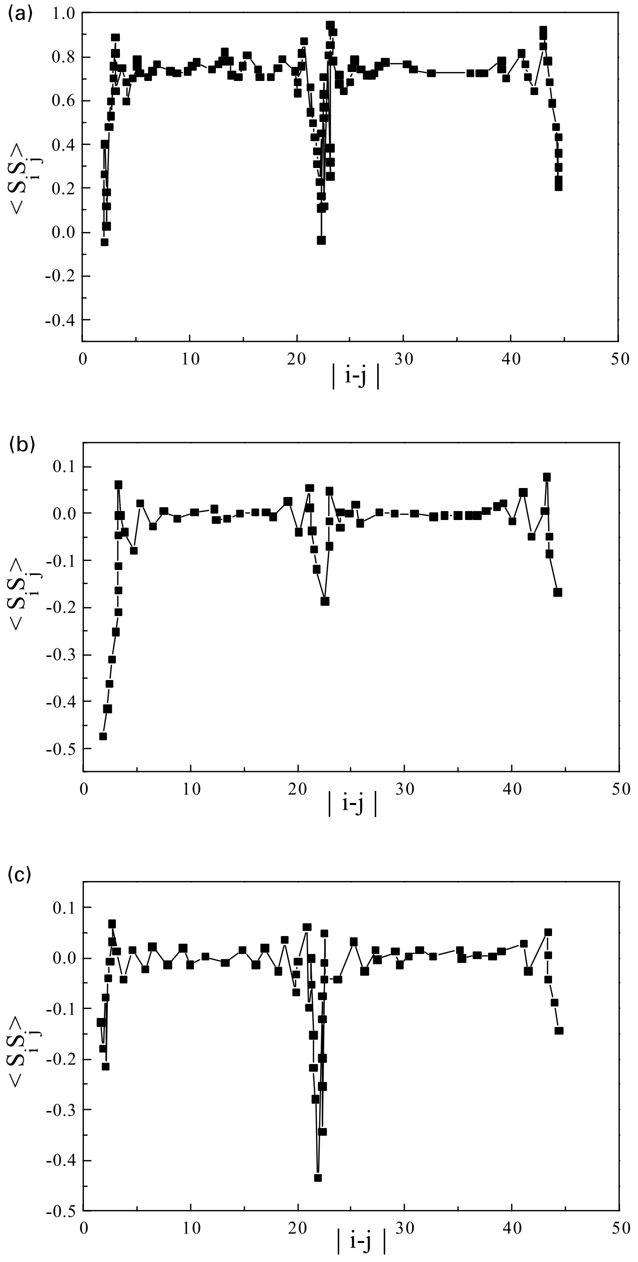


Fig. 5. Spin–spin correlations versus intersite separation for (a) undistorted, (b) *cis*-distorted ($\delta = 0.1$), and (c) *trans*-distorted polyacene ($\delta = 0.1$), for $U/t = 4.0$.

From these figures, we can make the following remarks:

For $U/t = 2.0$, the correlation function falls off very rapidly.

For $U/t = 4.0$, the correlation length appears extremely small for the bond-alternated states (see Fig. 5(b) and (c)), in comparison with work of Srinivasan et al. [12,20,21], the system starts developing antiferromagnetic fluctuations. Moreover, the existence of phase transition, through the behavior of correlation functions, is considered as a signature of the existence of quantum fluctuations, which might restore the broken-symmetry of the ground state. In fact, it is well known that the broken-symmetry ground-state in the presence of the electron–phonon interaction is BOW state, or charge density wave (CDW) state, while that in the presence of the electron–electron interactions is spin-density wave (SDW) state. From the works done on the one-dimensional conducting systems [9,22], both of BOW and CDW states can exhibit long range ordering in the ground state, and for very large U, the antiferromagnetic correlation decay algebraically which means that an antiferromagnetic ordering has occurred.

For undistorted case (Fig. 5(a)), the amplitude for SDW distortion is noticeable while in the distorted system this amplitude is nearly vanishing. This indicates that in polyacene the BOW and SDW are mutually exclusive. This, result is similar to our calculation done on polyacetylene [10,11]. The charge–charge correlations, as expected, show that the charge density fluctuation is negligible, and rule out (CDW) states in both the distorted and the uniform polyacene [23].

4. Summary

We have studied bond–bond and spin–spin correlations functions of a polyacene systems with up to 11 rings within the Hubbard model, using a quantum Monte-Carlo simulation.

We have employed the determinantal method based on the Hubbard–Stratonovich transformation, because it provides numerically highly accurate results for the calculated observables. We can summarize our main results as follows:

- Electron correlations tend to enhance the effect of bond alternation. Moreover, the correlation strength at which a maximum of the bond–bond correlation function occurs is seen to be shifted to larger values of U/t with increase in the bond-alternation parameter.
- The calculation of the bond–bond correlations indicates that the system has no tendency to destroy the imposed bond-alternation ($\delta = 0.1$ in our case). It also shows that the *cis* distortion is favored over the *trans* distortion.
- The undistorted polyacene has a tendency to form a SDW state for large interaction strength. Our system has no tendency to form CDW state for the parameters studied.

References

[1] Chiang CK, Fincher Jr CR, Park YW, Heeger AJ, Shirakawa H, Louis EJ, Gau SC, MacDiarmid AG. Phys Rev Lett 1977;39:1098.
[2] Su WP, Schrieffer JR, Heeger AJ. Phys Rev Lett 1979;42:1698.
[3] Rice MJ. Phys Lett 1979;71A:152.
[4] Peierls RE. Quantum theory of solids. Oxford: Clarendon; 1955.
[5] Coulson CA, Dixon WT. Tetrahedron 1961;17:215.
[6] Mazumdar S, Dixit SN. Phys Rev Lett 1983;51:292.
[7] Dixit SN, Mazumdar S. Phys Rev B 1984;29:1824.
[8] Hirsch JE. Phys Rev Lett 1983;n/volume-nr > :296.
[9] Baeriswyl D, Maki K. Phys Rev B 1985;31:6633.

[10] Goumri-Said S, Moussa R, Dufour J-P, Salomon L, Aourag H. Physica B 2001;296:377.

[11] Goumri-Said S, Aourag H, de Fornel F, Salomon L. Physica B 2001; 301:299.

[12] Srinivasan B, Ramasesha S. Phys Rev B 1998;57:8927.

[13] Trotter HF. Proc Am Math Soc 1959;10:545.

[14] Buendia GM. Phys Rev B 1986;33:3519.

[15] Hirsch JE. Phys Rev B 1985;31:4403.

[16] White SR, Scalapino DJ, Sugar RL, Loh EY, Gubernatis JE, Scalettar RT. Phys Rev B 1989;40:506.

[17] Hirsch JE, Sugar RL, Scalapino DJ, Blankenbecler R. Phys Rev B 1982;26:5033.

[18] Ruan JZ, Litt MH. In: Bowden MJ, Turner SR, editors. Polymers for high technology. Washington, DC: ACS; 1987.

[19] Canuto S, D' Albuquerque de Castro J, Paixao FJ. Electronic structure of atoms and molecules and solids. Singapore: World Scientific; 1990.

[20] Srinivasan B, Ramasesha S, Krishnamurthy HR. Phys Rev B 1996;54: R2276.

[21] Srinivasan B, Ramasesha S, Krishnamurthy HR. Phys Rev B 1997;56: 6542.

[22] Hayden G, Mele E. Phys Rev B 1985;32:6527.

[23] Garcia-Bach MA, Valenti R, Klein DJ. Phys Rev B 1997;56:1751.