

# STRUCTURAL INSTABILITY IN POLYACENE: A PROJECTOR QUANTUM MONTE CARLO STUDY

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## Abstract

We have studied polyacene within the Hubbard model to explore the effect of electron correlations on the Peierls' instability in a system marginally away from one-dimension. We employ the projector quantum Monte Carlo method to obtain ground state estimates of the energy and various correlation functions. We find strong similarities between polyacene and polyacetylene which can be rationalized from the real-space valence-bond arguments of Mazumdar and Dixit. Electron correlations tend to enhance the Peierls' instability in polyacene. This enhancement appears to attain a maximum at  $U/t \sim 3.0$  and the maximum shifts to larger values when the alternation parameter is increased. The system shows no tendency to destroy the imposed bond-alternation pattern, as evidenced by the bond-bond correlations. The cis- distortion is seen to be favoured over the trans-distortion. The spin-spin correlations show that undistorted polyacene is susceptible to a SDW distortion for large interaction strength. The charge-charge correlations indicate the absence of a CDW distortion for the parameters studied.

## 1 Introduction

The structural instabilities of one-dimensional systems, first predicted by Peierls[1] have been subjects of long standing interest to theoreticians and experimentalists. Initial studies of the Peierls' instability focussed on quasi-one-dimensional inorganic and organic charge-transfer solids such as KCP and TTF-TCNQ[2, 3, 4]. However, later studies have concentrated on polyacetylene, the archetypal one-dimensional system. Subsequent to the initial Hückel theoretic descriptions of polyacetylene[5], much interest has been generated by the possibility of novel solitonic and polaronic excitations in polyacetylene, the former suggested first in the work of Pople and Wamsley[6] and taken up again by Rice[7] and Su, Shrieffer and Heeger[8]. The importance of including electron-electron interactions in interpreting the electronic spectra of finite polyenes has been demonstrated. Therefore there has been much interest in studying the effect of electron correlations on the Peierls' instability in polyacetylene. Early work in this direction which described dimerization within a real space valence-bond approach was carried out by Coulson and Dixon[9].

The ordering of excited states has been studied in interacting models and the correct ordering of excited states in long polyenes( $2^1A_g$  below the optically allowed  $1^1B_u$  state) is obtained only at moderate to strong correlation strengths[10]. The effect of electron correlations on the ground state of polyacetylene is not obvious and contradictory results were obtained from different approximate theoretical approaches. Mean-field and Hartree-Fock

approaches in general predict a decrease in dimerization on including electron correlations even at the minimal level i.e. the Peierls-Hubbard model. However, going beyond mean-field theory, a real-space picture of dimerization was gained by the valence-bond analysis of Mazumdar and Dixit[11]. They found that while correlations enhance dimerization and this persists over a large range of correlation strength, the stabilization has a maximum for  $U \sim 4t$ . Hirsch[12] studied finite rings within the Peierls-Hubbard model using a checkerboard Monte Carlo technique and obtained a similar maximum in the enhancement. The variational calculation of Baeriswyl and Maki[13] agrees well with the quantum Monte Carlo results. The numerical renormalization group studies of Hayden and Mele[14] predict a similar maximum. Thus, it is now widely held that electron correlations enhance the instability in Peierls-Hubbard systems. The  $XY$  spin model maps on to a non-interacting spinless fermion model and is hence expected to show a similar instability. The spin analogue of the Hubbard model is the  $XYZ$  model or Heisenberg model. In spin-Peierls' systems, the effect of dimerization is to introduce a gap in the excitation spectrum[15]. The spin-Peierls' instability of the spin-half system has been extensively studied by probing this gap.

Another aspect of interest in Peierls' systems is the effect of dimensionality on the instability. In non-interacting systems, this aspect has been studied quite generally in the framework of energy band theory and it is well recognized that the strength of the instability depends upon the extent of nesting of the Fermi surface. The effect of increase in dimensionality on the spin-Peierls' instability has been explored by studying spin ladders and dimerized spin chains with next-nearest-neighbour interactions[16].

The effect of dimensionality on the Peierls-Hubbard system can also be studied by dealing with coupled Hubbard chains[17]. However, Hubbard ladders have been studied extensively mainly to explore other kinds of instabilities such as the pairing instability. Experimentally realizable systems which closely resemble Hubbard ladders are the polyacenes (Fig. (1a)). In the laboratory, polyacenes with up to seven rings have already been synthesized [18]. Early studies of the Peierls' instability in polyacenes were carried out by Salem and Longuet-Higgins[19], within the Hückel approximation. They considered the stabilities of the cis- form of bond-alternated polyacene (Fig. (1b)) and observed that the instability in these systems is only conditional, that is it could occur only below a critical force constant for a given electron-lattice coupling strength. This is unlike the prediction in one-dimension where the distorted state is more stable than the undistorted state independent of the magnitude of the force constant and the strength of electron-lattice interaction. Boon[20] considered the trans- form of bond-alternated polyacene(Fig. (1c))

and argued that this should be the more stable distortion. Misurkin and Ovchinnikov[21] predicted that very long polyacenes should have an antiferromagnetic spin structure. The calculations of Whangbo, Woodward and Hoffmann[22] indicate that the trans- form is energetically stabilized. The more detailed CNDO calculations of Tanaka et al[23] indicate that polyacene prefers the trans- distorted ground state.

There have been some theoretical studies on the electronically driven structural instability in polyacenes which include electron correlations in the mean field approximation. Kivelson and Chapman[24] studied the possibility of bond alternation, magnetic ordering and a superconducting transition as possible broken symmetry states of polyacene. Their mean-field calculations indicated that the bond-alternated state is not favoured. It has been conjectured that polyacene might show interesting conducting properties in view of the small excitation gap. Electron correlations were explicitly included by O'Connor and Watts-Tobin[25] in their study of polyacene which employed a modified Gutzwiller variational ansatz. Their study showed that mean field phase diagram for the ground state is only quantitatively modified and that the instability is only conditional. However, the variational ansatz used by them makes assumptions about the structure of the wavefunction and does not provide unbiased correlations. Besides these studies there also exist other theoretical studies of polyacene which pertain to the origin of the band gap and the crossover of these systems to the metallic state[26, 27, 28].

The issue of the effect of electron correlations on the instability predicted by non-interacting theories is far from being resolved. A proper study of this aspect would require the use of reliable numerical techniques for the ground state of the interacting model Hamiltonian for fairly large system sizes. In recent years, the projector quantum Monte Carlo 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 PQMC studies on the role of electron correlations on the different dimerization instabilities in polyacene. The PQMC method provides a treatment of the Hubbard model that is exact within statistical errors and makes no assumptions about the structure of the wavefunction in estimating correlation functions. The technique also allows us to study significantly larger system sizes than have been accessible through other approaches. The paper is organized as follows. We begin with a brief review of the results from the non-interacting model and then present our results and discussions. We end with a summary of our results in the last section.

## 2 Results and Discussion

Before discussing the interacting model, it would be worthwhile to present a brief outline of the analysis of the non-interacting model, due to Salem and Longuet-Higgins[19]. In the non-interacting picture, the Hamiltonian for polyacene (Fig. (1)) is given by

$$\hat{H}_0 = \sum_{\langle ij \rangle} \sum_{\sigma} t_{ij} (c_{i\sigma}^{\dagger} c_{j\sigma} + h.c.) \quad (1)$$

where  $c_{i\sigma}^{\dagger}$  ( $c_{i\sigma}$ ) is the creation (annihilation) operator for an electron with spin  $\sigma$  in the Wannier orbital at the  $i^{th}$  site and the summation  $\langle ij \rangle$  runs over bonded atom pairs. The bands of polyacene can be classified as symmetric or antisymmetric based on the symmetry property (reflection about the plane bisecting the rungs) of the MOs from which they are constructed. The ordering of the bands is such that the Fermi level lies between the antisymmetric and the symmetric bands. In the absence of any distortion, for all values of the interchain coupling, there is a degeneracy, at the Fermi level between the top of the antisymmetric band and the bottom of the symmetric band. A symmetric distortion of the polyacene leads to a symmetric perturbing potential. The matrix element of the perturbation between the degenerate states at the Fermi level vanishes by symmetry. Therefore, the response of the electronic system to a finite perturbation does not diverge, in second order. This divergence is essential for an unconditional Peierls' distortion, as is found in the polyenes. Thus, Hückel model studies indicate that the Peierls' instability in polyacene is conditional (the occurrence of the distortion depends on the magnitude of the force constant). Essentially the same result holds for a distortion in which the dimerization of the top chain is out of phase with the dimerization of the bottom chain (Fig. (1c)). A polymer with this type of distortion retains a  $C_2$  symmetry with the axis of symmetry being perpendicular to the molecular plane and passing through the center of the polymer and the above reasoning carries through because the matrix element between states of different symmetry vanishes when the operator has the same symmetry as one of the states.

We now present results from projector quantum Monte Carlo (PQMC) calculations of the ground states of polyacenes studied within the framework of the Hubbard model.

The Hubbard Hamiltonian is given by,

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \quad (2)$$

$$\hat{H}_1 = U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \quad (3)$$

where  $\hat{H}_0$  is the Hückel Hamiltonian described above and the notation is otherwise standard. The PQMC method[29] is a reliable method for obtaining ground state estimates of various properties of the Hubbard model. In a PQMC calculation, a Trotter decomposition of the projection operator  $exp(-\beta\hat{H})$  is followed by a discrete Hubbard-Stratonovich transformation which decouples the Hubbard interaction into the interaction of fermions with Ising-like fields. Expectation values are obtained as Monte Carlo averages by importance sampling the Ising configurations. Estimates obtained from the PQMC method are subject to a Trotter error and a statistical error, the first arising from the Trotter decomposition and the second from the Monte Carlo procedure. However, these can be controlled and it is possible to obtain accurate estimates of the energy and other correlation functions from the PQMC method. Further details of the method can be obtained from the literature[29, 30, 31] However, a caveat in using the PQMC method is that a single-configurational trial wavefunction is inadequate for "open-shell" systems[32], i.e. systems which have degenerate non-interacting ground states. Since the neutral polyacenes are "closed-shell", i.e. they possess unique non-interacting ground states, the PQMC method is expected to provide accurate estimates and would allow the simulation of fairly large systems.

We study polyacenes with up to eleven rings, with periodic boundary conditions. We have considered the undistorted and cis- and trans- distorted (about the cross-links) forms shown in Fig. (1). We study the effect of bond-alternation by imposing an alternation in the transfer integrals,  $\delta$ , as shown in Fig. (1). With this notation, the double lines between sites  $i$  and  $j$  in Fig. (1) would correspond to shorter bonds between these sites. Thus hopping between sites  $i$  and  $j$  would have a transfer integral  $(1 + \delta)t_{ij}$ . The transfer integrals corresponding to the other bonds are so modified as to keep the sum of transfer integrals constant to allow reasonable comparison of energies. We have studied the effect of increasing correlation strength, from weak through intermediate values ( $U/t=4.0$ ) for alternation parameter values  $\delta= 0.05, 0.1$  and  $0.2$ .

We have studied the instability in polyacene within the static lattice approximation. Our approach is to impose a bond alternation pattern and then to study the effect of electron correlations. The strength of the Hubbard interaction is systematically increased from the Hückel limit and the results obtained compared with the non-interacting results.

These studies are carried out for different values of the alternation parameter and for different types of distortions. The issues we address are the following: (i) the effect of electron correlations on the stability of the distorted states (ii) differences between systems with odd and even numbers of rings, if any (iii) whether any qualitative change occurs on increasing the alternation parameter (iv) effect of interactions on the imposed bond order wave (BOW) (v) comparison with polyacetylene and (vi) interpretation in terms of real-space pictures along the lines of Mazumdar and Dixit for polyacetylene rings.

We first use a naïve approach to the Peierls' distortion, entirely in terms of energetics. We study the gap  $\Delta E_A(N, \delta, U)$  [ $= E_A(N, \delta, U) - \Delta E(N, 0, U)$ ;  $A = \text{cis-}, \text{trans-}$ ] between the distorted and undistorted state, varying the number of rings ( $N$ ), the alternation parameter ( $\delta$ ) and the strength of electron correlations ( $U$ ). In Figs. (2) and (3), we present the variation of  $\Delta E_{cis}(N, \delta, U)/N$  and  $\Delta E_{trans}(N, \delta, U)/N$  with number of rings in the system. With our definition, a negative value of  $\Delta E$  would imply stabilization of the distorted state. We observe that the distorted state is stabilized with respect to the undistorted state even for  $U/t = 0.0$ . At  $U/t = 0.0$ , increasing the alternation parameter  $\delta$  tends to increase the stabilization. At the level of the Hückel model, the cis- and trans-distortions are stabilized to the same extent. There is a difference in the behaviour of systems with odd and even numbers of rings even within the Hückel picture. Introducing electron-electron interactions appears to increase the stabilization of the distorted state, for both cis- and trans- distortions. We digress at this point to establish a connection between polyacene and coupled polyacetylene chains, which will be useful in interpreting most of the results.

We note that an  $N$ -ring polyacene with periodic boundary conditions has  $4N$  sites. If we view an  $N$ -ring polyacene as coupled polyacetylene chains with missing alternate rungs, it is evident that systems with odd numbers of rings would correspond to coupled  $4n + 2$  rings and that systems with even numbers of rings would correspond to coupled  $4n$  "polyacetylene" rings ( $2n + 1 = N$ ). The larger stabilization of the even- $N$  polyacenes relative to the odd- $N$  polyacenes (Figs. 2, 3 and 4) can be rationalized using the real space arguments of Mazumdar and Dixit (MD). They showed that for cyclic polyenes, in the space of covalent functions, the  $4n$  ring systems have a stronger propensity for dimerization since the fraction of covalent VB states that favour uniform bonds is zero for all  $n$ . However, for the  $4n + 2$  ring systems, this fraction decreases to zero from a finite value as  $n \rightarrow \infty$ . This explains the opposite trend in the stability of the even- $N$  polyacenes compared to the odd- $N$  polyacenes as a function of the system size,  $N$  upon introducing dimerization. The data shown in Figs. (2 - 4) clearly indicate that marked

differences exist between systems with even and odd numbers of rings. If we interpret a larger stabilization energy as being indicative of a greater susceptibility to distortion, systems with even numbers of rings are seen to be more susceptible to distortion and their stabilization decreases with increasing system size. The opposite trend can be noted for systems with odd numbers of rings from Figs. (2 - 4). In polyacene, the most favourable extended conjugation pattern can be obtained by treating it as coupled polyacetylene chains within the given structural framework. Introducing "double bond" paths along the rungs would only lead to break in conjugation and thus an overall destabilization. This would account for the similarity in the results for polyacene and polyacetylene.

We now examine the effect of correlations on the stabilization of polyacene systems with odd numbers of rings. As can be seen from Figs. (2) and (3), these systems are further stabilized by a non-zero  $U/t$ . This stabilization is seen to increase initially with increasing  $U/t$ , but appears to reach a maximum at  $U/t = 3.0$ , whereupon the effect of  $U/t$  is to relatively destabilize the distorted state. Furthermore, upon increasing  $\delta$  to 0.2, it can be seen from Fig. (4) that the maximum value of the stabilization is not attained even at  $U/t = 4.0$ . As shown by Mazumdar and Dixit, introducing the Hubbard interaction increases the tunneling barrier between the structures with two opposite phases for dimerization. This leads to an increase in the energy difference between the dimerized and undimerized structure upon increasing the Hubbard parameter  $U/t$ . This increased stabilization gradually reduces at larger on-site correlation strengths as the energy scale in the problem changes from the transfer integral  $t$  to  $J = 2t^2/U$ . Since the quantities presented here are differences in energies, they are more difficult to measure accurately than just ground state energies. Furthermore, it is well known that the PQMC method becomes increasingly inaccurate with increasing correlation strength. Since the system shows the interesting turn-around behaviour in  $U/t$  even at  $\delta = 0.1$ , we concentrate on this case without any loss in generality. We observe that systems with even numbers of rings also show an increase in stabilization energy with increasing  $U/t$ . However, there is no discernible maximum in the stabilization energy, for the system sizes and correlation strengths that we have studied. It is evident that the system size variations are strong even at 10 rings for polyacenes with even numbers of rings. However, the extrapolated stabilization energies for the infinite system size obtained from the results for the even-N polyacenes do show a maximum between  $U/t = 3.0$  and 4.0. However, it is not clear at what system size this effect will be observed for finite systems. The trends observed in the stabilization energy with  $\delta$  and  $U/t$  can be compared to the behaviour observed in polyacetylene. As mentioned previously, a variety of analyses, based on QMC methods,



the real-space VB analysis, the variational approaches and numerical RG methods have indicated that the effect of electron correlations is to enhance the Peierls' instability in polyacetylene.

A physical picture of the ground state can be obtained by analyzing the various correlation functions. The rest of our analysis concentrates on systems with odd numbers of rings and specifically on the system of 11 rings, the largest that we have studied. The correlation functions of smaller systems with odd and even numbers of rings also show similar behaviour and we believe that the results of the chosen system are indeed representative of the infinite system. We have computed the bond-bond, spin-spin and charge-charge correlations of these systems. To study the existence of a BOW in systems which have degenerate ground states, the bond-bond correlation function defined as,

$$\langle b_i b_j \rangle = \langle \sum_{\sigma} (a_{i,\sigma}^{\dagger} a_{i+1,\sigma} + h.c.) (a_{j,\sigma}^{\dagger} a_{j+1,\sigma} + h.c.) \rangle, \quad (4)$$

should be studied. The bond order *per se* does not give information about the susceptibility to distortion in systems with possible degenerate distorted states, in the absence of an imposed distortion. Since the bond-bond correlation describes relative distortions of bonds in the system, in principle, its fourier transform would give the amplitudes for various kinds of BOW distortions. The system has five bonds per unit cell and hence there are fifteen possible bond-bond correlation functions. We do not consider all these fifteen correlation functions but instead consider only those correlation functions that correspond to the distortions shown in Figs. (1b) and (1c). For the numbering scheme shown in Fig. (1a), the bond which connects sites  $i$  and  $i + 1$  is labelled  $i$ , with the exception of those labelled  $2N$  and  $4N$ , which connect sites 1 with  $2N$  and  $4N$  with  $2N + 1$ .

In Figs. (5a-c) we present the bond-bond correlations  $\langle b_1 b_j \rangle$  for  $U/t = 2.0$  for the undistorted and  $\delta = 0.1$  cis- and trans- distorted forms of polyacene with 11 rings. To compare the effect of increased correlation strength, we present these correlations for  $U/t = 4.0$ , in Figs. (6a-c). In these figures,  $j = 2, \dots, 2N$  label the bond-bond correlation of the bond "1" with bonds on the upper chain and  $j = 2N + 1 \dots 4N$  label the correlation of bond "1" with bonds on the lower chain. From Figs. (5a) and (6a) we see no evidence for bond-alternation in the ground state of polyacene when it is not imposed in the Hamiltonian, independent of the strength of correlations. However in Fig. (5b) and (5c), we see that the bond-bond correlation reflects the cis- and the trans- bond alternation imposed on the system respectively. Increasing  $U/t$  to 4.0 does not bring about any qualitative change in the picture (Figs. (6b-c)). However, the amplitude for the cis- distortion is larger than that for the trans- distortion for the same imposed bond alternation  $\delta$ . It is

also seen that on going from  $U/t = 2.0$  to  $U/t = 4.0$ , the amplitude of the cis- distortion increases slightly while that of the trans- distortion decreases. Although energetically, the cis- and trans- distortions are favoured almost equally, the bond-bond correlation functions indicate a larger susceptibility to distortion of the cis type. It would be interesting to study the bond-bond correlation function of the doped system, since any domain walls resulting from change over in the phase of the distortion would be very clearly indicated. However, this would require the use of a multi-configurational trial wavefunction to obtain accurate open-shell ground state energies and would be the subject of a different study[31].

In Figs. (7a-c) we present the spin-spin correlations  $4\langle s_1^z s_j^z \rangle$ , where  $j = 2, \dots, 4N$ , for the numbering shown in Fig. (1a). The correlation function falls off very rapidly for  $U/t = 2.0$ . However, we observe from Figs. (8a-c) that while the uniform system starts developing antiferromagnetic fluctuations, the correlation length appears extremely small for the bond-alternated states. It is interesting to note that the amplitude for spin density wave (SDW) distortion is noticeable for the uniform case while in the distorted system this amplitude is nearly vanishing. This indicates that in polyacenes the BOW and SDW are mutually exclusive. The charge-charge correlations shown in Figs. (9a-c) and (10a-c) show that the charge density fluctuation is negligible and rules out charge density wave state in both the distorted and the uniform polyacenes.

### 3 Summary

We have studied polyacene systems with up to eleven rings within the Hubbard model, using the PQMC method. We compare our results with those known for polyacetylene and find strong similarities. We find that systems with even and odd numbers of rings exhibit different behaviour, as do polyacetylene systems with  $4n$  and  $4n + 2$  sites. We compare polyacene systems with odd numbers of rings to coupled  $4n + 2$  polyacetylene rings and systems with even numbers of rings to coupled  $4n$  polyacetylene rings. Electron correlations tend to enhance the effect of bond-alternation. This effect is seen to pass through a maximum for  $U/t \sim 3.0$ , the value for polyacetylene being  $U/t \sim 4.0$ . Furthermore, the correlation strength at which this maximum occurs is seen to be shifted to larger values of  $U/t$  with increase in the bond alternation parameter. A study of the bond-bond correlations indicates that the system has no tendency to destroy the imposed bond-alternation pattern. It also shows that the cis- distortion is favoured over the trans-distortion. The spin-spin correlations show that the undistorted polyacene has a tendency

to form a SDW for large interaction strength. The charge-charge correlations show no evidence for any CDW distortion for the parameters studied.

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## Figure Captions

1. **Figure 1:** Structure of (a) undistorted (b) cis- distorted and (c) trans- distorted polyacene.
2. **Figure 2:** (a)  $\Delta E_{cis}(N, \delta, U)/N$  and (b)  $\Delta E_{trans}(N, \delta, U)/N$ , with  $\delta=0.05$  for polyacenes with 3 to 11 rings.
3. **Figure 3:** (a)  $\Delta E_{cis}(N, \delta, U)/N$  and (b)  $\Delta E_{trans}(N, \delta, U)/N$ , with  $\delta=0.1$  for polyacenes with 3 to 11 rings.
4. **Figure 4:** (a)  $\Delta E_{cis}(N, \delta, U)/N$  and (b)  $\Delta E_{trans}(N, \delta, U)/N$ , with  $\delta=0.2$  for polyacenes with 3 to 11 rings.
5. **Figure 5:** Bond-bond correlations vs. bond separation for (a) undistorted (b) cis-distorted ( $\delta = 0.1$ ) and (c) trans- distorted polyacene ( $\delta = 0.1$ ) for  $U/t=2.0$ .
6. **Figure 6:** Bond-bond correlations vs. bond separation for (a) undistorted (b) cis-distorted ( $\delta = 0.1$ ) and (c) trans- distorted polyacene ( $\delta = 0.1$ ) for  $U/t=4.0$ .
7. **Figure 7:** Spin-Spin correlations vs. intersite separation for (a) undistorted (b) cis-distorted ( $\delta = 0.1$ ) and (c) trans- distorted polyacene ( $\delta = 0.1$ ) for  $U/t=2.0$ .
8. **Figure 8:** Spin-Spin correlations vs. intersite separation for (a) undistorted (b) cis-distorted ( $\delta = 0.1$ ) and (c) trans- distorted polyacene ( $\delta = 0.1$ ) for  $U/t=4.0$ .
9. **Figure 9:** Charge-charge correlations vs. intersite separation for (a) undistorted (b) cis- distorted ( $\delta = 0.1$ ) and (c) trans- distorted polyacene ( $\delta = 0.1$ ) for  $U/t=2.0$ .
10. **Figure 10:** Charge-charge correlations vs. intersite separation for (a) undistorted (b) cis- distorted ( $\delta = 0.1$ ) and (c) trans- distorted polyacene ( $\delta = 0.1$ ) for  $U/t=4.0$ .