A Peierls-extended Hubbard model study on quasi-one-dimensional alternant pi -conjugated high-spin hydrocarbon

A Peierls–extended Hubbard model study on quasi-one-dimensional alternant π-conjugated high-spin hydrocarbon

Z Fang†, Z L Liu†, K L Yao‡§‖ and Z G Li¶

† Department of Physics and National Laboratory of Laser Technology, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China
‡ Centre of Theoretical Physics, CCAST (World Laboratory), Beijing, People's Republic of China
§ International Centre of Material Physics, Academia Sinica, Shenyang 110015, People's Republic of China
‖ Department of Physics, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China‡‡
¶ National Laboratory of Laser Technology, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

Abstract. A Peierls–extended Hubbard model is used to study the possible high-spin ground state of a quasi-one-dimensional alternant π-conjugated hydrocarbon with unequal numbers of atoms on two sublattices, which has been predicted to be a good candidate for organic ferromagnets. Considering the strong electron–phonon (e–ph) coupling and electron–electron (e–e) interaction, allowing for full lattice relaxation, the system is optimized by a set of self-consistent iterative equations. The results of the calculation indicate that the system can show a high-spin ground state owing to the topological structure and the on-site e–e interaction. The intersite e–e interaction will cause a charge density distribution and consequently weaken the stability of the high-spin ground state. It is also found that the dimerization amplitude of the system will always decrease with increasing intersite e–e interaction for different e–ph coupling.

1. Introduction

In recent years, with the discovery of organic conductors and organic superconductors, the search for organic ferromagnets in which there are no ions of the type that are usually magnetic, has become a challenge that has attracted considerable attention [1–4]. The possibilities of the existence of such organic ferromagnets have been demonstrated by the synthesis of some ferromagnetic polymer fragments, such as poly-BIPO [5], m-PDPC [6] and p-NPNN [7].

McConnell [8] first proposed the production of intermolecular ferromagnetic interaction in organic molecules in 1963. Mataga [9] reported another strategy to prepare organic ferromagnets based on intramolecular ferromagnetic interactions in very large molecules. The basic idea of this proposal is the synthesis of alternant hydrocarbon in the high-spin ground state. Then Ovchinnikov [10] considered some large alternant hydrocarbon molecules, wherein the atoms can be subdivided into two groups or sublattices usually

‡‡ Mailing address for correspondence.

called the starred and the unstarred respectively. Ovchinnikov showed that if the numbers of atoms in the two sublattices are unequal, the ground state of the system will be a high-spin state due to the topological nature of the molecular orbitals. Forming domains by such hydrocarbon molecules themselves, an organic ferromagnetic material can be obtained. Several theoretical methods [11, 12] have been used to study the possible high-spin ground state, and a qualitative agreement in that these approaches all predicted a certain high-spin class of molecules was found. However, owing to the complicated structure, the system is still very poorly characterized, and further studies are necessary.
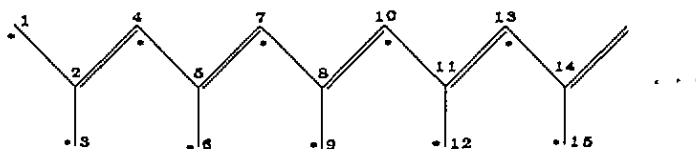

Figure 1. The simplified structure of a typical polymer that has a high-spin ground state in an alternant model. Starred and unstarred atoms belong to different sublattices.

The simplest model system with the essential features of this proposal is the quasi-one-dimensional (quasi-1D) structure shown in figure 1, where the dangling sites can be substituted by various organic free radicals, which contain unpaired electrons. In some cases, the unpaired electrons at free radicals are not conjugated with the π electrons along the main chain and it therefore can be treated as localized spin. For this kind of organic ferromagnetic polymer, we have developed a theoretical model and a self-consistent iterative method [13] to study them. However, in some other cases, the unpaired electrons at free radicals are still conjugated with the π electrons along the main chain and can therefore be itinerant along the chain instead of localized. What will happen for this kind of organic ferromagnetic polymer? This investigation will be the main purpose of this paper. We use here the simpler system (shown in figure 1) so that there is only a π-conjugated orbital associated with each dangling site. Based on the numerical method [13] developed by us, the high-spin ground state of the π-conjugated structure (shown in figure 1) will be studied by the Peierls–extended Hubbard model. The electron–electron (e–e) interaction and the electron–phonon (e–ph) coupling in the system will be considered self-consistently. Allowing for full lattice relaxation, a set of self-consistent iterative equations will be established to study this system. In section 2 we will give the model and the method. Results and discussion will be given in section 3.

2. The Peierls–extended Hubbard model and computational method

We consider the π-conjugated alternant hydrocarbon chain shown in figure 1. Each carbon atom of this system has a π orbital associated with a vertex or site. We use the generalized SSH Hamiltonian to describe the hopping of π electrons and the e–p coupling. The e–e interaction is introduced by the extended Hubbard model. Then the Peierls–extended Hubbard Hamiltonian that has been employed for modelling the polymer is given by

$$H = -\sum_{\langle i,j \rangle}\sum_{\sigma}[t_0 - \alpha Y_{ij}](C_{i,\sigma}^+ C_{j,\sigma} + \text{HC}) + \frac{K}{2}\sum_{\langle i,j \rangle}Y_{ij}^2 + U\sum_{i}n_{i\alpha}n_{i\beta} + V\sum_{\langle i,j \rangle}n_i n_j \qquad (1)$$

where i labels the ith lattice site, j labels the nearest-neighbour lattice site around the ith site and $\langle i, j \rangle$ means two nearest-neighbour sites, $\sigma = (\alpha, \beta)$ labels the direction of spin where α denotes up and β denotes down spin, $C_{i,\sigma}^+$ and $C_{j,\sigma}$ are the creation and the annihilation

operator for a π electron with spin σ on the ith site respectively, Y_{ij} is the displacement of the bond length between the ith and the jth lattice site from the equilibrium position, t_0 is the transfer or overlap integral between the original and the nearest-neighbour carbon sites for the undimerized chain and α is the corresponding rate of change of the overlap integral with distance, K is the effective spring constant between the adjacent units, U is the effective repulsive energy between two π electrons when they are on the same carbon atom and V is the intersite e–e interaction potential energy.

In order to minimize the total energy in our self-consistent calculation, it is convenient to use the following transformations:

$$h = H/t_0 \qquad u = U/t_0 \qquad v = V/t_0 \qquad \lambda = 2\alpha^2/\pi t_0 K$$
$$y_{ij} = (-1)^{i+j}(\alpha/t_0)Y_{ij}. \tag{2}$$

Then using the self-consistent iterative method and self-consistent field Hartree–Fock approximation [13], we can obtain the eigenenergies ε_i, the expansion coefficients $Z^\sigma_{\mu,i}$ of the molecular orbitals and the optimized geometry y_{ij} from the following self-consistent iterative equations:

$$-\sum_j [1 + (-1)^{i+j} y_{ij}] Z^\alpha_{\mu,j} + \left[u \sum_{\substack{\mu' \\ (occ)}} Z^{\beta^*}_{\mu',i} Z^\beta_{\mu',i} + v \sum_j \sum_\sigma \sum_{\substack{\mu' \\ (occ)}} Z^{\sigma^*}_{\mu',j} Z^\sigma_{\mu',j} \right] Z^\alpha_{\mu,i} = \varepsilon^\alpha_\mu Z^\alpha_{\mu,i} \tag{3}$$

$$-\sum_j [1 + (-1)^{i+j} y_{ij}] Z^\beta_{\mu,j} + \left[u \sum_{\substack{\mu' \\ (occ)}} Z^{\alpha^*}_{\mu',i} Z^\alpha_{\mu',i} + v \sum_j \sum_\sigma \sum_{\substack{\mu' \\ (occ)}} Z^{\sigma^*}_{\mu',j} Z^\sigma_{\mu',j} \right] Z^\beta_{\mu,i} = \varepsilon^\beta_\mu Z^\beta_{\mu,i} \tag{4}$$

$$y_{ij} = 2\pi\lambda(-1)^{i+j} \left[\sum_{\substack{\mu,\sigma \\ (occ)}} Z^\sigma_{\mu,i} Z^\sigma_{\mu,j} - \frac{1}{N} \sum_{\langle ij \rangle} \sum_{\substack{\mu,\sigma \\ (occ)}} Z^\sigma_{\mu,i} Z^\sigma_{\mu,i} \right]. \tag{5}$$

Here, periodic boundary conditions are used, and (occ) means those states occupied by electrons. New values of the dimerization order parameter y_{ij} are calculated by minimizing the total energy $E(y_{ij})$ of the system with respect to y_{ij}.

$$E(y_{ij}) = -\sum_{\substack{\langle ij \rangle \\ (occ)}} \sum_\sigma \left\{ [1 + (-1)^{i+j} y_{ij}] \sum_{\substack{\mu \\ (occ)}} [Z^{\sigma^*}_{\mu,j} Z^\sigma_{\mu,i} + Z^{\sigma^*}_{\mu,i} Z^\sigma_{\mu,j}] \right\} + \frac{1}{\lambda\pi} \sum_{\langle ij \rangle} y^2_{ij}$$
$$+ u \sum_i \sum_{\substack{\mu \\ (occ)}} \sum_{\substack{\mu' \\ (occ)}} |Z^\alpha_{\mu,i}|^2 |Z^\beta_{\mu',i}|^2 + v \sum_{\langle i,j \rangle} \sum_{\substack{\mu \\ (occ)}} \sum_{\substack{\mu' \\ (occ)}} \sum_{\sigma,\sigma'} |Z^\sigma_{\mu,i}|^2 |Z^{\sigma'}_{\mu',i}|^2. \tag{6}$$

From (3)–(5), we can obtain the optimized configuration and energy levels of the system self-consistently. We can also obtain the spin density and the charge density of electrons at every lattice site as

$$\delta n_i = (n^\alpha_i - n^\beta_i)/2 = \frac{1}{2} \left(\sum_{\substack{\mu \\ (occ)}} Z^{\alpha^*}_{\mu,i} Z^\alpha_{\mu,i} - \sum_{\substack{\mu \\ (occ)}} Z^{\beta^*}_{\mu,i} Z^\beta_{\mu,i} \right) \tag{7}$$

$$n_i = (n^\alpha_i + n^\beta_i) = \left(\sum_{\substack{\mu \\ (occ)}} Z^{\alpha^*}_{\mu,i} Z^\alpha_{\mu,i} + \sum_{\substack{\mu \\ (occ)}} Z^{\beta^*}_{\mu,i} Z^\beta_{\mu,i} \right). \tag{8}$$

The starting geometry in the iterative optimization process is usually the one with zero dimerization. The stability of the optimized geometry is always tested by using
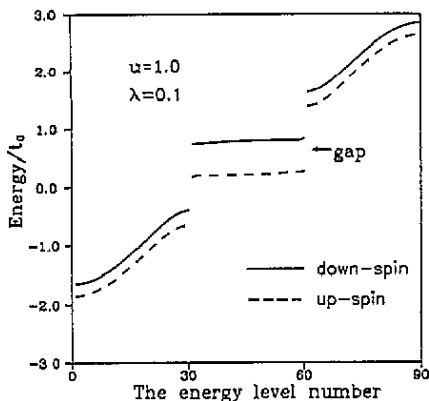
Figure 2. The energy levels of π electrons when $\lambda = 0.1$, $u = 1.0$, $v = 0.0$.
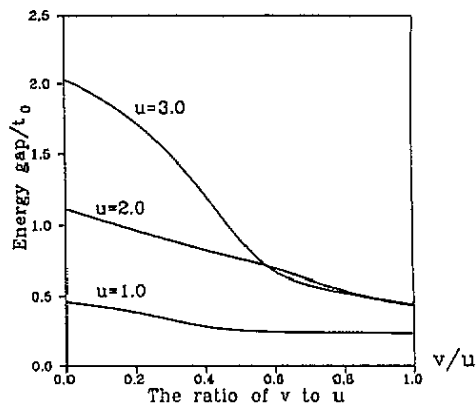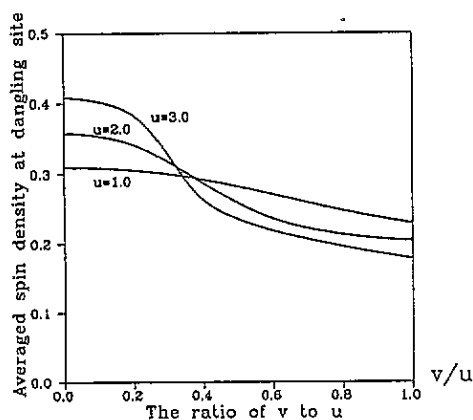
Figure 3. The energy gap between the localized up-spin and down-spin bands as a function of the intersite e–e interaction for different on-site e–e interactions with $\lambda = 0.1$.

another starting configuration and performing the optimization again. For all parameters included in this study, the same optimal ground state was reached, independent of the starting configuration. The criterion for terminating the optimization is that between two successive iterations, the difference is less than 10^{-5} Å for the dimerization order parameter.

3. Results and discussion

We now consider a periodic alternant π-conjugated hydrocarbon chain shown in figure 1, which contains 90 sites and 90 π electrons. This network can be subdivided into two groups shown as starred and unstarred. It is clear that the numbers of carbon atoms in the two groups are unequal. From (3) and (4), we know that the eigenvalue equations are asymmetric about spin owing to the on-site e–e interaction. So in this kind of system, the degeneration of spin has been lifted, and we must solve the given equations with different spins respectively. In order to study the ground state, we always fill the π electrons in the possible lowest levels in every iterative step.

In our calculations, there are three parameters, λ, u and v. Since the main chain of this network is the same as that of polyacetylene, we can estimate the parameters with parameters of polyacetylene as $\lambda = 0.0$–0.3, $u = 0.0$–3.0 and $v < u$ [14]. For a different system, such as different substituted organic free radicals, the parameters can vary. At first, we neglect the intersite e–e interaction ($v = 0$), and consider only the onsite e–e interaction. Figure 2 shows the energy levels of the system when $\lambda = 0.1$ and $u = 1.0$. We have three up-spin and three down-spin bands, each of which contains 30 energy levels. The up-spin bands have lower energy than the down-spin bands. The two lower bands (up and down spin) and the two upper bands (up and down spin) mainly originate from the π orbitals along the main chain, and the gap between the upper and the lower bands is the result of Peierls instability and the dimerization. We also have two highly degenerate bands (up and down spin) in the middle of the Peierls energy gap, which is qualitatively different from the π energy levels of [13]. This is because in [13] we treat the unpaired electrons at dangling sites as localized spins, but here the electrons at dangling sites can be itinerant along the

Figure 4. The spin density at the dangling site as a function of the intersite e–e interaction for different on-site e–e interactions with $\lambda = 0.1$.
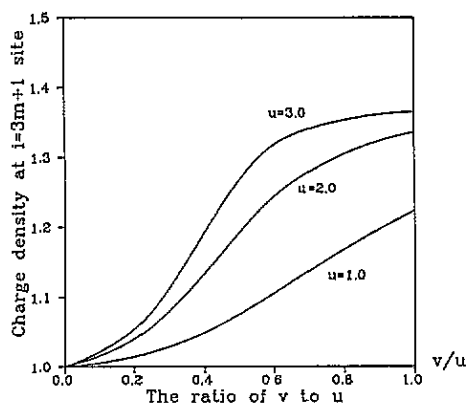
Figure 5. The charge density at the $i = 3m + 1$ site as a function of the intersite e–e interaction for different on-site e–e interactions with $\lambda = 0.1$.

chain instead of localized. That is to say the two high-degeneracy bands originate from the conjugated π orbitals at the dangling sites. Since we have 90 electrons, the two localized bands are just at the Fermi level. Then in the ground state, the two lower bands will be filled up by up- and down-spin electrons respectively, and for the two localized bands in the middle, only the up-spin branch is filled up by electrons. This kind of asymmetric distribution of π electrons of different spin causes a high-spin ground state. At this time, along the chain there appears a distribution of spin density, the amplitude of which will increase with increasing on-site e–e interaction u. At all the dangling sites, there appears up-spin density distribution. This parallel spin arrangement at dangling sites is simply a high-spin state. The indirect spin interactions between spins at dangling sites result in the antiparallel spin density distribution along the main chain. Here, the energy gap between the localized up-spin and down-spin bands is a very important parameter. The larger the gap is, the more stable the high-spin ground state is. If the gap vanishes, the high-spin ground state will no longer be stable.

In the following, we will consider the effect of the intersite e–e interaction on the high-spin ground state. Figure 3 shows the energy gap as a function of the intersite e–e interaction v for different on-site e–e interactions u. We can see clearly that for different u the energy gaps always decrease with increasing intersite e–e interaction v. This means that the intersite e–e interaction will weaken the stability of the high-spin ground state of the system. This can be confirmed by calculations of the spin density and the charge density. Figure 4 shows the averaged spin density at dangling sites as a function of the intersite e–e interaction. We can see clearly that the spin density will decrease with increasing intersite e–e interaction v. From the above discussions, we know that the high-spin ground state will become unstable. This is due to a charge density distribution appearing with addition of intersite e–e interaction. Figures 5–7 show changes of charge density distribution at three different sites, labelled by $i = 3m + 1$, $i = 3m + 2$ and $i = 3m$, respectively (shown in figure 1). The charge density n_i is averaged through the chain respectively. When $v = 0$, there is no charge density fluctuation at all the sites ($n_i = 1.0$ for all sites). With increasing intersite e–e interaction v, a charge density fluctuation appears. This charge density distribution will weaken the spin density distribution of the system, and consequently will weaken the high-spin ground state.
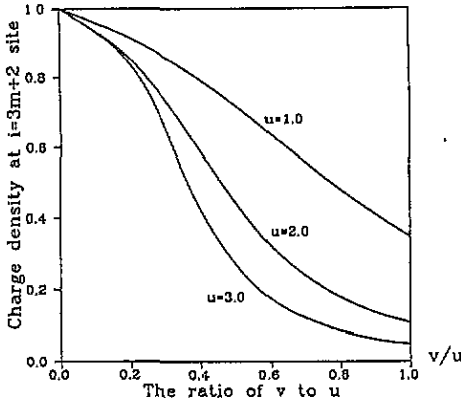
Figure 6. The charge density at the $i = 3m + 2$ site as a function of the intersite e–e interaction for different on-site e–e interactions with $\lambda = 0.1$.
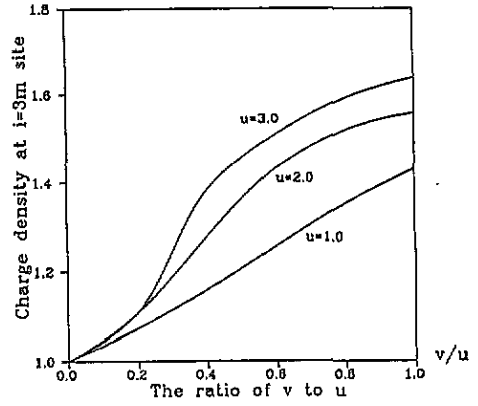

Figure 7. The charge density at the $i = 3m$ site as a function of the intersite e–e interaction for different on-site e–e interactions with $\lambda = 0.1$.
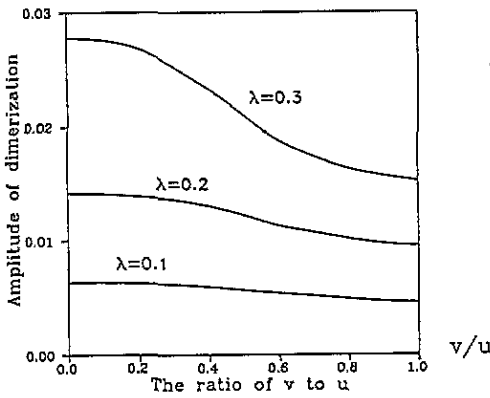

Figure 8. The dimerization amplitude of the system as a function of the intersite e–e interaction for different e–ph couplings with $u = 1.0$.
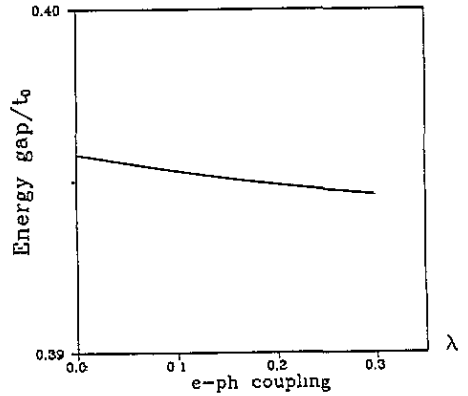

Figure 9. The evolution of the energy gap as a function of the e–ph coupling λ with $u = 1.0$ and $v = 0.2u$.

In conjugated polymers, the amplitude of dimerization is also quite important. Figure 8 shows the dimerization amplitude, expressed as $\langle y_{ij} \rangle$, as a function of the intersite e–e interaction v for different e–ph coupling λ. We can see clearly that the dimerization amplitude of the system will always decrease with increasing intersite e–e interaction v for different e–ph couplings λ. To give a qualitative comparison with the results on short oligomers in [11], figure 9 shows the evolution of the energy gap as a function of the e–ph coupling λ with $u = 1.0$ and $v = 0.2u$. Clearly the energy gap will decrease with increasing e–ph coupling λ. Since the dimerization amplitude of the system will be larger with increasing e–ph coupling λ (this can be seen from figure 8), we can be convinced that the dimerization of the system will weaken the stability of the high-spin state. This is consistent with the results on short oligomers in [11].

In summary, considering the strong e–p coupling and the e–e interactions, we have

studied the possible high-spin ground state of an alternant π-conjugated hydrocarbon chain by the Peierls–extended Hubbard model. Allowing for full lattice relaxation, a set of self-consistent iterative equations have been established to study the system. The results of calculation show that owing to the topological structure and the on-site e–e correlation, the system can show a high-spin ground state. The intersite e–e interaction will cause a charge density distribution along the chain and consequently weaken the stability of the high-spin ground state. The dimerization amplitude of the system will always decrease with increasing intersite e–e interaction for different e–ph coupling.

Acknowledgment

References

[1] Miller J S, Epstein A J and Reiff W M 1988 *Chem. Rev.* **88** 201; 1988 *Science* **240** 40
[2] Gatteschi D and Sessoli R 1992 *J. Magn. Magn. Mater.* **104–107** 2092
[3] Iwamura H and Miller J S (ed) 1993 *Proc. Int. Symp. on Chemistry and Physics of Molecular Based Magnetic Materials (Tokyo); Mol. Cryst. Liq. Cryst.* **232** 1, **233** 1
[4] Gatteschi D, Kahn O, Miller J S *et al* (ed) 1991 *Magnetic Molecular Materials, NATO ASI Series 198* (Dordrecht: Kluwer)
[5] Ovchinnikov A A and Spector V N 1988 *Synth. Met.* B **27** 615
[6] Nasu K 1986 *Phys. Rev.* B **33** 330
[7] Takahashi M, Turek P, Nakazawa Y *et al* 1991 *Phys. Rev. Lett.* **67** 746
[8] McConnell H M 1963 *J. Chem. Phys.* **39** 1910
[9] Mataga N 1968 *Theor. Chim. Acta* **10** 372
[10] Ovchinnikov A A 1978 *Theor. Chim. Acta* **47** 297
[11] Sinha B, Albert I D L and Ramasesha S 1990 *Phys. Rev.* B **42** 9088
[12] Klein D J, Nelin C J, Alexander S and Matsen F A 1982 *J. Chem. Phys.* **77** 3101
[13] Fang Z, Liu Z L and Yao K L 1994 *Phys. Rev.* B **49** 3916
[14] Heeger A J, Kivelson S, Schrieffer J R and Su W P 1988 *Rev. Mod. Phys.* **60** 781, and references therein