

LOCALIZATION LENGTH TUNED BY EXTERNAL MAGNETIC FIELD IN POLYPHENYLENE TYPE OF POLYMERS

R. Trencsényi

Department of Theoretical Physics, University of Debrecen
H-4010 Debrecen, Hungary

Abstract

The topic of present paper is given by the polyphenylene type of quasi-1D hexagon chains, whose ground states have been examined by exact methods. The main line of the study was investigating the reactions of the system in case of changing some circumstances, e.g. how can the physical properties of the chain be influenced by turning on or off an external magnetic field, or modifying the total number of electrons in the system?

I. Introduction

Polyphenylene stands as a collective noun for those quasi-1D polymer chains whose hexagonal cells are connected by a bond along a periodic structure. A lot of different representatives of polyphenylenes can be mentioned, for example polyphenylene oxide (PPO), polyphenylene sulfide (PPS), polyphenylene vinylene (PPV), polyarylene ether (PAE), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), etc.

Polyphenylenes are thermoplastic polymers having very special chemical and mechanical properties. Itemizing some aspects, for example PPO is a high-temperature thermoplastic, which resists to high heat, and has a good dimensional stability. It is rarely used in its pure form, it is usually mixed with polystyrene, creating in this way a homogenous mixture of

two polymers. It is remarkably interesting since polymers are mostly incompatible with each other, which means that they tend to disintegrate to separate phases in the course of mixing. The blend of PPO and polystyrene is widely used for example to produce printer cartridges. In addition, it can be applied in electronics, household and automotive items, and they are also used in medicine for sterilizable instruments made of plastic [1]. PPS is one of the most important high-temperature polymers because it shows such advantageous properties like resistance to heat, acids, abrasion, mildew, aging or sunlight, it can be molded, extruded or machined to high tolerances. PPS can serve as a good stock for fabricating synthetic fiber and textiles resisting to thermal and mechanical attack. It is highly proper for making filter fabric for coal boilers, papermaking felts, special membranes, gaskets and packings.

Beyond these, there are still a number of areas where polyphenylenes can be relevant in for example nanoscale junctions [2], light emission possibilities [4], frequency dependence in specific heat [5], temperature dependent elastohydrodynamic properties [6], fuel cell technology [7]. These applications take the intrinsic properties of polyphenylenes as a basic, but besides, they can also be used in diffusion pumps, aerospace applications, electronic connectors, high-temperature hydraulic systems or ultra high vacuum and heat transfer processes [8]-[10].

As regards the theoretical treatments, some studies have revealed the fact that inter-electronic correlations play a high important role in the physical processes taking place in chain structures [2],[3], so these correlation effects actually can not be neglected during the descriptions. In virtue of this statement, we aimed to consider genuine correlation effects, which has been carried out by making use of exact terms. Details can be found in [11].

II. Presentation of the starting points: the system and the method

II.1 The system

The structure of the studied system can be observed in Fig. 1. As seen, one primitive cell of the chain is given by one hexagon containing six sites

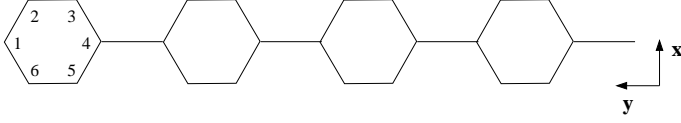


Figure 1: The structure of the studied polymers

denoted by number 1 to number 6. One carbon atom is placed on each site, and dependingly on the concrete nature of the matter, different groups of atoms can be attached to certain carbon sites. As an example, in case of polyphenylene oxide a methyl group (CH_3) joins to site 3 and site 5 in each cell of the chain. Hexagons are linked by bonds shaping hereby the periodic structure of the system. These bonds connecting hexagons can evolve chemically in various ways in different systems. For examples, at polyphenylene oxide an oxygen atom, while at polyphenylene sulfide a sulphur atom appears in each linking bond between hexagons. In Figure 1. four cells are depicted, but – since *polymer* structures are in focus – the number of cells denoted by N_c can be an arbitrary positive integer.

The Hamiltonian of the system is given by

$$\hat{H} = \hat{H}_0 + \hat{H}_U, \quad (1)$$

where

$$\begin{aligned} \hat{H}_0 &= \sum_{\sigma} \sum_{\mathbf{i}} \epsilon_{\mathbf{i}} \hat{n}_{\mathbf{i},\sigma} + \sum_{\sigma} \sum_{\mathbf{i},\mathbf{j}} (t_{\mathbf{ij}} e^{i\gamma_{\mathbf{ij}}} \hat{c}_{\mathbf{i},\sigma}^{\dagger} \hat{c}_{\mathbf{j},\sigma} + H.c.), \\ \hat{H}_U &= U \sum_{\mathbf{i}} \hat{n}_{\mathbf{i},\uparrow} \hat{n}_{\mathbf{i},\downarrow}. \end{aligned} \quad (2)$$

In (1,2) \hat{H}_0 yields the kinetic energy, while \hat{H}_U provides the potential energy of the system.

$\hat{c}_{\mathbf{i},\sigma}^{\dagger}$ creates an electron possessing spin projection σ on site \mathbf{i} , and $\hat{c}_{\mathbf{j},\sigma}$ annihilates an electron with spin projection σ from site \mathbf{j} . Accordingly, the product $\hat{c}_{\mathbf{i},\sigma}^{\dagger} \hat{c}_{\mathbf{j},\sigma}$ represents a hopping of an electron which eventuate from site \mathbf{j} to site \mathbf{i} . This hopping is characterized by the energy value $t_{\mathbf{ij}}$, near which the so-called Peierls phase factor $e^{i\gamma_{\mathbf{ij}}}$ emerges. With this exponential factor one can take into account an external magnetic field \vec{B} . In present case the

magnetic field is assumed to be perpendicular to the plane of the chain, i.e. the direction of vector \vec{B} is the same as which of axis z by Fig. 1. If \vec{A} the belonging vector potential via $\vec{B} = \text{rot}\vec{A}$, then γ_{ij} from the Peierls factor can be given by a linear integral as $\gamma_{ij} = (2\pi/\Phi_0) \int_j^i \vec{A} d\vec{l}$, where $\Phi_0 = \frac{hc}{e}$ denotes the flux quantum. In order to calculate the integral of γ_{ij} , one must choose an appropriate form for the vector potential. For mathematical convenience, \vec{A} was chosen with the components $A_x = A_z = 0$, $A_y = Bx$, so it was defined along the axis y .

In the first sum of \hat{H}_0 , $\hat{n}_{i,\sigma} = \hat{c}_{i,\sigma}^\dagger \hat{c}_{i,\sigma}$ represents the particle number operator which counts the electrons with spin projection σ occurring on site i , and the corresponding on-site potential is denoted by ϵ_i . By the meanings of them, these terms are the local one-particle contributions in \hat{H}_0 .

\hat{H}_U in (2) is written according to the Hubbard model, which means that short-range Coulomb repulsion is considered between electrons, i.e. only the on-site contributions are kept from the Coulomb function. U stands for the coupling constant characterizing the strength of the interaction having a repulsive nature, hence the sign of U is given by $U > 0$.

II.2 The method

The applied method for deducing exact ground states in the system makes use of the advantageous property of positive semidefinite operators that their spectrum has a well-defined lower bound. Namely, they possess a non-negative spectrum, thus the lowest eigenvalue of them is zero. Hence, it is expedient to transcribe the Hamiltonian (1,2) into a positive semidefinite structure by $\hat{H} = \hat{H}_P + K$, where \hat{H}_P is generated as a sum of positive semidefinite operators, \hat{P}_n , i.e. $\hat{H}_P = \sum_n \hat{P}_n$, and K is an additive scalar constant. After this, one should make an effort to construct the Ψ_0 ground state wave function of the system, applying the condition $\hat{H}_P \Psi_0 = 0$. If one succeeds in finding the most general wave function which can satisfy the requirement $\hat{H}_P \Psi_0 = 0$, then Ψ_0 will describe the exact ground state of the system, and K will provide the E_0 exact ground state energy, i.e. $K = E_0$.

III. Some thoughts about the results

Regarding the final form of the ground state wave function Ψ_0 , we obtained the expression

$$|\Psi_0\rangle = \prod_{\mathbf{i}} \hat{V}_{\mathbf{i},\sigma}^\dagger |0\rangle, \quad (3)$$

where \mathbf{i} runs over lattice sites, $|0\rangle$ denotes the bare vacuum state, and the operators $\hat{V}_{\mathbf{i},\sigma}^\dagger$ are built up as linear combinations of fermionic creation operators by

$$\hat{V}_{\mathbf{i},\sigma}^\dagger = \sum_j x_j \hat{c}_{\mathbf{i}_j,\sigma}^\dagger. \quad (4)$$

A given operator $\hat{V}_{\mathbf{i},\sigma}^\dagger$ can place one electron in the system with spin projection σ , which can occur on either of the sites \mathbf{i}_j . For example, the coefficient x_k is a numerical prefactor belonging to site \mathbf{i}_k , and $|x_k|^2$ yields the probability of occurring of the electron on site \mathbf{i}_k . Now it is clear that the total number of electrons, N in the system is fixed by the number of operators $\hat{V}_{\mathbf{i},\sigma}^\dagger$ in the product of (3).

Only one question has remained relating to expression (4). What may be the domain of variability of the index j ? In other words, how extended may be the domain where one electron can emerge?

III.1 $\vec{B} = 0$ case

In the first part of the study we have investigated the system without external magnetic field. Note that in this case one has to treat a Hamiltonian in (1,2) which does not contain Peierls phase factors because – via $\vec{A} = 0$, $\gamma_{ij} = 0$ – they disappear from \hat{H}_0 .

As seen in Fig. 2., in absence of \vec{B} , operators $\hat{V}_{\mathbf{i},\sigma}^\dagger$ possess a block-like structure, which means that the sum in (4) consists of only a few terms, since each $\hat{V}_{\mathbf{i},\sigma}^\dagger$ has only four sites. These blocks are illustrated by black dots encircled with rectangles in Fig. 2., and here it can be clearly observed that the blocks of operators $\hat{V}_{\mathbf{i},\sigma}^\dagger$ are completely separated from each other, i.e. they do not share common sites in the chain. Because of the special

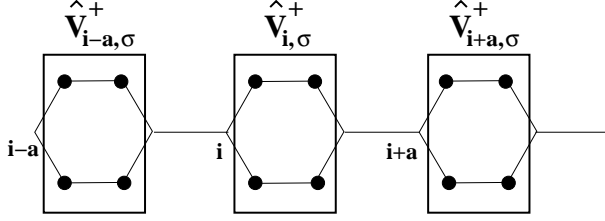


Figure 2: The structure of operators $\hat{V}_{i,\sigma}^\dagger$ in case of $\vec{B} = 0$. \mathbf{a} represents the Bravais vector of the lattice.

structure of $\hat{V}_{i,\sigma}^\dagger$, the region of occurrence of one electron is confined to one cell of the chain, thus the maximal number of electrons which can be present in the system is equal to the number of cells, N_c . In pursuance of the above, the block-structured operators $\hat{V}_{i,\sigma}^\dagger$ realise in-cell-localized electron states in the chain, which physically leads to a localized ground state. On the other hand, since the blocks of $\hat{V}_{i,\sigma}^\dagger$ are separated, no chance is given σ indices to be correlated. So, the spin projections of electrons are independent from each other, and this results in a paramagnetic ground state. This paramagnetic and localized property of the ground state is valid in the continual domain $N \leq N_c$ because varying N in the interval $N \leq N_c$, the separated characteristic of operators $\hat{V}_{i,\sigma}^\dagger$ remains.

III.2 $\vec{B} \neq 0$ case

Now, we switch an external magnetic field on the chain, which is perpendicular to the (x, y) plane presented in Fig. 1. Herewith, of course, the Peierls phase factors must be taken into account in \hat{H}_0 of the Hamiltonian (1,2).

Fig. 3. shows the structure of operators $\hat{V}_{i,\sigma}^\dagger$ in case of applying \vec{B} . Here it can be seen that $\hat{V}_{i,\sigma}^\dagger$ preserve their block-like nature, but in this case in the sum of (4) more contributions are present than which of situation $\vec{B} = 0$. Namely, now each $\hat{V}_{i,\sigma}^\dagger$ possesses ten sites, whereby a given operator $\hat{V}_{i,\sigma}^\dagger$ cover two neighbouring cells of the chain. Consequently, it can happen that two adjacent $\hat{V}_{i,\sigma}^\dagger$ share common sites, i.e. they touch each other. In

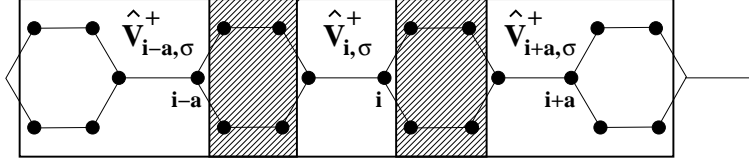


Figure 3: The structure of operators $\hat{V}_{i,\sigma}^{\dagger}$ in case of $\vec{B} \neq 0$. \mathbf{a} represents the Bravais vector of the lattice.

other words, they satisfy the so-called connectivity condition. The domains of the common sites of two neighbouring operators is pictured by the ruled, gray areas in Fig. 3. in case of $\hat{V}_{i-a,\sigma}^{\dagger}$, $\hat{V}_{i,\sigma}^{\dagger}$ and $\hat{V}_{i+a,\sigma}^{\dagger}$. If N is rather small, then it can be possible that the operators $\hat{V}_{i,\sigma}^{\dagger}$ separate from each other, composing a paramagnetic and localized ground state. But increasing the N number of electrons, bigger and bigger clusters can evolve in the system, and in border-line case, when $N = N_c$, each pair of adjacent $\hat{V}_{i,\sigma}^{\dagger}$ will overlap (see Fig. 3. again). Regarding the physical properties, it means that in case of $N = N_c$ extended electron states can come into existence, which makes the possibility for generating a delocalized ground state. Nevertheless, satisfying the connectivity condition has another important consequence. Namely, the σ spin indices of $\hat{V}_{i,\sigma}^{\dagger}$ become correlated, since the system tries for minimizing its energy, and in the interest of this, it eliminates the double occupied sites by fixing all of the electron spins at the same value. This circumstance, however, leads to a ferromagnetic ground state. Thus, enhancing the N number of electrons gradually, bigger and bigger ferromagnetic clusters can be created, and in case of $N = N_c$ the system turns into a saturated ferromagnet. So, it means that the localization length of the electron states can be changed by varying the total number of electrons, modifying in this manner the magnetic properties of the system.

Moreover, it must be emphasized, too that varying N is not the only way to alter the physical properties of the chain because – comparing subsection III.1 with III.2 – it is clear that applying an external magnetic field is as well as proper for tilting the system from a paramagnetic and localized ground state to a ferromagnetic and delocalized one, as long as $N = N_c$ holds.

IV. A short summary

Polyphenylene types of hexagonal chains have been analysed by means of a technique which is based on the positive semidefinite operators. We have deduced ground state wave functions in the system, and have studied the physical properties of them. The deduction of ground states has been carried out without, or rather in presence of external magnetic field, \vec{B} . It has turned out that if $\vec{B} = 0$, than in the continuous interval of $N \leq N_c$, the system behaves as a paramagnet generated by localized electrons. However, in case of $\vec{B} \neq 0$ the system can be transferred from a paramagnetic and localized ground state to an itinerant ferromagnet by increasing the total number of electrons. If N is fixed by $N = N_c$, then the localization length can be tuned by the external magnetic field.

First and last, note that the system can be switched between two phases having different physical properties by changing the total number of electrons or – when $N = N_c$ stands – by switching on or off an external magnetic field.

Acknowledgements

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