

SOME INTERESTING REMARKS RELATED TO PHASE DIAGRAMS OF POLYPHENYLENE STRUCTURES

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Abstract

Phase diagrams of exact ground states of polyphenylene types of quasi-1D hexagonal chain structures have been deduced and examined. During the calculations some special characteristics of the phase space have been revealed.

I. Introduction

This study deals with the polyphenylene types of hexagonal chains which are built up periodically by hexagons joint each other through intercell-bonds, constituting a quasi-1D organic polymer chain. Many different representatives of polyphenylenes can be mentioned, for example polyphenylene oxide, polyphenyl sulfide, polyphenyl ether, polyphenyl thioether, polyarylene ether, polyethylene terephthalate etc.

These types of hexagonal chains can have a wide range of application possibilities which is due to their special chemical and mechanical properties. Emphasizing some areas: aerospace applications, diffusion pumps, high-temperature hydraulic systems, electronic connectors, ultra high vacuum or heat transfer processes [1, 2, 3].

Focusing on the intrinsic physical properties of polyphenylenes, many investigations happened from quite diverse aspects, as for example lighth emission possibilities [4], application possibilities in fuel cell technology [5],

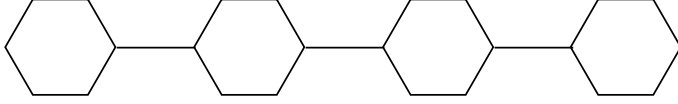


Figure 1: The structure of polyphenylene.

temperature dependent elastohydrodynamic properties [6], frequency dependence in specific heat [7], application possibilities in nanoscale junctions [8]. Some studies reveal also the fact that inter-electronic correlations play a high important role in the physical processes [8, 9], so they actually can not be neglected during the descriptions.

II. The Hamiltonian of the system

Let us have a look at Figure 1, which shows the line drawing of the polyphenylene chains. As seen, one primitive cell of the system is determined by one hexagon which contains six sites at the vertexes of the hexagon. On these sites single carbon atoms are located, but in several cases additional groups of atoms can be attached to certain carbon atoms in the chain (for example a CH_3 methyl group in case of polyphenylene oxide). The neighbouring hexagonal primitive cells are connected by intercell-bonds, which can be created by different atoms in different systems (for example an oxygen atom at polyphenylene oxide, or a sulphur atom at polyphenylene sulfide). Figure 1 illustrates the polyphenylene types of chains of course only schematically, and – although only four cells are depicted – the number of cells denoted by N_c can be an arbitrary positive integer.

The studied system is described by the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_U$, where

$$\begin{aligned} \hat{H}_0 &= \sum_{\sigma} \sum_{\mathbf{i}} \epsilon_{\mathbf{i}} \hat{n}_{\mathbf{i},\sigma} + \sum_{\sigma} \sum_{\substack{\mathbf{i},\mathbf{j} \\ \mathbf{i} \neq \mathbf{j}}} (t_{\mathbf{ij}} \hat{c}_{\mathbf{i},\sigma}^{\dagger} \hat{c}_{\mathbf{j},\sigma} + t'_{\mathbf{ij}} \hat{c}_{\mathbf{i},\sigma}^{\dagger} \hat{c}_{\mathbf{j},\sigma} + H.c.), \\ \hat{H}_U &= U \sum_{\mathbf{i}} \hat{n}_{\mathbf{i},\uparrow} \hat{n}_{\mathbf{i},\downarrow}. \end{aligned} \quad (1)$$

In expression (1) \hat{H}_0 gives the kinetic energy of the system, while \hat{H}_U demonstrates the Hubbard interaction between electrons. $\hat{c}_{\mathbf{i},\sigma}^\dagger$ creates an electron with spin projection σ on site \mathbf{i} , $\hat{c}_{\mathbf{j},\sigma}$ annihilates an electron with spin projection σ from site \mathbf{j} , and $\hat{n}_{\mathbf{i},\sigma} = \hat{c}_{\mathbf{i},\sigma}^\dagger \hat{c}_{\mathbf{i},\sigma}$ holds. $\epsilon_{\mathbf{i}}$ represents the one-particle on-site potential, t and t' denote the nearest and the next nearest hopping matrix elements, respectively, while the coupling constant U yields the strength of the Hubbard interaction. Hubbard interaction is essentially short-range Coulomb interaction between electrons, and due to the repulsive nature of it, U has to be positive, i.e. $U > 0$. The sum $\sum_{\mathbf{i}}$ runs over the N_c cells of the system.

In the Hubbard terms in (1) we have taken into account only on-site contributions from the Coulomb repulsion, i.e. interaction between electrons occurring on the same site. Interactions between first, second, third, ... neighbour electrons of course also exist in the system, but compared to the on-site terms they are smaller with one, two, three, ... orders of magnitude, thus the longer-range Coulomb contributions can be neglected during the calculations. By several estimations the value of the on-site Coulomb-repulsion in organic chain structures built up from hexagonal cells is around or above 10 eV [8, 9, 10, 11], so these data confirm that the on-site Hubbard repulsion is the highest interaction in the system.

III. About our method

As written in Section I., the inter-electronic correlation effects play a high important role in the evolving of physical properties of polymer structures, hence in order to reveal and understand the real physical aspects of these systems, the descriptions must be effectuated at an exact calculational level. Accordingly, we have applied such an exact method for deducing ground states in the system which utilizes the peculiarity of positive semidefinite operators. The operator \hat{P} has a positive semidefinite characteristic, if the $\langle \psi | \hat{P} | \psi \rangle \geq 0$ relation holds for any $|\psi\rangle$ wave vector of the Hilbert space. Making use of the $\hat{P}|\psi\rangle = p|\psi\rangle$ eigenvalue equation of \hat{P} , one can be led to the conclusion that $p \geq 0$, i.e. the set of the eigenvalues is non-negative, which means that the spectrum of \hat{P} has a well-defined lower bound, namely the zero. This fact was of capital importance in the development of our

exact method. The substance of the procedure is that we transcribe the Hamiltonian of the system from (1) to a positive semidefinite form by

$$\hat{H} = \hat{P} + C, \quad (2)$$

where \hat{P} is usually generated as a sum of positive semidefinite operators, $\hat{P} = \sum_q \hat{P}_q$, and C provides a constant value. Now, if the transformed Hamiltonian in (2) acts on an arbitrary $|\psi\rangle$ element of the Hilbert space, we get to the expression $\hat{H}|\psi\rangle = (\hat{P} + C)|\psi\rangle$, from where – considering the $p = 0$ lowest eigenvalue – through

$$\hat{P}|\psi\rangle = 0, \quad (3)$$

we obtain the $\hat{H}|\psi\rangle = C|\psi\rangle$ eigenvalue equation. At this point it must be emphasized that even condition (3) is the clue to deduce exact ground states in the system. Namely, if one succeeds in constructing the most general wave vector which satisfies (3), then $|\psi\rangle$ yields the effective ground state wave function of the system, i.e. $|\psi\rangle = |\psi_g\rangle$, and C provides the attached ground state energy, i.e. $C = E_g$.

The above reviewed method is very productive in many respects. On the one hand, its applicability is absolutely independent of the dimension and the number of constants of motion of the system. On the other hand, one has to make conscious that the transformation of \hat{H} into positive semidefinite form is not at all a trivial step. Namely, even though the lower bound of the spectrum of \hat{H} is unknown, however, one can determine the ground state energy of the system, since the lower bound of the spectrum of \hat{P} is known and fixed at zero. And as seen from (2), \hat{H} and \hat{P} differ only in the constant C , thus shifting the lower bound of \hat{P} with the constant C , one can gain all information about E_g .

In order to carry out the transformation in (2) effectively, one has to create a concretely given form of \hat{P} so that \hat{P} must reproduce \hat{H} identically. This comparison and identity always generates a system of equations, which contains the starting parameters of \hat{H} , the parameters of \hat{P} (they are usually coefficients), and the constant C . Totally generally these relations can be graphically incorporated in a function form by

$$F(\{\epsilon_1, \epsilon_2, \dots, \epsilon_m, t_1, t_2, \dots, t_n, U\}, \{s_1, s_2, s_3, \dots, s_k\}, C) = 0, \quad (4)$$

where $\epsilon_1, \epsilon_2, \dots, \epsilon_m, t_1, t_2, \dots, t_n$, and U the relevant on-site one-particle potentials, the hopping matrix elements, and the couple constant of the Hubbard interaction. The set of $s_1, s_2, s_3, \dots, s_k$ denotes generally the parameters of \hat{P} , and C is the constant from (2). In the equations of (4) $\epsilon_1, \epsilon_2, \dots, \epsilon_m, t_1, t_2, \dots, t_n, U$ are considered as known parameters, while $s_1, s_2, s_3, \dots, s_k$ and C must be deduced in order to determine \hat{P} and hereby perform condition (3) to obtain the ground state wave function $|\psi_g\rangle$. (4) usually leads to a non-linear complex algebraic system of equations, which are called matching equations. These matching equations usually contain more equations than unknown variables, thus after expressing the unknown $s_1, s_2, s_3, \dots, s_k$ and C parameters, some additional equations still remain, which determine extra conditions between the $\epsilon_1, \epsilon_2, \dots, \epsilon_m, t_1, t_2, \dots, t_n, U$ parameters. Then, these extra conditions define a special restricted D domain in the parameter space, where the relevant ground state wave function deduced based on (3) is valid. Of course, it can also happen that the matching equations have more than one possible solutions, and in this case each solution fixes the deduced ground state in different D', D'', \dots regions.

Moreover, we would like to underline that the transformation of the starting Hamiltonian in (2) can be carried out in many different ways, since the transcription of \hat{H} itself is determined by the chosen structure of \hat{P} (for example \hat{P} can be structured as $\hat{P} = \sum_i \hat{A}_i^\dagger \hat{A}_i$, where \hat{A}_i is a linear combination of fermionic annihilation operators). Consequently, each transformation generates different systems of equations $F_1 = 0, F_2 = 0, F_3 = 0, \dots$, which provide solutions in different D_1, D_2, D_3, \dots restricted domains of the parameter space, and the proper ground state wave functions $|\psi_{g,1}\rangle, |\psi_{g,2}\rangle, |\psi_{g,3}\rangle, \dots$ exist in these D_1, D_2, D_3, \dots domains, thus demonstrating:

$$\begin{aligned}
F_1(\{\epsilon_1, \epsilon_2, \dots, \epsilon_m, t_1, t_2, \dots, t_n, U\}, \{s_1, s_2, s_3, \dots, s_k\}, C) = 0 &\rightarrow D_1 \rightarrow |\psi_{g,1}\rangle \\
F_2(\{\epsilon_1, \epsilon_2, \dots, \epsilon_m, t_1, t_2, \dots, t_n, U\}, \{s_1, s_2, s_3, \dots, s_k\}, C) = 0 &\rightarrow D_2 \rightarrow |\psi_{g,2}\rangle \\
F_3(\{\epsilon_1, \epsilon_2, \dots, \epsilon_m, t_1, t_2, \dots, t_n, U\}, \{s_1, s_2, s_3, \dots, s_k\}, C) = 0 &\rightarrow D_3 \rightarrow |\psi_{g,3}\rangle \\
\vdots & \hspace{15em} (5)
\end{aligned}$$

The D_α domains can have various shapes and extensions in 1, 2 or 3 di-

mensions, which implies linear, surface or volumetrical regions in the phase space. The shape and extension of these domains depend on the concrete form and complicity of the extra conditions arising from the matching equations, which determine the relation(s) between the parameters of the starting Hamiltonian.

In pursuance of the above explanations, it is clear that either searching for different solutions of the matching equations from (4) at a fixed transformation of \hat{H} , or effectuating different transformations of the Hamiltonian into positive semidefinite form, and solving the resultant matching equations from (5), one can reach different D_α domains in the parameter space, where the different $|\psi_{g,\alpha}\rangle$ ground state wave functions with the same or different physical properties are present. In this manner one can scan the whole phase diagram globally, and it makes possible to talk about for example the magnetic phases or the electric features of the system.

We also note that constructing the global phase space from local solutions by exact methods is usually typical for non-integrable systems – in contrast to the integrable systems, where it is possible to obtain the exact ground states in a compact single solution for the whole parameter space.

IV. Results and conclusions

In the present paper we have investigated the polyphenylene types of hexagonal chains by the exact method presented in Section III.. The starting point of our examinations was a previous study [12], in which we obtained for polyphenylenes that there is a thin linear domain in the parameter space where the system behave in its ground state as a paramagnetic insulator. This linear domain denoted by L can be graphically observed in Figure 2, which is only a sketchy illustration in order to facilitate to imagine and understand the results. The t_1, t_2, ϵ_1 parameters of the axes exemplify only a possible case in general, when the extra condtions include requirements for t_1, t_2 and ϵ_1 . Based on our earlier results from [12], we aimed to study the phase space of the system more intimately and try to discover other domains, as well, where the deduced paramagnetic and insulating ground state can also exist. After decomposing the Hamiltonian from (1) into a positive semidefinite form by (2), we have solved the matching equations

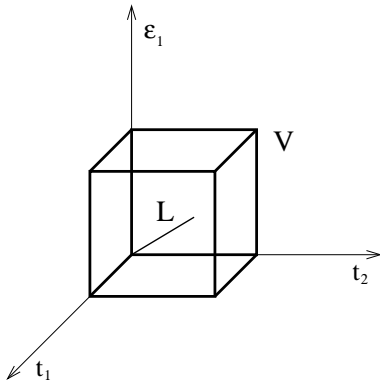


Figure 2: A schematic picture of possible domains in the parameter space.

from (4) in more different manners, and then we have performed the requirement (3). Collecting and comparing the received solutions, we realized that the paramagnetic insulator property of the system can be extended to a volumetrical region demonstrated by V in Figure 2. For convenience we have drawn a simple cubic in order to depict the volume, but otherwise V can have a more complicated shape. It means precisely that the paramagnetic and insulating ground state deduced in a narrow L linear domain remains stable in a much more extended V volumetrical region of the relevant phase space. As a further information we note that these results are valid in the low concentrational limit of the electrons. This treatment a non-trivial discussion for polyphenylene types of chain structures, because beside the enlargement of the physical knowledge, such a problem can also open the door to work out diversified methodological developments in the calculation techniques, as well. More details are available in [13].

As a summary once again, we report that in the current study many-particle, strongly correlated, quantummechanical, non-integrable polyphenylene types of quasi-1D organic periodic hexagonal chain structures were analyzed by means of an exact method which utilizes the special characteristics of the positive semidefinite operators. Applying this exact procedure, a paramagnetic and insulating ground state was deduced in the low concentration limit. In addition, we showed that this ground state can be observed not only in a slight linear region, but can be spread out to a considerable vol-

umetrical domain of the parameter space with the same physical behaviour. Beside the real physical aspects this investigation is also important in point of some calculational improvements.

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References

- [1] M. Joaquim, *Polyphenyl Ether Lubricants*, in: *Synthetic Lubricants and High-performance Functional Fluids*, edited by R. L. Rudnick and R. L. Shubkin (Marcel Dekker, New York, 1999).
- [2] B. Jakobsen, K. Niss, and N. B. Olsen, *J. Chem. Phys.* **123**, 234511 (2005).
- [3] S. Hamid and S. A. Burian, *Polyphenyl Ether Lubricants*, in: *Synthetics, Mineral Oils, and Bio-based Lubricants: Chemistry and Technology*, edited by Leslie R. Rudnick (Taylor and Francis Publisher, Abingdon, 2006).
- [4] A. Ruini, M. J. Caldas, G. Bussi, and E. Molinari, *Phys. Rev. Lett.* **88**, 206403 (2002).
- [5] D. Xing and J. Kerres, *Polym. Adv. Technol.* **17**, 591 (2006).
- [6] T. Reddyhoff, H. A. Spikes, and A. V. Olver, *Tribol. Lett.* **36**, 69 (2009).
- [7] B. Jakobsen, N. B. Olsen, and T. Christensen, *Phys. Rev. E* **81**, 061505 (2010).
- [8] J. P. Bergfield, M. Solis, and C. A. Stafford, *ACS Nano* **4**, 5314 (2010).

- [9] G. Brocks, J. van den Brink, and A. F. Morpurgo, Phys. Rev. Lett. **93**, 146405 (2004).
- [10] Z. Vardery and J. Tanc, Phys. Rev. Lett. **54**, 1844 (1985).
- [11] D. Baeriswyl, D. K. Campbell, and S. Mazumdar, Phys. Rev. Lett. **56**, 1509 (1986).
- [12] R. Trencsényi, K. Gulácsi, E. Kovács, and Z. Gulácsi, Ann. Phys. (Berlin) **523**, 741 (2011).
- [13] R. Trencsényi and Z. Gulácsi, Phil. Mag. **92**, 4657 (2012).