



HUNGARIAN UNIVERSITY OF AGRICULTURE AND LIFE SCIENCES

The bare band structure and physical properties of
solar cell polymers

PhD thesis

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by

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LIST OF SYMBOLS, ABBREVIATIONS

$\hat{c}_{i+\vec{r}_n,\sigma}^\dagger; \hat{c}_{i+\vec{r}_n,\sigma}$	creation and annihilation operator at site $\vec{l} + \vec{r}_n$ (the \vec{r}_n site of the i -th cell) with σ spinprojection	[-]
$\hat{c}_{n,\vec{k};\sigma}^\dagger; \hat{c}_{n,\vec{k};\sigma}; \vec{k}; k$	Fourier component of the $\hat{c}_{i+\vec{r}_n,\sigma}^\dagger; \hat{c}_{i+\vec{r}_n,\sigma}$ creation and annihilation operators respectively and the wave number vector and its length	[-; 1/m]
E_g	the energy of the ground state	[eV]
$\epsilon_n; t; t'; \tau; q; \tilde{\epsilon}_n$	the value of the on-site potential at site $\vec{l} + \vec{r}_n$ resp. the value of the hopping matrix element between the corresponding sites, the hopping term between the polythiophene pentagons, and the energy per unit cell; finally $(\epsilon_n - q)$	[eV]
η_{max}	maximum efficiency	[W]
$\Phi; \Phi_0; \mathbf{B}$	magnetic flux, flux quantum and magnetic induction respectively	[Wb;Wb;T]
$\hat{H}; \hat{H}_0; \hat{H}_U$	the entire Hamiltonian operator resp. its kinetic as well as its interaction part	[eV]
<i>HOMO; LUMO</i>	highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively	[eV]
$N(E)$	Experiential, measured energy dependence of AM 1.5 incident solar photon flux	[-]
$ \Psi_g\rangle; 0\rangle$	the wave function of the ground state, the <i>Fock</i> vacuum	[-]

1. INTRODUCTION AND OBJECTIVES

1.1. Timeliness and relevance of the chosen topic

The conversion of radiant energy from the sun into electricity is a natural, fundamental and nowadays urgent engineering task, both because of the increased demand for energy from renewable sources and the changing attitudes towards nuclear power. The domestic potential is illustrated by a new calculation published in 2017, which shows that the potential of solar PV (486 TWh at 10% efficiency) is almost 11 times the annual energy consumption in 2017 (45.05 TWh).

While efficiency is the most important characteristic of solar panels, they can also be divided into three generations based on economics, technology and installation. For example, the maximum efficiency of the most commercially used silicon solar cells (1st generation solar cells) is close to 27%, but they are difficult to install on uneven surfaces, which is why the much lower efficiency (max. 13 %), but flexible, environmentally friendly and cheaper polymer-based (organic) solar cells (3rd generation) - which can be installed on backpacks, tent roofs, human body - are at the forefront of research and development, both theoretical and experimental. My doctoral thesis concerns theoretical investigations of these polymer materials.

1.2. Objectives

The aim of my doctoral thesis is to carry out fundamental, multi-directional theoretical investigations of solar polymers, which are crucial for efficiency improvement, to reveal the as yet poorly studied properties of these materials and to provide a basis for future research work. These studies will provide a basis for practical ("engineering") research. The chosen polymers will also be studied in the presence of an external magnetic field in the so-called Hubbard model: the band structure and the ground state will be determined and derived. The external magnetic field was chosen for several reasons: on the one hand, the efficiency of organic solar cells can be increased in the presence of an external magnetic field, unlike silicon-based ones, and internal photovoltaic processes can be studied in a separate way, and on the other hand the so-called Peierls phase factors can be used to link them to symmetry studies in later research work.

A further important aim is to show that the Hubbard model, although developed for a deeper understanding of the phenomenon of magnetism in theoretical physics and applied primarily to obtain deeper theoretical results, can also be used directly to estimate the efficiency of polymer-based solar cells. The latter, to the best of my knowledge, has not yet been investigated.

The areas of the PhD thesis under investigation are:

- Investigation of the band structure and ground state of solar cell polymers in an external permanent magnetic field,
- Investigation of the improvability of polythiophene-fullerene based organic solar cells based on maximum efficiency estimates,

Phenomenological study of the spin-track coupling effect for the oxidation of polythiophene (derivation of a specific ground state).

2. MATERIAL AND METHOD

In this chapter of my thesis, I describe the solar polymer materials that are the focus of my research and the mathematical methods used to study them.

2.1. The solar cell polymers studied

In this section, i will first present the types of solar cell polymers i have studied and referred to in terms of my investigation methods. I will first do this by giving their (aromatic) skeletal structure (Figure 1):

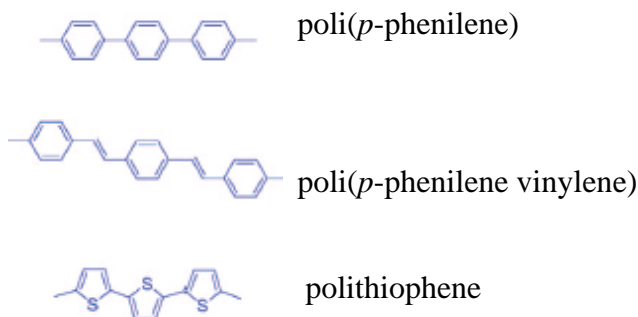


Fig. 1. Aromatic skeletal structure of the polymer types studied (Cheng et al., 2009)

In my thesis, I considered systems where different side groups are connected to the frame structure. These appear in the most common solar applications as shown in Figures 2 and 3. (with images from Sigma Aldrich):

During the measurements, the temperature rise of the heating cycle was examined. An average of 51.15 W was used to heat the collector circuit, and the speed of the collector circuit pump was 316 min⁻¹, which was 0.0059 kg s⁻¹ in terms of mass flow.

Poly(p-phenylene vinylene) derivatives:

MDMO PPV]: (poly [2-methoxy-5-(3', 7'-dimethyloctyloxy)-1,4-phenylene vinylene])

Results

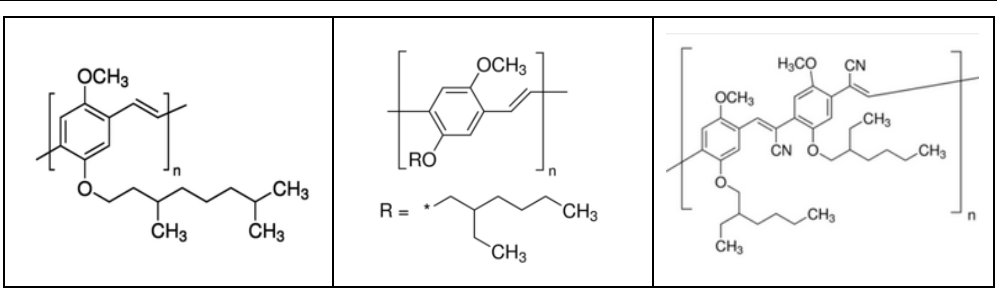


Fig. 2. MDMO PPV (poly [2-methoxy-5- (3', 7'-dimethyloctyloxy) -1,4-phenylene vinylene]: -, MEH PPV (Poly [2-methoxy-5- (2-ethylhexyloxy) -1,4-phenylene vinylene] and CN PPV (Poly [5- (2-ethylhexyloxy) -2-methoxycyanoterephthalylidene])

Some members of P3AT (poly (3-alkylthiophene)) derivatives:

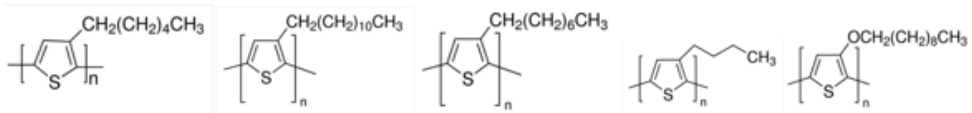


Fig. 3. Structural formula of some members of the P3AT polymer family. In order: P3HT (poly (3-hexylthiophene-2,5-diyl)); P3DDT (poly (3-dodecylthiophene-2,5-diyl), P3OT (poly (3-oxylthiophene-2,5-diyl); P3BT ((poly (3-butylthiophene-2,5-diyl)); Poly (3 -decyloxythiophene -2,5-, diyl).

Side group engineering can fundamentally change the chemical and physical properties. Some members of P3AT (poly (3-alkylthiophene)) derivatives: of the "pure" polymer, e.g. conductivity, solubility, regioregularity, LUMO and HOMO energy levels, emitted light frequency, thermoelectric properties, In my PhD work I consider side groups with the Hubbard model node potential parameter.

2.2. The Hubbard model and the Positive Semidefinite Operators method

The paper investigates the properties of solar cell polymers mathematically using quantum mechanical tools. For the analysis I use the Hubbard model, which is the simplest model that takes into account the interaction between electrons in the description of the system under study. The central element of the calculations is the Hamiltonian operator of the system, which is written in a so-called second-quantized form and its shape:

$$\hat{H} = \hat{H}_0 + \hat{H}_U,$$

where \hat{H}_0 is the kinetic part of the full Hamiltonian operator \hat{H} in the one-electron approximation and \hat{H}_U is the repulsive and shielded Coulomb interaction. In our case, \hat{H}_0 also consists of two parts: the energy of the

electron "hopping" (tunneling) between nodes (so-called hopping terms with parameter t) and the energy of the stay on the sites (ϵ with on-site potential parameter). The method indicated in the title was used to derive the ground state wave function of the polymer under study. The method is based on the fact that the Schrödinger equation for the ground state can be rewritten as:

$$\hat{H} = (\hat{H} - E_g \hat{1}) + E_g \hat{1} = \hat{P} + E_g \hat{1},$$

where E_g is the energy of the ground state. Then the problem reduces to solving

$$\hat{P}|\Psi_g\rangle = 0$$

where Ψ_g is the wave function of the ground state. The great advantage of the method is that it is completely general, requiring no dimensional constraints on the Hamiltonian operator. The method can be used to obtain accurate (exact, non-perturbative approximate) results for so-called non-integrable systems (e.g. ground state of polymers). The latter implies that the number of degrees of freedom of the system is orders of magnitude larger than the number of constants of motion. In the following, the steps of the method are described in general.

Main steps of the method:

1. Writing down the Hamiltonian operator of the system in second quantized form $\hat{c}_{i,\sigma}^\dagger \hat{c}_{j,\sigma}$ by linear combinations of the multiplications of the so-called multiplications of the substitution and vanishing operators). The parameters of the Hamiltonian operator are t_{ij} ; ϵ_l and U_n , the so-called hopping, nodal potential and interaction energy parameters, the latter with positive values:

$$\hat{H} = \hat{H}(t_{ij}; \epsilon_l; U_n). \quad (2.1)$$

2. Transcription of the Hamiltonian operator into a positive semidefinite form:: $\hat{H} = \hat{P} + E_g \hat{1}$, where \hat{P} is a positive semidefinite operator, E_g is the ground state energy. The \hat{P} operator is expressed as the sum of the operator multiplicities of the form either $\hat{A}^\dagger \hat{A}$ or $\hat{A} \hat{A}^\dagger$. In the first case, it is sufficient to rewrite only the kinetic part, since the interaction part is already positive semidefinite. We search for the operators \hat{A} in the form $\hat{A}_{i\sigma} = (a_1 \hat{c}_{i1,\sigma} + a_2 \hat{c}_{i2,\sigma} + \dots)$ acting on the sites (i_1 ; i_2 ; ...) in the form of the so-called block operator. In this way we rewrite the Hamilton operator into the form $\hat{H} = \hat{P} + E_g \hat{1}$ with new parameters:

$$\hat{H} = \hat{H}(a_1; a_2; \dots; b_1; b_2; \dots; \dots; E_g). \quad (2.2)$$

3. Since the two Hamiltonian operators must be rigorously equal, the new parameters will be some function of the initial ones:

$$\begin{aligned} a_i &= f_i(t_{ij}; \epsilon_l; U_n), \\ b_j &= g_j(t_{ij}; \epsilon_l; U_n), \\ &(\dots), \\ E_g &= h(t_{ij}; \epsilon_l; U_n). \end{aligned} \quad (2.3)$$

These function relations are called matching equations. These equations can only be solved over certain parts of the initial parameter range.

4. Derivation of the ground state wave function. This is found as a linear combination of electron-generating operators at certain lattice points of the polymer and then their multiplications per unit cell:

$$\begin{aligned} \prod_{\sigma_j} \prod_j \hat{X}_j^\dagger |0\rangle &= \prod_{\sigma_j} \prod_j (x_1 c_{jm1,\sigma_j}^\dagger + x_2 c_{jm2,\sigma_j}^\dagger \\ &+ \dots x_k c_{jmk,\sigma_j}^\dagger) |0\rangle \end{aligned} \quad (2.4)$$

where $|0\rangle$ is the vacuum state (Fock vacuum) i.e. the lattice is completely empty and $\sigma_j = \uparrow, \downarrow$ are the appropriate states of the spinprojection

5. Demonstrate the unicity of the ground state (I refer to the literature at this point in the paper).

2.3. Calculation of the bare band structure of polymers in the Hubbard model

The bare band structure of the polymers is obtained by Fourier transforming the generating and vanishing operators in the kinetic part of the Hamiltonian operator \hat{H}_0 according to the following formula:

$$\hat{c}_{i+r_n,\sigma} = \frac{1}{N_C} \sum_{k=1}^{N_C} e^{-ik(i+r_n)} \hat{c}_{n,k,\sigma}$$

The Hamiltonian operator just considered will thus have the following form:

$$\hat{H}_0 = \sum_{\sigma} \sum_{k=1}^{N_C} (\hat{c}_{m,k,\sigma}^{\dagger}; \dots; \hat{c}_{1,k,\sigma}^{\dagger}) \tilde{M} \begin{pmatrix} \hat{c}_{m,k,\sigma} \\ \vdots \\ \hat{c}_{1,k,\sigma} \end{pmatrix},$$

where m is the number of sites in a unit cell, N_C is the number of unit cells. The wavenumber vector \mathbf{k} points along the axis of the chain and has possible length values within a unit cell: $|\mathbf{k}| = \frac{2m\pi}{aN_C}$; $m = 0; 1; 2; \dots; N_C - 1$; and $|\mathbf{a}| = a$ is the lattice constant.

The bare band structure is given by the k -dependent eigenvalues (graph) of the matrix \tilde{M} .

3. RESULTS

3.1. Band structure of polyphenylene-vinylene derivatives in a constant external magnetic field

Aim of the study: can the band structure of PPV derivatives also become completely straight under the influence of an external magnetic field? This phenomenon has already been predicted in the literature for polyphenylene chains („Material and Method”)

By plotting the commonly considered Hamiltonian operator of polyphenylene-vinylene (PPV) derivatives in the Hubbard model in second-quantized form with the notation and geometric data in Figure 4. and then Fourier transforming the non-interaction (kinetic) part to the band structure, I obtained the following results:

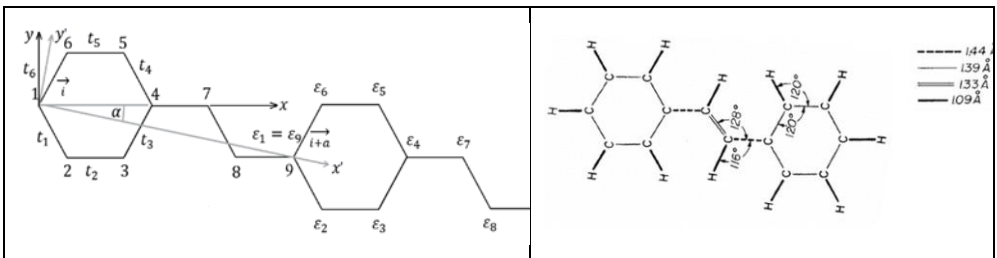


Fig. 4. Hubbard model and geometry of PPV derivatives

The simultaneous straightening of all bands of the band structure is given at conditions (C) :

$t_2 = t_5$; $t_1 t_3 = t_4 t_6$ and at the same time $\epsilon_5 = (\text{or } \epsilon_2 \text{ or } \epsilon_3)$ and correspondingly $\epsilon_6 = (\text{or } \epsilon_3 \text{ or } \epsilon_2)$ (C)

by the enclosed magnetic flux by the phenylene hexagon

$$\Phi = \left(\frac{2l + 1}{2} \right) \Phi_0, (l \in \mathbf{Z})$$

(here $\Phi_0, = \frac{h}{e}$; h is the Planck constant and e is the charge of the electron).

The result is the same with the results obtained for polyphenylene chains consisting of the interconnection of “only” hexagons (Trencsényi et al., 2011), thus independent of the presence of a longer and special-position vinylene chain connecting the hexagons. I illustrated this with a concrete example:

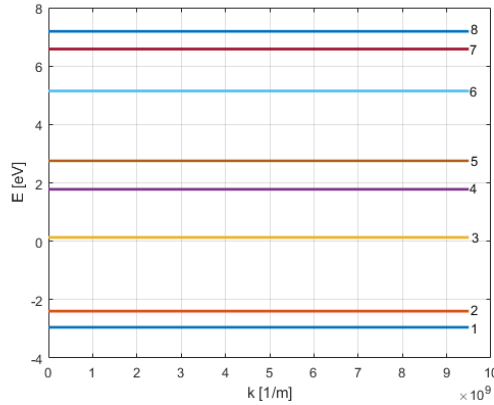


Fig. 5. PPV with a completely flat band structure under the given conditions: $t_1=t_2=t_3=t_4=t_5=t_6=2.4$ eV, $t_7=t_9=2.2$ eV, $t_8 = 2.6$ eV, $\epsilon_1 = \epsilon_4=0.5t_1$; $\epsilon_2 = \epsilon_3= \epsilon_5= \epsilon_6= \epsilon_7= \epsilon_8=1.1t_1$

Minimum magnetic induction required to form a completely flat band structure:

for $l = 0$: $B = 4,1085 \cdot 10^4 T$.

which is an unattainable value for technology. This is primarily due to the side angles of a few angstroms of the hexagon, and hence the hexagon, which is considered regular, is also derived from the area of a few angstrom squares. In order to take advantage of the effect, it would be necessary to increase the enclosed area 10^4 times. However, the advent of high-power lasers (\geq

$10^{21} \frac{W}{cm^2}$) allows the production of magnetic fields of up to MT strength in the laboratory!

3.2. Bare band structure of the most important solar polyphenylene-vinylene derivatives in a constant external magnetic field

It is essential for the research to conclude that in the case of MEH-PPV and MDMO-PPV, which are most common in solar applications, complete flattening cannot take place, ie minimal dispersion will always be present in one of the bands, as the condition imposed on ϵ_5 és ϵ_6 cannot be met. This statement is shown in Figure 6 using a Hubbard parameter that does not satisfy condition (C). In the case of two bands: the lowest (1.) and the middle (5.) band we examined whether there is a magnetic induction value \mathbf{B} at which the examined band becomes completely straight. The chosen parameters: $t_1=t_2=t_3=t_4=t_5=t_6=2.4$ eV, $t_7=t_9=2.2$ eV, $t_8 = 2.6$ eV, $\epsilon_1= \epsilon_4= \epsilon_7= \epsilon_8=1.2$ eV, $\epsilon_2=4.8$ eV, $\epsilon_3= \epsilon_6=2.64$ eV, $\epsilon_5=7.2$ eV.

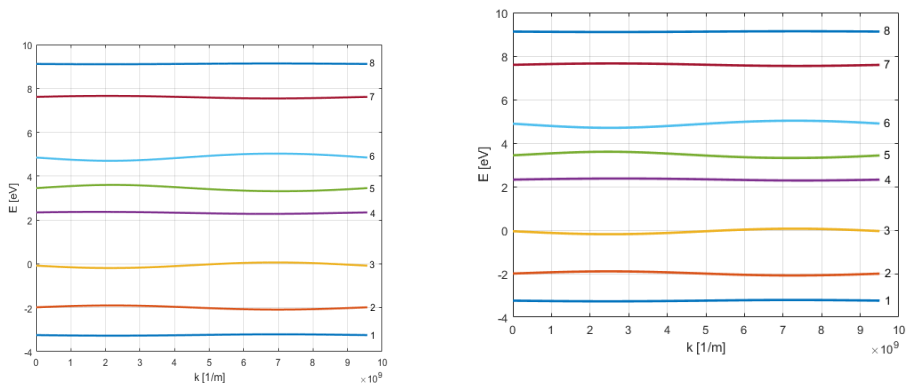


Fig. 6. Illustrative example of the absence of a completely flat band structure for the lowest and 5th bands

The “flattest” case occurs at the lowest band at $\mathbf{B} = 2.8798 \cdot 10^5$ T, then the bandwidth is 0.061 eV. For band 5, the minimum dispersion occurs at $\mathbf{B} = 6,98 \cdot 10^5$ T, the bandwidth at 0.2865 eV. In addition, the value of \mathbf{B} giving the smallest deviation and the so-called also an error function that “measures” the deviation from a completely straight band as a polynomial of degree 0 as well as its periodicity. The period of the error function is $\Delta\mathbf{B} = 9.9 \cdot 10^5$ T (Fundamentals of the computer approach is the work of János Tóth.)

3.3. Ground state of polyphenylene-vinylene derivatives in the case of an external magnetic field.

The transcription of the Hamiltonian operator into a positive semidefinite form as mentioned earlier in the chapter on Materials and Methods is described by the introduction of block operators. I performed a linear combination of the annihilation operators acting as space operators on the sites of each block according to Figure 7. *It is important to emphasize that we only had to rewrite the kinetic part \hat{H}_0 of the total Hamiltonian the interaction part \hat{H}_U is already a positive semidefinite operator!* The transcription took in the form $\hat{A}^\dagger \hat{A}$.

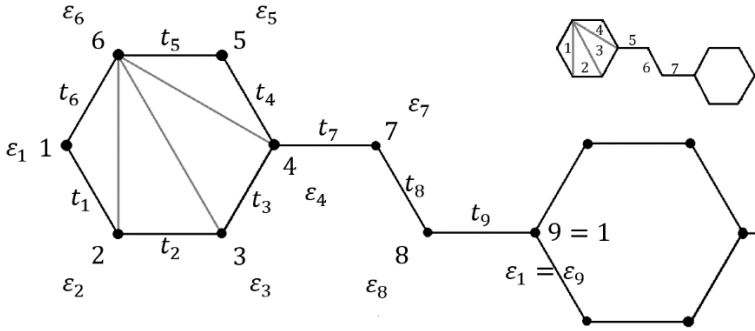


Fig. 7. Structure of the selected block operators

The most important consequence of the solvability conditions of the matching equations (see chapter Material and Method) is that in the case of the applied resolution we can get a solution only for the discrete values of \mathbf{B} which are related to the corresponding values of the magnetic flux penetrating the hexagon ring.

- a) In the case of $\mathbf{B} = 0$ $\Phi = 0$ follows and the positivity of C is realized in the case of an odd number of negative t_k .
- b) However $\Phi = \left(\frac{(2l+1)}{2}\right)\Phi_0$; (l is an arbitrary integer) an even number of t_k must be negative. This case does not exist at $\mathbf{B} = 0$.

The set of possible Φ flux values obtained by us and the corresponding \mathbf{B} magnetic induction quantities includes the Φ and \mathbf{B} values ($k = 2l + 1$) obtained for polyphenylene polymers in the literature (Trencsényi et al., 2011). As a consequence of the coverage equations, I obtained an implicit correlation for the energy q per unit cell, and a constraint relationship remained between the initial parameters, which must be satisfied initially for the method to be applicable.

3.4. The specification of the electronic structure of the ground state

Specifying the electronic structure of the ground state following the procedure described in the Material and Method section, I introduced new $\hat{X}_{\vec{i},\sigma}^\dagger$ operators according to Figure 8. These new operators $\hat{X}_{\vec{i},\sigma}^\dagger$ must satisfy the relations $\{\hat{A}_{\vec{i},\sigma,j}, \hat{X}_{\vec{i},\sigma}^\dagger\} = 0$ for all index values \vec{i}, σ and j .

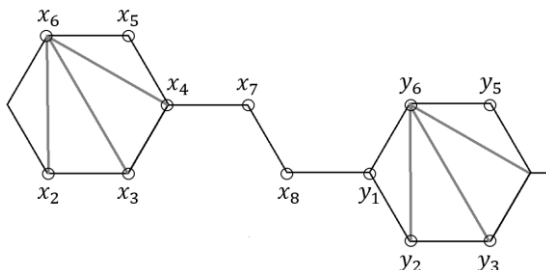


Fig. 8. Sites and coefficients corresponding to the operator $\hat{X}_{\vec{i},\sigma}^\dagger$

The derived ground state is saturated ferromagnetic, assigning one electron to each unit cell (bottom band half-charged). *The correlation of the ground state electron spin projection was forced by the \hat{H}_U interaction term, which describes the spin-independent, node-shielded Coulomb repulsion. Although the obtained ferromagnetism occurred in the presence of an external magnetic field at the possible B values, its origin is still different from that which has been observed in practical life e.g. experienced when placing the soft iron in a magnetic field.* In our case, the polymer has no magnetic atoms or other details with which the external magnetic field could directly interact, e.g., Zeeman interaction on spins was excluded from our studies. The external magnetic field changes the hopping energy term of electron jumps (tunneling) from a real to complex value through Peierls factors. *The ferromagnetism was realized with the flattening of the lowest band in such a way that the ground state at the same time fulfills the so-called correlation condition (this is fulfilled at sites 2,3,5 and 6), therefore our solution is called It was realized in the form of Mielke-Tasaki.*

3.5. Estimates of the maximum efficiency of polythiophene-fullerene type solar cells

The aim of the study is to apply the Hubbard model to a specific solar system to estimate the maximum efficiency of solar cells of the type indicated in the title based on the formula and notations in Figure 9. I investigated how the maximum efficiency of a polythiophene: fullerene solar cell changes as a function of a selected parameter of the model, the E_3 node potential associated with alkyl side groups.

$$\eta_{max} = \frac{E_{g,i} \int_{E_{g,absorber}}^{\infty} N(E) dE}{\int_0^{\infty} EN(E) dE}$$

Fig. 9. Formula and interpretation of efficiency estimation

The literature data we have chosen:

$HOMO_p = -4.7$ eV, $LUMO_p = -2.7$ eV, $HOMO_n = -6.2$ eV, $LUMO_n = -3.8$ eV are chosen (P3HT: PCBM based solar cell).

Hubbard data for the starting P3HT literature (Table 1, for $E_{gp} = 2.2$ eV):

E_1	E_2	E_5	t	t'	t''	τ
-1	0	-3,8	-3,5	-2,5	-2,8	-3,2

The τ -parameter was adjusted to the $E_{gp} = 2$ eV we chose ($\tau' = -3,5$ eV, $E_{offset} = -3,972$ eV).

The results of the calculation are shown in Figure 4.13. The figure shows:

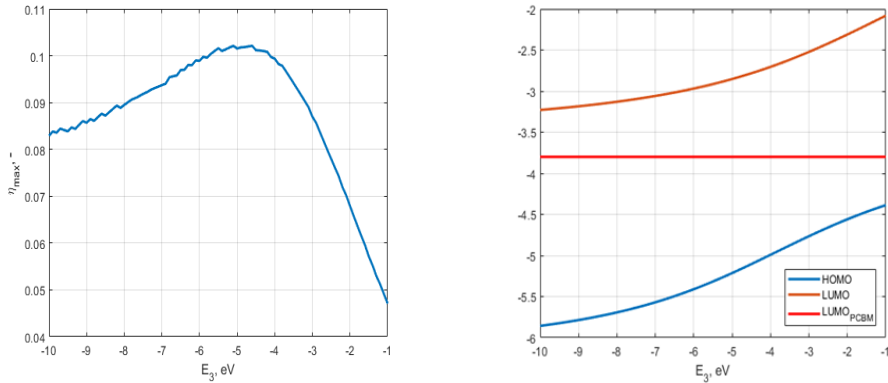


Fig. 10. Variation of the maximum efficiency (left figure) and the HOMO and LUMO levels of the studied polymer family (right figure) as a function of the E3 node potential. P3HT is at $E_3 = -3.97$ eV

From the graph on the left it can be read that the optimum of the maximum efficiency is approx. $E_3 = -4.6$ eV which would mean the synthesis of a side

group with a slightly stronger acceptor function than the hexyl group. However, the ca. 10% max. efficiency up to $E3 = -6$ eV can be taken to be essentially the same, i.e. P3HT is essentially at the optimum point for the maximum achievable efficiency at E3 on-site potential. In this range, the practically favorable efficiency is not the energy levels but other, e.g. morphological characteristics may decide.

Further studies should take into account that energy levels when donor and acceptor materials are combined into a solar cell may shift due to the appearance of a so-called surface dipole due to the phenomenon called by vacuum level shift, which should be taken into account in further modeling.

3.6. Oxidation of polythiophene considering spin-orbit coupling

Increasing the spin-orbit coupling effect can increase efficiency for polymer-based solar cells. This e.g. can be accomplished by implanting heavy metal atoms (e.g., Pt) into the polymer backbone. The spin-orbit coupling effect was investigated phenomenologically according to Figure 11: in the Hamiltonian operator between the sites $\vec{l} + \vec{r}_4$ és $\vec{l} + \vec{a} = \vec{l}$ (Born-Karman condition) the spin-dependent $t_c^{\uparrow\uparrow}$; $t_c^{\downarrow\downarrow}$; $t_c^{\uparrow\downarrow}$; $t_c^{\downarrow\uparrow}$ with hopping factors resp. $\epsilon_1^{\uparrow\uparrow}$; $\epsilon_1^{\downarrow\downarrow}$; $\epsilon_4^{\uparrow\uparrow}$; $\epsilon_4^{\downarrow\downarrow}$ was also considered with spin-dependent node potentials. The “mixed” potentials were taken as $\epsilon_1^{\uparrow\downarrow}$; $\epsilon_1^{\downarrow\uparrow}$; $\epsilon_4^{\uparrow\downarrow}$; $\epsilon_4^{\downarrow\uparrow} = 0$ (Kucska and Gulácsi, 2018). For the sake of simplicity, I treat $t_c^{\uparrow\downarrow}$; $t_c^{\downarrow\uparrow}$ parameters as independent parameters, my investigations are aimed at how the appearance of these parameters affects the applicability of the Positive Semidefinite Method. Based on the literature, the oxidation was taken into account by recording the site $\vec{l} + \vec{r}_6$ and the associated Hubbard parameters.

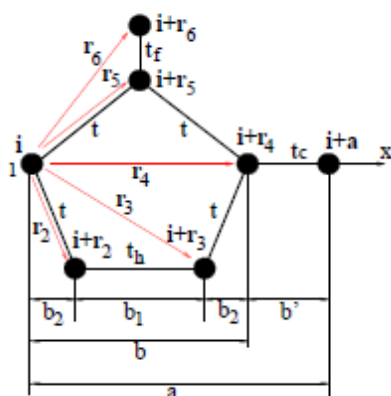


Fig. 11. Hubbard model of polythiophene

For two specific parameter groups of the initial parameters, I gave the translatability to the positive semidefinite form. The degree of spin-orbit

Results

coupling differs by order of magnitude between the two groups. with the help of I solved the coverage equations of the form $\hat{A}^\dagger \hat{A}$ leading to a high concentration ground state, with their help I gave the ground state. The filling rate of the system corresponds to the half-filled upper band case.

4. NEW SCIENTIFIC RESULTS

1. Bare band structure of polyphenylene-vinylene derivatives in the presence of a constant external magnetic field

Based on the antecedents of the literature, I set up a model for the general mathematical study of polyphenylene-vinylene (PPV) derivatives in the presence of an external, permanent magnetic field. These derivatives differ in the side groups attached to the polymer backbone. The parameters of the model are arbitrary. I have also shown that for these PPV polymer derivatives, the model parameters for hopping and on-site potentials are: $t_2 = t_5$; $t_1 t_3 = t_4 t_6$ és $\epsilon_5 = \epsilon_2$; ϵ_3 and accordingly $\epsilon_6 = \epsilon_3$; ϵ_2 under this condition, all the bands of the band structure can become straight at the same time (completely flat band structure), similarly to the cases previously predicted for polymers with polyphenylene chains. I defined the conditions for becoming completely flat for the parameters. I have given the set of magnetic induction values for total precipitation, I have shown that this set is the same as the set of induction values obtained for polyphenylene chains. I proved that the overall precipitation is not affected by the longer vinylene chain, only the flux through the hexagonal phenylene ring is decisive. However, I have shown in detail the effect of the vinylene chain on the band structure.

2. The bare band structure of the most important polyphenylene-vinylene derivatives in solar applications in the presence of a permanent external magnetic field

I have shown that in the case of the most important solar polymers, MEH-PPV, MDMO-PPV, the completely dispersion-free band structure cannot occur. In an illustrative counterexample, where the conditions for all bands to become straight at the same time do not exist, I demonstrated by computer simulation for two bands that although the magnetic field flattens the bands, there always remains dispersion. With a specific example, the parameters are: $t_1=t_2=t_3=t_4=t_5=t_6=2.4$ eV, $t_7=t_9=2.2$, $t_8=2.6$; $\epsilon_1= \epsilon_4= \epsilon_7= \epsilon_8=1.2$; $\epsilon_2=4.8$; $\epsilon_3= \epsilon_6=2.64$, $\epsilon_5=7.2$ eV.

if chosen, the lowest band approximates the line best at $B = 2.8798 \cdot 10^5$ T with a bandwidth of 0.061 eV. For the 5th band (calculated from below), the smallest deviation from the line occurs at $B = 6,98 \cdot 10^5$ T, the bandwidth then: 0.2865 eV. I determined the period of the lane structure. In the specific case mentioned, it is: $\Delta B = 9.9 \cdot 10^5$ T.

3. The ground state of polyphenylene-vinylene derivatives in the presence of a constant external magnetic field

Using the method of positive semidefinite operators, I derived a saturated ferromagnetic ground state wave function satisfying the correlation condition for the investigated PPV derivatives. The system contained 1 delocalized π -electron per cell (the lowest band is half-filled). I have given the conditions for the applicability of the method. These are: $\tilde{\epsilon}_5; A; B; C; K; H; G > 0$; real numbers where

$$A = \frac{\tilde{\epsilon}_3 \tilde{\epsilon}_2 - t_2^2}{C t_2^2 + \tilde{\epsilon}_3}; B = \frac{C t_2^2 + \tilde{\epsilon}_3}{C \tilde{\epsilon}_2 + 1}; C = -\frac{(t_6'^*)(t_3'^*) \tilde{\epsilon}_5}{(t_1')(t_2')(t_4')(t_5)'};$$

$$K = \tilde{\epsilon}_1 - \frac{t_1^2}{A}; H = \tilde{\epsilon}_8 - \frac{t_9^2}{K}; G = \tilde{\epsilon}_7 - \frac{t_8^2}{H}$$

One of the most important of these is that a constraint remains between the initial parameters:

$$\frac{t_6^2}{t_1^2} A + \frac{t_6^2}{t_1^2 t_2^2} A^2 B + \frac{t_4^2 t_5^2}{t_3^2 \tilde{\epsilon}_5^2} ABC + \frac{t_5^2}{\tilde{\epsilon}_5} = \tilde{\epsilon}_6.$$

I have shown that the method, with the resolution I use, is only possible for discrete magnetic induction values, I have determined the set of these values. Regarding the magnitude of the flux through the hexagon chain:

$$\Phi = \frac{k}{2} \Phi_0$$

This set contains the set of previously published magnetic induction values for polyphenylene chains: $\Phi = \left(\frac{(2l+1)}{2} \right) \Phi_0$; , but more so. In the case of this former subset, since the whole band structure becomes straight and the correlation condition is satisfied, the ferromagnetic ground state is realized in the Mielke-Tasaki sense. I have given the general, implicit form of the ground state qNc energy: q should be expressed from the equation:

$$\frac{t_3^2}{ABC} + \frac{t_4^2}{\tilde{\epsilon}_5} + \frac{t_7^2}{G} = \tilde{\epsilon}_4$$

I have shown that the ferromagnetism was caused by a spin-independent Coulomb interaction between the electrons, and the system did not contain magnetic atoms or other magnetic details with which the external magnetic field could have directly interacted. I generalized my method to polymers in

which the adjacent carbon rings are connected by a chain longer than the vinylene chain (several alternating single and double bonds).

4. Estimates of the maximum efficiency of polythiophene-fullerene type solar cells

I determined the maximum efficiency of PCBM-accepting solar cells of polythiophene derivatives in the Hubbard model of polythiophene as a function of the E3 on-site potential model parameter belonging to the linking carbon atom of alkyl side groups. Based on the P3HT: PCBM data selected from the literature and the Hubbard parameters of the P3HT literature, I obtained a function with a local maximum for maximum efficiency. I found that P3HT is located near the optimum according to the model parameter, thus the molecular construction methods involving the change of the model parameter only slightly increase the maximum achievable efficiency. I have shown that the nature of the changes in the HOMO, LUMO energy levels of the described polythiophene derivatives is similar to the nature of the changes of certain poly (3-alkylthiophenes) measured in the alkyl side group other than P3HT, therefore the model parameter can be identified by different synthesized side groups. I pointed out other identifiable possibilities. I raised the possibility of computer simulation refinement of the results for the shift of vacuum levels of donor and acceptor materials suggested in the literature.

5. Oxidation of polythiophene with respect to spin-orbit coupling

As a specific case, I derived a ground-state wave function for the oxidation of polythiophene by the method of positive semidefinite operators based on the characteristic literature data according to the Hubbard model, taking into account the effect of spin-orbit coupling. I gave two solutions that differed in magnitude in the degree of spin-orbit coupling. The electron concentration of the system is high, referring to the upper band is half-filled. Certain parameters were obtained due to the method of resolution and transcription to the positive semidefinite shape. I supported the correctness of the order of magnitude of the specific values with literature data. With the given examples I proved that the method of positive semidefinite operators can be applied to specific solar studies for mixed spin hopping members in the order of 10^{-4} eV and 0.1 eV energy respectively.

5. CONCLUSIONS AND SUGGESTIONS

During my doctoral work, I derived a wave function for the low-state ground state of PPV derivatives. Using this, I propose to draw conclusions about the driving properties of the ground state in the so-called by calculating the ground state expected value of a long-term hopping matrix element (between two nodes that are in different cells but have the same relative position). Having the ground state, I propose an exact interpretation of the absorption coefficient of PPV derivatives in the framework of the Hubbard model based on the literature, taking into account the low concentration state. The analysis of PPV derivatives was performed by the method of Positive Semidefinite Operators (PSZO). I suggest examining the possibilities of extending the method to the so-called in the case of copolymers. The essence of quasi-one-dimensionality is that electron tunneling (hopping, hopping) can also take place between the individual chains. I propose to investigate the derivation of the ground state for this two-dimensional system by including inter-chain hopping members in the Hamilton operator compared to the studies performed on two-dimensional highly correlated systems already published by the PSZO method. I also recommend a two-dimensional extended study of the band structure. The efficiency of polymer-based solar cells can be increased by the external magnetic field. Against the background of these possibilities, the so-called There is a Zeemann effect (fission), in which the external magnetic field acts directly on the spins of the electrons. I propose to extend the PSZO method to take into account the Zeeman effect (by including so-called Zeemann members in the Hamiltonian operator). In my dissertation, I give estimates of the maximum achievable efficiency of polymer-based solar cells based on the energy levels given in the literature, without concentrators within the framework of the Hubbard model. I propose to refine the results to take into account the effect of vacuum shift based on the model proposed in the literature. I propose to extend the method to the so-called. fully polymeric solar cells (both the donor and acceptor material are polymeric, especially if they are derivatives of the same polymer).

6. SUMMARY

My doctoral dissertation deals with the magnetic field properties of solar polymers, the estimation of the efficiency of polymer-based solar cells, and the phenomenological study of the effect of the spin-orbit coupling effect on the solvability of the method leading to the exact ground state. In the first topic, I deduced an exact, saturated ferromagnetic ground state for polyphenylene-vinylene (PPV) derivatives in the presence of a constant, external magnetic field. This ferromagnetism was created by the spin-independent Coulomb repulsion, the polymer did not contain magnetic atoms or other magnetic details with which the external magnetic field could have interacted directly. The magnetic field transformed the hopping parameter of the model into a complex number, I disregarded the direct effect on spin projections. Transcribability to the positive semidefinite form (PSO method) resulting from the polymer resolution I chose was only possible with discrete magnetic induction values. Other important computational results came from studies of the band structure of PPV derivatives. I have found that all energy bands can become dispersion-free at the same time, in which case the energy is independent of the wave number vector at certain parameter conditions and specific values of magnetic field induction, which are the same as the magnetic induction values mentioned above. This means that in these cases the ferromagnetism is called It is realized in the mind of Mielke-Tasaki. The lowest magnetic induction value is very high, not yet achievable for current technology. Due to the conditions of the band structure, the most important solar PPV derivatives (MEH-PPV, MDMO-PPV) cannot be completely precipitated. In the second topic, starting from the literature parameters of poly3-hexylthiophene (P3HT), I investigated the maximum achievable efficiency of polythiophene / fullerene-based solar cells based on the efficiency formula reported in the literature based on a selected (associated with the alkyl group) parameter of the model. In the dissertation, in addition to specific literature values, I derived a ground state for the oxidation of polythiophene, resp. I investigated the applicability of the PSZO method by including energy members modeling spin-orbit coupling.

7. MOST IMPORTANT PUBLICATIONS RELATED TO THE THESIS

Referred articles in foreign languages

1. **Nikolényi I. R.**, Tóth J. (2021): Magnetic field study of poly (*p*-phenylenevinylene) derivatives, *Journal of Magnetism and Magnetic Materials*, Volume 517, <https://doi.org/10.1016/j.jmmm.2020.167281> (IF: 2,717)
2. Mészáros Cs., **Nikolényi I. R.**, Bálint Á. (2020): Symmetry analysis of some basic structural properties of incommensurately modulated crystals by projective representations of unimodular groups, *Physica Status Solidi B-Basic Research* Vol. 257, No. 3, Paper 1900403, p. 7. (IF: 1,481 2019/2020)
3. **Nikolényi I. R.**, Mészáros Cs. (2018): *Symmetry-based study of quasi-one-dimensional systems relevant to solar cell applications*. *Hungarian Agricultural Engineering*, Vol 33., pp. 43-47. ISSN 0864-7410

Referred articles in Hungarian

4. **Nikolényi, I.R.**, Tóth J., Farkas I. (2020): Investigation of the maximum efficiency of polythiophene-fullerene-based organic solar cells, *Energiagazdálkodás* Vol. 61, No. 3, pp. 2-7.
5. **Nikolényi I. R.**, Tóth J., Farkas I. (2020): The effect of the magnetic field on the efficiency of polycrystalline solar cells, *Energiagazdálkodás*, Vol. 61, No. 4, pp. 30-36.