Symmetry of the pentacene molecule and classification of electron states studied in the frame of group action on a set

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Abstract: Pentacene have recently become the subject of intense studies due to their physical properties which follow from the states of their outer-shell electrons that are able to take part in molecule bonding. The symmetry of these molecules provides the classification of quantum states according to the group theory method. In this paper, we apply a molecular state-space factorization scheme for the classification of pentacene molecules based on the structure of their electron states.

Keywords: Pentacene, symmetry of molecules, quantum states, group theory

1 Introduction

Organic solids are promising materials for electronic devices since they demonstrate properties similar to amorphous silicon [1]. From among many new organic compounds [2–4] which manifest interesting semiconducting parameters, the pentacene was selected as the most promising for FET [5].

Usefulness of organic crystals for the production of FET transistors depends upon good parameters that characterize the electric conduction in such crystals. Primary among such parameters is a large mobility of charge. In single ambipolar pentacene transistors, the electron mobility approaches 1 cm^2/Vs, while in other n-type channel organic materials the n mobility is restricted to 0.1 cm^2/Vs for naphtalenetetracarbolixylic

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materials and C^{60} and to 0.01 cm^2/Vs for fluorinated copperphtalocyanine [6].

The electronic properties and theirs stability depend strongly on the structure and ordering of pentacene thin films. Crystal defects, grain boundaries and disorder dominate charge transport properties in layers.

The mobility parameter has a strong correlation to electron-phonon coupling, because the mechanism of conductivity can be either by hopping or polaron. Microscopic descriptions of the model being discussed are still unclear even though theoretical investigations are up-to-date. To work the problem out correctly it is necessary to create a classification of both, electron and phonon states for the pentacene crystals being investigated.

Using the Born–Karman condition for pentacene molecules, the symmetry of this molecule can be considered in the frame of the line group formalism [7]. The possible breakdown of translational symmetry of a chain (which may, for example, lead to the change of band structure and the corresponding driving modes) can be analysed using the general principles of "action of a group on a set" [8]. This method is based on a mathematical structure as are, for example, the subgroup lattice, epicernel, stratum etc.

Pentacene molecular crystals of conjugated aromatic hydrocarbons are grown in the herringbone structure [1] forming triclinic [9] crystallographic systems. The van der Waals forces between molecules forming crystals or solids are considerably weaker than covalent bonds acting between atoms in molecules. Therefore, the properties of individual molecules are expected to contribute considerably to the overall properties of the solid. In the case of pentacene (as in other polyacenes), the electronic properties of molecules are determined mainly by π- orbitals since they are the highest occupied as well as the lowest empty orbitals. In a crystal, the later degenarated orbital forms a band caused by interaction between neighbouring molecules. However, in organic crystals the π carbon atomic orbitals as well as the hydrogen 1s, 2s and 2p orbitals contribute in overlapping effects of adjacent molecules. Such calculations for the overlap of H orbitals with the π system of carbon atoms of neighbouring molecules were done recently by Mattheus [9] for the herringbone arrangement in pentacene crystals. It seems to us that precise insight into the symmetry of the orbital studied should give more information about the conductivity mechanism in these crystals as well as about the mobility anisotropy of the charge carriers as is measured in paper [10], for example.

In this paper we describe the pentacene molecule using the principles of "action of a group on a set". We also propose a classification of the electron states of pentacene because of its widespread application as semiconducting layers in FET transistors. The classification introduced in the present paper is based on factorization algorithm of the molecular orbital representation proposed earlier by Lulek [11] and applied for classification of normal vibrations [12]. This method was successfully used earlier for benzene, naphthalene and polyacenes of higher order [13].

2 Action of group on the set

Let Δ be a set and G be a group. An action P of the group G on the set Δ is a homomorphism of this group into the group $\sum(\Delta)$, which is made up of all permutations of all elements of the set Δ

$$P : G \to \sum(\Delta). \tag{1}$$

Action P forms a permutation representation of the group G

$$P(G) = (\tfrac{\delta}{P(g/\delta)}) \qquad \delta\epsilon\Delta, g\epsilon G, \tag{2}$$

where $P(g/\delta)$ is an image of an element $\delta\epsilon\Delta$ for permutation $P(g)\epsilon\sum(\Delta)$. The set Δ represents a group, lattice, linear space etc. The action P decomposes the set Δ into separate subsets called orbits:

$$O[\delta_0] = \{P(g/\delta)|g\epsilon G\}\epsilon\Delta, \tag{3}$$

where $\delta_0 \in \Delta$ is a representative of the orbit $O[\delta_0]$.

The set $T \subset \Delta$ of orbits representatives is called a travers, when orbits fulfill the relations

$$\Delta = \bigcup_{\delta_0 \in T} O[\delta_0], \tag{4}$$

$$O[\delta_0] \cap 0[\delta_0'] = 0 \text{ for } \delta_0 \neq \delta_0'.$$

The set of all orbits forms a quotient set

$$\Delta/P = \{O[\delta_0]|\delta_0\epsilon T\} \approx T. \tag{5}$$

The travers classifies uniquely this set of orbits.

The set Δ can be a lattice of subgroup G (a lattice of group G is a set $La(G)$ of all subgroup G).

The natural action τ of the group G on the lattice $La(G)$ is given as

$$\tau(g) = \left(\frac{H}{gHg^{-1}}\right) \qquad H \in La(G), \qquad g \in G. \tag{6}$$

This leads to the new lattice

$$\tau(g) = La(G)/\tau.$$

The action P of the group G on the set Δ can be reduced to the $O[\delta_0]$ orbit. This action creates a transitive representation characterized by element $K\epsilon T(G)$ appointed by the stability group $H[\delta]$ of one element δ of the orbit $O[\delta_0]$

$$H[\delta] = \{g\epsilon G|P(g/\delta) = \delta\}\epsilon La(G). \tag{7}$$

The orbit $O[\delta_0]$ is a type K and we denote it as $\tau(O[\delta_0]) = K$. If the set Δ includes orbits of the type $K\epsilon\tau(G)$, then K is the epicernel of the representation P

$$ekP = \{\tau(H[\delta])\epsilon\tau(G)|\delta\epsilon\Delta\} \subset \tau(G), \tag{8}$$

is a subset of the lattice $\tau(G)$.

A set of all orbits of type $K\epsilon ekP$ is a stratum of the set Δ in relation to the action P

$$S(K) = \{O\epsilon\Delta/P|\tau(O) = K\}.$$

The quotient set Δ/P can be decomposed on strata

$$\Delta/P = \bigcup_{K\epsilon ekP} S(K). \tag{9}$$

This decomposition is called stratification of the set Δ, generated by the action P of the group G.

Similarly, the stratification of any set can be conducted by using theory of combinations, e.g.

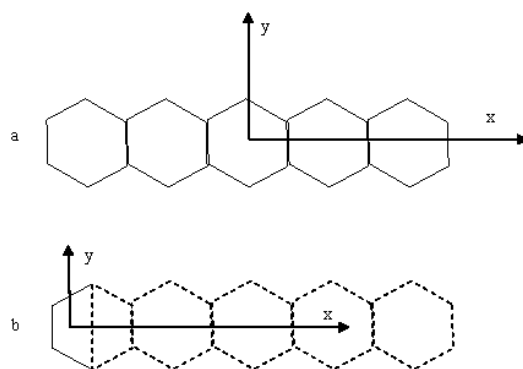$$T_{\beta x\beta y\beta z} = T_{\beta x}^x T_{\beta y}^y T_{\beta z}^z, \tag{10}$$

where $T_{\beta\alpha}^\alpha$ are travers that describe strata on the Cartesian axis $\alpha = \{x, y, z\}$, $\beta_\alpha = \{1, 2, ...k_\alpha\}$, k_α is a number of stratums for α.

3 Symmetry of the pentacene molecule

The point group of the pentacene molecule Fig. 1 is $D_{2h} = \{$E, $C_{2(x)}$, $C_{2(y)}$, $C_{2(z)}$, I, $\sigma_{(xy)}, \sigma_{(xz)}$, $\sigma_{(yz)}\}$. The D_{2h} group is a subgroup of the symmetry group of benzene rings — D_{6h}. The pentacene molecule consists of five benzene rings. If we use the Born–Karman condition, the symmetry of pentacene can be considered in the frame of the line group formalism [7]. The line group $L(a)$ is defined as an extension of point group P by a one-dimensional translational group $T(a)$. The elements of this group are denoted as $l = (t+v(q), q)$ where t is an integer number describing primitive translation ta (a – lattice constant), q is an element of the quotient group $Q(a) = L(a)/T(a)$, $v(q)$ is a fractional translation defining the mapping $v : Q(a) \rightarrow R$ of the group $Q(a)$ into a field of real numbers R. The mapping v is determined by the line group structure and the choice of the origin of the coordinate system. According to the notation used in paper [7] the line group of pentacene is $L(a)$=L21/mcm. The set of $v(q)$ is given in Table 1 for the coordinate system chosen in Fig. 1.

4 Orbits and stratification of pentacene

The calculated orbits, travers and epicernels for all axis and the single pentacene unit cell are collected in Tables 2 and 3 respectively. For the elementary pentacene cell we have obtained six stratums: one three-dimensional, two two-dimensional, two one-dimensional and one zero-dimensional.

Fig. 1 Pentacene as a molecule (a) and as a finite chain of C_4H_2 units (b).

Table 1 Symmetry elements of the pentacene line group.

$(t + v(q), q)$	$v(q)$	q	$V(q)$ interpretation
(t, E)	E	0	neutral element
$(t + \frac{1}{2}, C_{2(z)})$	$C_{2(z)}$	$\frac{1}{2}$	two-fold axis
$(t + \frac{1}{2}, C_{2(y)})$	$C_{2(y)}$	$\frac{1}{2}$	two-fold axis
$(t, C_{2(x)})$	$C_{2(x)}$	0	two-fold axis
$(t + \frac{1}{2}, I)$	(t, I)	$\frac{1}{2}$	inversion
$(t + \frac{1}{2}, \sigma_{(yz)})$	$(t, \sigma_{(yz)})$	$\frac{1}{2}$	mirror plane
$(t, \sigma_{(xz)})$	$(t, \sigma_{(xz)})$	0	mirror plane
$(t, \sigma_{(xy)})$	$(t, \sigma_{(xy)})$	0	mirror plane

Table 2 Stratification of the x, y, z axes by symmetry group $Q(a)$.

Axis α	Typical orbits	Travers T^{α}_{β}	Number elements in orbit	Number of stratum β	Epicernel K^{α}_{β}	Isomorphic point group
	$\{x, -x, x + \frac{1}{2}, -x + \frac{1}{2}\}$	$(0, \frac{1}{4})$	4	1	$\{E, \sigma_{(xy)}\}$	C^z_s
x	$(0, \frac{1}{2})$	$\{0\}$	2	2	$(E, C_{2(y)}), \{\sigma_{(xy)}, \sigma_{(xz)}\}$	C^y_{2v}
	$\{\frac{1}{4}, \frac{3}{4}\}$	$\{\frac{1}{4}\}$	2	3	$\{E, C_{2(z)}, \sigma_{(xy)}, I\}$	C^z_{2h}
y	$\{-y, y\}$	$(0, \infty)$	2	1	$\{E, C_{2(y)}, \sigma_{(yz)}, \sigma_{(xy)}\}$	C^y_{2v}
	$\{0\}$	$\{0\}$	1	2	$Q(a)$	D_{2h}
z	$\{-z, z\}$	$(0, \infty)$	2	1	$\{E, C_{2(z)}, \{\sigma_{(yz)}, \sigma_{(xz)}\}$	C^z_{2v}
	$\{0\}$	$\{0\}$	1	2	$Q(a)$	D_{2h}

A zero-dimensional stratum $S(C^z_{2h})$ composed with the point 0 and 1/4 lie on the z axis. A one-dimensional stratum $S(C^y_{2v})$ is the y axis without the point $(0,0,0)$ and stratum $S(C^z_2)$ is the line parallel to the z axis passing through the point $(1/4,0,0)$. A two-dimensional stratum $S(C^x_s)$ is the yz plane, and $S(C^z_2)$ is a part of the xy plane contained between two lines perpendicular to the x axis, passing through the points $(-1/4, 0, 0)$

Table 3 Stratification and epicernels of the pentacene single unit cell by symmetry group $Q(a)$.

Stratum	Stratum dimension	$T_{\beta1}^x \; T_{\beta2}^y \; T_{\beta3}^z$	$K_{\beta1}^x \cap K_{\beta2}^y \cap K_{\beta3}^z$	ek
$S(C_1)$	3	$(0, \frac{1}{4}) \times (0, \infty) \times (0, \infty)$	$C_s^z \cap C_{2v}^y \cap C_{2v}^z$	
		$\{\frac{1}{4}\} \times (0, \infty) \times (0, \infty)$	$C_{2h}^z \cap C_{2v}^y \cap C_{2v}^z$	C_1
		$(0, \frac{1}{4}) \times \{0\} \times (0, \infty)$	$C_s^z \cap D_{2h} \cap C_{2v}^z$	
		$(0, \frac{1}{4}) \times (0, \infty) \times \{0\}$	$C_s^z \cap C_{2v}^y \cap D_{2h}$	
$S(C_s^z)$	2	$\{\frac{1}{4}\} \times (0, \infty) \times \{0\})$	$C_{2h}^z \cap C_{2v}^y \cap D_{2h}$	C_s^z
		$(0, \frac{1}{4}) \times \{0\} \times \{0\}$	$C_s^z \cap D_{2h} \cap D_{2h}$	
$S(C_s^z)$	2	$\{0\} \times (0, \infty) \times (0, \infty)$	$C_{2v}^y \cap C_{2v}^y \cap C_{2v}^z$	C_s^x
		$\{0\} \times (0, \infty) \times \{0\}$	$C_{2v}^y \cap D_{2h} \cap C_{2v}^z$	
$S(C_2^z)$	1	$\{\frac{1}{4}\} \times (0, \infty) \times \{0\}$	$C_{2h}^z \cap D_{2h} \cap C_{2v}^z$	C_2^z
$S(C_{2v}^y)$	1	$\{0\} \times \{0\} \times (0, \infty)$	$C_{2v}^y \cap C_{2v}^y \cap D_{2h}$	C_{2v}^y
		$\{0\} \times \{0\} \times \{0\}$	$C_{2v}^y \cap D_{2h} \cap D_{2h}$	
$S(C_{2h}^z)$	0	$\frac{1}{4} \times \{0\} \times \{0\}$	$C_{2h}^z \cap D_{2h} \cap D_{2h}$	

and $(1/4, 0, 0)$, respectively. A three-dimensional stratum $S(C_1)$ contains two planes parallel to the yz plane (passing through the points $(-1/4, 0, 0)$ and $(1/4, 0, 0)$) with space contained between these planes.

5 Electron states and vibrational modes of pentacene

Let the set of molecular orbitals [14] forms the Hilbert space M of quantum electronic states of the pentacene molecule. Such a space is a direct product of two subspaces [13]: P (described by a positional representation) and A (described by an atomic representation) spanned by positions of groups of C-H atoms in the molecule and by atomic orbitals of carbon atoms, respectively:

$$M = P \otimes A,$$

where subspace A is a sum of A_σ and A_π subspaces of σ and π atomic orbitals. Basis vectors of the Hilbert space M, P, and A are formed by vectors $|\Gamma w\gamma\rangle$, $|\Lambda\lambda\rangle$ and vectors, respectively. The positional representation P and orbital representation A decomposes into irreducible representations Λ and Δ of the group G:

$$P = \sum_\Lambda \oplus n(P, \Lambda)\Lambda, A = \sum_\Delta \oplus n(P, \Delta)\Delta. \tag{11}$$

We can calculate the product of all such irreducible representations and create a decomposition of the type

$$\Lambda \otimes \Delta = \sum_\Gamma \oplus c(\Lambda, \Delta, \Gamma)\Gamma. \tag{12}$$

The basis vectors of the molecular space M can be determined using the Clebsch–Gordan procedure as

$$|\Lambda t, \Delta d, \Gamma w\gamma\rangle = \sum_{\lambda\delta} \begin{bmatrix} \Lambda & \Delta & \Gamma w \\ \lambda & \delta & \gamma \end{bmatrix} |\Lambda t\lambda| \Delta d\delta\rangle, \tag{13}$$

where $t = 1, 2, \ldots, n(P, \Lambda)$, $t = 1, 2, \ldots, n(A, \Delta)$, $w = 1, 2, \ldots, c(\Lambda, \Delta, \Gamma)$ are repetition indices of the first (t, d) and second range (w), and the matrix is the Clebsch–Gordan coefficient. The vectors $|\Lambda t\lambda\rangle$ and $|\Delta d\delta\rangle$ are given by:
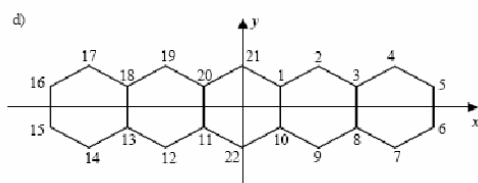
$$|\Lambda t\lambda\rangle = \sum_{i=1}^{N} b_{\Lambda t\lambda}^{i}|i\rangle, \tag{14}$$

$$|\Delta d\delta\rangle = \sum_{\alpha} a_{\Delta d\delta}^{\alpha}e^{\alpha}, \tag{15}$$

where e^{α} is a three-dimensional Cartesian basis.

The symmetry group decomposes all carbon positions i Fig. 2 into orbits of actions of the group D_{2h} on a set $\{i\}$ for all $g\epsilon\ D_{2h}$: $O_r = \{gr\}$ where $r\epsilon\{i\}$ is a generator of orbit O_r as following: $O_1 = \{1, 10, 11, 20\}$, $O_2 = \{2, 9, 12, 19\}$, $O_3 = \{3, 8, 13, 18\}$, $O_4 = \{4, 7, 14, 17\}$, $O_5 = \{5, 6, 15, 16\}$, $O_{21} = \{21, 22\}$.

There are five four-element orbits and one two-element orbit for each molecule.

Fig. 2 Pentacene molecule with numerations of the carbon atoms.

The character of atomic A and positional P representations for pentacene as well as the irreducible representation of D_{2h} group are given in table 4.

The irreducible basis vectors $|\Lambda\lambda\rangle$ of the positional representation (according to enumeration of carbon atoms as in Fig. 2) are given in Table 4.

The basis vectors for A representation of the pentacene molecule are as follows:

$$|B_{2u}b_2\rangle = \frac{1}{\sqrt{2}}(\varphi_{\sigma b} - \varphi_{\sigma c}),$$

$$|B_{3u}b_3^{(1)}\rangle = \varphi_{\sigma a},$$

$$|B_{3u}b_3^{(2)}\rangle = \frac{1}{\sqrt{2}}(\varphi_{\sigma b} - \varphi_{\sigma c}), \tag{16}$$

where $\varphi_{\sigma a}$, $\varphi_{\sigma b}$, $\varphi_{\sigma c}$ are normalized σ- type atomic orbitals [14].

Examples of the symmetry orbitals calculated for pentacene using vectors from Table 5 and basis vectors for A representation 16 as well as formula 13 are given in Table 6, where for abbreviation we denote $|a\rangle \equiv \varphi_{\sigma a}$, $|b\rangle \equiv \varphi_{\sigma b}$ and $|c\rangle \equiv \varphi_{\sigma c}$.

Table 4 Irreducible representations of the D_{2h} group, atomic and positional representation of the pentacene molecule.

	E	$C_{2(x)}$	$C_{2(y)}$	$C_{2(z)}$	I	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$	Decomposition
				Irreducible representations					
A_g	1	1	1	1	1	1	1	1	-
B_{1g}	1	−1	−1	1	1	1	−1	−1	-
B_{2g}	1	−1	1	−1	1	−1	1	−1	-
B_{3g}	1	1	−1	−1	1	−1	−1	1	-
A_u	1	1	1	1	−1	−1	−1	−1	-
B_{1u}	1	−1	−1	1	−1	−1	1	1	-
B_{2u}	1	−1	1	−1	−1	1	−1	1	-
B_{3u}	1	1	−1	−1	−1	1	1	−1	-
				Atomic representation					
A	4	0	−2	−2	−4	2	2	0	$B_{1u} + B_{2u} + 2B_{3u}$
A_σ	3	1	−1	−3	−3	3	1	−1	$B_{2u} + 2B_{3u}$
A_π	1	−1	−1	1	−1	−1	1	1	B_{1u}
				Positional representation					
P	22	0	2	0	0	22	0	2	$6A_g + 5B_{1g} + 6B2u + 5B_{3u}$
				Vector representation					
V	3	−1	−1	−1	−3	1	1	1	$B_{1u} + B_{2u} + B_{3u}$

Table 5 Summary of the most frequently used pore size classifications.

orb it	N	$|A_g a_g\rangle$	$|B_{1g} b_{1g}\rangle$	$|B_{2u} b_{2u}\rangle$	$|B_{3u} b_{3u}\rangle$
O_1	$\frac{1}{2}$	$|1\rangle + |10\rangle + |11\rangle + |20\rangle$	$|1\rangle - |10\rangle + |11\rangle - |20\rangle$	$|1\rangle - |10\rangle - |11\rangle + |20\rangle$	$|1\rangle - |10\rangle - |11\rangle - |20\rangle$
O_2	$\frac{1}{2}$	$|2\rangle + |9\rangle + |12\rangle + |19\rangle$	$|2\rangle - |9\rangle + |12\rangle - |19\rangle$	$|2\rangle - |9\rangle - |12\rangle + |19\rangle$	$|2\rangle - |9\rangle - |12\rangle - |19\rangle$
O_3	$\frac{1}{2}$	$|3\rangle + |8\rangle + |13\rangle + |18\rangle$	$|3\rangle - |8\rangle + |13\rangle - |18\rangle$	$|3\rangle - |8\rangle - |13\rangle + |18\rangle$	$|3\rangle - |8\rangle - |13\rangle - |18\rangle$
O_4	$\frac{1}{2}$	$|4\rangle + |7\rangle + |14\rangle + |17\rangle$	$|4\rangle - |7\rangle + |14\rangle - |17\rangle$	$|4\rangle - |7\rangle - |14\rangle + |17\rangle$	$|4\rangle - |7\rangle - |14\rangle - |17\rangle$
O_5	$\frac{1}{2}$	$|5\rangle + |6\rangle + |15\rangle + |16\rangle$	$|5\rangle - |6\rangle + |15\rangle - |16\rangle$	$|5\rangle - |6\rangle - |15\rangle + |16\rangle$	$|5\rangle - |6\rangle - |15\rangle - |16\rangle$
O_6	$\frac{1}{\sqrt{2}}$	$|21\rangle + |22\rangle$		$|21\rangle - |22\rangle$	

Table 6 Examples of σ- type symmetry orbitals of pentacene.

Λt	Δd	$\Gamma\gamma$	N	Symmetry orbitals
$A_g 1$	B_{2u}	$\frac{1}{2\sqrt{2}}$	$|1b\rangle - |1c\rangle + |10b\rangle - |10c\rangle + |11b\rangle - |11c\rangle + |20c\rangle - |20c\rangle$	
$A_g 1$	$B_{3u} 1$	$\frac{1}{2}$	$|1a\rangle + |10a\rangle + |11a\rangle + |20a\rangle$	
$A_g 1$	$B_{3u} b_{3u} 5$	$\frac{1}{2\sqrt{2}}$	$|1b\rangle + |1c\rangle + |10b\rangle + |10c\rangle + |11b\rangle + |11c\rangle + |20c\rangle + |20c\rangle$	
$B_{3u} 5$	$B_{1g} b_{1g}$	$\frac{1}{2\sqrt{2}}$	$|5b\rangle - |5c\rangle + |6b\rangle - |6c\rangle + |15b\rangle - |15c\rangle + |16c\rangle - |16c\rangle$	
$B_{3u} 5$	$A_g a_g$	$\frac{1}{2}$	$|5a\rangle + |6a\rangle + |15a\rangle + |16a\rangle$	
$B_{3u} 5$	$A_g a_g$	$\frac{1}{2\sqrt{2}}$	$|5b\rangle + |5c\rangle + |6b\rangle + |6c\rangle + |15b\rangle + |15c\rangle + |16b\rangle + |16c\rangle$	

The mechanical representation Me [11] is a simple product:

$$Me = P \otimes V,$$

where V is of the vector representation for the D_{2h} group symmetry in a three-dimensional

Cartesian basis (Table 4).

The decomposition of the mechanical representation (Me) into an irreducible representation of the D_{2h} group gives normal modes for the pentacene molecule.

$$Me = (6A_g + 5B_{1g} + 6B_{2u} + 5B_{3u}) \otimes (B_{1u} + B_{2u} + B_{3u}) =$$

$$11A_g + 11B_{1g} + 5B_{2g} + 6B_{3g} + 5A_u + 6B_{1u} + 11B_{2u} + 11B_{3u}.$$

This decomposition includes a representation connected with the translation and rotation of the pentacene molecule. There are sixty normal modes corresponding to the vibrational representation: $11A_g + 10B_{1g} + 4B_{2g} + 5B_{3g} + 5A_u + 5B_{1u} + 10B_{2u} + 10B_{3u}$.

6 HOMO-LUMO energy gap of pentacene

The carrier mobility in pentacene, besides structural factors such as defect density and domain boundaries, is ultimately determined by the strength of spin-orbit coupling and the electronic band structure responsible for carrier localization.

The spin-orbit coupling of the ground and excited states of pentacene has been investigated early in the all-valence-electron CNDO/S approximations [16]. In the work [16], the spin-orbit coupling matrix elements were calculated, including one- and two-electron contributions to the single- and multi-center integrals. The spin-dependent transport properties of pentacene have been measured, for example, in magnetic multilayers of the form FM/pentacene/FM', where FM and FM' are inorganic magnetic metals [17]. In [17], we see a reduction of the effects of interfacial scattering as well as an allowance for a much thicker pentacene spacer layer. Due to this weak intralayer, a spin-flip scattering was observed that suggested a low spin-orbit coupling for pentacene. Results for a spacer layer of a small molecule of pentacene show $a > 1\%$ change (at room temperature) in the magnetoresistance for thicknesses well over 100 nanometers. The relation between transport properties of the pentacene single crystal and its electronic structure were studied in detail, for example in [18]. The band structure of pentacene crystals or layers has been calculated by other authors, mainly by using first-principles density function theory — DFT (for example in [15, 19]). Unfortunately, the results of calculations of energy gap presented in literature are smaller than those obtained in experiment (2.2 eV [20]). For example, the value of a Kohn–Sham band gap calculated in works [15, 21] is near 0.8 eV. The calculated band gap of the pentacene crystal at the Γ point is $0.95 - 0.98$ eV [15, 22]. The energy gap in a pentacene molecule is directly related to the difference between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels.

The energy of molecular states can be calculated in principle by using the Hückel theory [14]. This theory was originally introduced to permit qualitative studies of the π-electron systems in planar, conjugated hydrocarbon molecules. It is therefore most appropriate for molecules such as pentacene, but the approach and concepts have wider applicability. The basic form of the secular equation for the bonding arising from the

overlap of 22 π- orbitals is:

$$\begin{bmatrix} \alpha_1 - E & \beta_{1\ 2} & . & \beta_{1\ 22} \\ \beta_{2\ 1} & \alpha_2 - E & . & \beta_{2\ 22} \\ . & . & . & . \\ \beta_{2\ 21} & \beta_{2\ 22} & . & \alpha_{22} - E \end{bmatrix} = 0, \tag{17}$$

where $\alpha k = \int \phi_k \hat{H} \phi_k$ are Coulomb integrals and $\beta_{ij} = \int \phi_i \hat{H} \phi_j$ are resonance integrals (φ_n denotes n-th atomic orbital).

We make the next basic assumptions:

(1) The Coulomb integrals α_k [14] for all the carbon atoms in a pentacene molecule are assumed to be identical ($\alpha_1 = \alpha_2 = \ldots = \alpha_{22} = \alpha$) i.e. small differences in these values due to the different chemical environment of C atoms in the molecule are neglected.

(2) All resonance integrals β_{ij} [14] between directly-bonded atoms are assumed to be the same ($\beta_{ij} = \beta$, if atoms i and j are directly σ-bonded); while those between atoms that are not directly bonded are neglected ($\beta_{ij} = 0$, if atoms i and j are non-bonded).

In order to solve the secular equation (17), we put that energy E as a function of a new variable $x : E = \alpha - x\beta$. For this condition, equation (17) can be transformed into a new form in which only 0, 1 and x are present. In the last step, we used factorization of the secular equations by group theory [23].

The calculated value of the gap between the HOMO and LUMO levels by this method is 1.13 eV. This value is about 45% higher than the Kohn–Sham energy gap obtained according to the principle of DFT theory in work [15], but it is still drastically smaller than experimental data.

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References

[1] M. Pope and C.E. Swenberg: *Electronic Processes in Organic crystals and Polymers*, 2nd ed., Oxford University Press, New York, 1999.

[2] S. Reynolds, J.T. Shepherd, C. Main, J.M. Marshall and J.M. Maud: "A comparative study of photoconductivity and carrier transport in oligomeric films", *J. Non-Cryst. Sol.*, Vol. 266-269, (2000), pp. 994–998.

[3] V.C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R.L. Willet, T. Someya, M.E. Gershenson and J.A. Rogers: "Elastomeric Transistor Stamps: Reversible Probing of Charge Transport in Organic Crystals", *Science*, Vol. 303, (2004), pp. 1644–1646.

[4]   M.S. Liao and S. Scheiner: "Electronic structure and bonding in metal phthalo-cyanines, Metal=Fe, Co, Ni, Cu, Zn, Mg", *J. Chem. Phys.*, Vol. 114, (2001), pp. 9780–9791.

[5]   S. Schreinert and G. Paasch: "Fabrication and analysis of polymer field-effect tran-sistors", *Phys. Status Solidi A*, Vol. 201(6), (2004), pp. 1263–1301.

[6]   Z. Bao, A.J. Livinger and J. Brown: "New Air-Stable n-Channel Organic Thin Film Transistors", *J. Am. Chem. Soc.*, Vol. 120(1), (1998), pp. 207–208.

[7]   M. Vujicic, I.B. Bozovic and F. Herbut: "Construction of symmetry groups of poly-mer molecules", *J. Phys. A- Math. Gen.*, Vol. 10, (1977), pp. 1271–1279.

[8]   L. Michel: "Symmetry defects and broken symmetry. Configurations Hidden Sym-metry", *Rev. Mod. Phys.*, Vol. 52, (1980), pp. 617–651.

[9]   C.C. Matthews: *Polymorphism and electronic properties of pentacene*, Dissertation, Groeningen, 2002.

[10] J.H. Schon, C. Kloc and B. Batlogg: "Hole transport in pentacene single crystals", *Phys. Rev. B*, Vol. 63, (2001), art. 245201.

[11] T. Lulek: "Classification of symmetric coordinates for point clusters. I. The metod", *Acta Phys. Pol. A*, Vol. 57, (1980), pp. 407–414.

[12] M. Kuzma, I. Kumplowski and T. Lulek: "Classification of symmetric coordinates for point clusters. II. Examples: a regular tetrahedron and a cube", *Acta Phys. Pol. A*, Vol. 57, (1980), pp. 415–428.

[13] M. Labuz, A. Wal, G. Wisz and M. Kuma: "Symmetry and classification of electron states in polyacenes", *J. Phys.: Conference Series*, Vol. 30, (2006), pp.325–332.

[14] F.A. Cotton: *Chemical Applications of Group Theory*, Warsaw, PWN, 1973 (in Polish).

[15] K. Hummer and C. Ambrosch-Draxl: "Electronic properties of oligoacenes from first principles", *Phys. Rev. B*, Vol. 72, (2005), art. 205205.

[16] Yu.F. Pedash, O.V. Prezhdo, S.I. Kotelevskiy and V.V. Prezhdo: "Spin-orbit cou-pling and luminescence characteristics of conjugated organic molecules. I. Poly-acenes", *J. Mol. Struct. Theochem*, Vol. 585, (2002), pp. 49–59.

[17] S.J. Etzkorn, W.C. Pirkle, J. Yang, L. Dai and A.J. Epstein: "Book of abstract - March Meeting 2004, (March 22-26, 2004), Palais des Congres de Montreal, Montreal, Quebec, Canada, abstract #J23.012 (oral presentation)", American Physical Society, Montreal, 2004.

[18] J. Cornil, J.Ph. Calbert and J.L. Brédas: "Electronic Structure of the pentacene Single crystal: relation to transport properties", *J. Am. Chem. Soc.*, Vol. 123, (2001), pp. 1250–1251.

[19] G.A. Wijs, C.C. Mattheus, R.A. Groot and T.M. Palstra: "Anisotropy of the mobility of pentacene from frustration", *Synthetic Met.*, Vol. 139, (2003), pp. 109–114.

[20] E.A. Silinsh: *Organic Molecular Crystals, their electronic states*, Berlin, Springer Verlag, 1980.

[21] M.L. Tiago, J.E. Northrup and S.G. Louie: "Ab initio calculation of the electronic and optical properties of solid pentacene", *Phys. Rev. B*, Vol. 67, (2003), art. 115212.

[22] R.G. Endres, C.Y. Fong, L.H. Yang, Ch. Wöll and G. Witte: "Structural and electronic properties of pentacene molecule and molecular pentacene solid", *Comp. Mats Sci.*, Vol. 29, (2004), pp. 362–370.

[23] W.B. Byers: "On the Factorization of Secular Equations by Group Theory", In: Per-Olov Löwdin(Ed.): *Quantum Theory of Atoms, Molecules, and the Solid State A Tribute to John C. Slater*, Academic Press, New York, 1966, pp. 123–133.