Symmetry and classification of electron states in polyacenes

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Abstract. Organic materials have been recently the object of the intense studies due to their opto-electronic properties which follow from the states of the outer-shell electrons, taking part in molecule bonding. The symmetry of molecules provides the classification of quantum states according to the group theory method. We apply molecular state space factorizaton scheme for the states structure classification of selected polyacenes.

1. Introduction

Organic semiconductors are strongly studied from many years and a great progress was made in the performance of organic devices particularly in organic field-effect transistors (FET). The key element in FET transistors is thin semiconductor organic film. From many new organic compounds such as thienylene – vinylene oligomers (TVB, TVC, TVD) [1], rubrene [2], metal phthalocyanines (MP) [3-5], which manifest interesting semiconducting parameters, the pentacene was selected as the most promising for FET. Such organic electronics will result in many low-cost and large area applications. The low-temperature processes of devices in relation to the nonorganic semiconductors industry result in applications of extraordinary substrates as flexible, large area, low-weight polymeric or even biological plates for integrated electronic structures. The possibility of submicron scale of integrated electronic circuits is the next feature of organic electronics, which overcome the possibilities of standard microelectronics.

Usefulness of organic crystals for FET transistors production depends on good parameters that characterise the electric conduction in such crystals, first of all large mobility of charge. The mobility is in strong relation with electron-phonon coupling, because the mechanism of conductivity can be hopping or polaron one. Microscopic description of the model being discussed is still unclear and theoretical investigations are nowadays up-to-date. To work the problem out correctly it is necessary to create classification of both electron and phonon states for the organic crystals being investigated. The properties of charge carriers depend on the electronic properties of molecules as well as the kind of interactions between them. As regards to aromatic hydrogencarbon molecules the \( \pi \) orbitals were studied mainly, which determine not only bonding between carbon atoms, but they also control other electronic properties of the molecule. However, in organic crystals the \( \sigma \) carbon atomic orbitals as well as the hydrogen 1s, 2s and 2p orbitals contribute in overlap effects of adjacent molecules. Such calculations for overlap of H orbitals with \( \pi \) system of carbon atoms of neighbour molecule were done recently by Mattheus [6] for herringbone arrangement in pentacene crystals. It seems to us that precise insight into symmetry of orbital studied should give more information about the conductivity mechanism in these crystals as well as charge carriers mobility anisotropy measured e.g. in paper [7]. In our paper we propose classification of the electron states in cyclic molecules of aromatic
hydrocarbons and derivatives because of its major application as semiconducting layers in FET transistors. In particular, we focus our attention on the classification of molecular electron states in benzene and naphthalene, which play the role of the model investigations of pentacene widely applying in FET transistors [8,9]. The classification introduced in the paper bases on factorization of molecular orbital representation, the algorithm related to that, proposed earlier by Lulek [10] and applied for classification of normal vibrations [11].

2. Molecular orbitals and LCAO approximation

The LCAO method [12-14] introduces molecular orbitals $\Psi_m$ expressed by the formula

\[ \Psi_m = \sum_i c_{im} \phi_i . \]  

Introducing symmetry orbitals $\psi_k$

\[ \psi_k = \sum_i a_{ik} \phi_i , \]  

we obtain the series (1) as

\[ \Psi_m = \sum_k b_{km} \psi_k , \]  

where $\phi_i$ denotes $i$-th atomic orbital. Coefficients $c_{im}$ can be obtained from the eigenvalue problem simplified by group-theory, whereas $a_{ik}$ coefficients can be found directly from group-theory calculations.

The eigenvalue problem of the system

\[ (\hat{H} - E_m) \Psi_m = 0 \]  

is reduced to the secular equation:

\[ \begin{vmatrix} H_{11} - E_m & \ldots & H_{1k} - E_m S_{1k} \\ \vdots & \ddots & \vdots \\ H_{k1} - E_m S_{k1} & \ldots & H_{kk} - E_m \end{vmatrix} = 0 , \]  

where $H_{ii} = \int \phi_i \hat{H} \phi_i d\tau$, $H_{ij} = \int \phi_i \hat{H} \phi_j d\tau$, $S_{ij} = \int \phi_i \phi_j d\tau$ are Coulomb, interaction and overlap integrals respectively and can be evaluated, e.g. also using some approximation method (e.g. Hückel method). The solution of this eigenvalue problem results in determining of energies $E_m$ and $c_{im}$ coefficients and thereby the strict form of orbital molecules.

Let the set of molecular orbitals forms Hilbert space $M$ of quantum electronic states of the aromatic hydrocarbons. Such a space is a direct product of two subspaces: $P$ and $A$ spanned by positions of C-H atom groups in the molecule and by atomic orbitals of carbon atoms, respectively:

\[ M = P \otimes A . \]  

Furthermore the subspace $A$ is a sum of $A_{\pi}$ and $A_{\sigma}$ subspaces of $\pi$ and $\sigma$ atomic orbitals:

\[ A = A_{\pi} \oplus A_{\sigma} . \]  

Thus:

\[ M = (P \otimes A_{\pi}) \oplus (P \otimes A_{\sigma}) . \]
The group $G$ of symmetry of the molecule acts in the space $\mathbb{M}$ forming representation $\mathbb{M}$, whereas representations $\mathbb{P}$ and $\mathbb{A}$ act in subspaces $\mathbb{P}$ and $\mathbb{A}$, respectively.

Let vectors $|\Gamma w \gamma \rangle$, $|\Lambda t \lambda \rangle$ and $|\Delta d \delta \rangle$ form basis of the Hilbert space $\mathbb{M}$, $\mathbb{P}$, and $\mathbb{A}$ respectively. The positional representation $\mathbb{P}$ and orbital representation $\mathbb{A}$ decomposes into irreducible representations $\Lambda$ and $\Delta$ of the group $G$:

$$\mathbb{P} = \sum_{\Lambda} \oplus n(\mathbb{P}, \Lambda) \Lambda$$  \hspace{1cm} (9)

$$\mathbb{A} = \sum_{\Delta} \oplus n(\mathbb{A}, \Delta) \Delta$$  \hspace{1cm} (10)

Taking into account the decomposition

$$\Lambda \otimes \Delta = \sum_{\Gamma} \oplus c(\Lambda, \Delta, \Gamma) \Gamma,$$  \hspace{1cm} (11)

the basis vectors of the $\mathbb{M}$ (molecular) space are determined using Clebsch-Gordan procedure as:

$$|\Lambda t, \Delta d, \Gamma w \gamma \rangle = \sum_{\Lambda, \Delta, \Gamma} \left[ \begin{array}{ccc} \Lambda & \Delta & \Gamma w \\ \lambda & \delta & \gamma \end{array} \right] |\Lambda t \lambda \rangle |\Delta d \delta \rangle,$$  \hspace{1cm} (12)

where $t = 1, 2, ..., n(\mathbb{P}, \Lambda), \ d = 1, 2, ..., n(\mathbb{A}, \Delta), \ w = 1, 2, ..., c(\Lambda, \Delta, \Gamma)$ are repetition indices of the first ($t$ and $d$) and second range ($w$). The symbol $\left[ \begin{array}{ccc} \Lambda & \Delta & \Gamma w \\ \lambda & \delta & \gamma \end{array} \right]$ is Clebsch-Gordan coefficient. The vectors on the right side of the equation (12) are

$$|\Lambda t \lambda \rangle = \sum_{i=1}^{N} b^{\Lambda t \lambda}_{i} |i\rangle$$  \hspace{1cm} (13)

$$|\Delta d \delta \rangle = \sum_{\alpha} a^{\Delta d \delta \alpha}_{\alpha} \varphi^{\alpha}$$  \hspace{1cm} (14)

3. Electron states of benzene

In the case of benzene molecular orbitals, the electron configuration of each carbon atom is $1s^22s^22p^2$. In the language of chemical bonding the $sp^2$ hybridisation is a set of three (so called $\sigma$) atomic orbitals $\varphi_x, \varphi_y, \varphi_z$ (figure 1b). However in the symmetry with three-fold axis in the carbon position (as in the case of benzene ring) it is convenient to introduce orbitals $\varphi_{\sigma_a}, \varphi_{\sigma_b}, \varphi_{\sigma_c}$ (figure 1c) [15]

$$\varphi_{\sigma_a} = \frac{1}{\sqrt{3}} \left( \varphi_x + \sqrt{2} \varphi_y \right)$$

$$\varphi_{\sigma_b} = \frac{1}{\sqrt{3}} \left( \varphi_x + \frac{3}{2} \varphi_y - \frac{1}{\sqrt{2}} \varphi_z \right)$$

$$\varphi_{\sigma_c} = \frac{1}{\sqrt{3}} \left( \varphi_x - \frac{3}{2} \varphi_y - \frac{1}{\sqrt{2}} \varphi_z \right)$$

$$\varphi_{\pi} = \varphi_y$$  \hspace{1cm} (15)

The geometry of $\varphi_{\sigma}$, $\sigma = (\sigma_a, \sigma_b, \sigma_c)$ vectors is introduced in figure 1c. They are situated along $a$, $b$, $c$ axis, which form $120^\circ$ angle with each other. The $\varphi_y$ atomic orbital remains unchanged and is
The set of atomic orbitals \( \varphi_\sigma \) and \( \varphi_\pi \) spans the Hilbert space, which we call the atomic orbital space \( A \) with basis vectors \( \varphi_\sigma \). The action of symmetry group \( D_{6h} \) of benzene molecule on the set \( \{ \varphi_\sigma \} \) forms the atomic representation \( A \). Vector \( \varphi_\pi \) does not mix with the vectors \( \varphi_\sigma \), therefore the representation is one-dimensional and \( \varphi_\pi \) changes its sign by operations \( C_2', C_2'', I, S_3, S_6, \sigma_h \) (table 1). The characters of the representation \( A \) and its decomposition into irreducible representations of the group \( D_{6h} \) are collected in table 1. Table 1 the structure of \( A_\sigma \) and \( A_\pi \) representations is presented too. The positions \( (i = 1,...,6) \) of carbon atoms in benzene (figure 1a) constitute basis vectors \( |i\rangle \) of positional space \( P \).

The elements of the group \( D_{6h} \) acting in this space form positional representation \( P \) with characters included in table 1.

![Figure 1. Benzene. a) symmetry elements of benzene ring, b) orbitals \( \varphi_{px}, \varphi_{py}, \varphi_{pz} \) and c) \( \varphi_{\sigma_x}, \varphi_{\sigma_y}, \varphi_{\sigma_z} \) of carbon atoms.](image_url)

| \( D_{6h} \) | \( E \) | \( 2C_6 \) | \( 2C_3 \) | \( C_2 \) | \( 3C_2' \) | \( 3C_2'' \) | \( I \) | \( 2S_3 \) | \( 2S_6 \) | \( \sigma_h \) | \( 3\sigma_3 \) | \( 3\sigma_6 \) | Decomposition |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| \( P \) | 6 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 6 | 0 | 2 | \( A_{1g} + E_{2g} + B_{1u} + E_{1u} \) |
| \( A \) | 4 | 1 | 1 | -2 | 0 | -2 | -4 | -1 | -1 | 2 | 0 | 2 | \( A_{2u} + B_{1u} + E_{1u} \) |
| \( A_\sigma \) | 3 | 0 | 0 | -3 | 1 | -1 | -3 | 0 | 0 | 3 | -1 | 1 | \( B_{1u} + E_{1u} \) |
| \( A_\pi \) | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 | 1 | 1 | 1 | \( A_{2u} \) |

The positional representation \( P \) decomposes into irreducible ones as follows (see table 1):
\[
P = A_{1g} + E_{2g} + B_{1u} + E_{1u}, \tag{16}
\]
whereas atomic representation decomposes as (see table 1):
\[
A = A_\sigma + A_\pi = A_{2u} + B_{1u} + E_{1u}, \tag{17}
\]
where \( A_\pi = A_{2u} \). The irreducible basis vectors of the positional subspace for benzene are:
\[
|A_{1g}\rangle = \frac{1}{\sqrt{6}} \left( |1\rangle + |2\rangle + |3\rangle + |4\rangle + |5\rangle + |6\rangle \right)
\]
\[ |B_{1u} b_1 \rangle = \frac{1}{\sqrt{6}} \left( |1\rangle - |2\rangle + |3\rangle - |4\rangle + |5\rangle - |6\rangle \right) \] (18)
\[ |E_1 e_1 \rangle = \frac{1}{\sqrt{12}} \left( 2|1\rangle + |2\rangle - |3\rangle - 2|4\rangle - |5\rangle + |6\rangle \right), \quad |E_1 e_2 \rangle = \frac{1}{2} \left( |2\rangle + |3\rangle - |5\rangle - |6\rangle \right) \]
\[ |E_2 e_1 \rangle = \frac{1}{\sqrt{12}} \left( 2|1\rangle - |2\rangle - |3\rangle + 2|4\rangle - |5\rangle - |6\rangle \right), \quad |E_2 e_2 \rangle = \frac{1}{2} \left( |2\rangle - |3\rangle + |5\rangle - |6\rangle \right). \]

4. Electron states of naphthalene and polyacenes of higher order
Naphthalene, anthracene, tetracene and pentacene consists of two, three, four and five benzene rings respectively. Due to the adjoin of \( k \) benzene rings together, these molecules show symmetry \( D_{2h} \), which is subgroup of the \( C_{6v} \) group symmetry of benzene. The symmetry of all polyacenes is the same independently on the number \( k \) of benzene rings (figure 2). The symmetry group decomposes all carbon positions \( i \) into orbits of action of group \( G=D_{2h} \) on a set \( \{i\} \) (table 2) for all \( g \in D_{2h} \):
\[ O_r = \{gr\}, \quad (19) \]
where \( r \in \{i\} \) is a generator of orbit \( O_r \). There are \( k \) four-element orbits and one two-element orbit for each molecule (table 4).

Characters of atomic \( A \) and positional representations \( P_k \) are collected in table 3, where symbol \( k=II \) concerns naphthalene, \( k=III \) – anthracene, \( k=IV \) – tetracene and \( k=V \) – pentacene. The decomposition of these representations into irreducible ones are presented in this table as well.

![Figure 2](image)

**Figure 2.** Enumeration of carbon atoms in: a) naphthalene, b) anthracene, c) tetracene, d) pentacene.

**Table 2.** Enumeration of orbits in polyacenes.

| Polyacene   | Orbits                        |
|-------------|-------------------------------|
| Naphthalene | \( O_1 = \{1,4,5,8\}, O_2 = \{2,3,6,7\}, O_3 = \{9,10\} \) |
| Anthracene  | \( O_1 = \{1,6,7,12\}, O_2 = \{2,5,8,11\}, O_3 = \{3,4,9,10\}, O_{13} = \{13,14\} \) |
| Tetracene   | \( O_1 = \{1,8,9,16\}, O_2 = \{2,7,10,13\}, O_3 = \{3,6,11,14\}, O_4 = \{4,5,12,13\} O_{17} = \{17,18\} \) |
Pentacene \( O_1 = \{1,10,11,20\} \), \( O_2 = \{2,9,12,19\} \), \( O_3 = \{3,8,13,18\} \), \( O_4 = \{4,7,14,17\} \), \( O_5 = \{5,6,15,16\} \), \( O_{21} = \{21,22\} \).

Table 3. The characters of atomic representation \( \mathbf{A} \) and positional representations \( \mathbf{P}_{\text{II}}, \mathbf{P}_{\text{III}}, \mathbf{P}_{\text{IV}}, \mathbf{P}_\nu \) of higher order polyacenes.

| \( D_{2h} \) | \( E \) | \( C_2(z) \) | \( C_2(y) \) | \( C_2(x) \) | \( I \) | \( \sigma(x) \) | \( \sigma(y) \) | \( \sigma(z) \) | Decomposition
|---|---|---|---|---|---|---|---|---|---|
| \( \mathbf{A} \) | 4 | -2 | -2 | 0 | -4 | 2 | 2 | 0 | \( B_{2u} + B_{3u} + 2B_{3u} \)
| \( \mathbf{A}_\sigma \) | 3 | -3 | -1 | 1 | -3 | 3 | 1 | -1 | \( B_{2u} + 2B_{3u} \)
| \( \mathbf{A}_\pi \) | 1 | 1 | -1 | -1 | -1 | 1 | 1 | 1 | \( B_{1u} \)
| \( \mathbf{P}_{\text{II}} \) | 10 | 0 | 2 | 0 | 0 | 10 | 0 | 2 | \( 3A_4 + 2B_{1u} + 3B_{2u} + 2B_{3u} \)
| \( \mathbf{P}_{\text{III}} \) | 14 | 0 | 2 | 0 | 0 | 14 | 0 | 2 | \( 4A_4 + 3B_{1u} + 4B_{2u} + 3B_{3u} \)
| \( \mathbf{P}_{\text{IV}} \) | 18 | 0 | 2 | 0 | 0 | 18 | 0 | 2 | \( 5A_4 + 4B_{1u} + 5B_{2u} + 4B_{3u} \)
| \( \mathbf{P}_\nu \) | 22 | 0 | 2 | 0 | 0 | 22 | 0 | 2 | \( 6A_4 + 5B_{1u} + 6B_{2u} + 5B_{3u} \)

According to enumeration of carbon atoms as in figure 2 the irreducible basis vectors \( |\Lambda \lambda \rangle = N \sum_{G=1}^{G} b_{\lambda \lambda}^G |i \rangle \) (where \( N \) is normalization factor) of positional representation are collected in table 4.

Table 4. Irreducible basis \( |\Lambda \lambda \rangle \) of the positional representation for polyacenes.

| Representation | Molecule | Orbit | \( N \) | \( |A_g A_g \rangle \) | \( |B_{2u} B_{2u} \rangle \) | \( |B_{3u} B_{3u} \rangle \)
|---|---|---|---|---|---|---|
| Naphthalene | \( O_1 \) | 1/2 | \( |1\rangle + |4\rangle + |5\rangle + |8\rangle \) | \( |1\rangle - |4\rangle - |5\rangle - |8\rangle \) | \( |1\rangle + |5\rangle - |8\rangle \) | \( |1\rangle + |4\rangle - |5\rangle - |8\rangle \)
| | \( O_2 \) | 1/2 | \( |2\rangle + |3\rangle + |6\rangle + |7\rangle \) | \( |2\rangle - |3\rangle - |6\rangle - |7\rangle \) | \( |2\rangle + |3\rangle - |6\rangle - |7\rangle \)
| | \( O_3 \) | \( \sqrt{1/2} \) | \( |9\rangle + |10\rangle \) | \( |9\rangle - |10\rangle \) | \( |9\rangle - |10\rangle \) | \( |9\rangle - |10\rangle \)
| Anthracene | \( O_1 \) | 1/2 | \( |1\rangle + |6\rangle + |7\rangle + |12\rangle \) | \( |1\rangle - |6\rangle | |7\rangle - |12\rangle \) | \( |1\rangle + |6\rangle - |7\rangle - |12\rangle \)
| | \( O_2 \) | 1/2 | \( |2\rangle + |5\rangle + |8\rangle + |11\rangle \) | \( |2\rangle - |5\rangle - |8\rangle - |11\rangle \) | \( |2\rangle + |5\rangle - |8\rangle - |11\rangle \)
| | \( O_3 \) | \( \sqrt{1/2} \) | \( |3\rangle + |4\rangle + |9\rangle + |10\rangle \) | \( |3\rangle - |4\rangle - |9\rangle - |10\rangle \) | \( |3\rangle + |4\rangle - |9\rangle - |10\rangle \)
| | \( O_4 \) | \( \sqrt{1/2} \) | \( |13\rangle + |14\rangle \) | \( |13\rangle - |14\rangle \) | \( |13\rangle - |14\rangle \) | \( |13\rangle - |14\rangle \)
| Tetracene | \( O_1 \) | 1/2 | \( |1\rangle + |8\rangle + |9\rangle + |16\rangle \) | \( |1\rangle - |8\rangle | |9\rangle - |16\rangle \) | \( |1\rangle + |8\rangle - |9\rangle - |16\rangle \)
| | \( O_2 \) | 1/2 | \( |2\rangle + |7\rangle + |10\rangle + |15\rangle \) | \( |2\rangle - |7\rangle - |10\rangle - |15\rangle \) | \( |2\rangle + |7\rangle - |10\rangle - |15\rangle \)
| | \( O_3 \) | \( \sqrt{1/2} \) | \( |3\rangle + |6\rangle + |11\rangle + |14\rangle \) | \( |3\rangle - |6\rangle - |11\rangle - |14\rangle \) | \( |3\rangle + |6\rangle - |11\rangle - |14\rangle \)
| | \( O_4 \) | \( \sqrt{1/2} \) | \( |4\rangle + |5\rangle + |12\rangle + |13\rangle \) | \( |4\rangle - |5\rangle - |12\rangle - |13\rangle \) | \( |4\rangle + |5\rangle - |12\rangle - |13\rangle \)
| | \( O_5 \) | \( \sqrt{1/2} \) | \( |17\rangle + |18\rangle \) | \( |17\rangle - |18\rangle \) | \( |17\rangle - |18\rangle \) | \( |17\rangle - |18\rangle \)
| Pentacene | \( O_1 \) | 1/2 | \( |1\rangle + |10\rangle + |11\rangle + |20\rangle \) | \( |1\rangle - |10\rangle - |11\rangle - |20\rangle \) | \( |1\rangle + |10\rangle - |11\rangle - |20\rangle \)
| | \( O_2 \) | 1/2 | \( |2\rangle + |9\rangle + |12\rangle + |19\rangle \) | \( |2\rangle - |9\rangle - |12\rangle - |19\rangle \) | \( |2\rangle + |9\rangle - |12\rangle - |19\rangle \)
| | \( O_3 \) | \( \sqrt{1/2} \) | \( |3\rangle + |8\rangle + |13\rangle + |18\rangle \) | \( |3\rangle - |8\rangle - |13\rangle - |18\rangle \) | \( |3\rangle + |8\rangle - |13\rangle - |18\rangle \)
| | \( O_4 \) | \( \sqrt{1/2} \) | \( |4\rangle + |7\rangle + |14\rangle + |17\rangle \) | \( |4\rangle - |7\rangle - |14\rangle - |17\rangle \) | \( |4\rangle + |7\rangle - |14\rangle - |17\rangle \)
| | \( O_5 \) | \( \sqrt{1/2} \) | \( |5\rangle + |6\rangle + |15\rangle + |16\rangle \) | \( |5\rangle - |6\rangle - |15\rangle - |16\rangle \) | \( |5\rangle + |6\rangle - |15\rangle - |16\rangle \)
| | \( O_6 \) | \( \sqrt{1/2} \) | \( |21\rangle + |22\rangle \) | \( |21\rangle - |22\rangle \) | \( |21\rangle - |22\rangle \) | \( |21\rangle - |22\rangle \)

The basis vectors of atomic representations for all polyacenes are as follows:
\[ |B_{2u}b_2\rangle = \frac{1}{\sqrt{2}} (\varphi_{\sigma_v} - \varphi_{\sigma_c}) \equiv \frac{1}{\sqrt{2}} (|b\rangle - |c\rangle) \]
\[ |B_{3u}b_3^{(1)}\rangle = \varphi_{\sigma_v} \equiv |a\rangle \]
\[ |B_{3u}b_3^{(2)}\rangle = \frac{1}{\sqrt{2}} (\varphi_{\sigma_v} + \varphi_{\sigma_c}) \equiv \frac{1}{\sqrt{2}} (|b\rangle + |c\rangle), \]

where for abbreviation we denote \( \varphi_{\sigma_v} \equiv |a\rangle, \varphi_{\sigma_b} \equiv |b\rangle, \varphi_{\sigma_c} \equiv |c\rangle. \)

Using formula (12) and taking into account the vectors from the table 4 as well as the ones expressed in (20) we obtain the symmetry orbitals \( |\Lambda, \Delta, \Gamma\rangle \). Some of the symmetry orbitals calculated for pentacene are presented in table 5, where \( |il\rangle \ (l = a, b, c) \) denotes product \( |i\rangle |l\rangle \).

| \( \Lambda \) | \( \Delta \) | \( \Gamma \) | \( N \) | \( |\Lambda, \Delta, \Gamma\rangle \) |
|---|---|---|---|---|
| \( A_{g1} \) | \( B_{2u} \) | \( B_{2u}b_{2u} \) | \( 1/2\sqrt{2} \) | \( \begin{array}{c} |l\rangle = |b\rangle - |c\rangle \\ |10b\rangle + |11b\rangle + |20c\rangle \end{array} \) |
| \( B_{3u1} \) | \( B_{3u}b_{3u} \) | \( 1/2 \) | \( \begin{array}{c} |1a\rangle + |10a\rangle + |20a\rangle \\ |11a\rangle \end{array} \) |
| \( B_{3u2} \) | \( B_{3u}b_{3u} \) | \( 1/2\sqrt{2} \) | \( \begin{array}{c} |l\rangle = |b\rangle + |c\rangle \\ |10b\rangle + |11b\rangle + |20c\rangle \end{array} \) |
| \( A_{g2} \) | \( B_{2u} \) | \( B_{2u}b_{2u} \) | \( 1/2\sqrt{2} \) | \( \begin{array}{c} |l\rangle = |b\rangle - |c\rangle \\ |10b\rangle + |11b\rangle + |20c\rangle \end{array} \) |
| \( B_{3u1} \) | \( B_{3u}b_{3u} \) | \( 1/2 \) | \( \begin{array}{c} |1a\rangle + |10a\rangle + |20a\rangle \\ |11a\rangle \end{array} \) |
| \( B_{3u2} \) | \( B_{3u}b_{3u} \) | \( 1/2\sqrt{2} \) | \( \begin{array}{c} |l\rangle = |b\rangle + |c\rangle \\ |10b\rangle + |11b\rangle + |20c\rangle \end{array} \) |
| \( B_{3u4} \) | \( B_{2u} \) | \( B_{1g}b_{1g} \) | \( 1/2\sqrt{2} \) | \( \begin{array}{c} |l\rangle = |b\rangle - |c\rangle \\ |7b\rangle + |7c\rangle + |14b\rangle + |14c\rangle + |17c\rangle \end{array} \) |
| \( B_{3u1} \) | \( A_{g1}a_{g1} \) | \( 1/2 \) | \( \begin{array}{c} |4a\rangle + |7a\rangle + |14a\rangle + |17a\rangle \\ |4a\rangle \end{array} \) |
| \( B_{3u2} \) | \( A_{g1}a_{g1} \) | \( 1/2\sqrt{2} \) | \( \begin{array}{c} |l\rangle = |b\rangle + |c\rangle \\ |7b\rangle + |7c\rangle + |14b\rangle + |14c\rangle + |17c\rangle \end{array} \) |
| \( B_{3u5} \) | \( B_{2u} \) | \( B_{1g}b_{1g} \) | \( 1/2\sqrt{2} \) | \( \begin{array}{c} |l\rangle = |b\rangle - |c\rangle \\ |5b\rangle + |5c\rangle + |6b\rangle + |6c\rangle + |15b\rangle + |15c\rangle + |16c\rangle \end{array} \) |
| \( B_{3u1} \) | \( A_{g1}a_{g1} \) | \( 1/2 \) | \( \begin{array}{c} |5a\rangle + |6a\rangle + |15a\rangle + |16a\rangle \\ |5a\rangle \end{array} \) |
| \( B_{3u2} \) | \( A_{g1}a_{g1} \) | \( 1/2\sqrt{2} \) | \( \begin{array}{c} |l\rangle = |b\rangle + |c\rangle \\ |5b\rangle + |5c\rangle + |6b\rangle + |6c\rangle + |15b\rangle + |15c\rangle + |16c\rangle \end{array} \) |

5. Conclusions
The factorization of the symmetry orbitals subspace into positional and orbital subspaces is a useful tool for the group-theory classification of such orbitals. However, in the case of molecules consisted of large number of atoms and having a low symmetry, this procedure does not allow to classify orbits entirely because of the large number of irreducible representations included in the reducible ones (e.g. in the case of pentacene the index of multiplicity \( t = 5 \) or \( 6 \)). Nevertheless, for aromatic hydrocarbons such index can be satisfactorily connected with the orbit numbers of carbon atoms. This provides almost complete distinction of symmetry orbitals. Only the indices of multiplicity \( d \) for atomic representation have no group-theory grounds.

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