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Condensed Graph: Determination of Eigenspectra and Band Gap of Cylindrical Poly(*p*-phenylene) Systems

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ABSTRACT

The compounds of poly(*p*-phenylene) are important materials for electro-optical and electronic applications. Algorithms for the calculation of the eigenspectra of cylindrical poly(*p*-phenylene) systems have been developed in analytical forms considering its condensed graphs. Rotational symmetry is utilized to construct the condensed graphs of the cylindrical poly(*p*-phenylene) systems. Calculation of band gap, chemical potential and hardness from the corresponding energy eigenvalues of HOMO and LUMO of such cylindrical poly(*p*-phenylene) systems are shown here.

KEY WORDS: cylindrical poly(*p*-phenylene); eigenspectra; condensed graphs; band gap; chemical potential; hardness.

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1. INTRODUCTION

In few years the discovery of organic polymers with high conductivities has been generated substantial research interest among the physicists and chemists. Among the conducting polymers linear and cylindrical poly(*p*-phenylene) systems are very attractive because these compounds are supposed to be promising candidates for low cost and easy processing materials for electro-optical and electronic applications[1,2]. In our present study, we focus our attention on cylindrical poly(*p*-phenylene) that is a conjugated polynuclear hydrocarbon consisting of 'n' number of benzene rings connecting through para positions. The eigenspectra of a graph are the zeros of its characteristic polynomial, $|x\boldsymbol{I} - \boldsymbol{A}|$. Here $\boldsymbol{A}$ is the adjacency matrix of the graph is just equal to the Hückel matrix through proper scaling of energy that means coulomb integral $(\alpha)$is expressed as zero of energy and resonance integral (β) is expressed as unit of energy. Therefore with proper scaling of the energy, graph eigenvalues become exactly equal to the Hückel molecular orbitals (HMO) of the corresponding molecule. There are a large number of graph theoretical methods for the determination of eigenspectra for large graphs. In a series of papers, Hall[3] provided the basis of determination of eigenvalues in alternate hydrocarbons using embedding rules. Pairing theorem[4] is also applied to predict the nature of eigenvalues in case of alternant hydrocarbons.

A weighted graph[5,6] is defined as a graph in which at least one vertex or edge has some weight(s) that is an weighted graph must have at least one edge of weight other than unity or one vertex of weight other than zero. A number of research works on eigenspectra was done using weighted graphs also. Mandal[7] developed graph theoretical procedure to obtain the eigenspectra of linear chains and cycles with alternant vertex weights and same edge weights in analytical form. He further studied on the linear chain having one or two terminal edge(s) of weigh $\sqrt{2}$ times that of remaining edge. Again the eigenspectra of vertex and edge–weighted graphs of linear chains, cycles and stars have been determined and subsequently analyzed to calculate some important properties of those corresponding graphs by Mandal[8].

2. CONSTRUCTION OF CONDENSED GRAPH OF CYLINDRICAL POLY(*P*-PHENYLENE)

Cylindrical poly(*p*-phenylene) in which 'n' number of benzene rings are connected through para position has 'n' fold rotational symmetry.

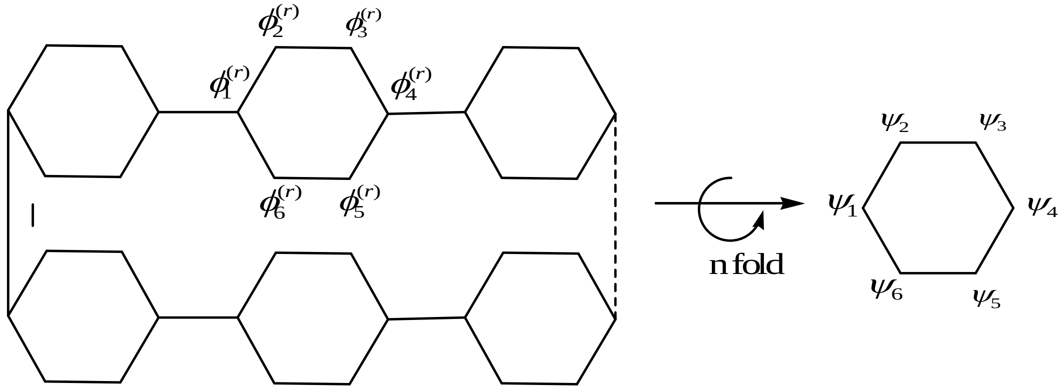


Figure-1: Graph of cylindrical poly(*p*-phenylene) and its condensed graph

$\phi_i^{(r)}$ represents the *i*th *p*-atomic orbital of *r*th ring. Each ϕ_1 from each benzene ring *(r)* of the polymer graph contributes to ψ_1 of condensed graph. Here '*r*' changes from 1 to *n*. Similarly $\phi_2, \phi_3, \phi_4, \phi_5$ and ϕ_6 from each ring contributes to form $\psi_2, \psi_3, \psi_4, \psi_5$ and ψ_6 those represent the wave functions of the condensed graph.

Thus we can write the equation for the *t*th irreducible representation as follows:

$$\psi_j^{(t)} = \frac{1}{\sqrt{n}} \sum_{r=1}^{n} \varepsilon^{rt} \phi_j^{(r)}$$

$$\varepsilon = \frac{2\pi rt}{n}, t = 1,2,3 \ldots n$$

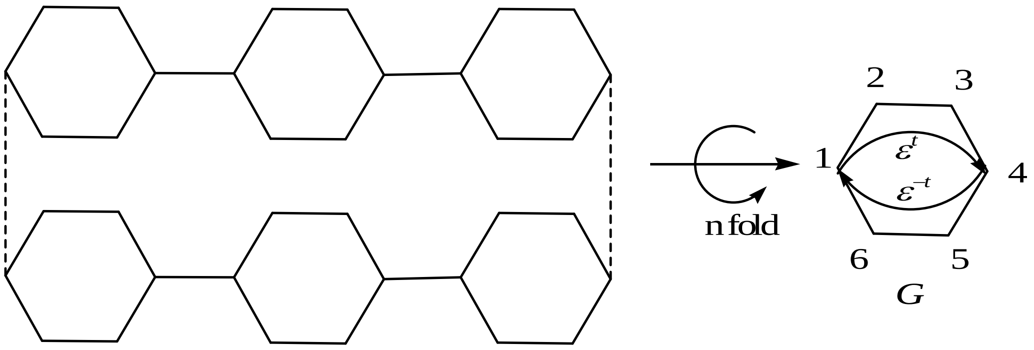
Now vertex weights and edge weights of the condensed graph can be calculated solving the following integrations where the expression of $\psi_j^{(t)}$ is used

$$\lambda_{tr} = \left\langle \psi_k^{(t)} \middle| A \middle| \psi_j^{(t)} \right\rangle$$

$$= \left\langle \frac{1}{\sqrt{n}} \sum_{r=1}^{n} \varepsilon^{rt} \varphi_k^{(r)} \middle| A \middle| \frac{1}{\sqrt{n}} \sum_{r=1}^{n} \varepsilon^{rt} \varphi_j^{(r)} \right\rangle$$

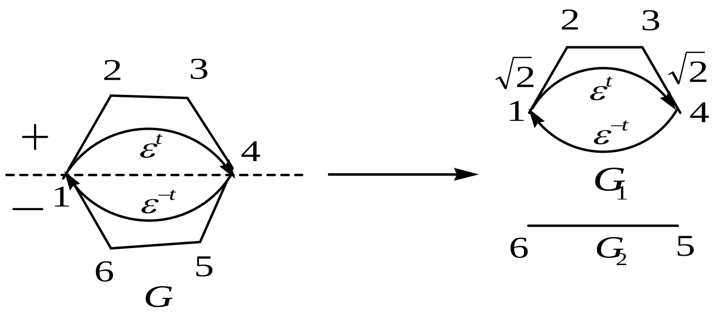
Using the above equation the condensed graph (G) is obtained and it is shown in scheme-1

3. DETERMINATION OF EIGENSPECTRA FOR CYLINDRICAL POLY(*P*-PHENYLENE)



Scheme-1

Now two subgraphs i.e. G_1 and G_2 are obtained, employing plane of symmetry fragmentation method as shown in scheme-2. Present work is an attempt to calculate the eigenvalues of cylindrical poly(*p*-phenylene) compounds having any number of benzene ring.



Scheme-2

Secular determinants of graph G_1 and graph G_2 will be given as follows

$$\left.\begin{aligned} A(G_1) &= \begin{vmatrix} x & -\sqrt{2} & 0 & -\varepsilon^{-t} \\ -\sqrt{2} & x & -1 & 0 \\ 0 & -1 & x & -\sqrt{2} \\ -\varepsilon^{t} & 0 & -\sqrt{2} & x \end{vmatrix} \\[2ex] A(G_2) &= \begin{vmatrix} x & -1 \\ -1 & x \end{vmatrix} \end{aligned}\right\} \qquad (2)$$

Solving the equations corresponding to these determinants (2) we obtain the eigenspectra as follows

We obtain eigenvalues as four bands for G_1

$$x = \pm\sqrt{3 \pm 2\sqrt{2}\cos\frac{\pi t}{n}}, \qquad t = 1,2,3\ldots,n. \qquad (3)$$

Similarly the other highly degenerate eigenvalues of all ethylenic group (G_2) will be

$$x = \pm 1 \qquad (4)$$

4. BAND GAP OF CYLINDRICAL POLY (*P*-PHENYLENE)

The band gap generally refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. Band gap is important in determining physical properties such as photoconductivity and electroluminescence of different systems[9-11]. Linear or cylindrical poly(*p*-phenylene), linear or cyclo poly-phenacene compounds are good example of one-dimensional conjugated polymeric semiconductors. The band gap type, be it direct or indirect, is characteristic of the extended systems not on molecules[12]. Band structure calculations have provided significant information for controlling the band gap size of organic semiconductors. The energy difference between valence band and conduction band provide the band gap and it is equal to the energy difference between HOMO and LUMO. All the eigenvalues of this graph are to be derived from the expressions given by equation (3) and (4). Using these expressions energy eigenvalue of HOMO and LUMO can be calculated, so that we should have the band gap value for this compounds.

5. CALCULATION OF ENERGY EIGENVALUE OF HOMO AND LUMO

As energy of HOMO means the minimum negative energy, therefore energy eigenvalue for HOMO will be calculated as follows

$$\varepsilon_t = \pm\sqrt{3 \pm 2\sqrt{2}Cos\frac{\pi t}{n}}$$

$$\frac{d\varepsilon_t}{dt} = \frac{d}{dt}\left(\pm\sqrt{3 \pm 2\sqrt{2}Cos\frac{\pi t}{n}}\right)$$

$$\frac{d\varepsilon_t}{dt} = \frac{1}{2}\left(3 \pm 2\sqrt{2}Cos\frac{\pi t}{n}\right)^{-1/2}(\pm)2\sqrt{2}\frac{\pi}{n}Sin\frac{\pi t}{n}$$

So far energy value of HOMO is concerned therefore $\frac{d\varepsilon_t}{dt} = 0$

This is only possible if $Sin\frac{\pi t}{n} = 0$

$$Sin\frac{\pi t}{n}=0$$

$$Sin\frac{\pi t}{n}=Sink\pi, k=0,1,2,3...$$

$$\frac{\pi t}{n}=k\pi$$

$$t=nk$$

Now $\varepsilon_{HOMO}=+\sqrt{3\pm 2\sqrt{2}Cos\pi k}\beta$, as β is itself negative

$\varepsilon_{HOMO}=+\sqrt{3+2\sqrt{2}Cos\pi k}\beta$ if k is odd

$\varepsilon_{HOMO}=+\sqrt{3-2\sqrt{2}Cos\pi k}\beta$ if k is even

But in both cases magnitude of ε_{HOMO} is the same and it is $\sqrt{3-2\sqrt{2}}\beta$

$$\varepsilon_{HOMO}=\sqrt{3-2\sqrt{2}}\beta \qquad (5)$$

Now because of alternant property of this polymer (bipartite in nature) its all eigenvalues occur in pair with opposite sign (pairing theory). So eigenvalues of bonding molecular orbitals and antibonding molecular orbitals are just the mirror images of one another means magnitude is the same but opposite in sign. In this way, we can obtain the eigenvalue of LUMO given in equation (6) as

$$\varepsilon_{LUMO}=-\sqrt{3-2\sqrt{2}}\beta \qquad (6)$$

6. BAND GAP

So band gaps $(E_{gap}=E_{LUMO}-E_{HOMO})$ of cylindrical poly(*p*-phenylene) is $-2\sqrt{(3-2\sqrt{2})}\beta$

The chemical potential (μ) is defined by Pearson as the rate of change of total energy E with electron count *N*.

$$\mu=\left(\partial E/\partial N\right)_v, \quad v \text{ implies a constant nuclear potential (i.e. fixed nuclei).}$$

According to Hückel theory chemical potential reduces to

$$\mu\approx\alpha+\frac{1}{2}(E_{LUMO}+E_{HOMO})\beta$$

Therefore chemical potential value of cylindrical poly(*p*-phenylene) is $\alpha + 0.4142\beta$

And the hardness η is the second derivative of the energy or the first derivative of chemical potential. Softness is the reciprocal of hardness. Now in orbital model η can be approximated as a function of the orbital energies.

$$\eta \approx \frac{1}{2}(E_{LUMO} - E_{HOMO}) \qquad (7)$$

Hardness parameter for all cylindrical poly(*p*-phenylene) is $\eta \approx -\sqrt{3-2\sqrt{2}}\beta$ i.e. -0.4142β. The value is not very high means molecule is quite soft. Soft molecules are more reactive and polarizable also.

7. CONCLUSION

Poly(*p*-phenylene) are belong to a polycyclic aromatic hydrocarbon compounds (PHA) which are planar sets of linearly fused benzene rings. Several molecules of this family are known to have interesting electronic, thermodynamic and optical properties potentially applied to new materials, e.g. of highly conductive, semi conductive, photoconductive and ferro-magnetic properties. This method of condensed graph formation using rotational symmetry is very useful for evaluation of eigenspectra of some cylindrical poly(*p*-phenylene) graphs. The spectra of graphs, which are the zeros of their corresponding characteristic polynomials, have many chemical applications for instance, they have been used in chemical kinetics[13], quantum chemistry, dynamics of oscillatory reactions and in determining the stabilities of reaction networks[14], estimating the stabilities of conjugated systems and the electronic structure of organic polymers. On the other hand, HOMO and LUMO energies, band gap, chemical properties are also calculated for such molecules.

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