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Foreword

It is indeed a proud moment for the University Publication Centre (UPENA) of UiTM Pulau Pinang for having realised the publication of the sixth volume of the Esteem Academic Journal UiTM Pulau Pinang. In fact, it is the undivided support and all-round commitment from all those who were directly and indirectly involved in this project that was the pivotal factor for this success.

On behalf of UPENA UiTMPP, I would like to, first and foremost, express my sincerest gratitude to Associate Professor Mohd Zaki Abdullah, Director of UiTM Pulau Pinang, Associate Professor Dr Mohamad Abdullah Hemdi, Deputy Director of Academic Affairs and Associate Professor Ir. Damanhuri Jamalludin, Deputy Director of Research, Industry Linkages, Development & Maintenance for their unwavering support and being such a driving force towards this successful endeavour.

Not to be forgotten also is the service rendered by the distinguished panel of external reviewers for their constructive comments and criticisms in ensuring that the papers published in this issue would be of the highest quality. Similarly, the panel of language editors who had worked tirelessly towards ensuring that the papers published were linguistically perfect. To both these groups, UPENA is in awe of your efforts and salutes you!

UPENA is also impressed with the nature of papers submitted for publication. While this issue comprises all engineering based articles, it covers a wide array of sub-engineering disciplines. Kudos to these writers! UPENA sincerely appreciates their efforts and hopes more of our staff will follow in their footsteps.

Finally, research and publication are integral parts of an academic's life at any institution. Apart from being an institutional requirement, it is also essential for our own continuous self-development and knowledge expansion. To this effect, UPENA hopes to play a significant role by providing the platform upon which our staff can realise their dream. So, it is our hope at UPENA UiTMPP that lecturers will take up the challenge and start to publish more vigorously from now on.

Rasaya Marimuthu
Chief Editor
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Organic Semiconductor Characterization Using Linear Combination of Atomic Orbital (LCAO)

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ABSTRACT

The electronic structure of conjugated polymer (π-polymer) is calculated using Linear Combination of Atomic Orbital (LCAO). LCAO is a quantum superposition technique to calculate energy level of molecular orbital (MO). This article discusses the electronic structure of naphthalene and polyacetylene (PA). Naphthalene and its derivative are aromatic molecules that are widely used as a hole transport layer in most organic light emitting diode (OLED) applications. In calculating energy level, the basic electronic molecule frame work and Secular determinant must be determined. The band energy of PA is calculated using Ritz Method where H_{ii} determines the interaction of electrons in an isolated $2p_z$ orbital while S_{ij} measures the overlapping between basis function. In microscopic level, the important parameters are Highest Occupied Molecular Orbital (HOMO) which is equivalent with conduction band and Lowest Unoccupied Molecular Orbital (LUMO) which is equivalent with valence band. For Naphthalene, the positive and negative changing in

coefficient of LCAO shows the changing in wavefunction in every monomer unit and its effects on the electronic properties. In polyacetylene, Fermi Energy levels lay between -0.9 eV and -1.1eV.

Keywords: *LCAO, tight binding calculation, HOMO, LUMO*

Introduction

In 1977, Alan MacDiarmid, Hideki Shirakawa and Alan J. Heeger discovered polyacetylene conducting polymer which had the ability to be doped and enhanced the conductivity (Shirakawa et al., 1977). From this invention, such polymer has become a new material for electronic and optoelectronic application. The electron and hole mobility of organic semiconductor materials is lesser than inorganic semiconductor materials. Transport process in crystalline inorganic semiconductor can be described as band transport while in the organic semiconductor most of its transport properties can be described as hopping transport (Summerfield et al., 1982; Yoon et al., 1995). Some researchers suggested that the transport properties in conjugated polymer are due to weak Coulomb interaction with electron-phonon coupling (Pakbaz et al., 1994). Conjugated polymers have unique properties which show a combination of electronics characters of semiconductor and metals.

The electronic structure of material has been discussed in solid state physics using different approaches such as, tight binding, Muffin-Tin Potential, augumanted plane wave theory, Orthogonalized plane wave theory, Korringa, Kohn and Rostoker (KKR) method as well as Mott-Davis Model. By using mathematical software and programming, most of material structures were identified and solved. However, since the discovery of conjugated conducting polymer, lots of macromolecules and high performance polymers have been synthesized for the requirement to the device operation. Hence, many theoretical physicists and chemists have been trying to solve the unique properties of the electronic structure. Ab initio Hartree-Fock is one of the famous computational theories used to calculate the electronic structure of molecule and solid. Hatree-Fock method was also applied to Schrodinger's equation and the relation between eigen value and Fock function was identified (Rauk, 1994). Another theory used to investigate the electronic structure of many-body systems in molecule and condensed phase is the density functional theory (DFT) (Drezles, 1995). Besides that, the improvement of Hückel

Molecular Orbital (HMO) method by Hoffmann (1963) has made the electronic structure of conjugated materials more reasonable.

Calculation Electronic Structure using Hückel Theory

The simple operation of wave function using Hamiltonian operator will produce the eigen value. The linear combination atomic orbital (LCAO) is given by equation (1). While, the eigen value is given by equation (2).

$$\psi(y) = c_A\varphi_A + c_B\varphi_B \tag{1}$$

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\int(c_A\varphi_A + c_B\varphi_B)\hat{H}(c_A\varphi_A + c_B\varphi_B)d\tau}{\int(c_A\varphi_A + c_B\varphi_B)^2 d\tau}$$

$$= \frac{c_A^2 H_{AA} + 2c_A c_B H_{AB} + c_B^2 H_{BB}}{c_A^2 S_{AA} + 2c_A c_B S_{AB} + c_B^2 S_{BB}} \tag{2}$$

Where

$$\int(\varphi_A\hat{H}\varphi_A)d\tau = H_{AA}, \quad \int(\varphi_A\hat{H}\varphi_B)d\tau = H_{AB} = \int(\varphi_B\hat{H}\varphi_A)d\tau = H_{BA},$$

$$\int(\varphi_B\hat{H}\varphi_B)d\tau = H_{BB}, \quad \int(\varphi_A\varphi_A)d\tau = S_{AA}, \quad \int(\varphi_B\varphi_B)d\tau = S_{BB} \text{ and}$$

$$\int(\varphi_A\varphi_B)d\tau = S_{AB}.$$

For getting the minimum values of energy, $dE/dc_A = 0$ and $dE/dc_B = 0$. In term of Secular equation;

$$\begin{bmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{bmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{3}$$

$$\left[\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} - \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}E\right]\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{4}$$

In the matrix form;

$$(\mathbf{H}_{ij} - \mathbf{S}_{ij}\mathbf{E})\mathbf{C}_{ij} = 0 \tag{5}$$

The following steps are the general procedure for calculating HMO (Yates; 1978 and Heilronner; 1976);

i.   Draw the basic electronic molecule frame work;
ii.   Set up the Secular determinant;
iii. Choose the symmetrical basis set;
iv.   Determine the Molecular coefficient;
v.   Determine the eigen value.

Result and Discussion

Electronic Structure of Naphthalene

Result

Naphthalene and its derivative are widely used as a hole transport layer in OLED application. Secular determinant (no show) for naphthalene is 10x10. In solid and gas phase, naphthalene has D_{2h} plane of symmetry. Naphthalene consists of two aromatic rings. In order to set up Secular determinant, we consider only π-backbone as shown in Figure 1.
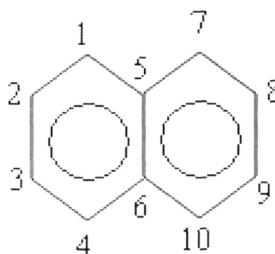
Figure 1: Molecule Frame Work for Naphthalene

In microscopic level, the important parameters to determine the electronic structure are Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). In solid state application, HOMO is equivalent with valence band while LUMO is equivalent with conduction band. The energy difference between HOMO and LUMO is called the band gap. The band gap is another important parameter which is able to characterize the electronic spectra of the molecule. Node is a point where destructive interference occurs, showing

a minimum amplitude. From Figure 2, HOMO and LUMO for naphthalene molecule, have zero coefficients implying that both wavefunctions have nodes. LUMO has alternating changing positive and negative. As a result, more nodes could be found in LUMO. Compared with HOMO, the changing in polarity positive and negative coefficient is lower than LUMO.
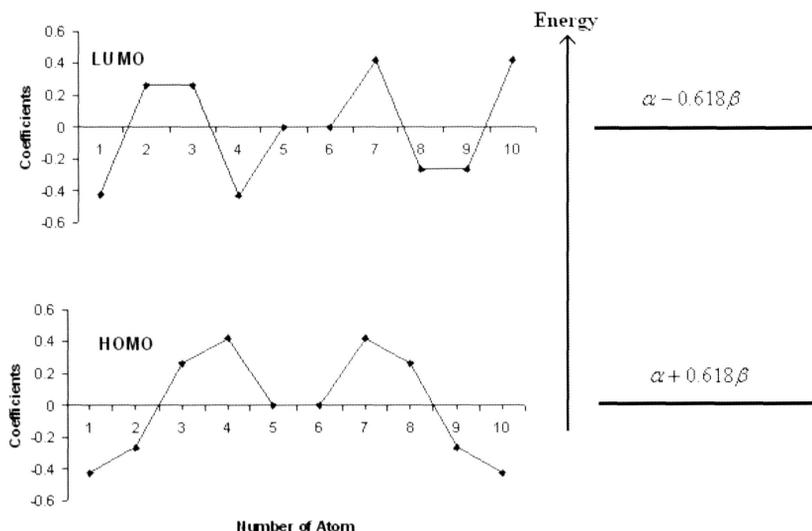
Figure 2: The Coefficients and Energy Levels HOMO and LUMO for Naphthalene

Discussion

According to the classical result of the molecular orbital theory, the distribution of π-electrons in alternant conjugated hydrocarbons (which include benzenoid hydrocarbons) is uniform, i. e., the π-electron cloud is uniformly distributed over the entire conjugated systems (Gutman; 2003). The total π-electrons energy is one of the factors which contribute the saturated character of conjugated compounds. The total π-electrons energy is depend upon the structure of molecules (Gutman, 1977). In organic semiconductor application, the charge injection that occurs in organic solid crystal depends on the degree of chain ordering, density of chemical structure and electronic structure of molecules (Laquindanum; 1996). HOMO and LUMO are resulted from interaction between adjacent

chains in the molecule. HOMO is produced from the situation where the adjacent atomic orbital has the same sign lobes. On the other hand, LUMO is produced from antibonding situation where the adjacent atomic orbital has different sign lobes. Figure 3(a) shows the illustration of the antibonding-bonding interaction between two carbon atoms. While, Figure 3(b) shows the Huckel Molecule for naphthalene at HOMO and LUMO level. At HOMO and LUMO level, the positive and negative changing in coefficient of LCAO shows the changing in wavefunction in every monomer unit. The changing in coefficient has produced the interaction between atomic orbital localized over the carbon-carbon double bond within the aromatic rings.

If the changing polarity in coefficient is greater, electrostatic repulsion could occur. Besides that, the energy level splitting in LUMO will become smaller (Bredas, 2002). It can be concluded that, the energy splitting for naphthalene in HOMO is greater than LUMO. This implies that the hole mobility is greater than electron mobility, in agreement with the experimental results reported by Karl (2003). His results showed that the value for hole mobility was higher than electron mobility. His experimental results also indicated that, the mobility for electron and hole depended on temperature, electrical field and effective mass.
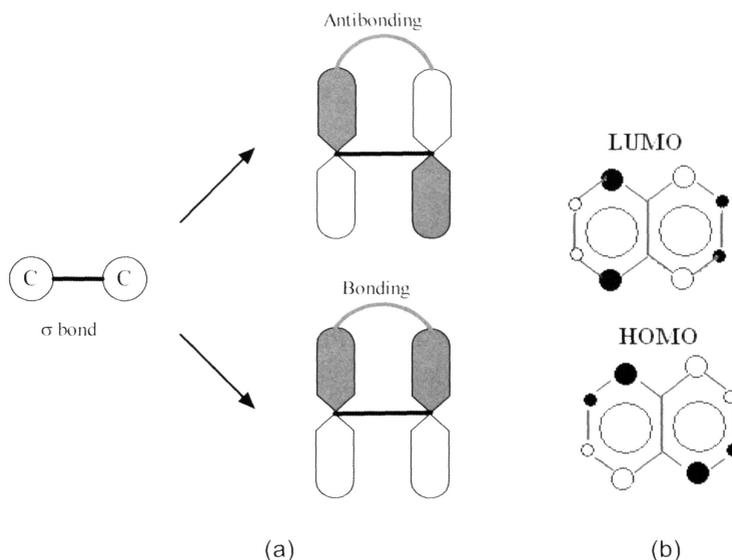

Figure 3: (a) Bonding and Antibonding Formation (b) Huckel Molecular for Naphthalene

Electronic Structure of Polyacetylene

Result

Polyacetylena has π-electron system which has n atomic orbital, Hückel determinant for n-row and n column can be written as in equation (3).

$$\begin{Vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & \vdots \\ 0 & 0 & \cdots & \ddots \end{Vmatrix} = 0 \tag{6}$$

$$x = \frac{\varepsilon - \alpha}{\beta} \tag{7}$$

The boundary condition is $x_n^N - x_{N+1}^N = 0$. The polynomial can be expanded in the form of polynomial. Basic equation for n^{th} root is $x_j = 2\cos\left(\frac{\pi}{n+1}j\right)$ where j is integer. In order to calculate our band structure in accordance with Dispersion Laws, we only consider the parameters as given in Table 1. The Coulomb and resonance integrals employed in our calculation are the same as Levin (1977) and Meyer (2003).

Figure 4 shows the energy band for s_σ-band, p_σ-band and p_π-band based on numerical calculation from Table 1.
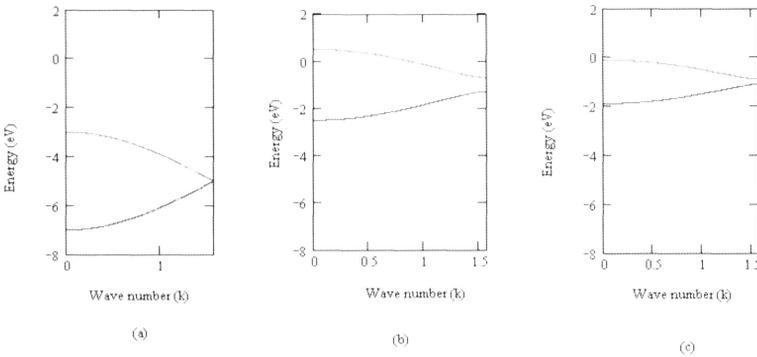
Figure 4: The Energy Band for (a) s_σ-band (b) p_σ-band and (c) p_π-band. Blue Line Indicates Bonding while Red Line Indicates Antibonding

Table 1: Energy Band Function for σ and π Bonding

Basis	Equation
Band-s σ	$E_{s\sigma}(k) = \sqrt{\beta_{s\sigma1}^2 + \beta_{s\sigma2}^2 + 2\beta_{s\sigma1}\beta_{s\sigma2}\cos(2ka)}$ $E_{Bs\sigma+}(k) = \alpha_{s\sigma} + E_{s\sigma}(k)$ $E_{Bs\sigma-}(k) = \alpha_{s\sigma} - E_{s\sigma}(k)$
Band-p σ	$E_{p\sigma}(k) = \sqrt{\beta_{p\sigma1}^2 + \beta_{p\sigma2}^2 + 2\beta_{p\sigma1}\beta_{p\sigma2}\cos(2ka)}$ $E_{Bp\sigma+}(k) = \alpha_{p\sigma} + E_{p\sigma}(k)$ $E_{Bp\sigma-}(k) = \alpha_{p\sigma} - E_{p\sigma}(k)$
Band-p π	$E_{p\pi}(k) = \sqrt{\beta_{p\pi1}^2 + \beta_{p\pi2}^2 + 2\beta_{p\pi1}\beta_{p\pi2}\cos(2ka)}$ $E_{Bp\pi+}(k) = \alpha_{p\pi} + E_{p\pi}(k)$ $E_{Bp\pi-}(k) = \alpha_{p\pi} - E_{p\pi}(k)$
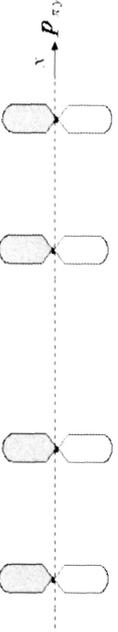
Discussion

An ideal polymer chain, conjugated has repeating unit which is formed periodicity. Monomer is assumed to become unit cell. Carbon orbital $1s^2$ $2s^2$ $2p^2$ has four neighbouring atom forms chemical binding. In conjugated polymer, carbon has sp^2 or sp hybrid state. The orientation of σ – bonding is perpendicular with π – bonding. The translation in monomeric unit can also be applied by using Bloch function. Brillouin Zone in the region – σ $/a \leq k \leq \pi /a$ where a is the lattice space. Translation on wavefunction is given in equation (8).

$$\psi (r) = u(r) \exp (ikr) \tag{8}$$

$u(r)$ in equation (8) is the lattice potential and k is the crystal momentum. Based on Hückel theory, the notation for lattice direction Γ, $E = \alpha \pm 3\beta$; M, $E = \alpha \pm \beta$ and K, $E = \alpha$ (Plsanty, 1991). In solid state physics, we classify the conductivity of metal, semiconductor and insulator based on the schematic of occupied electrons on the allowed band. Electrons in polymer also obey Fermi-Dirac statistic. The occupation probability $f(E)$ in distribution function at equilibrium is given by equation (9).

$$f(E) = \frac{1}{1 + \exp\left(\left(E - E_F\right)/kt\right)} \tag{9}$$

E_F is the Fermi energy which is related to the chemical potential. In Fermi-Dirac distribution, at $T = 0K$, electrons have the lowest energy state. The probability of electron to be occupied is zero at $E > E_F$. If we consider at $T > 0K$ and $E = E_F$, the probability of electrons to be occupied is ½. This means that some of the electrons have been excited to the highest energy levels.

If we apply to the single atom, electrons have discrete energy levels. Unperturbed energy level for 1s and 2s has a single degenerate energy level which can be filled by two electrons with different spins. While 2p orbital has three degenerate energy levels. When interactions occur, the energy levels are disturbed and split into the entire solid. If the number of unit cell is very large, sublevel of perturbation energy level is so close to each other to create energy band.

The s_σ band is located at the bottom. While the p_σ band is located below the p_π band. σ-bonding backbone of polymer bound the neighboring atom tightly at the parallel orientation. So, it is very hard to see electronic

conduction in σ – bonding. At the boundary k = 1.57, s_σ – bonding meets s_σ – antibonding. However for p_π – bonding, p_π – antibonding shifted (distort) upwards. Energy band distortion due to stabilizing deformation of molecule disturbs degenerate state in molecule. This effect is called Jahn-Teller theory (Stoneham, 1975). In solid state, band energy distortion near the Brillioun Zone at one-dimension was described by Peierls, in which the energy distortion occurs at the Fermi Energy levels (Kittel, 1987). Thus, it is expected that the Fermi Energy levels lay between -0.9 eV and -1.1eV. In thermodynamic definition, Fermi level is the energy of half filled which is the highest occupied level (HOMO) (Hoffmann, 1991).

For our calculation, energy gap between π and π^* (Eg(π)) is less than energy gap between σ and σ^* (Eg(σ)). In this case, π orbital delocalized while σ orbital localized in backbone of polymer. The maximum Eg(π) at direction 0 is about 1.8 eV implying that the conjugated polymer has semiconductor properties. According Salaneck et al. (1999) the difference between Eg(π) and Eg(σ) is due to the polymer chains rather easily oxidized or reduced and the polymer chemically doped. Meanwhile, chemical doping process increases the conductivity of polymer. However, the challenges to determine the electronic structure of polymer proposed by Dissado (1992) and Hoffmann (1991) are as follows:

1. The polymer chains are not rigid and have strong segment motion above the glass transition;
2. Periodicity limitation in space group. Most of polymers contain non-periodic sequences. Therefore, the ideal band structure will be interrupted;
3. Pendent group in polymer changes the backbone of polymer. Electron density for polymer also can be affected;
4. Disorder and dangling bond;
5. Plasmon and phonon phenomena;
6. Charge localization due to the transient polarization effect. In this situation, there are exist extended states in a solid polymer which create new energy levels so-called trap levels;
7. Bond order and polymer backbone kinks also affected the electronic structure.

Conclusion

In this paper, the energy of conjugated organic semiconductor was calculated using Hückel Method. In conjugated organic semiconductor, carbon has sp^2 or sp hybrid state. In this calculation the Coulomb and resonance integrals for s_σ, p_σ and p_π were different. The Fermi Energy level was predicted using Peierls Distortion which was laid between -0.9 eV and -1.1eV. Usually, monomer assumed as a unit cell. In our calculation, the monomer assumed that an ideal periodicity lattice structure. As for the HOMO and LUMO level, positive and negative changing in coefficient of LCAO showed the changing in wavefunction in every monomer unit. The changing in coefficient has produced the interaction between atomic orbital localized over the carbon-carbon double bond within the aromatic rings.

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