

A theoretical investigation of band gaps of conducting polymers - polythiophene, polypyrrole and polyfuran

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ABSTRACT

Theoretical calculations of band gaps for conducting polymers namely polythiophene, polypyrrole and polyfuran are presented and discussed. Theoretical band gaps of the conducting polymers are obtained by combining Density Functional Theory (DFT) and extended nearly free electron model with a new extrapolation technique. The calculated band gap values are compared with experimentally estimated values and it was found that with a single correction all theoretical values can be successfully brought to their corresponding experimental range.

1. INTRODUCTION

Conducting polymers have dynamic optical properties which enable wide range of applications such as in microelectronic devices, sensors, rechargeable batteries, electrochromic displays, solar devices, etc, [1-20]. Therefore over the past decades conducting polymers have been attracting large interest. In devising these conducting polymers, it is very important to know their electrical properties. The key factor that determines the intrinsic properties of the polymers are their band structures, particularly the positions of the conduction and valence bands and the gap between them. Therefore in the context of conducting polymers, the knowledge of the positions of highest occupied molecular orbital level (HOMO, π^*) and the lowest unoccupied molecular orbital level (LUMO, π) together with the energy gap between them is crucial. Therefore, the π electrons in conducting polymers play a major roll in determining their electrical conductivity and band structure.

The conducting polymers chosen for this study, polythiophene, polypyrrole and polyfuran have always been the most promising candidates among the commercially available conducting polymers, because they have high stability at both its doped and undoped states, being generally easy for structural modifications and controllable electrochemical behavior. In addition, it is easier to prepare the molecules that can be dissolved in a wide range of organic solvents [9,10,15,17,18]. But many difficulties are encountered in the synthesise of new materials.

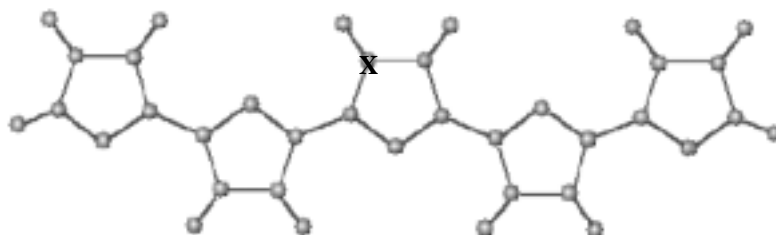


Figure 1: Description of aromatic five-ring geometries used in this calculation X= N,S,O

Theoretical studies are used to overcome these difficulties by investigating their band structural properties theoretically before they are tried out in applications. Many theoretical calculations have been carried out on short chain conjugated oligomers with increase in chain lengths using extrapolation methods. Only few theoretical calculations have been carried out on bulky polymers as normally the geometries of bulky polymers are not well characterized and even if they are well characterized, the calculations become very expensive. In this context it is well known that the Density Functional Theory (DFT) methods within the local density approximations (LDA) produce accurate equilibrium geometries for both conjugated oligomers and bulky polymers [12, 19-27]. DFT methods produce quite satisfactory results at relatively low computational cost when compared to other methods for solving the quantum mechanical many-body problems (Hartree Fock, Perturbation methods etc).

Therefore in order to establish an appropriate and simple theoretical method that can be used to predict the band positions and the band gap values of conducting polymers, we developed a technique by combining DFT methods with an extrapolation scheme. In order to check the accuracy of this new technique we studied well-known polymers such as polypyrrole, polythiophene and polyfuran as testing materials and compared their band gaps with the available values obtained from experimental studies

2. METHOD

This study on the band gaps of polymers consists of three major steps. During the first step, the oligomer structures were geometrically optimized using of Qchem 2.0 electronic structure package [28]. In the second step band gaps of optimized structures were calculated by taking in to account the energy difference of the HOMO and LUMO levels. In the third step, the band gap values of polymers were obtained using the nearly free electron model and the extrapolation techniques on the oligomers.

Step 1:

The electronic and optical properties of conducting polymers depend on their geometrical structure which is defined by bond lengths and bond angles of the oligomers. It is well known that the density functional theory (DFT) methods within the local density approximations (LDA) produce accurate equilibrium geometries for both conjugated organic oligomers and polymers [15,20,22]. Therefore, in order to obtain the equilibrium geometrical structure, the geometry optimization was performed on isolated oligomers of each polymer, using DFT methods within the LDA with various basis sets, exchange methods and correlation methods to figure out the optimal method. For the calculations on the conjugated organic oligomers, which are studied here, the best basis set was found to be is 6-31G**. It is large enough to give fairly good results while small enough to be used with a computer with 1GB RAM. The Becke Exchange and Lee-Yang-Parr Correlation methods were found to be most suitable for obtaining the equilibrium geometry.

Step 2:

The energies corresponding to the HOMO and the LUMO were extracted from these final equilibrium geometries of each oligomer. Thereafter, ΔE , which is the energy difference between the HOMO and the LUMO, was calculated for each oligomer.

Step 3:

Since we are interested in the electronic band gaps of polymers, we need to extrapolate results obtained for finite length oligomers to infinite length oligomer chains. However, the simple extrapolation, taking the limit $\lim_{n \rightarrow \infty} \Delta E(n)$, where n is the number of monomer units, does not correctly express the actual asymptotic behavior of the band gaps.

The oligomers studied in this study can be considered as conjugated one-dimensional π systems. The free electron model is often used to model such systems. But free electron model does not recover finite band gaps at infinite lengths. A more realistic method was introduced by Hans Kuhn [21] by replacing free electron model with a *sine* shaped potential along the chain. In this model the easily displaceable π electrons are assumed to be moving along the zigzag chain of single and double bond pairs and that they are in an one dimensional potential field which has a *sine* wave variation along the chain. Then the ΔE , the energy difference between the HOMO and the LUMO is given by,

$$\Delta E = \frac{h^2}{8mL^2} (N+1) + V_0 \left(1 - \frac{1}{N} \right) \quad \text{-----(1)}$$

where, h is the Plank's constant, m is the mass of the electron, N is the number of π electrons, L is the chain length (or the extension of the π conjugated system) and V_0 is the amplitude of the *sine* wave variation of π electrons. The chain length L is more precisely given by, $L = (N+l)d$ where d is the averaged C-C and C=C bond length and l is the effective length of the conjugated π system.

Here we can see that V_0 is equal to ΔE for very large N as the number of π electrons N , increases with the number of monomer units (i.e. the length of the chain L). Therefore, V_0 can be considered as the band gap of the corresponding infinitely long chain of the isolated oligomer. Now we rewrite the equation (1) in the following form.

$$V_0(n) = N(n) \left\{ \Delta E - \frac{h^2}{8mL^2} (N(n)+1) \right\} / (N(n)-1) \quad \text{-----(2)}$$

where n is the number of monomer units.

By applying the HOMO - LUMO band gap ΔE which was obtained in step 2, to the equation (2), V_{0s} is calculated for each oligomer. Then by plotting $V_0(n)$ vs. $1/n$ and extrapolating $V_0(n)$, the value for $V_0(\infty)$ is obtained. This $V_0(\infty)$ is now corresponding to the band gap of the polymer.

3. RESULTS AND DISCUSSION

Initially we carried out geometry optimization calculations on oligomers of Thiophene, Pyrrole, and Furan as described in step 1, For all the DFT calculations, Becke Exchange and Lee-Yang-Parr Correlation methods were used. The 6-31G** basis set was used in the calculations.

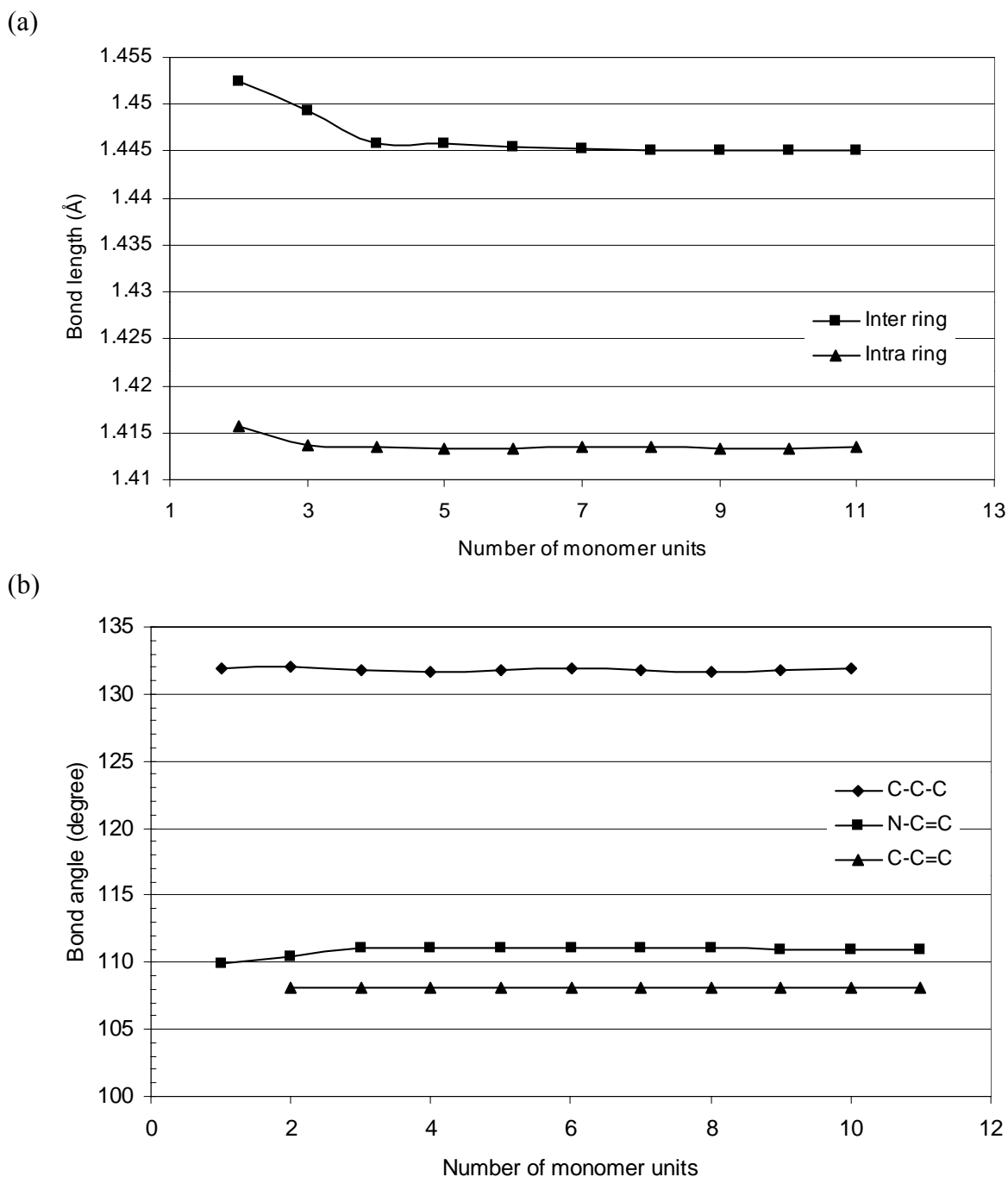


Figure 2 Convergence of (a) inter and intra ring C-C bond lengths and (b) C-C-C, N-C=C and C-C=C bond angles of pyrrole

In Figure 2 (a) which shows a comparison of C-C bond lengths in oligopyrrole, a fast convergence of bond length alteration for both intra-ring bonds and inter-ring bonds as a function of the number of monomer units can be observed. Bond lengths have been converged within 0.01Å. Convergence of bond angles as a function of the number of monomer units are shown in Figure 2 (b). The bond angles have been converged within 1°. Same types of convergences were observed in the bond lengths and angles of the other oligomers.

Then the band gaps of the corresponding polymers were calculated by extrapolation as described in steps 2 and 3. The estimated values of V_0 using the formula (2), corresponding to oligomers of each polymer were plotted against the reciprocal of the number of monomer units and shown in Figure 3.

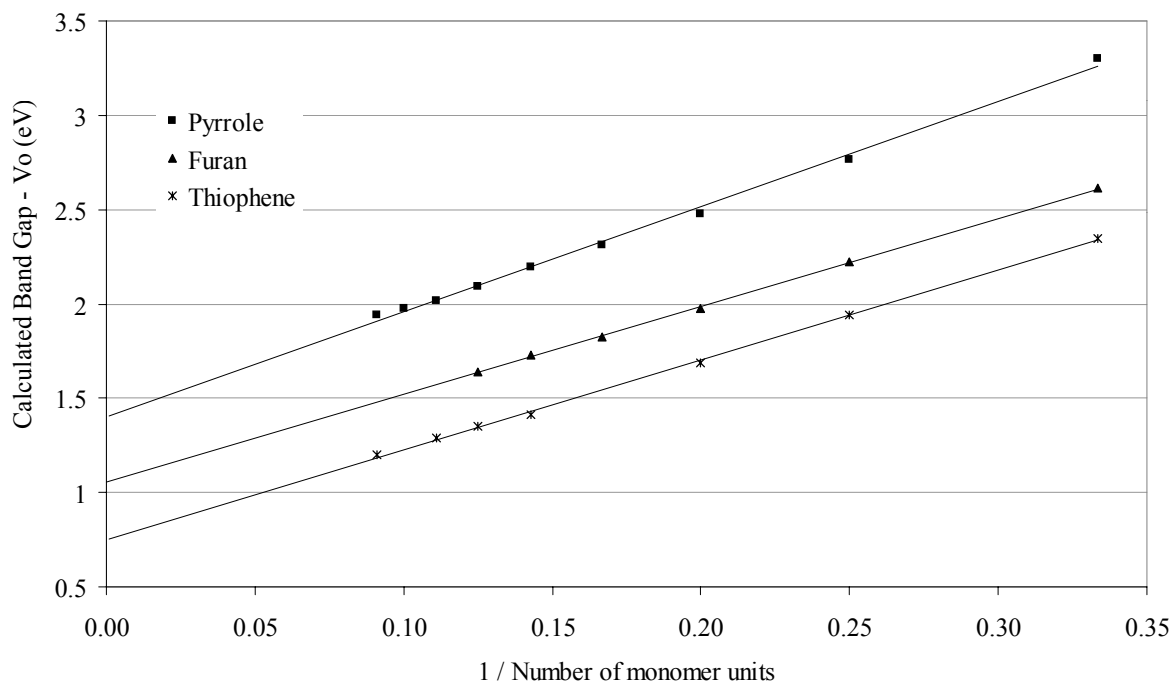


Figure 3: Plot of the calculated band gaps of oligomers against the reciprocal of corresponding oligomer lengths, i.e. the number of monomer units

By finding the value of V_0 where each line intersects the y-axis in Figure 3, $V_0(\infty)$ or the band gaps of the corresponding polymers were estimated.

Table 1 shows the calculated values from this method with the previously reported experimental values in the literature.

Table 1: Comparison of calculated band gaps with reported experimental values

Molecule	V_0 (eV)	V_0 (Corrected) (eV)	Exp (eV)	Reference
Polythiophene	0.75	1.8	1.8 - 2.21	[8,12,15,19]
Polypyrrole	1.4	3.3	2.9-3.2	[30,14, 12]
Polyfuran	1.05	2.5	1.94- 2.7	[12,14,31]

The discrepancy between experimental and theoretical values obtained from DFT/extrapolation method is obvious. However, experimental trend is correctly predicted by the theoretical calculations despite the fact that the complicated nature of the potential under which electrons move along the chain was simplified to a simple *sine* potential and the effects of disorder and three dimensional interactions of polymer chains were totally ignored. On the other hand, it is evident from the table1 that by ignoring above mentioned and other effects, theoretical values of the band gaps are nearly 42% smaller than the experimental values. However when the theoretical values are corrected, they are in fairly good agreement with experimental values. Using the above-described method and the corrections, we have predicted the band gap value for poly 3-methyl furan for which the experimental band gap values are not available in the literature.

4. CONCLUSION

We have demonstrated that DFT method along with extrapolation technique and the correction can be successfully applied to calculated energy band gaps of conducting polymers such as polythiophene, polypyrrole and polyfuran. Since structures of individual oligomers have been optimized using DFT methods with large basis sets, a good accuracy was achieved for the calculated bond lengths, bond angles and electronic band gaps. Consequently, our extrapolation method along with these accurately calculated band gap values produced reasonably accurate band gaps for each polymer. In general, extrapolation methods are not accurate enough to predict band crossings and localized bands correctly. However, by applying our extrapolation method on calculated electronic band gaps of oligomers and carrying out the correction described earlier, we were able to bring theoretically calculated values to the experimentally observed range of band gap of each polymer.

However, true success of this method can only be determined after testing the method described here with many other conducting polymers for which experimental data of band gaps is available.

Currently we are developing techniques to predict band positions by extending the method described here in this paper. Once we succeeded we would be able to use this method to design new polymers with different subgroups in their monomer units having appropriate band gaps and band positions for various applications.

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