

RESEARCH NOTE

A theoretical investigation of band gaps of conducting polymers with heterocycles

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This study reports a new method developed for calculating band gaps of conducting polymers. The method consists of three major steps. In the first step, the geometry optimization of the oligomer structures was carried out. The optimized oligomer structures were then used as input in the second step. In the second step band gaps of oligomers were calculated by taking into account the energy difference of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. In the third step, the nearly free electron model and the extrapolation techniques on the oligomers were used to obtain the band gap values of polymers.

Geometry optimization was performed on isolated oligomers of polypyrrole, polythiophene, polyfuran and some of their derivatives, using density functional theory (DFT) methods with Becke exchange (Becke, 1988) and Lee-Yang-Parr correlation (Lee *et al.*, 1988) methods within the local-density approximation (LDA). Several geometry optimization calculations were carried out with various basis sets such as STO-3G, 6-31G, 6-31G*, 6-31G** and 6-311G to figure out the optimal basis set. For calculations on the conjugated organic oligomers, which are studied here, the best basis set was found to be 6-31G** and was used in both geometry optimizations and band gap calculations. 6-31G** was large enough to give fairly good results while small enough to be used with a computer with 1 gigabyte random access memory (RAM). The energies corresponding to the HOMO and LUMO were extracted from the final equilibrium geometries of each oligomer. Thereafter, ΔE , which is the energy difference between the HOMO and LUMO, was calculated for each oligomer.

To obtain the electronic band gaps of polymers, it is necessary to extrapolate results obtained for finite length oligomers to infinite length oligomer chains. Conjugated one-dimensional π systems such as the oligomers used in this study are often modelled by a free electron model. But a free electron model does not recover finite band gaps at infinite lengths. Hans Kuhn (1949) introduced a more realistic method by replacing free electron model with a *sine* shaped potential along the chain. Assuming that the easily displaceable π electrons are moving along the zigzag chain of single and double bond pairs and that they are in a one dimensional potential field, which has a *sine* wave variation along the chain, Kuhn's result (Mintmire, 1988) can be obtained as,

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

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, $L = (N+1)d$, where d is the averaged C-C and C=C bond length and l is the effective length of the conjugated π system (*i.e.* l is the total number of double bond-single bond pairs along the chain).

The V_0 can be considered as the band gap of the corresponding infinitely long chain of the isolated oligomer. Now equation (1) can be written in the following form.

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

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where n is the number of monomer units. For each oligomer, by using equation (2), V_0 is calculated from the HOMO - LUMO band gap ΔE , which was obtained by DFT methods as described before. In other words, V_0 represents the band gap of the infinite chain, which produces correct ΔE of the finite 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.

First geometry optimization calculations were carried out on oligomers of thiophene, pyrrole, furan, 3-methyl thiophene, 3-methyl pyrrole, and 3-methyl furan and then the band gaps of the corresponding polymers were

calculated by extrapolation. Becke exchange and Lee-Yang-Parr correlation methods (Becke, 1988; Lee *et al.*, 1988) were used for all the DFT calculations.

The estimated values of V_0 using equation (2) corresponding to oligomers of each polymer were plotted against the reciprocal of the number of monomer units (Figure 1). By finding the value of V_0 where each line intersects the y-axis in Figure 1, $V_0(\infty)$ or the band gaps of the corresponding polymers were estimated. Table 1 shows the calculated values based on this method along with the previously reported experimental values in the literature.

Table 1: Theoretically calculated band gaps of conducting polymers with heterocycles

Molecule	V_0 (eV)	V_0 (Corrected) (eV)	Experimental (eV)	Reference
Polythiophene	0.75	1.8	1.8 - 2.21	Mintmire <i>et al.</i> , 1988 and Kaeriyama <i>et al.</i> , 1989
Polypyrrole	1.4	3.3	2.9 - 3.2	Mintmire <i>et al.</i> , 1988 and Zotti <i>et al.</i> , 1992
Polyfuran	1.05	2.5	1.94 - 2.7	Mintmire <i>et al.</i> , 1988 and Breeze <i>et al.</i> , 2001
Poly 3-methyl thiophene	0.71	1.7	1.7 - 2.4	Nguyen-Cong <i>et al.</i> , 1993
Poly 3-methyl pyrrole	1.23	2.9	2.93	Kaeriyama <i>et al.</i> , 1989
Poly 3-methyl furan	0.90	2.1		

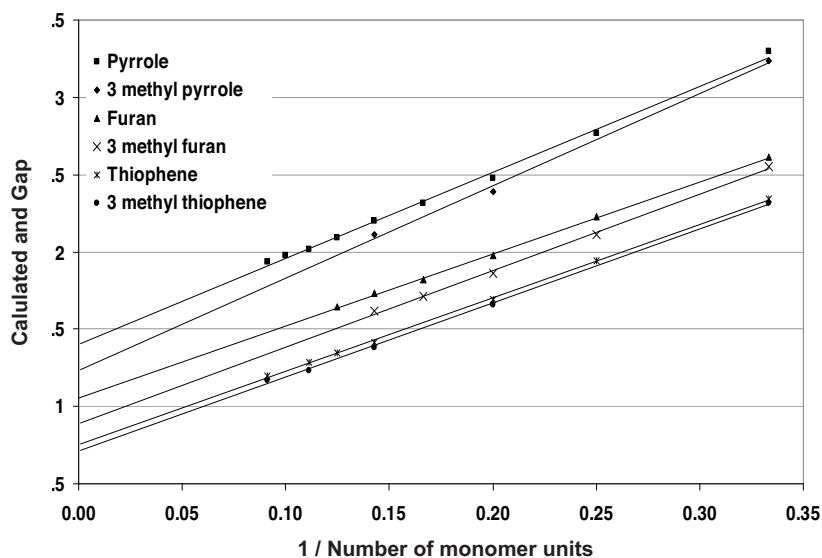


Figure 1: Plot of the calculated band gaps of oligomers against the reciprocal of corresponding oligomer lengths, i.e. the number of monomer units

Although there is a discrepancy between experimental and theoretical values, 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 Table 1 that by ignoring above mentioned and other effects, theoretical values of the band gaps are nearly 42% smaller than the experimental values.

It is known that although the density functional methods accurately determine equilibrium geometries of polymers, they underestimate HOMO-LUMO gaps. Therefore, the above discrepancy is expected. However, in this study it was found that the discrepancy can be corrected with a single parameter. This single parameter is calculated by fitting with theoretically calculated band gaps with experimental band gaps of polythiophene, polypyrrole and polyfuran. Then the band gaps of poly 3-methyl thiophene, poly 3-methyl pyrrole, and poly 3-methyl furan were estimated by the correction parameter. The first two are in fairly good agreement with experimental values. The predicted band gap value for poly 3-methyl furan cannot be tested as experimental band gap values for poly 3-methyl furan are not available in the literature.

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