AB INITIO AND DENSITY FUNCTIONAL STUDIES OF POLYTHIOPHENE ENERGY BAND GAP

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ABSTRACT – The energy band gap of intrinsic thiophene monomer and dimer were calculated using Hartree-Fock (HF) and density functional theory (DFT) methods employing various combinations of exchange and correlation functionals with electron core potential (ECP) split valence basis sets. HF overestimates band gap by up to 6.10 eV for thiophene monomers and dimers. DFT calculations with hybrid functionals (B3LYP and B3P86) give an excellent results (4.06 eV and 4.11 eV) which are in good agreement with the experimental energy band gap (4.05 eV).

KEYWORDS -- Energy band gap; density functional theory; *ab initio*; HOMO-LUMO; thiophene.

1. Introduction

Due to its chemical stability, high conductivity upon doping, and their non-linear optical properties, polythiophene is among the widely studied conjugated organic polymers, experimentally and theoretically [1]. During the recent years systematic efforts were aimed at investigating the molecular and electronic structure of thiophene oligomers and its derivatives [2, 3, 4, 5, 6, 7].

The energy gap between valence and conduction band of polymer is related to the lowest allowed energy of its monomer units and to the bandwidth resulting from the overlap between the monomer orbitals as shown in Figure 1 [2]. The energy band gaps obtained from band structure calculations for solids are analogous to Highest Occupied Molecular Orbital (HOMO) – Lowest Unoccupied Molecular Orbital (LUMO) energy differences in molecules.

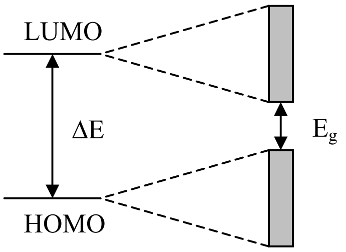

Figure 1. Relationship between HOMO-LUMO levels of finite and band gaps of the infinite system.

To design a low band gap polymer, it is desirable to start with monomer units with small excitation energies. A prior idea on the estimate is often useful. One way to obtain excitation energies is to calculate the energy of the ground and excited state explicitly and to take the energy difference. The commonly accepted structure of polythiophene is a linear chain of monomers α - α' (2, 5) bounded by carbon [3] as shown in Figure 2.

An initial estimate of the band gap can be carried out using density functional theory (DFT). DFT is very attractive in calculations involving finite system because even the lowest level of DFT – the Local Spin Density Approximation (LSDA) – includes some electron correlation. This is extremely important in the design of conducting organic polymers which have an extended π system. Although the LSDA eigenvalue differences underestimate the band gap compared to experiment, the shift is almost vertical and very systematic [2].

DFT method had successfully been used to study band gaps of conjugated organic polymers where the HOMO/LUMO difference provide good estimate of the excitation energy. While there is some controversy surrounding the interpretation of DFT orbitals energies, we find that HOMO/LUMO energy difference offers a very good estimate of band gaps. It should be noted that the HOMO/LUMO energy difference at *ab initio* level does not closely relate to excitation energies due to the absence of orbital relaxation effects [8].

2. Computational Details

Initial geometries were optimized at Hartree-Fock (HF) level of theory and further reoptimized using DFT methods to include correlation corrections. In this study, an exchange functional which was proposed by Becke [11a] in 1988 using a gradient-corrected correlation functional of Lee, Yang and Parr [11b, 11c] was employed. Hybrid functional are also used, the Becke's three-parameter functional (B3) [11d] which defines the exchange functional as the linear combination of Hartree-Fock, local and gradient-corrected exchange terms. The B3 hybrid functional was used in combination with the correlation functionals of Lee, Yang and Parr and non-local correlation expression provided by the Perdew 86 (P86) [11e].

The type of basis set is that of Stephens/Basch/Krauss ECP split valence (CEP-31G), augmented with polarization functions on heavy atoms (CEP-31G*), diffused function (CEP-31+G) and polarized functions (6-31G**). These basis sets were employed because some previous calculations [6] suggest that their results are in good agreement with the experimental values of the energy band gap of different polymeric system.

The vibrational frequency calculations were carried out to characterize the stationary points. Symmetry constraints were applied whenever possible.

All calculations were performed using the Gausian '94 [9] and GAMESS [10] suites of quantum chemistry programs running under Beowulf cluster, SunSparc station, and DEC alpha machines.

3. Results and Discussion

3.1 Geometries

The optimized results using hybrid DFT functional (B3LYP/CEP-31G*) are shown in Figure 2. This is the stable geometry of thiophene monomer and dimer. With the HF/6-31G* and B3LYP/CEP-31G*, the bond length are up to ±0.025Å and ±0.046Å, respectively when compared to experimental values. The bond angles agree very closely (to within ±0.33^{o}) with experiment. Pure and hybrid functionals geometries are almost identical. Compared to HF theory, DFT yields longer C=C double bonds. Thus, at HF, π-electrons is more localized. This is most likely due to the neglect of electron correlation. For geometry calculations, HF revealed more accurate estimates, indicating that it may not be necessary to perform DFT calculations to obtain good geometries in this case. Complete documentation of geometries is listed in Table 1.

3.2 Energy Band Gaps

Spectroscopic data for organic π-systems are usually determined either in solution or in the solid state (crystal or thin film). Since our calculations are for isolated molecules in the gas phase, we have attempted to compare our calculation to experimental results in solution.

Table 2 summarizes the energy band gap of intrinsic thiophene monomers and dimers at HF, BLYP, B3LYP and B3P86 with various combinations of basis sets. As expected, the RHF energy band gap of intrinsic thiophene oligomers overestimates the excitation energy because of the absence of correlation contribution [16]. Little improvement of the energy band gap is obtained in applying a higher level basis set; the absolute error is 5.51-6.10 eV. It is expected that the percent error decrease with increasing length of polymers at this level of theory [9]. The pure DFT functional (BLYP) underestimate the energy band gap by up to 1.77 eV compared to the experimental excitation energy. Hybrid DFT method (B3LYP and B3P86) yielded HOMO-LUMO energy difference which are in good agreement with the experiment. The DFT (B3LYP and B3P86) energy band gaps for thiophene dimer give an error of only up to 0.22 eV and 0.17 eV, respectively. The two hybrid functionals lead to almost identical results. Applying more comprehensive basis ddid not significantly improve the energy band gap of thiophene oligomer. This study shows that by using hybrid DFT functionals, a substantial improvement in the excitation energy can be obtained. The same observation was also reported previously by other workers [1, 2] using different polymeric system.

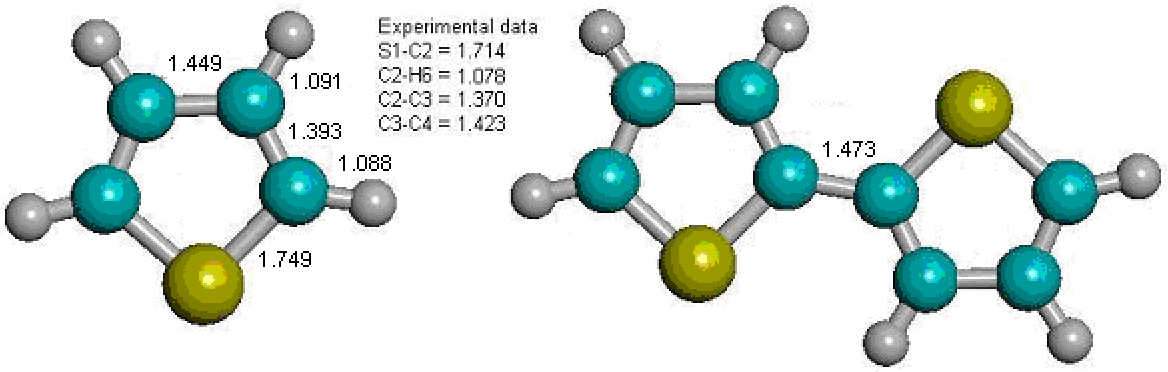

Figure 2. Structures of thiophene (a) monomer (b) dimer. Calculated bond distances are given in angstrom (Å) at B3LYP/CEP-31G.*

Table 1. Optimized structure of thiophene oligomers at 6-31G (HF) and CEP-31G* (DFT).*

Parameter	RHF	error	BLYP	error	B3LYP	error	B3P86	error	Expt.
Monomer									
Bond length									
$C_2 - H_6$	1.074	0.004	1.095	0.017	1.088	0.010	1.088	0.010	1.078
$S_1 - C_2$	1.726	0.012	1.764	0.050	1.749	0.035	1.737	0.023	1.714
$C_4 = C_5$	1.345	0.025	1.404	0.034	1.393	0.023	1.391	0.021	1.370
$C_3 - C_4$	1.437	0.014	1.455	0.032	1.449	0.026	1.443	0.020	1.423
Bond angle									
$S_1C_2C_3$	111.83	0.33	111.43	0.07	111.50	0.000	111.51	0.01	111.50
$C_2C_3C_4$	112.52	0.13	112.63	0.02	112.51	0.140	112.39	026	112.65
$C_4C_3H_7$	124.11	0.12	124.21	0.02	124.23	0.000	124.32	0.09	124.23
Dimer									
Bond length									
$S_1 - C_5$	1.736	0.012	1.766	0.042	1.750	0.026	1.739	0.015	1.724
$C_5 - C_2$	1.481	0.017	1.476	0.012	1.473	0.009	1.468	0.004	1.464
$C_4 = C_5$	1.367	0.014	1.403	0.050	1.391	0.038	1.390	0.037	1.353
$C_3 - C_4$	1.449	0.018	1.448	0.017	1.443	0.012	1.437	0.006	1.431
$C_4 - C_3$	1.375	0.019	1.414	0.058	1.402	0.046	1.339	0.043	1.356

Bond distances and bond angles are given in Å and degrees, respectively.

Table 2. HOMO-LUMO energy differences (energy band gap in eV) at various levels of theory.

	Monomer				**Dimer**			
	6-31G	*6-31+G*	*6-31G**	*6-31G***	*6-31G*	*6-31+G*	*6-31G**	*6-31G***
RHF	12.6066	11.4289	12.6888	12.6700	9.9676	9.5622	9.7031	10.1500
	CEP-31G	*CEP-31+G*	*CEP-31G**	*6-31G***	*CEP-31G*	*CEP-31+G*	*CEP-31G**	*6-31G***
BLYP	4.2298	4.2325	4.2415	4.4400	2.6741	2.2771	2.6790	2.8000
B3LYP	5.8426	5.8265	5.8570	6.1200	4.0491	4.0417	4.0572	4.2700
B3P86	5.9177	5.9153	5.9357	6.1800	4.1008	4.1049	4.1092	4.2200
Expt'l. value	5.2300[a]				4.0500[b]			

[a]ref. [18], [b]ref. [19]

4. Concluding Remarks

We have shown that a substantial improvement of DFT energy band gaps can be achieved with hybrid DFT functionals. Vertical excitation energies of thiophene oligomers were approximately reproduced with ±0.22 eV of the corresponding experimental results (solution phase).

Polythiophene presents special problems in computational modeling because of its extended molecular system. As a consequence, their properties may arise from secondary and tertiary structure effects, as well as from the primary microstructure. Their size and structure complexity causes the difficulty, even without worrying about inter chain-packing effect.

Energy band gap calculated using hybrid DFT functionals yielded estimates of excitations energies which are in good agreement with experimental value. The use of DFT hybrid functionals therefore will lead to a significant improvement of the energy band gap relative to those computed by HF methods. This study also indicated that the presences of polarized functions on heavy atoms as well as the corresponding diffused functions are crucial in the computations of the energy band gap of thiophene oligomers.

We hope that this contribution will stimulate the computational modeling community for the discussion of intrinsic polythiophenes as well as other conducting polymers. It is further suggested that longer thiophene oligomer chains up to 11 units or even longer with higher basis sets will be used so that a more accurate energy band gap could be predicted though this requires a very high computational cost.

Acknowledgments

We thank Prof. Ronald and Mr. Marvin Fernandez for many fruitful discussions. Likewise, thank is due to Mr. Allen S. Dahili for many helpful assistance. This study was conducted through the scholarship grant supported by the Commission on Higher Education – Mindanao Advanced Education Project (CHED-MAEP).

Reference

[1] Salzner, U., Lagowski, J. B., Pickup, P. G. and Poirier, A., *Synth. Met.* 96 (1998) 177-189.

[2] Salzner, U., Lagowski, J. B., Pickup, P. G. and Poirier, A., *J. Comp. Chem.* 18, 15, 1943-1953, 1997.

[3] Salzner, U., Lagowski, J. B., Pickup, P. G. and Poirier, A., *Synth. Met.* 98 (1999) 221-227.

[4] Nakanishi, H, *et al. J. Org. Chem.* 1998, 63, 8632-8633.

[5] Lathti, P. M., Obrzut, J., Karasz, F. E., *Macromolecules*, 1987, 20, 2023.

[6] Smith, James Richard, *Electrosynthesis of Novel Polyheterocycles*, Ph.D. Dissertation, Unpublished, School of Pharmacy & Biomedical Sciences, University of Portsmouth, Portsmouth, UK, 1995.

[7] Irle, Stephan and Lischka, Hans. *J. Chem. Phys.* 103 (4) 1995.

[8] Foresman, J. B. and Frisch, Æ., *Exploring Chemistry with Electronic Structure Methods, 2nd ed.* Gaussian, Inc., Pittsburgh, PA. 1995.

[9] *Gaussian 94, Revision B.2.* M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.

[10] GAMESS Version = 22 Nov 1995 from Iowa State University, M.W.Schmidt, K.K.Baldridge, J.A.Boatz, S.T.Elbert, M.S.Gordon, J.H.Jensen, S.Koseki, N.Matsunaga, K.A.Nguyen, S.J.Su, T.L.Windus, Together With M.Dupuis, J.A.Montgomer. *J. Comp. Chem.* 14, 1347-1363 (1993).

[11] (a) A. D. Becke, *Phys. Rev.*, A38, 3098 (1988). (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev.*, B37, 785-789 (1988). (c) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Rev. Lett*, 157, 200 (1989). (d) A. D. Becke, *J. Chem. Phys*. 98, 5648-5652 (1993). (e) J. P. Perdew, *Phys. Rev.* B33, 8822-8824 (1986).

[12] Slater, J.C., Quantum Theory of Molecules and solids, McGraw-Hill: New York, 1974, Vol. 4.

[13] Vosko, S.H., Wilk, L., Nusair, M., Can, *J. Phys.* 1980, 58, 1200.

[14] Becke, A.D., *J. Chem. Phys.* 1993, 98, 1372.

[15] P. Walters, M. Stahl, *BABEL Program (version 1.1)* Copyright ©1992, 93, 94, Dolota Research Group, Department of Chemistry, University of Arizona.

[16] Hyperchem ™ Release ^{3}. *Windows Molecular Modelling System*, Copyright ©1993, Hypercube, Inc. and Autodesk, Inc. Developed by Hypertube, Inc.

[17] R.M. Dreiler and E.K.U. Gross, *Density Functional Theory*, Springer, Berlin, 1990.

[18] Simmons, W.W., *Handbook of Ultraviolet Spectra*; Sdler Res. Lab.: Philadelphia.

[19] Colditz, R., Grebner, D., Helbig, M., Rentsch, S., *Chem. Phys.*1995, 201, 309.

[20] O. Kwong and M.L. McKee, *J. Phys. Chem.* B2000, 104, 1686-1694.

[21] Theoretical Studies of electronic Spectra of Organic Molecules, Roos, B.O., Fülscher, M., Malmqvist, P.-Å., Merchàn, M., Serrano-Andrès, L., in *Quantum Mechanical Structure Calculations with Chemical Accuracy*, Langhoff, S.R., Ed., Kluwer Academic Publishers: Boston, 1995; pp 357-438.