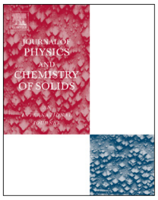
Journal of Physics and Chemistry of Solids 75 (2014) 212–223

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



# On site coulomb repulsion dominates over the non-local Hartree-Fock exchange in determining the band gap of polymers

Mausumi Chattopadhyaya [a], Sabyasachi Sen [b], Md.Mehboob Alam [a], Swapan Chakrabarti [a,*]

[a] Department of Chemistry, University of Calcutta, 92, A.P.C Road, Kolkata 700009, India
[b] Department of Physics, JIS College of Engineering, Block-A, Phase-III, Kalyani, Nadia 741235, India

ARTICLE INFO

*Article history:*
Received 6 April 2013
Received in revised form
11 September 2013
Accepted 19 September 2013
Available online 25 September 2013

*Keywords:*
A. Polymers
C. Ab initio calculations
D. Electronic structure

ABSTRACT

The present study deals with the relative performance of the various density functional approaches in evaluating the band gap of polymer materials. Several density functional approximations that includes pure generalized gradient approximated (GGA) functional, meta-GGA, hybrid and range separated hybrid functionals have been used to evaluate the electrical band gap or transport gap of the studied polymers and compared with that obtained using Hubbard U corrected GGA functional (GGA+U). It has been observed that the experimental band gap of the polymers studied is satisfactorily reproducible when GGA+U approach is adopted. The band gap analyses further suggest that range separated hybrid functional, CAM-B3LYP, largely overestimates the band gap of all the polymers studied while the performance of hybrid B3LYP functional and other range separated hybrid functional like HSE is moderate. Better performance of the GGA+U method clearly indicates that short range coulomb correlation plays more significant role over the non-local Hartree-Fock (HF) exchange in determining the electrical band gap of polymer materials. It is also noticeable that the Hubbard U parameter used for the various polymers under consideration is relatively large, indicating the semi-empirical nature of the GGA+U level of calculations. The present finding will help us design new low band gap polymer through estimating band gap by the GGA+U method and this could be very useful for solar cell research.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Low band gap, electrically conducting polymers have attracted substantial research interest over the past few decades because of their fascinating electronic and optical properties [1]. These materials find remarkable applications in almost every sphere of modern optoelectronic devices. Some of its major applications include design of light-emitting diodes [2], field effect transistors [3], nonlinear optical materials [4], photovoltaic solar cells [5], chemical sensors [6] and so forth. Amongst the wide variety of polymers available, polyacetylenes, polythiophenes, polyselenophenes, polytellurophenes, poly(*p*-phenylene vinylene) (PPV), poly-p-phenylene (PPP) and poly-pyrrole have drawn special attention of both the theoreticians and the experimentalists. The band gap engineering of these polymers through substitutions and heteroatom addition and vis-à-vis the prediction of new low band gap polymer is a very important domain of solar cell research since low band gap polymer ensures strong excitonic coupling and the concomitant higher life time of the excitons. Advancement of modern quantum chemical techniques has made it possible to predict the band gap of such materials with reasonably high accuracy. Of the many well known quantum chemical approaches, the most widely recognized technique used for large and periodic systems is the density functional theory (DFT).

Electronic structure calculation, band gap estimation, density of states analysis of periodic systems using density functional theory (DFT) has been highlighted in a number of literatures. Within DFT, the electrical band gap or transport gap for a system consisting of $N$ number ($N$ is integer) of electrons is obtained from the difference of ionization potential (I) and electron affinity (A). The electron affinity (A) and ionization potential (I) are achieved from the ground-state energy differences of the $N+1$ and $N-1$ electron systems versus the $N$ electron system. In presence of $n$ additional fractional electrons by the application of Perdew–Parr–Levy–Balduz condition in a Kohn Sham system, the electrical band gap is defined as the difference in orbital energies of LUMO ($\varepsilon_{\text{LUMO}}$; equivalent to conduction band minimum) and HOMO ($\varepsilon_{\text{HOMO}}$; equivalent to valence band maximum). As per hitherto known theoretical analysis, $\varepsilon_{\text{HOMO}}$ estimated with usual LDA and GGA functionals are much higher and $\varepsilon_{\text{LUMO}}$ estimated with same functionals are much lower and as a consequence the electrical band gap is largely underestimated. This feature arises due to the delocalization error connected to the convex energy curve. One simple example of this type of underestimation is, the undoped

---

* Corresponding author. Tel.: +91 33 23508386; fax: +91 33 23519755.
*E-mail address:* swapanchem@yahoo.co.in (S. Chakrabarti).

0022-3697/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jpcs.2013.09.018

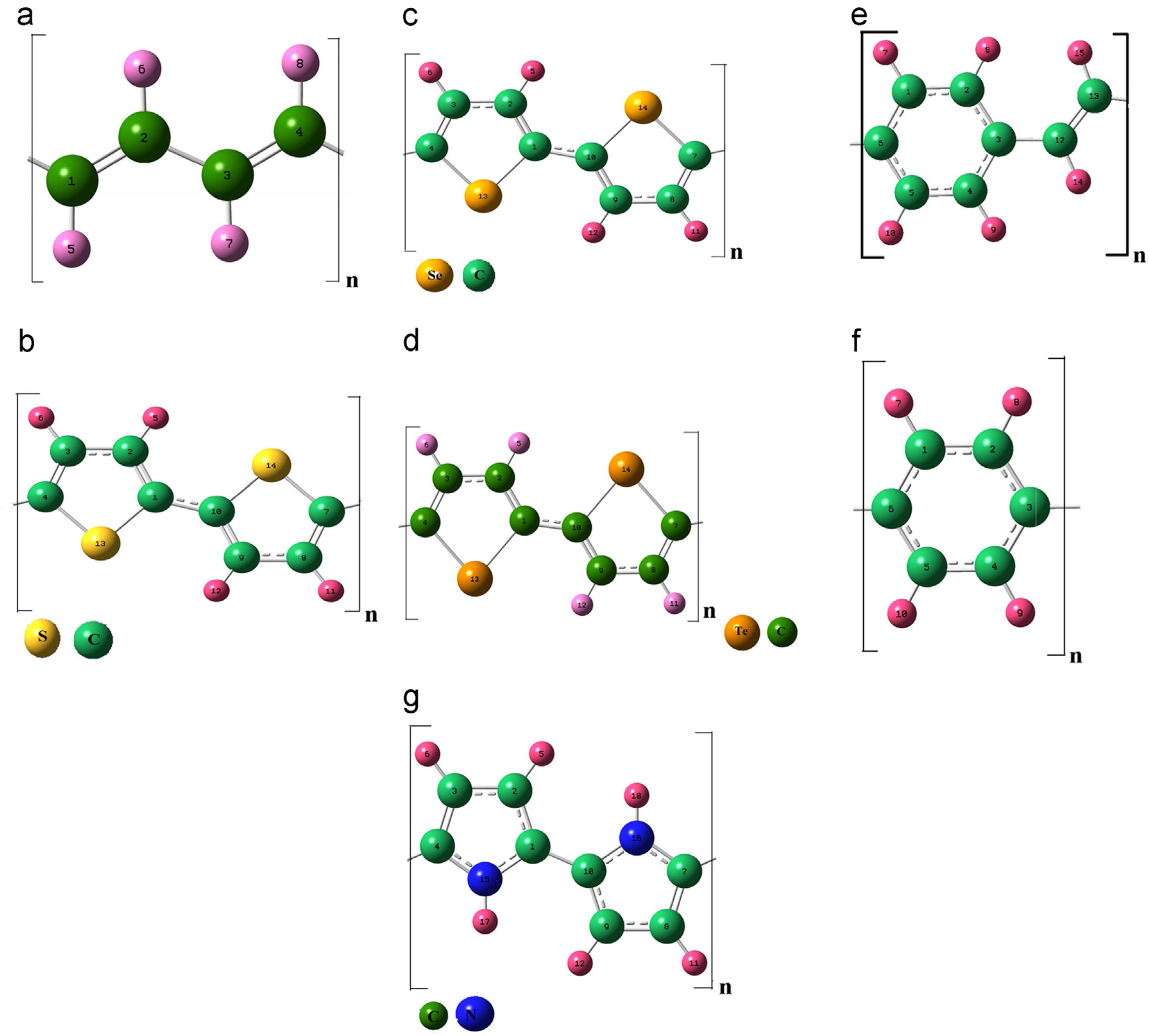


**Fig. 1.** Optimized unit cell geometries of (a) *trans*-polyacetylene, (b) polythiophene, (c) polyselenophene, (d) polytellurophene, (e) *p*-phenylene vinylene polymers (PPV), (f) poly-p-phenylene (PPP) and (g) poly-pyrrole.

cuprate high-temperature superconductors, $La_2CuO_4$, which has a band gap of 2 eV, but LDA, PBE, and PW91 predict that this material has metallic character (no band gap) [7]. According to previous theoretical analysis this limitation arises due to the derivative discontinuity of DFT exchange correlation functional with respect to the charge density [8]. On the contrary, the HF approximation gives less accurate energies due to the lack of electron correlation. The localization error involved in the HF method produces overestimation of the band gap. The addition of non-local HF exchange to GGA sometimes improves the band gap value to a satisfactory extent. Xiao et al. [9] found that hybrid functional, B3PW91, can produce reasonably good results in case of binary and ternary semiconductor. Screened hybrid functional like Heyd–Scuseria–Ernzerhof (HSE) [10] has been succeded in predicting the band gap of periodic systems. Recently, Song et al. [11] developed a hybrid exchange correlation functional using a short-range Gaussian attenuation (Gau-PBE) and checked its suitability for calculating the band gap in the solid state using periodic boundary conditions (PBC). Long range corrected functionals such as the Coulomb-attenuated method B3LYP (CAM-B3LYP) [12] is suitable for small molecular systems only. Apart from these existing well known approaches, some other methods such as modified LDA approach was developed by Zheng et al. [13] which is slightly better than LDA but has limitations in case of large gap ionic and noble gas crystals. In another approach, the potential difference is applied as a perturbation to the conduction-band states from a Kohn–Sham calculation with the local-density approximation, and a scissors-type band-gap correction is then obtained in a simple and efficient manner [14]. However, this technique is limited to insulating systems only. Improved methods such as all-electron full-potential exact exchange (EXX) functional performs successfully for noble gas solids but fails to predict correct the band gap of Si, Ge and GaAs crystals [15].

Apart from conventional DFT approaches, an alternative and efficient technique is the DFT+U method which has already proved its worth in predicting the correct band gap of strongly correlated 3d transition metals monoxides and sulfides. Here ‘U’ has the ability to capture the proper on site Coulomb repulsion and works in a similar way as it was originally proposed in Hubbard Hamiltonian. Hu et al. [16] applied the DFT+U method in exploring the electronic structure properties of ZnO magnetic semiconductor. Loschen et al. [17] successfully applied both the LDA+U and GGA (PW91)+U method for electronic structure calculation of cerium oxides ($CeO_2$ and $Ce_2O_3$). Although the DFT+U method has been applied on several metal oxide/sulfides successfully, its effectiveness in band gap prediction of low band gap polymer is still unknown.

In the present work, we employ the GGA+U technique for electronic band structure evaluation and density of states analysis of some well known polymers like, *trans*-polyacytelene,

Download English Version:

https://daneshyari.com/en/article/1516173

Download Persian Version:

https://daneshyari.com/article/1516173

Daneshyari.com