Computational Study of Nanomaterials Invoking DFT based Descriptors

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ABSTRACT

In modern day, nanotechnology and its application to the real field is an active field of research. In past few decades the advancement of the nanotechnology has opened so many research dimensions in the field of science and technology. The applications of nanomaterial in different forms are indispensable for advancement of the human civilization. The uses of nano-composite materials cover the major field of catalysis, semiconductor, microelectronics, biomedicine, aerospace application, defense, petrochemical, pharmaceutical, clean-energy sectors, photonics, and traditional glass and ceramic industries etc. Due to this diverse nature of applicability of nanomaterials, a number of researchers are actively involved in this domain. Now a days, theoretical and computational study of nano-materials has gained immense importance. Computational study of nano-materials invoking Density Functional based descriptors is very much popular in the concerned research domain. In this venture, we have studied a number of compound semiconductors using Density Functional Theory (DFT) methodology. As the band gap separation is an important index for correlating of any physico-chemical properties, we have computed the band gap of several semiconductors in terms of conceptual DFT based descriptors and tried to correlate with other available data. The nice correlation of our computed parameters with existing reported data supports the validity of our model.

Keywords: Bandgap, DFT, Physico-chemical properties, Semiconductor

1. INTRODUCTION

In recent day Nanomaterials have got a more focus due to its immense applications in the field of engineering and allied sciences. A number of scientists are actively involved in the research domain of computational nanomaterials. Nowadays, material doped semiconductors are extensively used as nano-clusters for their manifold applications. The band gap of material doped semiconductor is an important parameter for predicting its physic-chemical properties. Remediakis et al. (1999) reported basic structural calculation of some group of semiconductor invoking DFT theory. Recently Xiao et al. (2011) has reported an accurate band gap calculation of some set of

binary and ternary semiconductor in terms of DFT parameters. These particular set of semiconductors are popular for their wide application as photovoltaics and thermoelectrics.

In modern days Density Functional Theory (DFT) is immersed as a popular methodology to calculate the electronics structure of the molecules. Due to its computational friendly behavior researchers are interested to study the properties of any molecular system invoking DFT parameters. Conceptual DFT is an effort to correlate the experimental property of materials in terms of very simple DFT based descriptors. Nowadays, conceptual DFT is being extensively used in the research domain of calculation of band gap and other relevant properties of engineering nanomaterials.

In this venture we have calculated some set of nano-engineering materials taken from reference Xiao et al. (2011) In this study we have optimized the structure of instant nanomaterials using DFT methodology in terms of Local Density Approximation (LDA). From the optimized geometries some important DFT based descriptors viz. Global Hardness (η), Global Softness (S), Global Electrophilicity Index (ω) and Global Electronegativity (χ) have been calculated for the series of nanomaterials. Some correlation and effort has been made to correlate the experimental band gap with their computed counterparts.

2. METHOD OF COMPUTATION

In this report, we have collected 11 material doped semiconductors and reported them along with their experimental band gap in the table 1. The semiconductors are optimized in terms of LDA approximation invoking DFT with the help of ADF. From the optimized structure eigen value of the HOMO and LUMO have been calculated.

Invoking Koopmans' theorem, I and E have been calculated using the following ansatz-

$$I = - \varepsilon_{HOMO} \tag{1}$$

$$A = - \varepsilon_{LUMO} \tag{2}$$

Thereafter, using I and A, we have computed the electronegativity (χ), global hardness (η), molecular softness (S) and electrophilicity index (ω). For the computation of global reactivity descriptors, we have used the following equations-

$$\chi = - \mu = (I+A)/2 \tag{3}$$

where, μ represents the chemical potential of the system.

$\eta = \frac{1}{2} (I - A)$ (4)

$S = (1/(2*\eta))$ (5)

$\omega = (\mu)^2 / (2\eta)$ (6)

The above mentioned computed descriptors have been presented in the table 1.

3. RESULTS AND DISCUSSIONS

As compound semiconductors plays a vital role for its many fold applications, the experimental and theoretical research work on compound semiconductors have got immense importance. In this present venture we have studied a series of compound semiconductors in terms of computational methodology. The result is appended in the table 1.

Table 1: A Collection of computed global descriptors along with Experimental Band Gap of a series of Semiconductors

Species	Expt. (eV)	Electronegativity (eV)	Hardness (eV)	Softness (eV)	Electrophilicity Index (eV)
InP	1.42	3.744096	1.140099	0.43855841	1.872048
InAs	0.41	3.869262	1.121052	0.44600964	1.934631
ZnSe	2.83	2.187684	3.227106	0.15493758	1.093842
ZnS	3.84	5.4297555	0.224483	2.22734512	2.71487775
ZnTe	2.39	3.1849305	2.069321	0.24162521	1.59246525
CdS	2.58	3.1822095	2.042111	0.24484473	1.59110475
CdSe	1.85	3.120987	1.997214	0.25034874	1.5604935
$CuAlS_2$	3.46	4.021638	0.770043	0.64931439	2.010819
$CuGaS_2$	2.50	3.6937575	0.322439	1.55068331	1.84687875
$CuInS_2$	1.55	4.954941	1.039422	0.48103658	2.4774705
$CuAlSe_2$	2.65	5.06106	0.982281	0.50901931	2.53053
$CuGaSe_2$	1.67	4.59849	0.440802	1.1349612	2.299245

It has been well established a correlation between band gap and orbital energies of HOMO and LUMO for infinite solids (Perdew et al.(1983), sham et al. (1983)). The same correlation is being reflected in our computed data. There is slight exception only for case of ZnS, $CuInS_2$ and $CuAlSe_2$. As the band gap increases for infinite solids the hardness also increase hand in hand. The computed softness values exhibit an inverse relationship with the experimental band gap. There is

no direct correlation between experimental band gap and electronegativity and electrophilicity index.

Another striking fact is observe in the case of ZnS. The band gap of ZnS is the highest among the instant semiconductor and that existing band gap can be nicely correlated in terms of the highest electronegativity of the compound semiconductor.

4. CONCLUSION

Computational study of Nanomaterials is an active field of research. The engineering and other applications of nano-composite can be easily explained in terms of conceptual and theoretical parameters. DFT, a new paradigm of computational chemistry, is very much popular among the researchers due to its computational friendly manner. In this venture we have successfully studied a set of compound semiconductor invoking conceptual DFT based descriptors. From our calculation it is reveled for the most of the compound semiconductors there is a hand to hand relationship between experimental band gap and there computed global hardness. For ZnS the highest band gap among the instant compound, is nicely correlated in terms of the highest computed electronegativity.

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