

Calculation of the Band Structure for GaAs and ZnTe Nanoparticles from the Density Functional Theory Based on LDA, GGA and HSE06

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Abstract: The energy band structure and density of state (DOS) are calculated using density functional theory (DFT) for GaAs and ZnTe semiconductors for both the bulk and nanoparticles (NPs) and implemented in the CASTEP code. The calculations are employed within the local density approximation (LDA), generalized gradient approximation (GGA), and hybrid functionals of Heyd-Scuseria-Ernzerh of (HSE06). The DFT results within both LDA and GGA give lower values of band gap energies, while the HSE06 yields good results relative to the experimental data. Thus, HSE06 is employed to study the effect of size on band structures of semiconductor NPs. The results presented here illustrated that band gap increases with the reduction of NPs size due to the increase in lattice parameters.

Keywords: Nanoparticles, Energy Band Gap, Density of States, Density Functional Theory, HSE06

1. Introduction

Nanoscience and nanotechnology are known as priority fields of research since the last century, which are the studies and applications of very small things and produced materials of different kinds in nanoscale range (Feynman, 1992; Khan, Saeed, & Khan, 2017). Nanoparticles (NPs) are wide class of materials that include specific substances and they can be used in all fields of research, which have a size that is less than 100 nm (Laurent *et al.*, 2008; Mishra *et al.*, 2014) and classified as zero-dimensional, one dimensional, two-dimensional and three-dimensional nanostructures (Tiwari, Tiwari, & Kim, 2012; Zhu, Mu, van Aken, Maier, & Yu, 2015). NPs have also attracted attention in the materials community because their physics or catalytic properties are notably different from bulk materials (Gleiter, 2000; Jiang & Yang, 2008).

In general, semiconductors have appeared as the most promising group of materials which are subject of great interest for both theoretical and experimental points of view in designing semiconductor devices (Abdullah, Omar, & Jiang, 2017; Gunshor, 1997; Möller, 1991). Besides the typical group of IV elemental semiconductors, III–V and II–VI compounds are also widely used in a variety of electronic devices (Hur & Jeon, 2016; Ponce & Bour, 1997; Sze, 2008; Vurgaftman, Meyer, & Ram-Mohan, 2001) such as photovoltaic cells (Green & Bremner, 2017; Green *et al.*, 2017; Polman, Knight, Garnett, Ehrler, & Sinke, 2016). Semiconducting compounds such as GaAs and ZnTe have potential applications for making optoelectronic devices such as light emitting diodes, photovoltaic devices, laser diodes, infrared detectors (Boutaiba, Zaoui, & Ferhat, 2009; Gürel

& Ünlü, 2013; Sakly, Safta, Mejri, & Lamine, 2011). Thus, accurate study of their physical properties such as E_g is important in both experimental and theoretical studies particularly in designing semiconductor devices (Brothers, Izmaylov, Normand, Barone, & Scuseria, 2008; Zhao & Truhlar, 2009). The band gap affects the properties of solid materials. However, most material properties, such as intrinsic conductivity, optical transitions or electronic transitions are depending on energy gap (Meyers & Myers, 1997; Wooten, 2013).

Theoretical study of structure and electronic properties of semiconductors are often investigated by Ab-initio approaches such as the DFT (Hohenberg & Kohn, 1964; Kohn & Sham, 1965), which calculates the electronic structure from first-principles and empirical methods, such as the tight-binding method (Chadi & Cohen, 1975; Harrison, 1994; Vogl, Hjalmarson, & Dow, 1983), which requires empirical parameters to fit experimental data. Thus, DFT is currently the most efficient and popular first-principle method. In this work, the calculations have implemented in DFT within LDA (Kohn & Sham, 1965) and GGA (Langreth & Perdew, 1980) and more accurate hybrid exchange-correlation (XC) functions such as HSE06 (Heyd, Peralta, Scuseria, & Martin, 2005; Heyd & Scuseria, 2004; Heyd, Scuseria, & Ernzerhof, 2003), which improves band gaps over the standards like LDA and GGA (Henderson, Paier, & Scuseria, 2011; Marsman, Paier, Stroppa, & Kresse, 2008).

2. Theoretical Method and Computational Details

The Kohn-Sham-DFT approach describes the electronic states of atoms, molecules in terms of the three-dimensional electronic density of the system. The method is a great simplification over a wave function theory to perform electronic structure calculations in order to deal with solutions for many-electron systems (Kohn, Becke, & Parr, 1996; Kohn & Sham, 1965). In fact, the E_g calculated within the LDA or the GGA methods significantly have lower values relative to experimental data. To solve and get the better of this, HSE (Heyd, Scuseria, and Ernzerh) hybrid density functional method has been proposed and widely used for the calculation of semiconductor band gaps. In the hybrid functional calculations, the HSE06 function is performed that it has an effect on the predicted electronic properties. The use of the HSE06 yields improved electronic properties compared to both the LDA and GGA (Heyd *et al.*, 2003).

The first-principles methods are employed using DFT with the plane-wave pseudopotential method, which finds the solution to the Schrodinger equation. DFT has become an essential and a dominant first-principles approach that can be applied for a large variety of structures. The CASTEP code is implemented in the Material Studio to examine the E_g and DOS for GaAs and ZnTe compound using different forms of exchange-correlations function, including LDA, GGA, and HSE06. Using a dense Monkhorst-Pack k-grid (Monkhorst & Pack, 1976) in the Brillouin zone, the convergence of the calculations have verified and $6 \times 6 \times 6$ mesh values are used by a finite cut off energy of 850 eV.

The lattice constant in the bulk solid was reported by Omar (2007) as,

$$a(\infty) = \frac{4}{\sqrt{3}} d_{\text{mean}}(\infty) \quad (1)$$

and he has modified it for nanoscale (Omar, 2012) as,

$$a(r) = \frac{4}{\sqrt{3}} d_{\text{mean}}(r) \quad (2)$$

where $a(\infty)$ and $a(r)$ are the bulk and nanoparticles lattice constants, respectively; and d_{mean} refers to the mean bond length. The mean bond length $d_{\text{mean}}(r)$ at nanoscale is obtained by the following relation (Omar, 2012),

$$d_{\text{mean}}(r) = h - \Delta d_{\text{mean}}(r), \quad (3)$$

where h is the atomic diameter and its value can be calculated from $h = 1.429 d_{\text{mean}}(\infty)$ (Omar, 2016), and $\Delta d_{\text{mean}}(r)$ is the increase in mean bond length and is calculated as,

$$\Delta d_{\text{mean}}(r) = \Delta d_{\text{mean}}(r_c) \left[e^{\frac{-(S_m - R)}{(r_0 - r)^2}} \right]^{\frac{1}{2}} \quad (4)$$

where R is equal to $8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $\Delta d_{\text{mean}}(r_c)$ is the higher value in the mean bond length, using $d_{\text{mean}}(r_c) = h - \Delta d_{\text{mean}}(r_c)$, S_m bulk melting entropy (Zhang, Li, & Jiang, 2000), r the radius of the NPs, and r_0 denotes a critical radius which is calculated from $r_0 = (3 - d)h$, where $d = 0$ for NPs and r is the NPs radius (Zhao & Jiang, 2004).

3. Results and Discussion

DFT has been used to determine the band gap and DOS within LDA, GGA and HSE06. The method used to calculate the band structure properties is the plane wave pseudopotential method as employed in the CASTEP code. The crystal structure optimized in order to get both band gap and DOS, and the Brillouin zones are sampled by $6 \times 6 \times 6$ according to Monkhorst-Pack approach.

The experimental bulk values of E_g , the equilibrium lattice parameters and the results of the E_g within LDA, GGA, and HSE06 are presented in Table 1 for both bulk GaAs and ZnTe compound semiconductors. The calculated upper valence and lower conduction band structure are shown at the experimental equilibrium lattice constant. The results calculated at equilibrium lattice constant for band gaps are lower in values for LDA, GGA as shown in the Figures 1, 2, 4 and 5. Whereas HSE06 approach gives very accurate result in comparison to the experimental data for both GaAs and ZnTe as shown in the Figures 3 and 6. Thus, it is found that both band gap and DOS within HSE06 are in good agreement by less than (0.2 %) relative to the experimental values comparing to the calculated results from LDA and GGA, which are significantly underestimating by often more than (50 %) or more. Accordingly, HSE06 is applied to both GaAs and ZnTe compound semiconductor NPs due to the available experimental data of their quantum dots (QDs) (Jun *et al.*, 2001; Kher & Wells, 1996) by changing the lattice constant using Equations 2, 3 and 4. The results show that $E_g(D)$ gradually increases as the diameter of NPs decreases as illustrated in the Figures 7 and 8. The results obtained are compared with the experimental data and they have the same trend variation. The primary reason of this dependence on its size is that the band gap is a function of d_{mean} . The $d_{\text{mean}}(r)$ (where D is the NPs diameter and equals to $2r$) is constant for a bulk state, whereas it increases as the diameter of NPs drops which leads to increase in E_g .

Table 1: Calculated and experimental data (Kitai, 2011; Wei & Zunger, 1999) of energy band gaps for both GaAs and ZnTe within LDA, GGA and HSE06

Semiconductor	a (Å)	LDA	GGA	HSE06	Exp. Data
GaAs	5.633	0.318	0.525	1.427	1.43
ZnTe	6.101	1.469	1.804	2.385	2.39

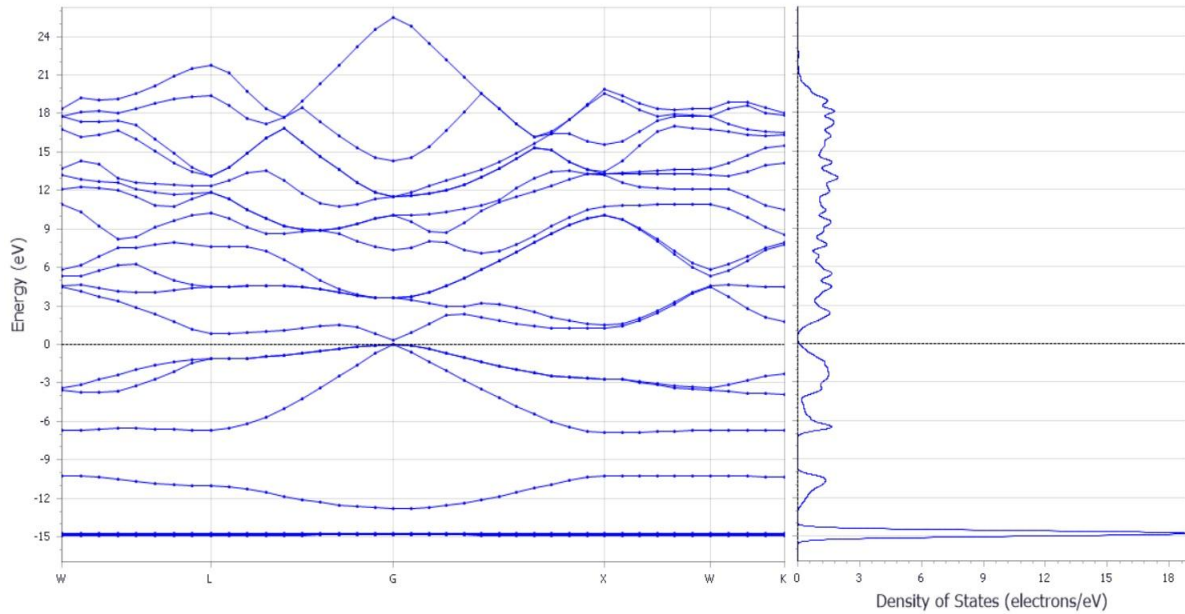


Figure 1: Band Structure diagram and DOS for GaAs semiconductor within LDA

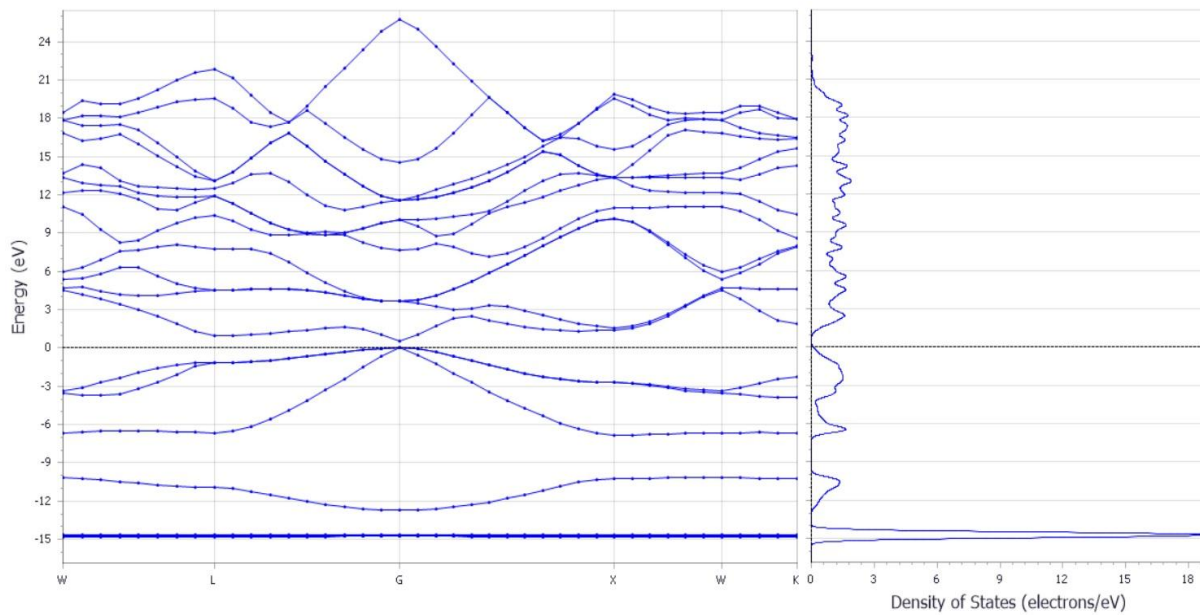


Figure 2: Band structure diagram and DOS for GaAs semiconductor within GGA

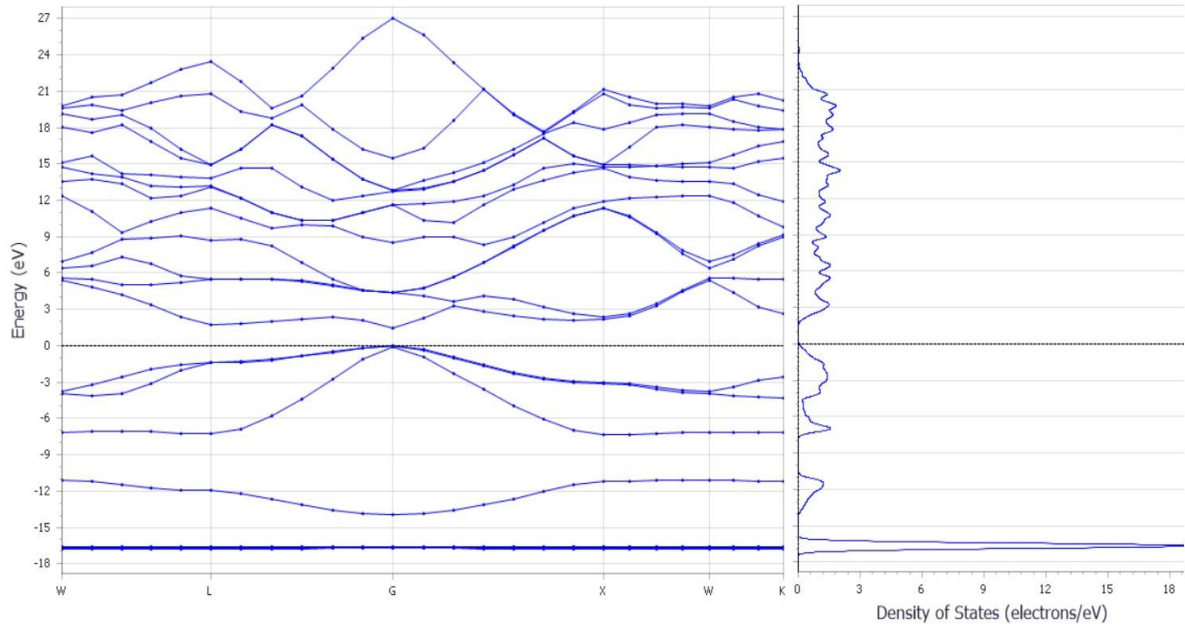


Figure 3: Band Structure diagram and DOS for GaAs semiconductor within HSE06

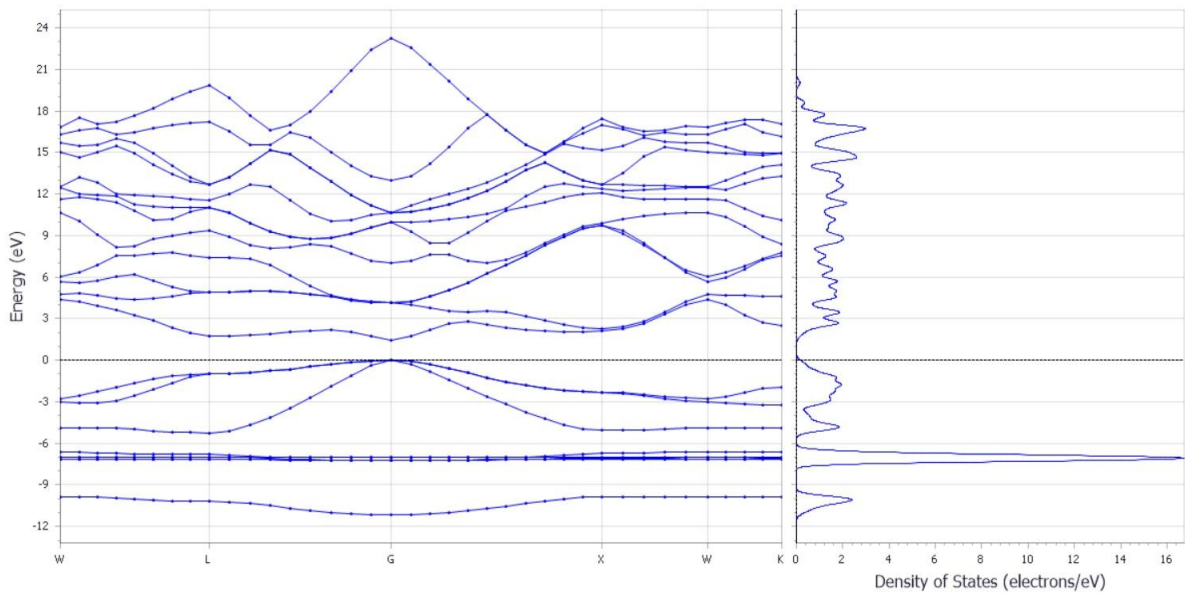


Figure 4: Band Structure diagram and DOS for ZnTe semiconductor within LDA

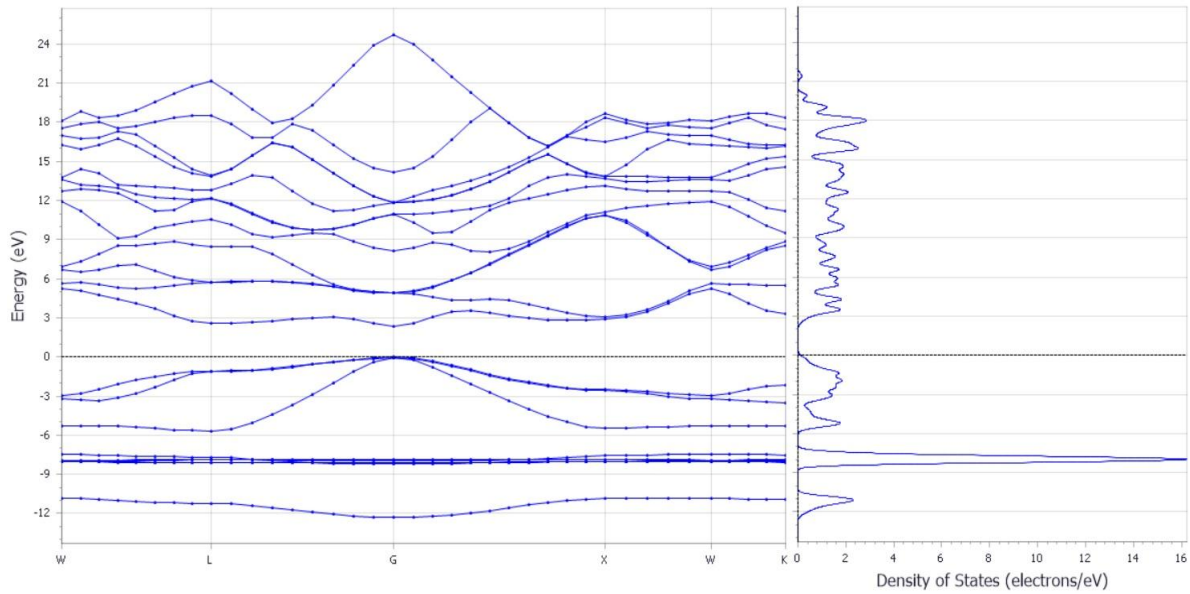


Figure 5: Band Structure diagram and DOS for ZnTe semiconductor within HSE06

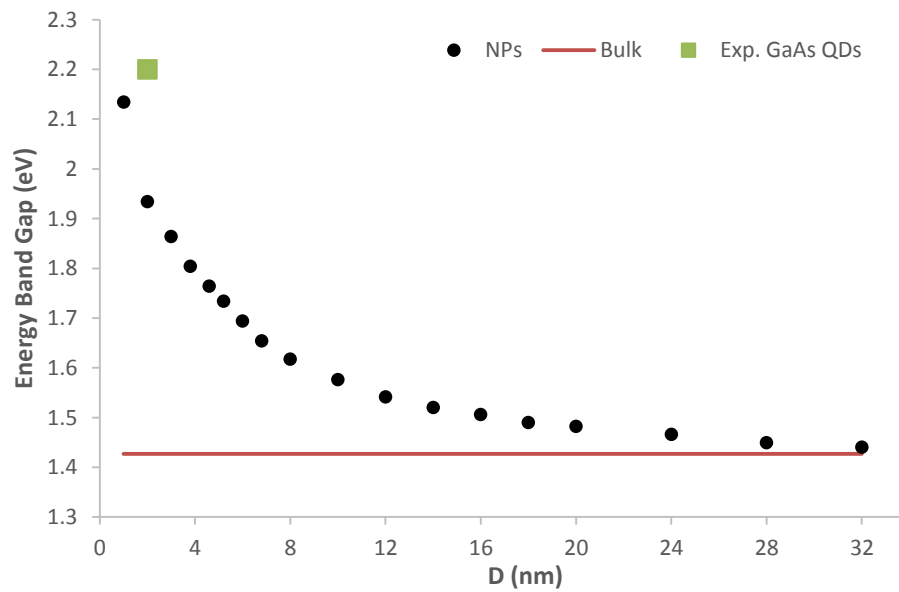


Figure 6: Diameter vs energy band gap for GaAs semiconductor NPs within HSE06. The experimental data taken from Kher & Wells (1996)

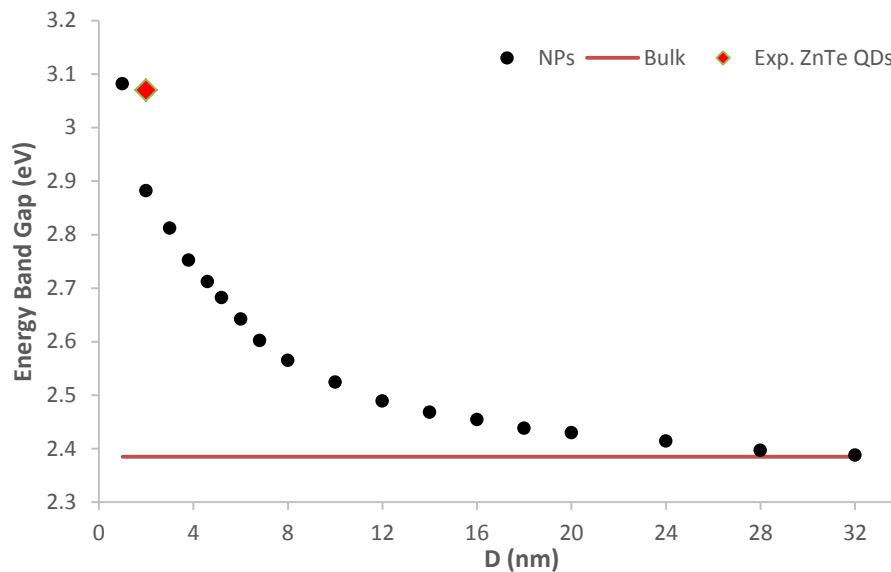


Figure 7: Diameter vs energy band gap for ZnTe semiconductor NPs within HSE06. The experimental data taken from Jun, Choi & Cheon (2001)

4. Conclusions

The study of bulk state and the variation of the size effects on the band gap of semiconductor NPs are implemented theoretically using first-principle calculations in the framework of DFT by LDA, GGA, and HSE06. The LDA and GGA are under estimated energy band gaps, while HSE06 gives correct values within an error of only (0.2%) for both bulk GaAs and ZnTe semiconductor. Thus, for DFT calculations, the exchange-correction is important to yield reasonable results relative to the experimental data for both bulk and NPs. The band gap obtained in the present study is in good agreement with experimental data with the function of diameter of NPs by considering the change in mean bond length. Further, it is found that the particle size can affect the mean bond length of semiconductor NPs, and this effect on the band gap becomes larger with decreasing particle size, that shift in the band gap plays an important role for effective industrial implementation.

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