

## Ab-initio study of structural, elastic, electronic and vibrational properties of PbSe in the rock-salt structure

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### Abstract

Structural, elastic, electronic and vibrational properties of rock-salt PbSe have been investigated theoretically within the framework of density functional theory (DFT). The generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) and revised Perdew-Burke-Ernzerhof (PBEsol) exchange correlation functional. The structure is shown to be mechanically and dynamically stable. The electronic properties show that the compound is a narrow direct band gap semiconductor. The PBE agrees better with the experimental elastic properties while PBEsol agrees better with the experimental structural, electronic and phonon properties.

**Keywords:** Ab-initio; Rock-salt PbSe; Elastic properties; Phonon; Electronic properties.

### Introduction

Lead chalcogenides or lead salts as they are often called have been studied extensively because of their numerous technological applications. In particular PbSe has been shown to find applications in sensors, solar cells, laser materials, optical filters (Lian *et al.*, 2018; Oh *et al.*, 2014; Kim *et al.*, 2015), laser technology (Preier, 1979) and as a thermoelectric material for conversion of waste heat into electricity (Khokholov, 2003; Bremholm *et al.*, 2003). PbSe is a narrow direct gap semiconductor which crystallizes at ambient conditions in the cubic NaCl structure. It has been synthesized using experimental methods such as epitaxial growth (Mariano and Chopra, 1967), in situ chloride passivation (Lian *et al.*, 2018), stepwise, post-synthesis, colloidal atomic layer deposition (Oh *et al.*, 2014), single step, cation-exchange reaction (Kim *et al.*, 2015), electrochemical deposition (Streltsov *et al.*, 1998) among others. Besides the experimental studies, some theoretical studies have been done on this material using several exchange correlation functional and different methods within density functional theory (DFT). Albanesi *et al.*, (2000), Hummer *et al.*, (2007) Amrane and Benkraouda (2013) and Lach-hab *et al.*, (2002) used full potential linearized augmented plane wave (FP-LAPW) method within the local density approximation (LDA) and generalized gradient approximation (GGA) including spin orbit coupling. Lach-hab *et al.*, (2002) also applied Slater-Koster (SK) tight-binding calculations, including the spin-orbit coupling in the SK Hamiltonian to get a better band gap.

Seetawan and Wattanasarn, (2012) used molecular dynamics (MD) method to study the mechanical properties of PbS, PbSe, CdTe and PbTe; Boukhris *et al.*, (2014) studied the structural, electronic and thermal properties of lead chalcogenides PbS, PbSe and BeTe using full-potential linear augmented plane wave (FP-LAPW) method, Herman *et al.*, (1968) used orthogonalized-plane-wave method, Overhob and Rossler (1970) used the relativistic Green's function method while Zaoui *et al.*, (2009) applied the hybrid full-potential augmented plane-wave plus local orbitals (APW+lo) method. Zhang *et al.*, (2009) used the GGA of Perdew and Wang (PW91) as implemented in the Vienna ab initio simulation package (VASP) using the projector augmented wave (PAW) pseudo-potential method. Bencherif *et al.*, (2011) used the pwscf code to calculate the lattice dynamics of PbSe using the Ceperley-Alder functional as parameterized by Perdew and Zunger.

### Materials and Methods

Interestingly, we could not find a theoretical result on electronic structure which uses plane wave method implemented by quantum espresso (QE) suit of codes. Also there was no report with the modified GGA of Perdew, Burke and Ernzerhof (PBE) developed to work better for solids, called PBEsol on both the electronic structure and phonon properties. To this effect, we wish to study the electronic structure, elastic properties and phonon properties of PbSe with the plane wave method using both PBE and PBEsol and see how our result

compares with other results as well as estimate accuracy of the results from ordinary PBEsol with respect to that from PBE. The paper is organized as follows, section 1 is a brief introduction, section 2 is our computational details, and section 3 is our results and discussions while section 4 is the conclusions.

We employ Kohn-Sham equation within the framework of Density Functional Theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) in our calculations. We performed ab-initio DFT non-spin polarized calculations in the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) (Perdew *et al.*, 1996a) and the revised Perdew-Burke-Ernzerhof (PBEsol) (Perdew *et al.*, 1996b) exchange correlation functional within the generalized gradient approximation (GGA) that improves equilibrium properties of densely packed solids. For the calculations, plane-wave self-consistent field (PWSCF) method, as implemented in the Quantum-Espresso program package (Giannozzi *et al.*, 2009) was used. Plane wave basis sets were used to represent wave functions and density of valence electrons with kinetic energy and augmented density cutoff of 40 Ry and 400 Ry respectively. At this cutoff, the total energy is converged to within 1 mRy/atom. Scalar relativistic ultrasoft pseudo-potentials (Vanderbilt, 1990) were used to describe the interaction between ions and valence electrons. Pb 6s, 6p, 5d and S 3s, 3p are treated as valence orbitals. Brillouin zone integration was done over 8 x 8 x 8 k-point grid sampled by Monkhorst-Pack scheme (Monkhorst and Pack, 1976). The optimization criteria for the ionic geometry relaxation was 0.0001 Ry for total energy and 0.001Ry/au for the Hellmann-Feynman forces. Linear response method proposed by Baroni *et al.*, (2001) a technique which uses density functional perturbation theory (Gonze and Lee, 1997) was used to compute directly dynamical matrix on already calculated grid of q points. Fourier transform is then applied on these dynamical matrices to determine interatomic force constant in real space. Dynamical matrices for phonon dispersion relations were calculated at a 4x4x4 grid of q-points. The elastic constants were calculated using the stress-strain method (Corso, 2016) and it has been confirm to work well with TMCs (Chibueze and Okoye, 2019). Elastic constants are used to obtain the strength and stability of a material. The tensor  $C_{ij}$  decides the

elastic property of the material. For the NaCl cubic structure, there are three components  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  needed to determine the mechanical stability. These three independent elastic constants are obtained by fitting the total energies of the strained crystal to a fourth order polynomial strain. For mechanical stability, the Born-Huang stability criteria (Born and Huang, 1954) are required. The conditions are:

$$C_{11}, C_{44} > 0, C_{12} < B < C_{11}, C_{11} - C_{12} > 0, C_{11} + 2C_{12} > 0 \quad (1)$$

Compressibility is measured using the bulk modulus B which is a measure of resistance to volume change on application of pressure given as

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (2)$$

Stiffness of a material is measured using the shear modulus G which is a measure of resistance to reversible deformation upon shear stress. G is obtained using three different approximations:

The Voigt approximation (Voigt, 1928) given by

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \quad (3)$$

The Reuss approximation (Reuss, 1929) given by

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{11} + 3(C_{11} - C_{12})} \quad (4)$$

And the Voigt-Reuss-Hill approximation (VRH) (Hill, 1952) which is a ratio of the first two and is given by

$$G = \frac{G_V + G_R}{2} \quad (5)$$

Young Modulus, a ratio of the linear stress to strain, which is another measure of stiffness is given by

$$E = \frac{9BG}{3G - B} \quad (6)$$

Another important quantity is the Poisson's ratio  $\nu$  is given by

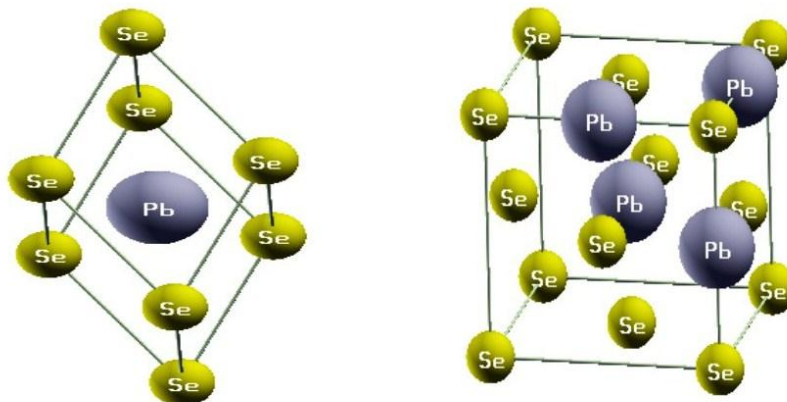
$$\nu = \frac{3B - 2G}{2(3B + G)} \quad (7)$$

For ductile materials  $\nu = \frac{1}{3}$  while for brittle material  $\nu < \frac{1}{3}$ . Zener anisotropy factor A is given by

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (8)$$

The ratio  $\frac{B}{G}$  is also used to determine if a material is brittle or ductile. A material is ductile if  $\frac{B}{G} > 1.75$

and brittle if  $\frac{B}{G} \leq 1.75$ . VRH approximation which is the average of Voigt and Reuss is used throughout our calculations.



**Figure 1:** (left) Primitive unit cell (right) conventional unit cell of the rock-salt structure of PbSe.

## Results and discussions

### Structural and elastic properties

**Table 1:** Lattice constant (a), Bulk modulus (B), Young modulus (E), Shear modulus (G), Poisson Ratio (n), band gap and elastic constants ( $C_{11}$ ,  $C_{12}$  and  $C_{44}$ ) of PbSe.

	a (Å)	Band gap (eV)	$C_{11}$ (GPa)	$C_{12}$ (GPa)	$C_{44}$ (GPa)	B (GPa)	E (GPa)	G (GPa)	n
PBE	6.2212	0.46	115.31	12.21	17.33	46.58	683.54	273.06	0.25
PBEsol	6.1044	0.29	138.77	11.57	17.64	53.972	764.82	304.21	0.26
Other	6.117 <sup>f</sup>	0.340 <sup>a</sup>	110 <sup>b</sup>	14.9 <sup>b</sup>	17.2 <sup>a</sup>	47.5 <sup>c</sup>			
calculated	6.196 <sup>a</sup>	0.318 <sup>c</sup>	120.8 <sup>a</sup>	8.9 <sup>a</sup>	21 <sup>b</sup>	49.187 <sup>b</sup>			
values	6.222 <sup>c</sup>	0.425 <sup>b</sup>	123.7 <sup>g</sup>	19.3 <sup>g</sup>	15.9 <sup>g</sup>	46.76 <sup>b</sup>			
	6.121 <sup>d</sup>	0.17 <sup>g</sup>				54.1 <sup>g</sup>			
	6.23 <sup>e</sup>								

<sup>a</sup>Lach-hab, (2002) <sup>b</sup>Boukhris *et al.*, (2014) <sup>c</sup>Zhang *et al.*, (2009) <sup>d</sup>Amrane *et al.*, (2013); <sup>e</sup>Albanesi *et al.*, (2000) <sup>f</sup>Mariano and Chopra, (1967) <sup>g</sup>Madelung *et al.*, (1983)

Our structural, elastic and mechanical properties are presented in Table 1. It is observed that the lattice constant obtained using the PBEsol pseudopotential is closer to the experimental value of 6.117 Å obtained by Mariano *et al.*, (1967) than the value we obtained using ordinary PBE. However our results from both PBE and PBEsol agrees fairly with other theoretical results. Our calculated elastic constants are presented in Table 1. For a cubic crystal, three elastic constants  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  are required to determine the stability and the values at equilibrium lattice constant are presented in Table 1.  $C_{11}$  characterize the elasticity in length,  $C_{12}$  and  $C_{44}$  typify the elasticity in shape. We see that for all the

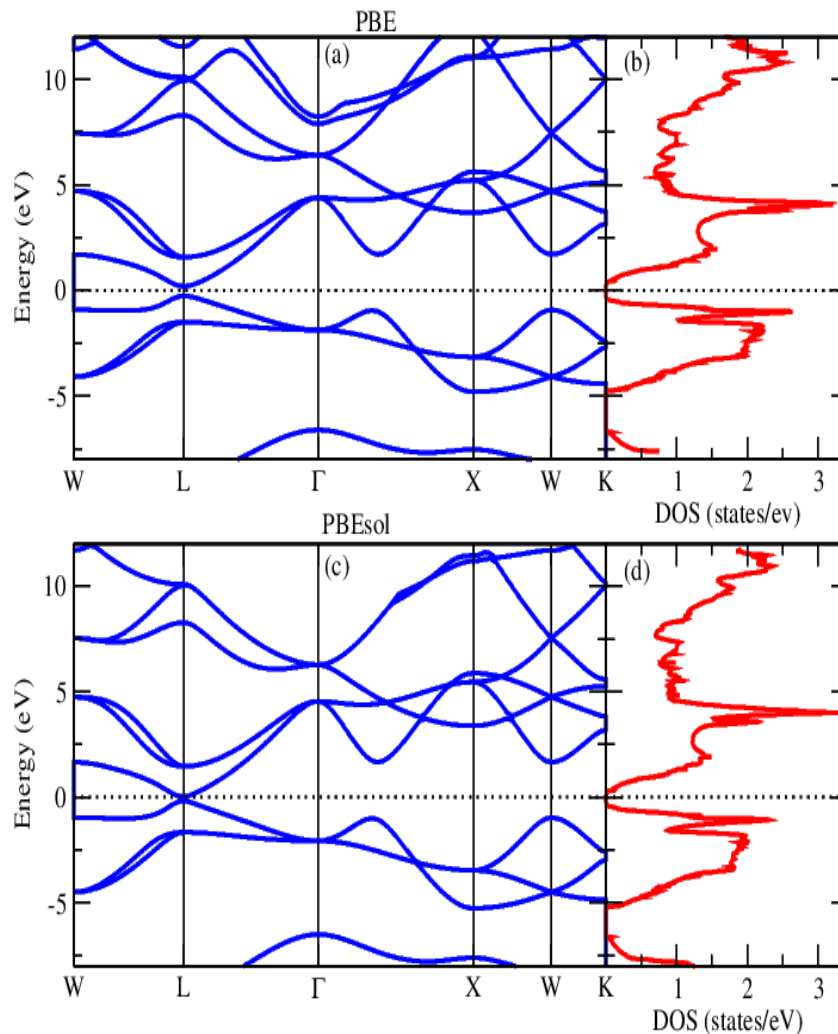
lattice constants considered, PbS satisfy the Born's stability criteria and therefore is mechanically stable. Our result shows that PbSe presents a stronger resistance to the unidirectional deformation (due to much higher value of  $C_{11}$  compared with the low value of  $C_{44}$ ) than resistance to the pure shear deformation. It is observed that the experimental elastic constants agree better with the values we obtained using ordinary PDE. However, the calculated bulk modulus obtained using PBEsol is in a very close agreement with the experimental result of Madelung *et al.*, (1967). We observe from Table 1 that the values of Bulk modulus, Young modulus, Shear modulus, and Poisson Ratio obtained using

PBEsol exchange correlation is relatively larger than that obtained using PBE exchange correlation but unfortunately we could not find any previous experimental or theoretical data to compare our elastic results. The Poisson ration shows that the structure is brittle both for PBE and PBEsol.

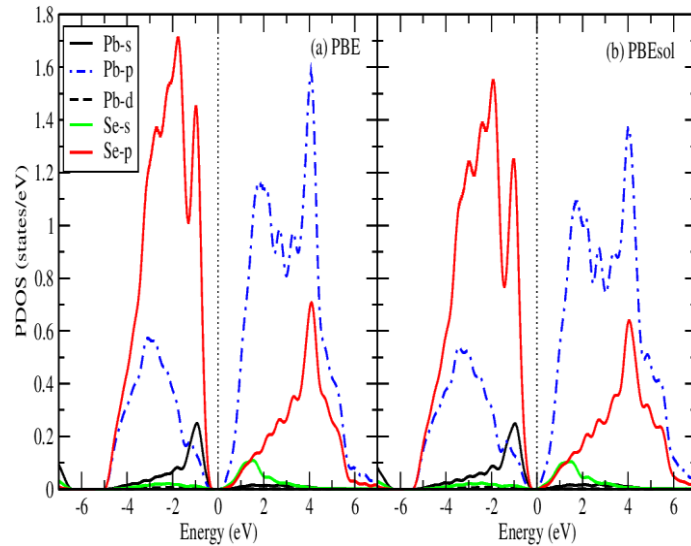
#### Electronic properties

The electronic properties were calculated using both the PBE and PBEsol exchange-correlations and presented in Figures 2 and 3 respectively. The calculated values of the band gap are presented in Table 1. The electronic band structure shows that the fundamental energy gap is direct at L symmetry point as seen in Figure 2. The bottom of the conduction and the top of the valence band is almost touching each other. The band gap of 0.29 obtained using PBEsol is in fair agreement with the

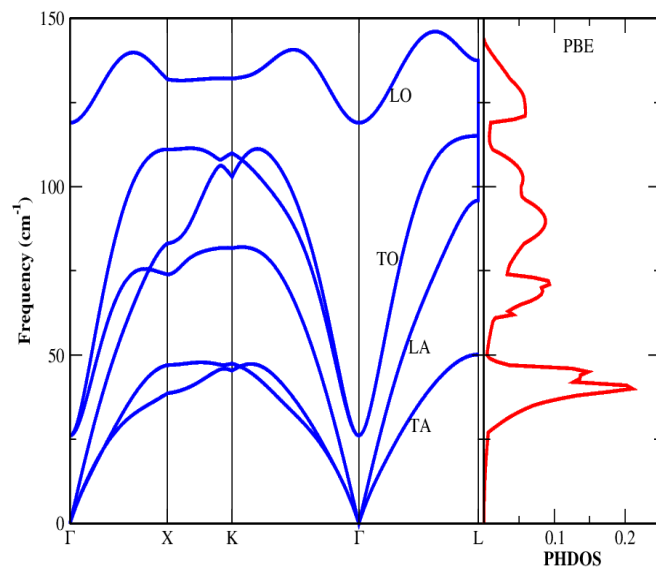
experimental value of 0.17 eV (Madelung *et al.*, 1983) and the theoretical value of 0.314 eV (Zhang *et al.*, 2009). The band gap obtained using the PBE is in agreement with the theoretical value of 0.425 eV obtained by Boukhris *et al.*, (2014). Our calculated values suggest that PBEsol provides a better electronic result than the PBE. It is worthy to mention that the band gap from the density of states (DOS) is slightly wider than that from the electronic band structure. To understand the states around the Fermi level and the general distribution of electronic states, we have presented the electronic density of states projected on the atomic orbitals (PDOS) in Figure 3. The PDOS reveal that the top of the valence band is dominated by Se-p states while the bottom of the conduction band is dominated by the Pb-p states.



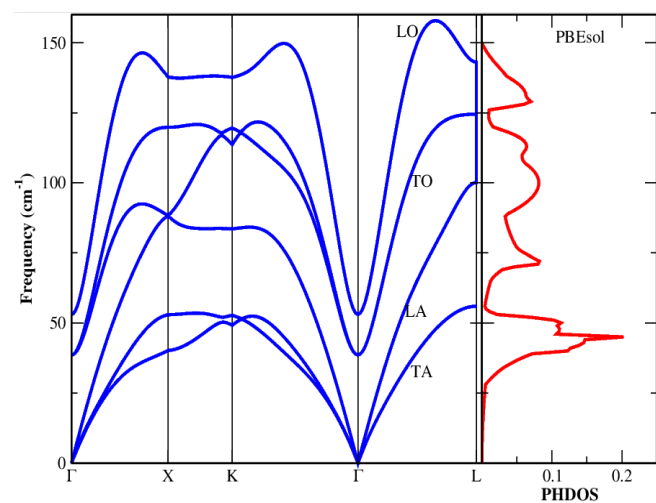
**Figure 2:** Electronic band structure of PbSe using PBE (c) using PBEsol and the total density of states (DOS) using (b) PBE and (d) PBEsol



**Figure 3:** Electronic density of states projected on the atomic orbitals using (a) PBE (b) PBEsol



**Figure 4:** Phonon energy dispersion (left panel) and phonon density of states (PHDOS) (right panel) for PbSe using ordinary PBE.



**Figure 5:** Phonon energy dispersion (left panel) and phonon density of states (PHDOS) (right panel) for PbSe using PBEsol.

In order to understand the lattice dynamical properties of PbSe, we did a phonon study using PBE and PBEsol exchange correlation. The phonon dispersion curves along the high symmetry directions together with the phonon density of states (PHDOS) are shown in Figures 4 and 5 where the longitudinal acoustical (LA), longitudinal optical (LO), transverse acoustical (TA) and transverse optical (TO) phonon modes have been clearly identified. Since we used two atoms in our unit cell, we obtained total of six phonon modes, three been acoustic and the remaining three optical. The calculations were performed using the PBE and PBEsol exchange correlations at the optimized lattice constant. The various phonon mode frequencies for the symmetry points are recorded in Table 2. For the two cases reported, there are no

negative frequencies observed which confirms that rock salt structure of PbSe is dynamically stable. The results reveal that the frequencies obtained for different phonon modes at L point using PBEsol are relatively higher when compared with that obtained using PBE while the frequency of LO at  $\Gamma$  point for PBEsol is lower than that of PBE.

It is very noticeable that there is pronounced anomalies in the transverse optical (TO) and longitudinal optical (LO) modes at the  $\Gamma$  point especially for the PBEsol. For the LO mode at the  $\Gamma$  point, the PBE result is closer to the result of Zhang *et al.*, (2009). However for all the other modes at both  $\Gamma$  and L points, the result from the PBEsol is closer to the result of Zhang *et al.*, (2009) than that from the PBE.

**Table 2:** Calculated values of TA, LA, TO, LO phonon modes for both PBE and PBEsol exchange correlation functional.

	Symmetry point	TA (cm <sup>-1</sup> )	LA (cm <sup>-1</sup> )	TO (cm <sup>-1</sup> )	LO (cm <sup>-1</sup> )
PBE	$\Gamma$ (0,0,0)	0.0	0.0	25.89	118.56
	L(0.5,0.5,0.5)	50.05	95.75	114.92	137.24
PBEsol	$\Gamma$ (0,0,0)	0.0	0.0	38.54	52.83
	L(0.5,0.5,0.5)	55.91	99.89	124.82	142.75
Others	$\Gamma$ (0,0,0)	0.0h	0.0h	48.0h	143.10h
	L(0.5,0.5,0.5)	54.37h, 50.0i	102.40h, 85.0i	122.75h, 130.0i	149.10h, 142.0i

<sup>h</sup>Zhang *et al.*, (2009) <sup>i</sup>Bencherif *et al.*, (2011)

### Conclusion

Structural, elastic, electronic and vibrational properties of rock-salt PbSe have been investigated theoretically within the framework of density functional theory using the PBE and PBEsol exchange correlation interaction in the present study. The elastic constants and the mechanical properties show that PbSe is mechanically stable in the rocksalt structure. Poisson ratio shows that the material is brittle. The electronic properties depicts that it is a narrow direct band gap semiconductor with the Se-p states dominating around the top of the valence band while Pb-p states dominate around the bottom of the conduction band. The phonon studies show that the material is dynamically stable with an abnormal behavior in the LO and TO phonon modes. The ordinary PBE exchange correlation potential best agrees with the experimental the elastic

properties while the PBEsol best describes the structural, electronic and phonon properties.

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