RESEARCH ARTICLE

Electronic properties of palladium diselenide by density functional theory

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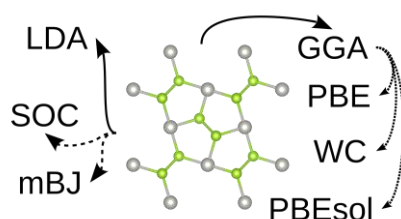[c] *Department of Physics, King Khalid University, Abha, Saudi Arabia*

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Graphical abstract

Abstract

The knowledge of the structural and electronic properties of a material is important in various applications such as optoelectronics and thermoelectric devices. In this study, we are using full potential linearized augmented plane wave method framed within density functional theory provided by WIEN2k to optimize the structure of $PdSe_2$ in orthorhombic (Pbca) phase and calculate its electronic properties. With the implementation of local density approximation (LDA), Perdew-Burke-Ernzerhof parameterization of generalized gradient approximation (PBE-GGA), Wu-Cohen parameterization of GGA (WC-GGA), and PBE correction for solid GGA (PBEsol-GGA), the computed results of lattice constants are found to be within 5% error with the experiment data. Also, our calculated indirect band gap energy was found to be ~0.24 eV by LDA along with modified Becke-Johnson potential functional (mBJ) with experimental lattice constants and ~0.52 eV by using PBE-GGA with optimized lattice constants. However, the effect of spin-orbit coupling is not found too much on the band gap energy. By analyzing the partial density of states, we identify that d-orbital of Pd is demonstrating a slightly more significant contribution to both the valence and conduction band near to Fermi level which is also in agreement with the previous first principles study.

Keywords: DFT, transition metal dichalcogenide, structural properties, electronic properties

INTRODUCTION

Recently, transition metal dichalcogenides have received a great attention as tempting candidates for thermometric and optoelectronic applications, due to their unique electronic and optical properties [1]. Their special crystal structures which make them possible to craft into two-dimensional (2D) materials, either semiconducting or metallic. The crystal structure of palladium diselenide ($PdSe_2$) has a long history and is being studied since the 1950s [2-3]. It retains its solid phase up to ~1000 K [4] and keeps on in crystallographic space group 61 Pbca under 6 GPa [5] (Fig. 1(a)). The structural and electronics parameters of a material are fundamental features from which the mechanical, magnetic, optical, and thermal properties are evaluated. Theoretically, these calculations are done using density functional theory (DFT) approaches as well. However, the quality of the results of the DFT approaches is sensitive to the suitable choice of the exchange-correlation energy/potential functional. For example, at the level of standard DFT, mostly material's band gap is severely underestimated [6-7]. Therefore, we examine here the performance of four non-empirical exchange-correlation (xc) functionals (local density approximation (LDA) [8], Perdew, Burke and Ernzerhof (PBE) [9] parameterization of generalized gradient approximation (GGA), Wu and Cohen (WC) parameterization of GGA [10], and PBE correction for solid (PBEsol) GGA [11]), for the calculations of the structural and electronics properties of $PdSe_2$. This study is performed by DFT framed

full potential linearized augmented plane wave (FP-LAPW) methodology as implemented in WIEN2k computational software.

COMPUTATIONAL METHODOLOGY

In FP-LAPW method, the contribution of potential is counted from all electrons (core electrons and valence electrons) and no shape approximation is imposed on the potential. However, in the core region, spherically symmetric form of the potential is assumed, where in the valence region, potential (where electrons are weakly bounded to nuclei) is expanded into spherically harmonics. Similarly, the valence electrons are treated using plane wave basis while the core electrons are treated using spherical harmonics times of the radial solution of Schrödinger equation in the core region [13].

The original structure file of $PdSe_2$ is generated using experiment data at 298 K, ambient pressure [5] where the lattice constants are $a = 5.7457$ Å, $b = 5.8679$ Å, and $c = 7.6946$ Å. The shifted k-mesh in the irreducible Brillouin zone was set to $11 \times 10 \times 8$ for LDA and PBEsol-GGA, $9 \times 9 \times 6$ for PBE-GGA and WC-GGA after the convergence test with increment of the total number of irreducible k-point and energy difference of 0.0001 Ry as the criteria. The RK_{max} which refer to the cut-off size of the basis sets was set to 7.7, 8.0, 7.8 and 7.7 for LDA, PBE-GGA, WC-GGA and PBEsol GGA respectively with convergent criteria of 0.01 Ry. While, G_{max} which specified the plane waves used as basis set and is set to 11.3 for LDA (± 0.00001 Ry), 12.0 for PBE-

GGA (± 0.00001 Ry), 8.47 for WC-GGA (± 0.0001 Ry) and 9.9 (minimum energy after first cycle of the energy increment) for PBEsol GGA. All the self-consistent field cycles stop with energy convergence limit 0.0001 Ry, force convergence limit 1.0 mRy/Bohr, and charge convergence limit 0.0001 e except in the structure optimization where the force convergence limit was noted to be 5.0 mRy/Bohr for the optimizing lattice constants and 0.5 mRy/Bohr for optimizing atomic positions.

We first optimized the lattice constants of $PdSe_2$ using one by one the XC functional listed before. After that, we optimized the atomic position using both optimized lattice constants and experimental lattice constants for comparison. Lastly, we calculated the band structure using k-path as shown in Fig. 1(b) and electronic density of states (DOS) using denser threefold k-mesh. The calculation of band structure and DOS were carried out including four different considerations; calculation without additional consideration (labelled as normal calculation), with consideration of spin-orbit coupling effect (SOC), with modified Becke-Johnson potential functional (mBJ) [14], and with both SOC and mBJ.
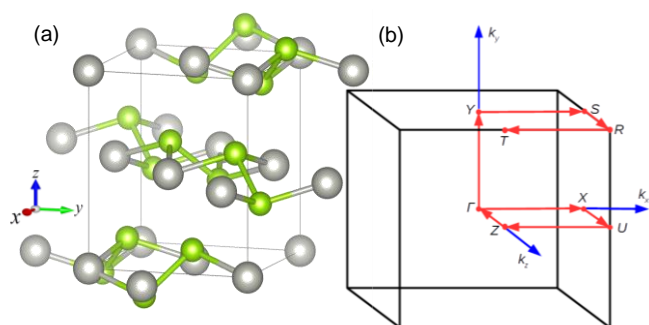

Fig. 1 (a) Unit cell of $PdSe_2$, Pd in grey colour and Se in green colour. (b) First Brillouin zone of $PdSe_2$, the red arrow is the k-path.

RESULTS AND DISCUSSION

Structural properties of $PdSe_2$

The optimized lattice constants are shown in Table 1. We found that estimated c is the largest source of errors for every XC functional because the bonding in the z direction is only due to the van der Waals forces. The lack of consideration of spontaneous charge density fluctuations and only the local properties are included to account XC energy [15]. a and b are shown overestimated as expected but the errors are less than 2.5 %. From the data in Table 2, all the atomic position calculated are accurate enough with the error less than 3.2 %. Despite the somewhat poor performance in optimizing lattice constants, PBE-GGA shows the best performance in minimizing the force in $PdSe_2$ unit cell.

Electronic properties of $PdSe_2$

The most obvious property in electronic properties is band gap energy E_g. From Table 3, we clearly have seen that without mBJ, non of the XC functional performs well. The literature [2-3] shows $PdSe_2$ is a semiconductor with $E_g = 0.4$ eV which contradicts with the metallic nature results shown in Table 3. But with adding mBJ, $PdSe_2$ showed the semiconducting nature. Although underestimation is around $40-58$ %, our results appear to be more accurate as compared to previous attempts [6-7]. This may due to larger basis sets we are used compared to previous works [6-7].

In order to demonstrate the ability of DFT to be more *ab initio*, we also use the optimized lattice constants to calculate E_g. Although PBE-GGA gives the largest error in the band gap calculations using experimental lattice constants, interestingly, here, PBE-GGA shows the semiconducting character of $PdSe_2$ with $E_g = 0.5189$ eV (without SOC), 0.5172 eV (with SOC). Moreover, results are too close to the experimental value of the E_g than the results of band gap reproduced from the experimental lattice constants. On the other hand, mBJ results become worse in this case (0.7956 eV (without SOC), 0.7922 eV (with SOC)). We suspect that the overestimation of the value of the lattice constant, c might be the reason to show correct semiconducting nature of the $PdSe_2$ within PBE-GGA. We test this by using optimized a, b, and experimental c, the result shows metallic. This also suggests we can modify E_g of $PdSe_2$ by modifying the strain on the z-axis.

As can be seen from the Fig. 2, the nature of the band gap is of indirect, as the valance band maximum is located at Γ and conduction band minimum is located between Y and S. Moreover, the SOC impact is also not considerable toward E_g.

The calculated density of states (DOS) is shown in Fig. 3. Pd atoms and Se atoms are contributing almost equivalent to the states near to the Fermi level. The most valance orbitals, which are 4d orbitals of Pd and 4p orbitals of Se occupied more states near to Fermi level as expected.

**Table 1** Lattice constants of $PdSe_2$, percent of error is compared to [5].

XC Functional	a (Å)	b (Å)	c (Å)
LDA	5.8304 (1.47 %)	5.8874 (0.33 %)	6.8498 (10.98 %)
PBE GGA	5.7867 (0.71 %)	5.9635 (1.63 %)	8.6076 (11.87 %)
WC GGA	5.8878 (2.47 %)	5.9512 (1.42 %)	6.9522 (9.65 %)
PBEsol GGA	5.8720 (2.20 %)	5.9386 (1.20 %)	6.9436 (9.76 %)

Table 2 Atomic-position of the $PdSe_2$ in the unit cell along with percent error of calculations in comparison to [5]. The atomic-position is represented in fractional coordinate system.

XC Functional	x	y	z
LDA	0.11212 (0.78 %)	0.11504 (2.50 %)	0.39286 (3.17 %)
PBE GGA	0.11107 (0.16 %)	0.12041 (2.05 %)	0.41399 (2.04 %)
WC GGA	0.11233 (0.97 %)	0.11593 (1.74 %)	0.39465 (2.74 %)
PBEsol GGA	0.11193 (0.61 %)	0.11557 (2.05 %)	0.39465 (2.73 %)

Table 3 *Eg* calculated using experimental lattice constants from different xc functional with different considerations, unit used is eV.

	LDA	PBE-GGA	WC-GGA	PBEsol GGA
Normal			Metallic	
SOC			Metallic	
mBJ	0.2407	0.1689	0.2141	0.2177
SOC + mBJ	0.2404	0.1686	0.2134	0.2170
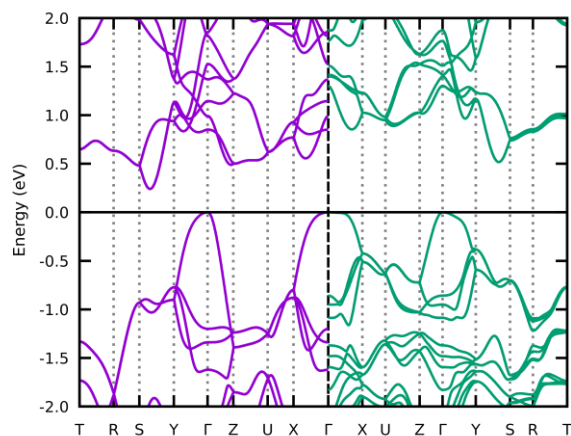
Fig. 2 Band structure of PdSe$_2$, purple line represents the band structure calculated using LDA with an experimental lattice constant and mBJ, the green line represents the band structure calculated using PBE-GGA with an optimized lattice constant and SOC. The Fermi level is set to zero.
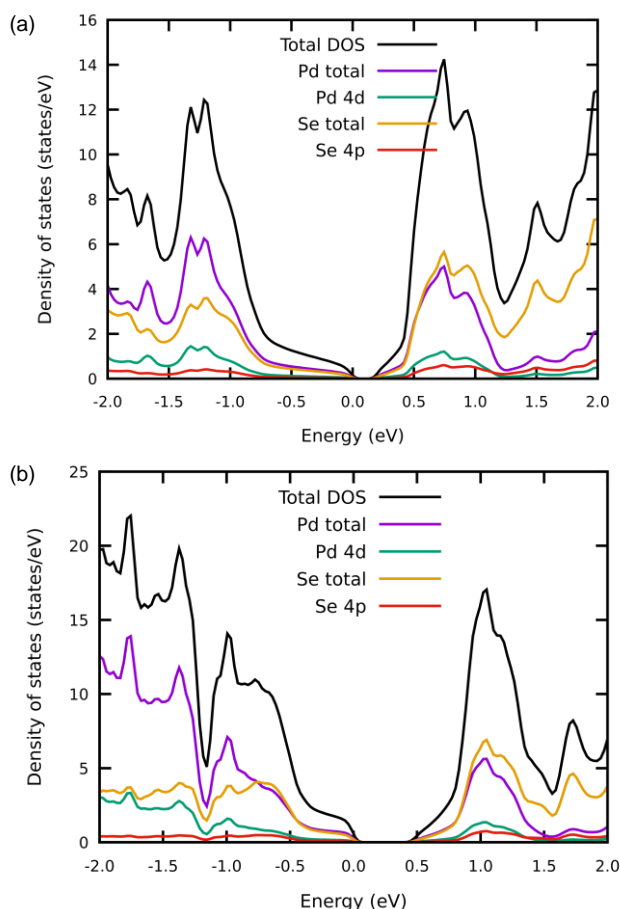
Fig. 3 (a) Density of states of PdSe$_2$ using LDA with an experimental lattice constant and mBJ. (b) The density of states of PdSe$_2$ using PBE-GGA with an optimized lattice constant and SOC. The Fermi level is set to zero.

CONCLUSION

In summary, we have investigated the structural and electronic properties of PdSe$_2$ by using WIEN2k framed within DFT. All the XC functional studies can accurately calculate the lattice constants and atomic position except lattice constant *c* because of the inability to take into account van der Waals force. For the case of electronic properties, SOC is not found important for PdSe$_2$ calculations. The mBJ revealed its ability to significantly improve results of E_g for the case of using experimental lattice constants. It is also possible to reduce the dependencies on experimental data to calculate the electronic properties which is demonstrated in the calculation of E_g using optimized lattice constant with PBE-GGA.

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