Numerical simulation of structural, electronic and optical properties of vanadium diselenide (VSe_2)

Elkana Rugut[1], **Daniel Joubert**[1] **and Glenn Jones**[2]

1. The National Institute for Theoretical Physics, School of Physics and Mandelstam Institute for Theoretical Physics, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa, Tel: +27117176804; Fax: +27117176879
2. Johnson Matthey Research (PTY) Limited, Scientia, CSIR Campus, Meiring Naude Road, Brummeria, Pretoria, South Africa.

E-mail: `elkanatawich@gmail.com`

Abstract. VSe_2 belongs to a group of compounds called transition metal dichalcogenides. This group of compounds have been exploited by several researchers both computationally and experimentally because of their intriguing properties such as low resistance, high chemical and mechanical stability and ease of synthesis. These properties make them candidates for various applications ranging from catalysis, electronics, aerospace engineering to plasmonics, just to mention a few. In this study we numerically simulated some of the properties of VSe_2. In this regard, a structural study of VSe_2 was undertaken using Density Functional Theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional with two flavours of van der Waal's interaction corrections namely Grimme (D2) and Tkatchenko-Scheffler (TS) to describe the inter-layer interactions of VSe_2 accurately. From the structural data obtained, PBE+D2 describe the structural parameters of VSe_2, when compared to experimental data, best. Vibrational properties via phonon calculations, mechanical properties through elastic constant calculations and energetic properties using the formation and the cohesive energies confirmed that VSe_2 is mechanically, dynamically and energetically stable in its trigonal phase. Furthermore, from electronic band structure and density of states, VSe_2 exhibits metallic character. Optical properties computed using many-body perturbation theory at the BSE level of approximation show that the compound is optically anisotropic with different absorption behaviour in-plane and out-of-plane. From the obtained values of the screened plasma frequency, VSe_2 is a promising plasmonic material.

1. Introduction

After the discovery of the notable electrical, physical, mechanical and optical properties of graphene [1], investigations of the physical properties of layered transition metal dichalcogenides [2] have been a continous source of interesting research. This family of compounds has a general formula MX_2 where M is a transition metal and X is chalcogen. This study is based on VSe_2. Levy and Froidevaux [3] studied VSe_2 experimentally when they were investigating $V_xTi_{1-x}Se_2$ and $Ta_xTi_{1-x}Se_2$ at various concentration levels and environmental conditions. From their analysis, VSe_2 is easy to alloy and crystallyzes in a stable octahedral co-ordination of cations. Close packed sheets of metal atoms (V) are sandwiched between sheets of chalcogen atoms (Se) with stacking sequence Se-V-Se and an inter-layer spacing of about 7 Å. The anisotropy can be attributed to strong intra-layer and weak inter-layer bonding. Wiegers [4] noticed that VSe_2

shows anomalous properties at around 110 K attributed to charge density waves. Due to its application in various fields such as lithium batteries [5] where powdered VSe_2 is one of the cathode components [6], an improved understanding of VSe_2 is valuable. Thus, this study is intended to advance the understanding of the properties of VSe_2. Although bulk VSe_2 has been studied before [7, 8], little has been reported on optical properties [9].
This paper is organized as follows; section 2 is devoted to methodology, section 3 is composed of a presentation of results obtained and a brief discussion whereas a summary and major conclusions of this study are presented in section 4 and lastly acknowledgements are noted in section 5.

2. Methodology

This study is based on a Density Functional Theory (DFT) implementation which solves Kohn-Sham equations using a projector augmented wave method. The generalized gradient approximation in the scheme of Perdew-Burke-Ernzerhof (PBE) [10] was used for the exchange-correlation energy functional as implemented in the Vienna *ab initio* Simulation Package (VASP) code [11, 12, 13]. It is noteworthy that the standard PBE does not describe the long range van der Waal's interaction between the individual layers of VSe_2. In this regard, we used the PBE+D2 method of Grimme [14] and the PBE+TS method proposed by Tkatchenko and Scheffler [15] to account for inter-layer interaction. The two approximations include long range van der Waal's interactions in an empirical manner. Ionic relaxation was done using a conjugate gradient minimization method [16] to minimize the Hellman-Feynman forces among the constituent atoms to less than 1 meV/Å. The cut-off energy for the plane wave basis and self-consistent threshold were set at 700 eV and 10^{-8} eV respectively, in order to achieve good convergence. For the structural study, a gamma centered grid of size 12 × 12 × 4 was used to sample the Brillouin-zone. Phonon calculations were done by applying a finite displacement method using a 3 × 3 × 3 supercell with 81 atoms. By varying the size of the cell from unit cell to supercell, one needs to re-adjust the number of k-points in the irreducible part of the Brillouin-zone. In this regard, the k-mesh was changed from 12 × 12 × 4 to 4× 4 × 1. We applied a stress-strain approach for calculating elastic constants whereby, after extracting our stiffness matrix, it was analyzed to obtain average properties such as bulk (B), Young's (E) and shear (G) modulus as well as Poisson's ratio (ν) among other mechanical properties. In order to calculate optical properties of the material, we had to go beyond the ground state calculation by considering excited state properties of the system. A DFT calculation was performed to obtain the ground state structure of the material of interest by solving the Kohn-Sham equations. DFT [17] output was then used as ingredients for self consistent GW_0 [18] calculations in which only the quasi-particle eigen-energies of the Green's function were updated while keeping the screened coulomb interaction fixed at its initial DFT value. Lastly, a Bethe Salpeter Equation (BSE) [19] calculation based on the GW_0 data was performed to determine optical absorption spectra which include excitonic effects.

3. Results and discussion

3.1. Structural and energetic properties

Table 1. Structural and energetic parameters

Functional	a (Å)	c (Å)	V_0 (Å^3)	α (°)	γ (°)	E_{coh} (eV/atom)	E_{form} (eV/atom)
PBE	3.3520	6.9970	68.10	90	120	-4.314	-0.694
PBE+TS	3.3350	5.9490	57.30	90	120	-4.582	-0.962
PBE+D2	3.2240	6.7300	60.58	90	120	-4.578	-0.958
Exp[3]	3.3480	6.1220	59.43	90	120	-	-
Exp[4]	3.3587	6.1075	59.67	90	120	-	-
Exp[20]	3.3400	6.1200	59.13	90	120	-	-

Table 1 shows structural data of VSe_2. Although PBE described the lattice parameter a well, it overestimated the value of lattice parameter c. On the other hand, PBE+TS underestimated both a and c lattice constants which automatically translates to the volume being underestimated as compared to the given experimental values. PBE+D2 underestimated the a lattice parameter but overestimated the c lattice parameter hence compensating each other resulting in ground state volume that is closer to experimental. Therefore, PBE+D2 gives a better overall description of the structural parameters of VSe_2. The calculated cohesive and formation energies obtained were negative for all the approximations of the exchange-correlation energy used, suggesting that trigonal VSe_2 is energetically stable against decomposition into its constituent atoms and elemental solids. Thus, further studies of VSe_2 were done using PBE+D2 since it reproduces the structural properties better.

3.2. Mechanical properties

Table 2. Calculated independent elastic coefficients (GPa)

C_{11}	C_{12}	C_{13}	C_{14}	C_{33}	C_{44}
133.62	22.30	21.79	-6.76	58.39	18.60

Table 3. Calculated eigenvalues (GPa)

λ_1	λ_2	λ_3	λ_4	λ_5	λ_6
17.410	17.629	49.472	56.856	112.290	164.830

From the calculated elastic coefficients tabulated in Table 2, the elastic constants for VSe_2 fulfilled all the Born stability criterion for trigonal structures [21]. All eigenvalues of the stiffness matrix given in Table 3 were positive which validates its mechanical stability. Three averaging schemes were used in computing B, G, E, ν and B/G, namely, Voight, Reuss and Hill methods [22]. The different schemes help to make comparisons and to check the accuracy of the computed values. From the literature [23], the Voight method gives an upper limit to numerical data since it assumes a uniform strain whereas the Reuss method gives a lower limit to numerical data since it assumes a uniform stress. The Hill method on the other hand gives an average of the two. This trend is consistent with the results of this current study.

Table 4. Calculated B, E, G, ν and B/G

Scheme	B	E	G	ν	B/G
Voight	50.819	87.152	35.890	0.2142	1.42
Reuss	43.950	66.557	26.674	0.2476	1.65
Hill	47.384	76.919	31.282	0.2295	1.51

Pugh proposed that if the B/G value is less than the critical value (1.75), the material is considered brittle [24], otherwise it is ductile. The B/G values obtained using the three averaging schemes were less than 1.75 as shown in Table 4 implying that VSe_2 is brittle.

3.3. Dynamical and electronic properties

VSe_2 is metallic since the valence band maxima and conduction band minima coincide as shown in Figure 1 and 2 which is consistent with existing literature [25]. Moreover, it is dynamically stable in its trigonal phase as backed by phonon dispersion curves in Figure 3 and 4 in which only positive frequencies are noticeable.

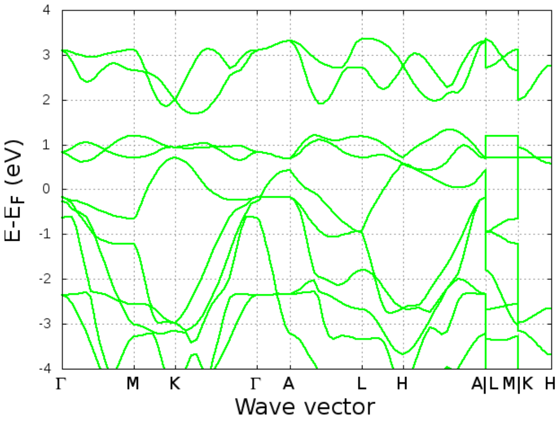

Figure 1. Electronic bands

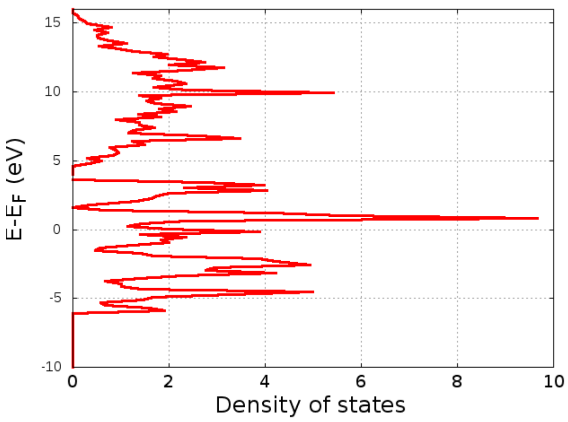

Figure 2. Electronic DOS

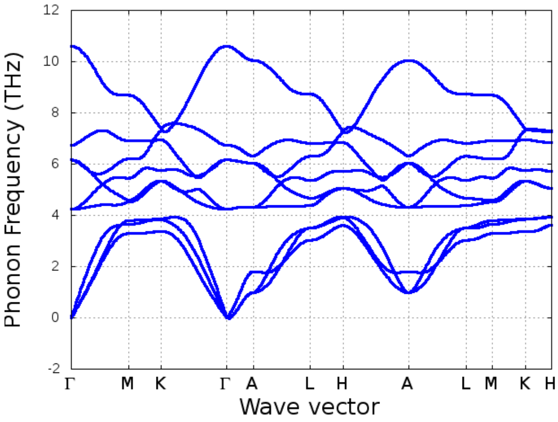

Figure 3. Phonon bands

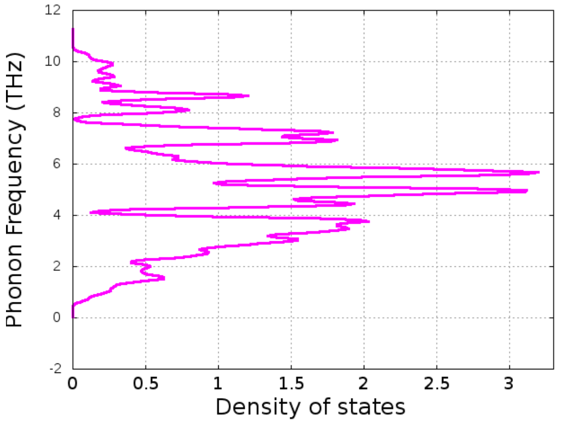

Figure 4. Phonon DOS

3.4. Optical properties

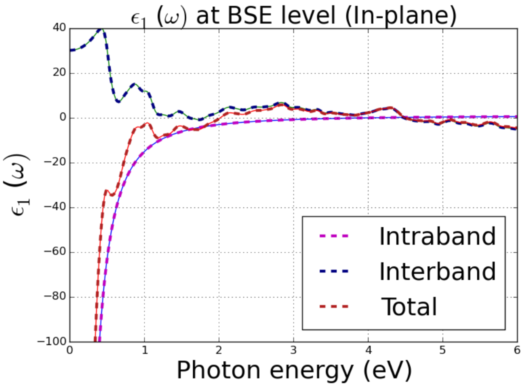

Figure 5. Real part of dielectric function at BSE

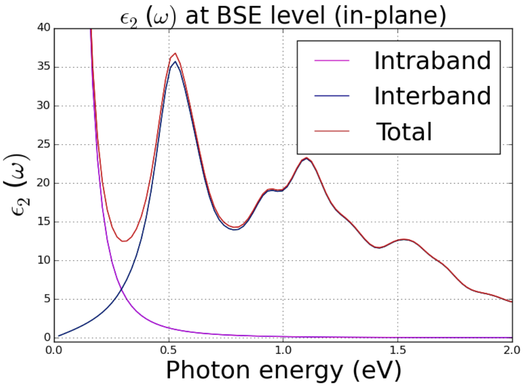

Figure 6. Imaginary part of dielectric function at BSE

At very low photon energies ($0 < \omega \leq 1$ eV) for the imaginary part and ($0 < \omega \leq 3$ eV) for the real part of dielectric function at the BSE level shown in Figure 5 and 6 respectively, it is evident that the intraband contribution is important for a good description of the optical behaviour of metallic systems [26]. In higher energy ranges, its contribution is negligible. Hence, the dielectric constant used in optical analysis should include both intraband and interband contributions.

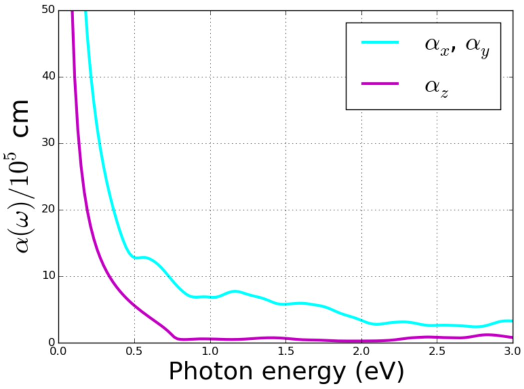

Figure 7. Absorption coefficient

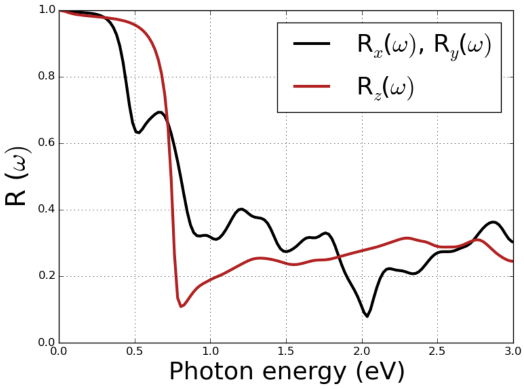

Figure 8. Reflectivity

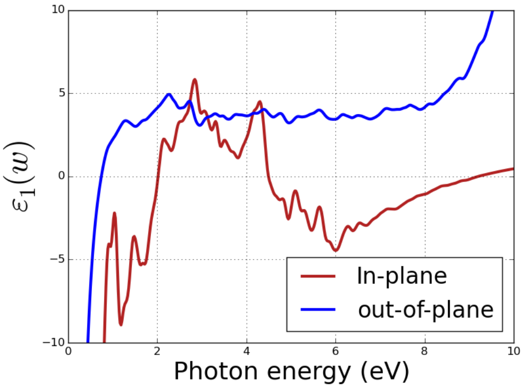

Figure 9. Real part of dielectric

The behaviour of the dielectric function is similar in the two in-plane (x- and y-) directions and we show only in-plane and out-of-plane (z-) values for the optical properties. Within a photon energy range of 0 eV to 3 eV, absorption in-plane is larger that absorption out-of-plane as shown in Figure 7. There is no distinguishing pattern for reflectivity. Within the visible range, maximum absorption peaks occur at the edge of the visible range both in-plane and out-of-plane. The out-of-plane plasma frequency is in infrared region at around 0.7 eV, whereas for in-plane, it is found at around 2 eV, 4.25 eV and 9 eV as shown in Figure 9. From the obtained values of screened plasma frequency, VSe_2 is a promising plasmonic material for radiation polarized for in-plane absorption because its in-plane screened plasma frequencies lie within the visible and ultraviolet region. This is in agreement with a DFT study done by Cudazzo *et al.* [9]. For plasmonic applications, high plasmonic quality in the UV-visible frequency regime is desired [27]. Recall that the screened plasma frequency is located at the point where the total contribution from the intraband and interband contributions to the real part of the dielectric matrix is zero.

4. Summary and conclusion

In this study, we have performed first principles computations on trigonal VSe_2 including structural, elastic, electronic, vibrational and optical properties using DFT and post-DFT many-body perturbation theory. We have established that the lattice parameters obtained after relaxation are in good agreement with existing experimental and theoretical data. From the mechanical properties, VSe_2 is brittle material hence can easily be used to craft components for optical communication, computers and other technological devices. Bulk VSe_2 is metallic and its plasma frequency is located within the visible range, hence it can be applied in plasmonic field which incorporates optics onto nanotechnology.

5. Acknowledgement

This study was financially supported by the Johnson Matthey Technology Centre (Pretoria) under contract number JM6473. We acknowledge Centre for High Computing, Cape Town for computational resources.

References

[1] Neto A C, Guinea F, Peres N M, Novoselov K S and Geim A K 2009 *Reviews of modern physics* **81** 109.
[2] Wang Q H, Kalantar-Zadeh K, Kis A, Coleman J N and Strano M S 2012 *Nature nanotechnology* **7** 699-712.
[3] Levy F and Froidevaux Y 1979 *Journal of Physics* C: *Solid State Physics* **12** 473.
[4] Wiegers G A 1980 *Physica* B+C **99** 151-165.
[5] Whittingham M S 2004 *Chemical reviews.* **104** 4271-4302.
[6] Ōnuki Y, Inada R, Yamanaka S and Kamimura H 1981 *Japanese Journal of Applied Physics* **20** 1583.
[7] Reshak A H and Auluck S 2004 *Physica* B: *Condensed Matter* **349** 310-315.
[8] Zunger A and Freeman A J 1979 *Physical Review* B **19** 6001.
[9] Cudazzo P, Gatti M and Rubio A 2014 *Physical Review* B **90** 205128.
[10] Perdew J P, Burke K and Ernzerhof M 1996 *Physical review letters* **77** 3865.
[11] Kresse G and Hafner J 1993 *Physical Review* B **47** 558.
[12] Kresse G and Hafner J 1994 *Physical Review* B **49** 14251.
[13] Kresse G and Furthmüller J 1996 *Physical Review* B **54** 11169.
[14] Grimme S 2006 *Journal of computational chemistry* **27** 1787-1799.
[15] Bučko T, Lebègue S, Hafner J and Ángyán 2013 *Physical Review* B **87** 064110.
[16] Stich I, Car R, Parrinello M and Baroni S 1989 *Physical Review* B **39** 4997.
[17] Hohenberg P and Kohn W 1964 *Physical review.* **136** B864.
[18] Aryasetiawan F and Gunnarsson O 1998 *Reports on Progress in Physics* **61** 237.
[19] Liegener C M 1981 *Physics Letters* A **85** 324-326.
[20] Hayashi K and Nakahira M 1978 *Journal of Solid State Chemistry* **24** 153-161.
[21] Mouhat F and Coudert F X 2014 *Physical Review* B **90** 224104.
[22] Shein I R and Ivanovskii A L 2008 *Journal of Physics: Condensed Matter* **20** 415218.
[23] Ching W Y, Rulis P and Misra A 2009 *Acta Biomaterialia* **5** 3067-3075.
[24] Pugh S F 1954 *The London, Edinburgh and Dublin Philosophical Magazine* **45** 823-843.
[25] Ruitao L, Robinson J, Sun D, Mallouk T and Terrones M 2014 *Accounts of chemical research* **48** 56-64.
[26] Kim J, Jhi S H and Ryeol K 2011 *Journal of Applied Physics* **110** 083501.
[27] Blaber M G, Arnold M D and Ford M J 2009 *arXiv preprint arXiv* 0908.3707.