Electronic and Optical Properties of monolayer MX_2(M= Zr, Hf; X= S, Se) from first principles calculations

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Abstract. Transition metal di-chalcogenide (TMDC) monolayers have potential applications in electronic and optical devices. Work on these atomically thin semiconductors is an exciting emerging field of research. In this research the electronic and photo-absorption properties of monolayer ZrS_2, $ZrSe_2$, HfS_2 and $HfSe_2$ have been investigated using density functional theory (DFT) and many body perturbation theory at the level of the partially self consistent GW_0 approximation and of the Bethe-Salpeter equation (BSE) in the Tamm-Dancoff approximation. The structures were found to be semiconductors with band gaps within the visible range of the spectrum with strong optical absorption in the visible range. Exciton binding energies were estimated from a comparison of the GW and BSE results.

1. Introduction

MX_2(M= Zr, Hf; X= S, Se) belong to the family of layered transition metal chalcogenides (TMC's). Layers in these materials are bonded to one another by weak van der Waals forces [1,2], making them a possible source of 2-D (two-dimensional) crystals [3–6]. Recently there has been a growing interest in 2-D materials due to their potential applications in the field of photonic and electronic applications [7–10]. Some of these materials have been used successfully in the fabrication of inverters, logic circuits, low powered field effect transistors and memory cells [5, 7, 10–14].

TMC's are expected to have a strong excitonic effects due to reduced screening, which is expected to affect their optical properties. There is a need to accurately calculate and understand the many-body electronic properties of these TMC's. One of the common approaches that can be used to investigate the electronic properties of these systems is to calculate the electronic excitation energies based on for example, Green's function for many body perturbation theory (MBPT) in the GW approximation with self energy [15]. This method has been proven to be accurate for a number of materials [16, 17]. Results from the GW-MBPT electronic excitation energies are then used to study neutral excitations by solving the two particle Bethe-Salpeter equation (BSE) [18–20]. The later method has been reported to give a reasonable description of optical properties of quite a number of systems [21, 22]. To the best of our knowledge, such methods have not been used to study the electronic and optical properties of monolayer MX_2(M= Zr, Hf; X= S, Se) structures. The interest of this paper, is therefore, to use the

many body GW and BSE equations to study the electronic and optical properties of monolayer MX_2(M= Zr, Hf; X= S, Se) structures.

In their bulk state, MX_2(M= Zr, Hf; X= S, Se) are iso-structural [23,24], they crystallize in a 1T-CdI_2 type structure with space group *164,* $P\bar{3}m1$ in which the metal atom is sandwiched between two sheets of the chalcogen atoms leading to X-M-X layers. Atoms within a layer are strongly held together by a covalent bond with weak ionic bonding within the layers. A monolayer of the structure is depicted in Figure 1.

2. Computational Method

Our first principle calculations were performed using the Projector Augmented Wave (PAW) [25] method as implemented in the Vienna ab initio Simulation Packege (VASP) [26, 27]. Perdew, Burke and Ernzerhof (PBE) [28, 29] parametrization of the generalised gradient approximation (GGA) [30–33] is used for exchange correlation. 17 x 17 x 1 Monkhorst-Pack meshes were used in sampling the Brillouin zones with an energy cut-off of 520 eV and were found to be sufficient enough for the energy convergence. The Brilloin zone sampling was chosen in such a way that the convergence of free energy is less than 1 meV/atom. The monolayer was generated by creating a space wide enough between the adjacent layers in the z-direction of the relaxed bulk structure. A vacuum region of 19 Å was used to isolate the layers along the c-axis and was found sufficient to eliminate interaction between the layers. The monolayer was generated by creating a space wide enough between the adjacent layers in the z-direction of the relaxed bulk structure.

Frequency dependent GW calculation at the level of partially self-consistent GW_0 approximation were performed, where the quasiparticle energies were updated while keeping the DFT wave functions. To calculate the optical spectra, BSE calculations using Tamm Dancoff (TD) approximation on the basis of a free qausielectron-quasihole were performed. Five highest valence bands and five lowest conduction bands were found to be enough to converged the peaks of the A and B energy peaks.

3. Results and discussions

We have systematically calculated the electronic and optical properties of the monolayer MX_2(M= Zr, Hf; X= S, Se) structures, the electronic and optical properties of the structures are discussed in subsection 3.1 and subsection 3.2 respectively.The unit cell of the structure used in the calculation is depicted in Figure 1.

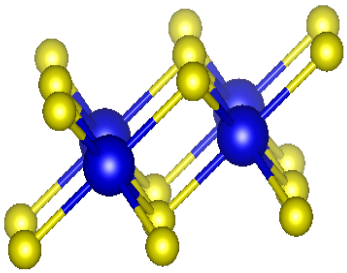


Figure 1: Monolayer MX_2(M= Zr, Hf; X= S, Se) relaxed structure: blue = M, yellow = X.

3.1. Electronic Properties

Our calculated fundamental electronic band gap of the monolayers MX_2(M= Zr, Hf; X= S, Se) structures are listed in Table 1. The PBE and GW calculated band gaps of ZrS_2, HfS_2 and $HfSe_2$ were found to be an indirect band gap semiconductors, their conduction band maximum lies at A and valence band maximum at Γ points of the high symmetry points in ZrS_2 and M in the case of HfS_2 and $HfSe_2$. $ZrSe_2$ was found to be a direct band gap material with both valence and conduction band at the Γ points of the high symmetry k-points. From the table we note that our calculated PBE electronic band gaps for the hafnium chalcogenides are in good agreement with those reported in [34]. The difference in our band gap in the zirconium compounds may be as a result of the choice of the lattice parameters used in the calculations. However, we have no experimental band gaps to compare our results with, the only available information we have is that of Li et. al [35], where the authors predicted the experimental band gap of monolayer ZrS_2 to be around 1.7 to 1.93 eV, which is in good agreement with our GW direct band results.

Table 1: Monolayer MX_2(M= Zr, Hf; X= S, Se) band gap in eV

	HfS_2	$HfSe_2$	ZrS_2	$ZrSe_2$
PBE	1.22	0.67	0.80	0.26
GW	2.02	0.93	1.95	2.53
Direct GW gap	3.07	2.31	2.83	2.53
Other PBE	1.27 [a]	0.61 [a]	1.10 [a]	0.45 [a]

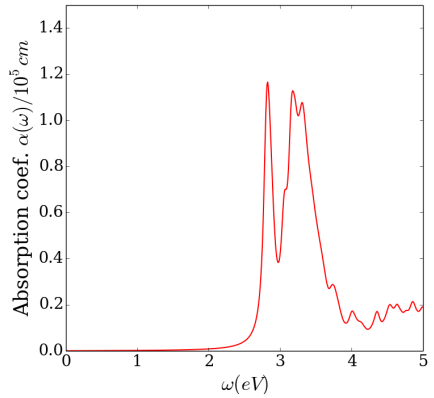
a = reference [34]

3.2. Optical Properties

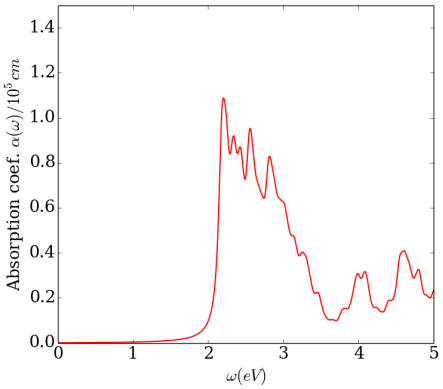
To determine the optical properties, absorption spectra of the ZrX_2 family structures were calculated at the BSE level of approximation. The results are plotted in Figures 2a, 2b, 2c and 2d. From Figure 2, we can note that HfS_2 and ZrS_2 start to absorb photons in the ultra-violet and infra red regions of the spectrum respectively and that there is downward shift in energy absorption energy in both zirconium and hafnium as we move from sulphur to selenium.

Table 2: Monolayer MX_2(M= Zr, Hf; X= S, Se) BSE calculated positions for A and B peaks in eV

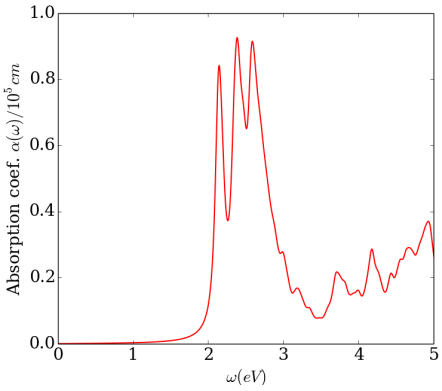
	HfS_2	$HfSe_2$	ZrS_2	$ZrSe_2$
E_A	2.84	2.20	2.15	1.57
E_B	3.17	2.60	2.40	1.71



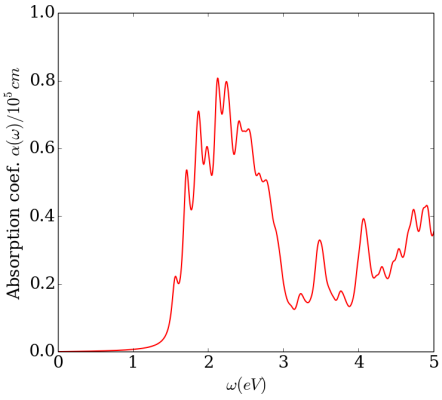
(a) HfS_2 optical absorption



(b) $HfSe_2$ optical absorption



(c) ZrS_2 optical absorption



(d) $ZrSe_2$ optical absorption

Figure 2: Monolayer MX_2(M= Zr, Hf; X= S, Se) optical absorptions

To determine the binding energies of the energetically lowest lying excitons, the energies of the peaks in the BSE calculated absorption coefficient were compared with the quasi-particle energies obtained from the GW calculations. The binding energies of the excitons can be estimated by subtracting the lowest BSE absorption peak energy listed in Table 2 from the GW direct band gap energy, i.e. E_A^a = GW direct gap -E_A and E_B^b = GW direct gap -E_B. The binding energies of the excitons are listed in Table 3. Negative binding energies suggest a resonant exciton at the corresponding energy level.

Table 3: Monolayer MX_2(M= Zr, Hf; X= S, Se) BSE calculated binding energy for A and B excitons in eV

	HfS_2	$HfSe_2$	ZrS_2	$ZrSe_2$
E_B^a	0.23	0.11	0.68	0.96
E_B^b	-0.1	-0.29	0.43	0.82

4. Conclusions

We have performed first principle calculations of the electronic and optical properties of monolayer MX_2(M= Zr, Hf; X= S, Se) structures. Three of structures were found to have indirect band gaps and $ZrSe_2$ was found to be a direct band gap material, with band gaps within the visible range of the spectrum. Strong optical absorption is predicted in the visible region. In a solar cell device, the monolayer structures will be mounted on a substrate which will affect the absorption properties. The results, however, suggest that it will be worthwhile investigating the MX_2(M= Zr, Hf; X= S, Se) further as potential components in second generation optical absorbers.

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