Exciton energies of chalcopyrites $AgAlX_2$(X=S,Se,Te) from GW and BSE calculations

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Abstract. Using state-of-the-art Density Functional and Many Body Perturbation Theories, we study electronic and optical properties of the chalcopyrites $AgAlX_2$(X=S,Se,Te). The Kohn-Sham Density Functional Theory (DFT) underestimates the fundamental and the optical gaps as a result of the particle number dependant discontinuity in the exchange-correlation potential [1]. Accurate estimates of fundamental gaps were obtained using post DFT Many Body Perturbation Theory at the GW level. Optical absorption spectra and optical gaps were determined from solutions of the Bethe-Selpeter Equation (BSE) in the Tamm-Dancoff approximation. Comparison of the BSE and the GW results were used to obtain exciton energies. The GW-level calculated bandgaps are in good agreement with experimental values. Exciton energies were estimated for the first time but we couldn't find any theoretical or experimental results for comparison.

1. Introduction

During the absorption of photons by the interband transitions, an electron and a hole are usually created in the conduction and valence bands respectively. The Coulomb interaction between the two particles leads to the formation of a new excitation in the crystal also known as exciton. It has been proved that these excitons can considerably impacted the optical properies of semiconductor materials and therefore are very important for opto-electronic applications [2,3]. The determination of the exciton energy has been a cumbersome task for the scientific community. Excitons are easily observed in pure samples. In real system, the impurities create unpaired electrons and holes which can screen the Couloumb interaction in the excitons and reduce the strength of the binding forces [2]. Hence, making the exciton very difficult to be observed experimentally. In theoretical point of view, accurate optical properties are not always directly accessible from first-principle DFT calculations. For example the eigenvalue energies $\epsilon_{v\mathbf{k}}$ and $\epsilon_{c\mathbf{k}}$ entering in the Fermi's golden rule expression [4]

$$\varepsilon_{2_M}(\omega) = \lim_{\mathbf{q}\to 0} \frac{8\pi^2}{\Omega \mathbf{q}^2} \sum_{vc\mathbf{k}} |\langle \mathrm{u}_{c\mathbf{k}+\mathbf{q}}|e^{i\mathbf{qr}}|\mathrm{u}_{v\mathbf{k}}\rangle|^2 \delta(\omega - (\epsilon_{c\mathbf{k}+\mathbf{q}} - \epsilon_{v\mathbf{k}})) \tag{1}$$

for calculating the absorption spectra correspond to the Kohn-Sham (KS) highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) respectively. The energy difference between HOMO and LUMO yields the KS bandgap. However, it is now well established that the KS bandgap is underestimated by more than 50% compared to the experimental measurement. As such, there is a need to go beyond the standard DFT in order to accurately predict the bandgap and the optical spectra. Reliable bandgap can be obtained by means of the GW approach by solving the *quasiparticle* (QP) equation [5]

$$[T + V_{ee} + V_{ext}]\,\varphi^{\mathrm{QP}}_{i,\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';\epsilon^{\mathrm{QP}}_{i,\mathbf{k}})\phi^{\mathrm{QP}}_{i,\mathbf{k}}(\mathbf{r}) = \epsilon^{\mathrm{QP}}_{i,\mathbf{k}}(\mathbf{r})\varphi^{\mathrm{QP}}_{i,\mathbf{k}}(\mathbf{r}) \tag{2}$$

where Σ is the self-energy which contains all the exchange and correlations effects among the electrons. Although this approach leads to a good approximation of the fundamental gap, it is still not sufficient for the correct description of the optical properties. For example in the case of silicon as described in Figure 1, GW gives a good onset of the optical absorption. However, the first peak occurs at a relatively high energy and its intensity is also underestimated as compared to that from experimental measurement. This is due to the fact that the GW only allows free electron-hole transition without accounting for the Coulomb interaction between the two particles. The electron-hole can be captured by solving the Bethe-Selpeter Equation (BSE) [8,9].

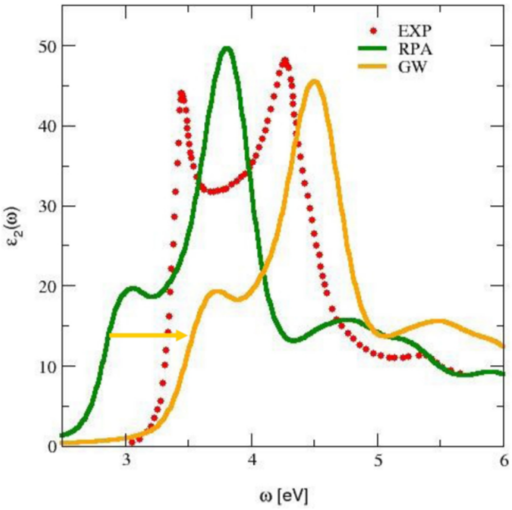

Figure 1. (Color online) Optical absorption of silicon from the experimental measurement (EXP), the GW and the DFT-LDA calculations within the random phase approximation (RPA) [6,7].

In most chalcopyrite materials, such an interaction is yet to be carefully examined in contrast to the bandgap and the electronic properties where a huge effort has been made. Most of the previous works have been limited to the calculation of the dielectric response function in the independent particle picture within local field effect [10–12]. This is due to the difficulty of including the electron-hole interaction in the calculations. Moreover, these calculations are very computationally demanding because of the high number of empty bands which need to be included in order to reach the convergence. We are not aware of any work done in that regard. Our goal in this paper is to first estimate the fundamental gap and secondly investigate the importance of the excitons in the chalcopyrite materials $\mathrm{AgAlX_2}$(X=S,Se,Te).

2. Methodology

All the relaxed structures were obtained from our previous work in Ref. [10]. In all the study, we use the plane wave projector augmented wave (PAW) [13] as implemented in the VASP package [14]. The self energy in Equation 2 is calculated using the many body perturbation theory at the GW level ($\Sigma = iGW$) [15]. At the first order of the approximation, the Green's function G is built from the Kohn-Sham (KS) orbitals and eigenvalue energies as

$$G_0(\mathbf{r}', \mathbf{r}; \epsilon) = \sum_i \frac{\varphi_{KS}(\mathbf{r})\varphi^*_{KS}(\mathbf{r}')}{\epsilon - \epsilon_i + i\eta \ \mathrm{sgn}(\epsilon_i - \mu)} \tag{3}$$

while the dynamically screened Coulomb potential is given by

$$W_0(\mathbf{r}, \mathbf{r}', \epsilon) = \int \varepsilon^{-1}(\mathbf{r}, \mathbf{r}_1, \epsilon) v(\mathbf{r}, \mathbf{r}') d\mathbf{r}_1 \tag{4}$$

with $v(\mathbf{r}, \mathbf{r}')$ the bare Coulomb potential and ε^{-1} the dielectric function calculated within the RPA [16] at the DFT level. The QP energies are therefore calculated as follow.

$$\epsilon^{QP}_{i,\mathbf{k}} = \mathcal{R}e\left[\left\langle \varphi^{\mathrm{QP}}_{i,\mathbf{k}} \middle| H_{KS} + \Sigma(\epsilon^{KS}_{i,\mathbf{k}}) - v_{xc} \middle| \varphi^{\mathrm{QP}}_{i,\mathbf{k}} \right\rangle\right] \tag{5}$$

where H_{KS} is the KS Hamiltonian and v_{xc} the exchange-correlation potential. It is worth mentioning that the exchange-correlation potential v_{xc} has to be subtracted from the expression for the QP energy since it is included in the Kohn-Sham Hamiltonian H_{KS}. The generalised gradient approximation PBEsol [17] is used as exchange-correlation functional. The excitonic effect was included in the calculation of the dielectric function by solving the BSE. We used 696 bands and 300 eV cutoff energy for the response function for the calculations.

3. Results and discussions

We start our study by performing a single shot $\mathrm{G_0W_0}$ calculation. Our results (see Table 1) show an underestimation of the fundamental bandgap despite the large number of empty bands included in the calculations. Aguilera et al. [18] in their study on the bandstructure and optical properties of $\mathrm{CuGaS_2}$ also found such a failure. They claimed that the underestimation is due to an important contribution of the d electrons at the upper most valence band with a strong hybridisation of the p orbitals that the $\mathrm{G_0W_0}$ is not capable of reproducing. Our previous study on the density of states of $\mathrm{AgAlX_2}$ [10] showed that the d and p orbitals from the Ag and chalcogenide (X) atoms respectively were also hybridised at the top of the valence band. Hence, it should also be at the essence of the failure of $\mathrm{G_0W_0}$. We therefore proceed by doing a semi self-consistent GW calculation ($\mathrm{GW_0}$) where screened Coulomb interaction $\mathrm{W_0}$ remains at the RPA level and the Green's function updated following the Dyson's equation [19]

$$G\left(\mathbf{r}', \mathbf{r}; E\right) = G_0\left(\mathbf{r}', \mathbf{r}; E\right) + \iint G_0\left(\mathbf{r}, \mathbf{r}_1; E\right) \Sigma\left(\mathbf{r}_1, \mathbf{r}_2; E\right) G\left(\mathbf{r}_2, \mathbf{r}'; E\right) d\mathbf{r}_1 d\mathbf{r}_2 \tag{6}$$

where $\mathrm{G_0}$ refers to the Green's function of the Kohn-Sham system. The bandgaps obtained from this approach are also summarised in Table 1. One can note the discrepancy with the $\mathrm{G_0W_0}$ and an agreement within 4% with the experimental results. Point to note here is that similar results in chalcopyrite based materials were obtained using the self-consistent Coulomb Hole Screened Exchange followed by $\mathrm{G_0W_0}$ (sc-COHSEX+$\mathrm{G_0W_0}$) [20, 21]. But this approach was not adopted in our study.

We present in Figure 2 the bandstructure from PBEsol and $\mathrm{GW_0}$ of $\mathrm{AgAlS_2}$. The two other compounds (not shown) have similar bandstructure. Both PBEsol and $\mathrm{GW_0}$ approximations show a direct bandgap at the Γ in accordance with experimental data [22]. The main difference between the bandstructure is the shift from 1.83 eV to 3.22 eV at the Γ. Note that, the bandgap does not only open because of the upshift of the conduction band as it seems to be the case in

Table 1. Bandgap from different methods, position of the exciton peak from BSE calculations and exciton binding energies of $AgAlX_2$. All the quantities are given in eV. * and * refer to Ref. [10] and Ref. [22] respectively.

	$AgAlS_2$	$AgAlSe_2$	$AgAlTe_2$
PBEsol*	1.83	1.11	1.03
G_0W_0	2.67	2.12	2.08
GW_0	3.22	2.46	2.22
EXP.**	3.13	2.55	2.27
First BSE peak	3.09	2.26	2.07
Binding energy	0.21	0.20	0.15

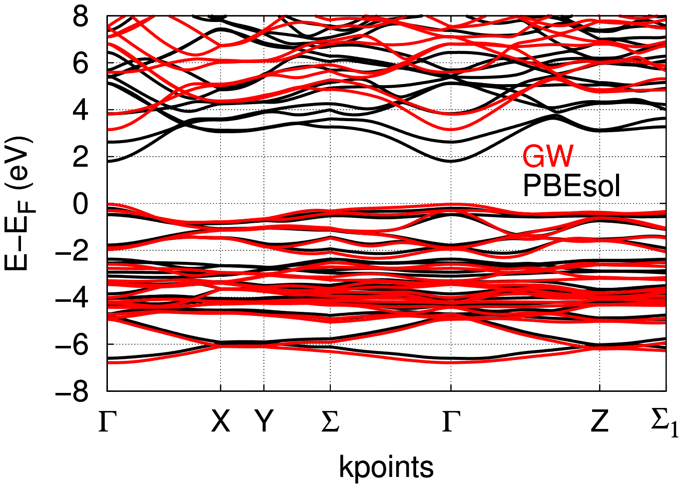

Figure 2. (Color online) Representative bandstrcture of $AgAlX_2$ from PBEsol and GW_0 calculation: Case of $AgAlS_2$.

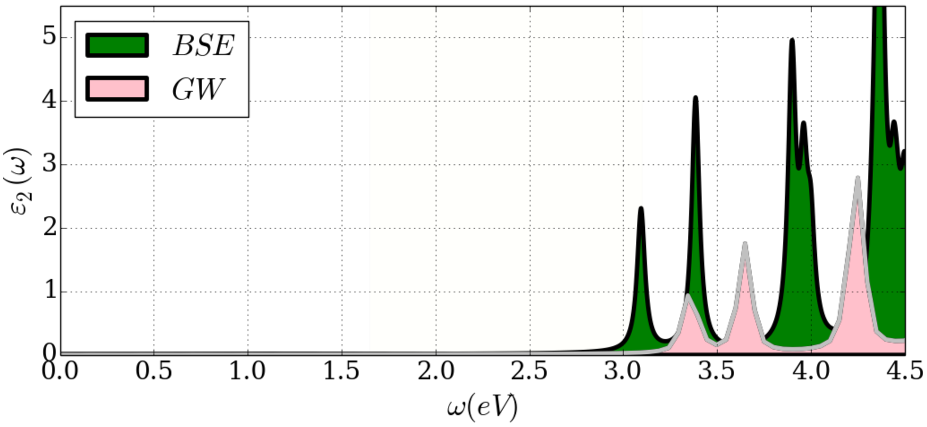

Figure 3. (Color online) $AlAgS_2$ imaginary part of the dielectric function (ε_2) from GW and BSE calculations.

Figure 2. Here the Fermi level is shifted to the upper valence band for the two approximations. Usually, the valence band also downshifts as a result of the cancellation of the delocalisation

error originated from the PBEsol wave function [10, 18]. We calculated the dielectric function in the frame work of many body pertubation theory at the GW and BSE level. We presented in Figure 3 the imaginary part of the dielectric ε_2 from the two approximations. Experimental data are not available for the sake of comparison. The onset of from GW lies at 3.19 eV, 2.44 eV, and 2.10 eV for $AgAlS_2$, $AgAlSe_2$ and $AgAlTe_2$ respectively. The values are in the range their respective bandgaps as seen in Table 1. However when the electron-hole interaction is incorporated in the calculation through the BSE, we observe a reduction of the onset with a peak appearing below the bandgap. Thus, attesting the presence of bound exciton in these materials. In direct bandgap materials, the binding energy of the exciton can easily be estimated. Here, electron and hole have the same group velocity ($v_{g_e}=v_{g_h}=\frac{1}{\hbar}\frac{\partial E}{\partial \mathbf{k}}$) since they appear at the same $\mathbf{k}$ vector [2]. In such condition the exciton energy can therefore be calculated as difference between the bandgap from GW and the position of the first excitonic peak from BSE. As summarised in Table 1, the excitonic binding energies range from 0.15 eV for $AgAlTe_2$ to 0.21 eV for $AgAlS_2$. Comparing the bandgaps and the excitonic binding energies, it turns out that the bigger the bandgap, the bigger the excitonic binding energy. Hence, the excitonic binding energy should be related to the nature of the chalcogenide atom in presence in the chalcopyrites.

4. Conclusion

We investigated the bandgap and optical spectra of the chalcopyrite materials $AgAlX_2$ by means of the many body perturbation theory at GW and BSE level. The single shot G_0W_0 method failed to predict correctly the bandgaps. Using the semi self-consistent GW_0, accurate bandgap within 4% agreement with the experimental data was obtained. The BSE calculation on top of the GW_0 allows us to predict the existence of exciton on these compounds. We also found that the excitonic energy was influenced by the size of the bandgap of the materials investigated.

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