Improved electronic structure prediction of chalcopyrite semiconductors from a semilocal density functional based on Pauli kinetic energy enhancement factor

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Received 1 June 2021, revised 26 September 2021
Accepted for publication 12 November 2021
Published 29 November 2021

Abstract
The correct treatment of \(d\) electrons is of prime importance in order to predict the electronic properties of the prototype chalcopyrite semiconductors. The effect of \(d\) states is linked with the anion displacement parameter \(u\), which in turn influences the bandgap of these systems. Semilocal exchange–correlation functionals which yield good structural properties of semiconductors and insulators often fail to predict reasonable \(u\) because of the underestimation of the bandgaps arising from the strong interplay between \(d\) electrons. In the present study, we show that the meta-generalized gradient approximation (meta-GGA) obtained from the cuspless hydrogen density (MGGAC) (2019 Phys. Rev. B 100 155140) performs in an improved manner in apprehending the key features of the electronic properties of chalcopyrites, and its bandgaps are comparative to that obtained using state-of-art hybrid methods. Moreover, the present assessment also shows the importance of the Pauli kinetic energy enhancement factor, \(\alpha = (\tau - \tau^W)/\tau^W\) in describing the \(d\) electrons in chalcopyrites. The present study strongly suggests that the MGGAC functional within semilocal approximations can be a better and preferred choice to study the chalcopyrites and other solid-state systems due to its superior performance and significantly low computational cost.

Keywords: Pauli kinetic energy, chalcopyrite semiconductors, correlation, hybrid functional, meta-GGA functional, band structures, density of states

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)
1. Introduction

In the last two decades, the $ABX_2$ [$A = I$ (Cu, Ag) or II (Be, Mg, Zn, Cd), $B = III$ (In, Ga, Al) or IV (Si, Ge, Sn), and $X = VI$ (S, Se, Te) or V (P, As)] chalcopyrite semiconductors based on the zinc-blend structure have emerged as highly promising advanced solar cells materials that allow the tweaking of macroscopic physical properties as function of microscopic chemical and structural degrees of freedoms [1–6]. In particular, Cu-based ternary and quaternary semiconductors and their alloys are now widely exploited as light absorbers in thin film solar cells [2, 7–10] and various non-linear optical devices [11–13]. Unfortunately, the theoretical predictions of the structural and electronic properties of Cu-based ternary or quaternary semiconductors remain far from being accurate because of the involvement of semicore $d$ or $f$ electrons, which play a decisive role in the determination of the properties of these materials [14, 15].

The straightforward applications of the Kohn–Sham (KS) density functional theory (DFT) [16] within the framework of the local density approximation (LDA) [17] or generalized gradient approximation (GGA) [18] often result in wrong predictions of bandgaps and band ordering as these suffer from the delocalization error [19]. Thus, the insufficiency and lack of appropriate theoretical approaches hinder the proper understanding of the inherent electronic properties of these systems. Although some plausible attempts have been made to correlate bandgap with the physical parameters in chalcopyrites such as CuInSe$_2$, CuInS$_2$ in various literature [14, 20], theoretical studies of such correlations and structural anomalies in relevant and important prototypes such as CuGaS$_2$, CuAlS$_2$, are still fragmentary.

Nevertheless, using hybrid functional schemes [21–28], improved bandgaps of chalcopyrites and other insulators have been reported. These schemes combine Hartree–Fock exchange with LDA/GGA correlation. Further, the semilocal exchange–correlation (XC) effect of strongly localized $d$-orbitals are treated at the mean-field level [29–32]. Although the hybrid density functionals have been applied and studied for a variety of systems, these schemes are often computationally expensive and prohibitive. On the other hand, the strong electron correlations and self-interaction related problems within semilocal approximation can be partially mitigated by the addition of separate Hubbard $U$ for the $d$ or $f$ localized electrons. This scheme may be expected to provide a qualitative assessment of the influence of the electronic correlations on the physical properties of a system [29, 30]. The DFT + $U$ method attempts to fix hybridization problems due to overly-delocalized orbitals and thereby has been recognized as a potent tactic to treat the strongly localized $d$ electrons in chalcopyrites [31, 32].

In addition to hybrid and DFT + $U$ schemes, the quasiparticle correction method within the many-body GW approximation is even more well-founded among different levels of theory which renders a relatively more accurate estimation of bandgaps [29, 30]. However, the calculations using the GW scheme are usually more computationally expensive than those using hybrid functionals.

Over the years, the search for efficient semilocal approaches which can predict the accurate electronic structure of systems, has become an important and fascinating research topic. The progress in semilocal density functionals in recent years shows that the accuracy of the material properties can be achieved from the advanced XC methods by satisfying more exact quantum mechanical constraints. The advent of these accurate semilocal density functionals [33–39] has also led to wide applicability of DFT in the condensed matter physics. In particular, the meta-GGA functionals have been found to be quite successful in overcoming the several challenges associated with the lower rung of functionals such as GGA, LDA etc [40–46].

Though the chalcopyrite systems have been studied using different functionals, the assessment, and performance of the advanced meta-GGA methods for these systems have not been reported to the best of our knowledge. Therefore, in this article, we investigate the performance of some advanced meta-GGA functionals such as (1) meta-GGA functional obtained from the cuspless hydrogen density (MGGAC) [35, 47], (2) strongly constrained and appropriately normed (SCAN) semilocal functional [33], and (3) Tao–Mo (TM) [34] semilocal functional. We assess the performance of these functionals in the study of structural and electronic properties, bandgaps, and enthalpy formation energies of chalcopyrite systems. It may be noted that both SCAN and MGGAC functionals have been found to be quite successful in overcoming the several drawbacks of the GGA functional such as severe underestimation of the bandgaps of the bulk and layered solids [48, 49]. In particular, our study shows that the MGGAC functional is quite advantageous to study the chalcopyrite semiconductors as it is computationally inexpensive and exhibits good performance. The aforementioned meta-GGA schemes span the third rung of the Jacob ladder of the XC approximation [50] owing to important features associated with them.

This paper is organized as follows. The methodologies used in this work are discussed in section 2. The structural properties, electronic properties, and enthalpy formation energies are discussed in sections 2–4 respectively. The results and the functional performances are further analyzed in section 6. Finally, the conclusions are presented in section 6.

2. Background of methodologies

In the present study, the XC contributions are included using semilocal XC functional schemes such as PBE [18], SCAN [33], MGGAC [35], and TM [34]. Unlike GGAs, the meta-GGA functionals SCAN, MGGAC, and TM are implemented in generalized KS (gKS) [51, 52] scheme because of their dependence on KS orbitals. Usually, the meta-GGAs are quite reliable as compared to GGAs as they can recognize and describe covalent, metallic, and non-covalent interactions [53, 54].

In general, the meta-GGA XC functional which depends on the density ($\rho$), gradient of density ($\nabla \rho$), and KS kinetic energy
density \((\tau(\mathbf{r}) = 4\sum_i |\nabla \psi_i|^2)\) can be presented as:

\[
E_{xc}[\rho, \tau] = \int d^3r \rho(\mathbf{r}) \varepsilon_{xc}^{1DA}(\rho, \rho^*, \nabla \rho, \nabla \rho^*, \tau, \tau^*),
\]

where \(\varepsilon_{xc}^{1DA}\) is the exchange energy density in uniform electron gas approximation and \(F_{xc}\) is the XC enhancement factor. In case of construction of SCAN [33] and MGGAC [35] functionals, one of the main ingredients in \(F_{xc}\) is the Pauli kinetic enhancement factor \(\alpha = (\tau - \tau^W)/\tau^{unif}\), where \(\tau^W = [\nabla \rho]/[8\rho]\) is the von Weizsäcker kinetic energy density, \(\tau^{unif} = (3\pi^2)^{2/3} \rho^{5/3}\) is the Thomas–Fermi kinetic energy density. It may be noted that the exchange of the SCAN functional uses both the \(\alpha\) and \(p = s = \frac{\sqrt{\rho^X}}{\rho_0 k_F}\) (with \(k_F = (3\pi^2\rho)^{1/3}\) is the Fermi wave vector) [33], while the exchange in MGGAC uses only \(\alpha\) [35]. The MGGAC exchange functional is constructed using the Becke–Roussel approach together with the cupsole hydrogen exchange hole density model, where the \(\alpha\) only parameter is used to model the exchange hole. The important difference between the SCAN and MGGAC for solid is that SCAN respects uniform electron gas as well as slowly varying fourth order gradient expansion, while MGGAC respects only the uniform electron gas norm. However, both SCAN and MGGAC respect the tightened bound of the exchange \((E_{xc} \leq 1.174 [33, 55])\) and possess negative slope with respect to \(\alpha(\partial E_{xc}/\partial \alpha < 0)\), important for the bandgap improvement in semilocal level [35, 48, 56, 57]. In section 6, we discuss the exchange enhancement factor \((F_{xc})\) and relevant features of both the functionals for solids, in details. For more details of the SCAN and MGGAC construction can be found in appendix and references [33, 35], respectively.

Another reliable meta-GGA semilocal functional was proposed by TM [34] which has been quite successful at providing reasonably accurate estimates of various quantum chemical and solid-state properties [34, 40, 58–61]. The TM and its revised version revTM [40] functionals, use both the meta-GGA ingredients i.e., \(z = \tau^W/\tau\) and \(\alpha\). However, these functionals satisfy looser bound of exchange [62–64] and suffer from the order-of-limit problem [37, 39].

In addition to aforementioned functionals, we have also used the hybrid functional HSE06 scheme propounded by Hyde, Scuseria, and Ernzerhof [21–24]. The HSE06 scheme is based on the inclusion of fixed amount of Hartree–Fock exchange. Briefly, the XC energy of the HSE06 functional is given by [21–24],

\[
E_{xc}^{\text{HSE}}(\alpha, \omega) = \alpha E_{xc}^{\text{HF,SR}}(\omega) + (1 - \alpha) E_{xc}^{\text{PBE,SR}}(\omega) + E_{xc}^{\text{PBE,LR}}(\omega) + E_{xc}^{\text{HSE}}.
\]

Here, the XC energy \(E_{xc}\) is range separated with the use of a screening potential. The parameter \(\alpha\) describes the fraction of the Fock exchange while \(\omega\) calibrates the range of the interaction. We have used the conventional \(\alpha = 0.25\) and \(\omega = 0.11\)Bohr\(^{-1}\) in computations with HSE06 [23, 24]. It may be noted that other variants of hybrid density functionals [25–28] have also been proposed.

In this work, we report the relative performance of HSE06, MGGAC, PBE, SCAN, and TM functionals by comparing the computed estimates of the structural parameters and properties of the Cu based chalcopyrite systems. In case of other systems, the structural properties are calculated only using MGGAC, PBE, SCAN, and TM functionals and the results are reported in supplementary material (https://stacks.iop.org/JPCM/34/075501/mmedia). Since, the main focus of the present work is the study of Cu based chalcopyrites, we do not relax the structures of Ag, Be, Cd, Mg, and Zn based chalcopyrites using HSE06 scheme, which is quite expensive computationally. For these systems the structures are optimized and lattice constants are computed using PBE (GGA) scheme.

In table 1, we list the I–III–VI\(_2\) and II–IV–V\(_2\) group systems which are considered in present work.

### 3. Structural properties

The \(ABX_2\) chalcopyrite compounds of composition I–III–VI\(_2\) or II–IV–V\(_2\) are iso-electronic analogues of the II–VI or III–V binary semiconductors, respectively [65]. The chalcopyrite lattice structure adopts the \(D_{4h}^{12}\) (No. 122) space group symmetry. The structure is a cation mutated super-structure of the cubic zinc-blende structure (\(T\_d\)), in which each of the two cations \((\text{A, B})\) are tetrahedrally coordinated by four anions \((\text{X})\), and each anion is coordinated by two \(\text{A}\) and two \(\text{B}\) cations [66]. The chalcopyrite structure can be described accurately by three structural parameters: (i) lattice constant \(a\), (ii) the tetragonal ratio \(\eta = c/2a \neq 1\), where \(c\) is the lattice constant in the \(z\)-direction, and (iii) the anion displacement parameter, \(u\). In general, \(\text{A}–\text{X}\) and \(\text{B}–\text{X}\) bond lengths, denoted by \(r_{\text{A}–\text{X}}\) and \(r_{\text{B}–\text{X}}\) (see figure 1), respectively, are not equal. In table 2, we present

### Table 1. I–III–VI\(_2\) and I–IV–V\(_2\) chalcopyrite semiconductor systems considered in this paper.

| Group | Systems |
|-------|---------|
| I–III–VI\(_2\) | CuInS\(_2\), CuInSe\(_2\), CuGaS\(_2\), CuGaSe\(_2\), CuAlS\(_2\), CuAlSe\(_2\), CuAlTe\(_2\), CuGaTe\(_2\), CuInTe\(_2\), AgAlS\(_2\), AgAlSe\(_2\), AgAlTe\(_2\), AgGaS\(_2\), AgGaSe\(_2\), AgGaTe\(_2\), AgInS\(_2\), AgInSe\(_2\), AgInTe\(_2\) |
| II–IV–V\(_2\) | BeSiP\(_2\), BeSiAs\(_2\), BeGeP\(_2\), BeGeAs\(_2\), BeSnP\(_2\), BeSnAs\(_2\), MgSiP\(_2\), MgSiAs\(_2\), MgGeP\(_2\), MgGeAs\(_2\), MgSnP\(_2\), MgSnAs\(_2\), ZnSiP\(_2\), ZnSiAs\(_2\), ZnGeP\(_2\), ZnGeAs\(_2\), ZnSnP\(_2\), ZnSnAs\(_2\), CdSiP\(_2\), CdSiAs\(_2\), CdGeP\(_2\), CdGeAs\(_2\), CdSnP\(_2\), CdSnAs\(_2\) |

### Table 2. Structural properties of Cu based chalcopyrites.

| Parameter | Value |
|-----------|-------|
| \(a\) | 0.5431 (CuInS\(_2\)) |
| \(\eta\) | 0.53 (CuInS\(_2\)) |
| \(u\) | 0.10 (CuInS\(_2\)) |

...
for details of the notations of the structural parameters of the semiconductor. The lattice vectors of the unit cell are \( \mathbf{u} \) length results in a tetragonal distortion parameter (\( \eta \)).

One may also note that the distortion parameter (\( u \)) describes the re-positioning of the anions in the \( x-y \) plane, sensitively influence the electronic bandgap of these materials [66].

The lattice constants (\( a \) and \( c \)), distortion parameter (\( u \)), and tetragonal ratio (\( \eta \)) of Cu based chalcopyrites computed using different XC schemes are listed in table S1 of the supporting information. The trend seen in the results obtained from semilocal functionals may be explained from the perspective of computed electronic properties.

In general, the computed lattice constants of solids obtained from PBE-like GGA XC functionals are reasonably accurate. However, the PBE–GGA computed lattice constants are generally found slightly overestimated because of the lack of slowly varying density correction, which is taken care of in its solid-state version PBEsol [67, 68]. Furthermore, the higher rung of functionals i.e., meta-GGAs are generally better than PBE–GGA functional for estimating the lattice constants. For instance, the SCAN meta-GGA performs reasonably well in predicting the lattice constants of different solids.

In figure 2, we show the relative error (in %) in parameters \( a \), \( c \), \( u \), and \( \eta \) of the Cu based chalcopyrites as obtained from different methods. As can be seen, the HSE06 performs better than other methods in predicting \( a \), \( c \), \( u \), and \( \eta \). However, within semilocal methods, the SCAN performs better than MGGAC and PBE for \( a \) and \( c \), while MGGAC performs better than SCAN for \( u \). Physically, this improvement in \( u \) obtained using MGGAC comes from bond lengths \( r_{\text{A-B-X}} \), which are also connected to the improved description of the Cu \( d \)-states. It may also be seen in figure 2 that the \( u \) parameters obtained from MGGAC are very close to those obtained using HSE06, indicates Cu–\( d \) states is well treated by both the MGGAC and HSE06 methods. We will further discuss this point in more detail in section 4. Further, in most cases, the MGGAC underestimates \( a \) and \( c \) parameters as compared to experimental and SCAN values. It may also be noted that for the tetragonal ratio (\( \eta \)), the MGGAC performs in a more balanced way than SCAN due to its tendency to underestimate both \( a \) and \( c \).

### Table 2. The fractional coordinates of the primitive unit cell of \( \text{ABX}_2 \) chalcopyrite semiconductors.

| Atoms | Coordinates |
|-------|-------------|
| \( A_1 \) | (0, 0, 0) |
| \( A_2 \) | (0.25, 0.25, 0.50) |
| \( A_3 \) | (0.50, 0.50, 0.00) |
| \( B_1 \) | (0.25, 0.25, 0.50) |
| \( X_1 \) | (0.25 + x, 0.125, 0.25) |
| \( X_2 \) | (0.25 + x, -0.375, 0.25) |
| \( X_3 \) | (-0.125, 0.25 + x, -0.25) |
| \( X_4 \) | (0.375, -x, -0.25) |

4. Electronic properties

The phenomenological treatment of \( p-d \) interaction in chalcopyrite systems depends on how good are the various approximations of XC for the \( d \)-electron of Cu. For instance, the LDA (or GGA) based methods tend to delocalize \( d \)-electrons which results in underestimation of \( p-d \) hybridization [14, 32].

Further, a significant shortcoming in standard DFT based methods is the presence of inherent self-interaction error (SIE) [14, 69]. In the case of chalcopyrites, this shortcoming results in shallow \( d \) states description for the cations, and in general, the absence of derivative discontinuity in the KS bandgap which is defined as the difference between eigenvalues of the CBM and VBM. As a consequence, the theoretical bandgap is severely underestimated as compared to the experimental bandgap (the difference between the ionization potential and electron affinity). The absence of the LDA/GGA computed bandgaps in some of the chalcopyrites and other material...
systems has been attributed to large ratio of SIE in exchange functionals. Hybrid functionals eliminate some amount of SIE and improve the performance and estimates of bandgaps [14, 69].

To evaluate the relative performances of different functionals, we first discuss the band structures as obtained from HSE06, MGGAC, PBE, and SCAN functionals. Following this, the density of states (DOS) and charge density will be analyzed and discussed. We have not included the performance of the TM functional as its performance is known to lie in between that of PBE and SCAN functionals. The bandgap values computed using TM functional are shown in table S1 of the supporting information. Overall, the performance of TM functional is found to qualitatively similar to that of the PBE functional.

In order to analyze the performance of different functionals, the band structures, charge density, and DOS of CuInS2 are computed using the HSE06, MGGAC, PBE, and SCAN functionals. In supporting information, we also present and analyze the electronic properties of CuInSe2. These two systems are particularly chosen since their electronic band structures, DOS, and charge densities are quite distinct from one another. Further, both these systems are known to exhibit strong interplay between structure and electronic properties [14].

4.1. Band structures

The bandgaps of different Cu-based chalcopyrite systems as obtained from different methods are shown in table S1 of the supporting information. As can be seen, the bandgaps computed using hybrid HSE06 method, are in close agreement with the experimental values. Further, among the semilocal functionals, MGGAC performs in a significantly better way than others, as it opens the bandgaps in CuInS2, CuInSe2, and CuInTe2. The bandgaps computed using SCAN, TM and PBE are found to be severely underestimated and thus these methods perform poorly.

Figure 3 shows the band structure of CuInS2 along high-symmetry directions in Brillouin zones (BZ). As can be seen, the bandgap computed using MGGAC is improved significantly and is quite close to that obtained using HSE06. The SCAN method though opens the bandgap for CuInS2, its magnitude comes out to be very small. The use of PBE results in zero bandgap.

It may be noted that the HSE06 functional has more often been used to study chalcopyrites as compared to other global hybrid functionals such as PBE0, because of the presence of screened Coulomb interaction, which reduces the computational cost significantly.

As can be seen in table S1 of the supporting information, excellent estimates of electronic properties are obtained from hybrid functional HSE06 with its default value of 25% fraction of Fock exchange.

Interestingly, among considered semilocal approximations, the MGGAC functional performs quite closely to HSE06 for most semiconductors [65]. A comparative plot of theoretical and experimental bandgaps is shown in figure 4 which clearly indicates that bandgap estimates obtained using MGGAC
are more accurate than those obtained using other semilocal functionals.

Based on the comparison of the results presented in this work with those in references [65, 71] for I–III–VI2 and II–IV–V2 chalcopyrite semiconductors, the performances of different functionals are twofold:

- **I–III–VI2 semiconductors.** The direct bandgaps are found to be most severely underestimated when computed using semilocal functionals like PBE, SCAN, and TM. For Ag based chalcopyrites too, a similar trend is observed. A consistent improvement in the bandgap magnitudes is observed, when computed using the MGGAC functional. This is expected due to the improvement in the description of p–d hybridization discussed earlier. In the case of CuAlTe2, the bandgap computed using MGGAC and HSE06 is found to be overestimated whereas PBE–GGA estimated bandgaps are closer agreement with the experiment. Further, for all the Te based systems, MGGAC overestimates the bandgaps as compared to HSE06. In particular, the MGGAC overestimates the bandgaps of CuAlTe2 and AgInTe2 by a large margin. Nevertheless, for other Te based systems, the performance of MGGAC is reasonably good with bandgap estimates closer to the experiments as compared to other semilocal methods.

- **II–IV–V2 semiconductors.** The computed PBE bandgaps are found to be in excellent agreement with the experiments [65] and earlier reported theoretical results [65]. The MGGAC computed bandgaps are found to be comparable with HSE06 computed bandgaps. However, both MGGAC and HSE06 overestimate the bandgaps for BeSiAs2, BeSiP2, CdGeAs2, CdSnP2. In case of these semiconductors, the SCAN functional performs well as compared to other semilocal (MGGAC, TM, GGA) methods (see reference [65] for details). As can be seen in figure 4, the MGGAC computed bandgaps are overestimated by more than 0.5 eV in case of CdSnAs2, CdGeAs2, ZnSnAs2, BeGeP2, BeSiAs2, and BeSiP2. Further the chalcopyrite semiconductors containing Be and Cd, the HSE06 bandgaps are comparable to the GW0 bandgaps as reported in reference [65]. However, for semiconductors containing Mg and Zn, all functionals estimate bandgaps close to the experimental values except for some semiconductors containing Zn.

Overall, it may be concluded from the calculations and above discussions that the bandgaps estimated by semilocal MGGAC are comparable to those estimated by hybrid functional HSE06 to a great extent with a minimal deviation (see figure 4).

Further, to visualize the variation of the bandgap with the distortion parameter (u), in figure 5 we plot the bandgaps of CuInS2 and CuInSe2 computed using different functionals as a function of u. One may note that the u parameter depends on the inverse of the square of the lattice parameter a via equation (3). Here, we consider the experimental lattice parameters (a = 5.523 Å and c = 11.12 Å for CuInS2 [72]; a = 5.78 Å and c = 11.62 Å for CuInSe2 [73]) for the calculation of u vs bandgap variation. The atomic coordinates are taken from the reference [74]. As given in table 2 (also in reference [74]) for a fixed values of x we have the fixed values of rA−X and rB−X. Here, we varied the parameter x within the range (0.20–0.25) that encompasses u within the experiment range. As can be seen, the bandgap increases almost linearly with u in range 0.2 < u < 0.25. For both the chalcopyrite systems, HSE06 bandgaps are improved over MGGAC bandgaps, which in turn are improved over SCAN bandgaps. For CuInS2 and CuInSe2, the SCAN bandgap opens for u > 0.2 and u > 0.22, respectively. As can be seen, the MGGAC and HSE06 bandgaps are finite for all values of u (in range shown) for both the chalcopyrites. The difference in the bandgaps...
Figure 4. Experimental versus theoretical bandgaps of I–III–VI$_2$ (upper panel) and II–IV–V$_2$ (lower panel) semiconductors as obtained from different methods. The values within dotted lines indicate the bandgaps within the error of ±0.5 eV of the experimental values. The experimental bandgaps of I–III–VI$_2$ are taken from reference [70] and II–IV–V$_2$ from reference [65].

obtained from different methods is expected due to strong interplay between the structure parameter $u$ and the hybridization of the $p$–$d$ orbitals [14]. We will revisit this point later in this paper.

In supporting information, we also discuss and analyze another chalcopyrite system CuInSe$_2$. As can be seen in supporting information, the MGGAC and HSE06 open the bandgap of this system, whereas it remains closed for PBE and SCAN functionals.

4.2. Charge densities

The charge density contours for CuInS$_2$ are shown in figure 6, which reveals the presence of both ionic and covalent bonds. The mixed bonding is seen irrespective of the XC functionals used. As can be seen, the electron density is more enhanced toward the side of the S-atom than that of the In-atom, which indicates that the In–S bond is more ionic. Further, the even distribution of the electron density in the case of the Cu–S bond indicates that the bonding is more covalent. The arrow labeled in the Cu–S bond (see figure 6) indicates the isosurface value. The size of the arrow is larger in the case of PBE and SCAN than the one for MGGAC and HSE06, which follows the bandgap enlargement rule as well as the differences in the $u$ parameter. The arrow size is related to the corresponding bond length and varying degrees of $p$–$d$ hybridization for these chalcopyrites. From table S1 of the supporting information, it can be seen that the calculated $u$ parameter, which depends on the bond length of Cu–S, is less for PBE and SCAN (0.218) than that for MGGAC (0.224) and HSE (0.226). The greater the isosurface arrow, the lower the atomic distance is, which indicates greater $p$–$d$ repulsion and thereby smaller bandgap. It is generally understood that methods (within the DFT framework) that do not take into account the self-energy correction, underestimate the bandgaps. However, in the case of MGGAC, the presence of internal screened coulomb energy $U$ results in bandgap estimates which are comparable to bandgaps obtained using hybrid functionals as well as state-of-the-art many-body perturbation technique. We will revisit and elaborate more on this point in a later section.

4.3. Density of states

The electronic structures of all chalcopyrite semiconductors are qualitatively similar. In the following, we present and discuss the electronic structure of CuInS$_2$. The electronic structure of CuInSe$_2$ is presented in the supporting information. The total DOS and partial DOS as computed with different XC functionals are shown in figure 7 and figure S3 of supporting information for CuInS$_2$ and CuInSe$_2$, respectively. As can be seen, the contribution from the valence Cu–4$s$ and Cu–3$p$ states near the VBM is negligible as compared to Cu–3$d$ states. The valence band region exhibits two main groups: up to around $-2$ eV from the VBM, the region is mainly composed of $p$ and $d$ states with primary contribution from Cu–3$d$ states. The deeper valence band in the energy range $-2$ eV to 0 eV results from strong hybridization of Cu–3$d$ and S–3$p$ states. The conduction band region is contributed by In–5$p$ and S–3$p$ states along with a minor contribution of Cu–3$d$ states. The dispersion of the valence and conduction bands are found to be almost the same for all semilocal functionals (PBE, SCAN, and MGGAC) with an exception that the band width (energy between the highest and lowest allowed levels), for which the MGGAC shows a wider range than that for PBE and SCAN.

To encapsulate the behavior of the VBM and CBM, we show the DOS plot for the respective functionals in the right panel of figure 7, in the energy range $-0.5$ eV $< (E − E_F) < 0.0$ eV. The enhancement in the bandwidth is evident in case of MGGAC as compared to that for SCAN and PBE semilocal functionals. In case of MGGAC, the CBM shifts to the higher energy level resulting in the opening of the bandgap. This may be related to the nature of the MGGAC enhancement.
factor as discussed in section 6. However, in case of PBE and SCAN, the 3d non-bonding region lies a little bit of the higher side on the energy scale, which results in the reduction of the bandgap as compared to that in case of MGGAC and HSE06. For HSE06, the relative bandgap enhancement compared to that for semilocal functionals happens because of the inclusion of the non-local HF exchange, which reduces the repulsion between Cu–3d and S–4p states and thereby results in the bandgap opening [69]. Importantly, the bandgap enlargement in the case of HSE06 as compared to other semilocal functionals (MGGAC, SCAN, TM, and PBE) may be attributed to (i) enlargement of bandwidth and the orbital spacing which directly influences the bandgap and (ii) the shift of non-bonding 3d states downward which reduce the p–d repulsion.

Generally, within semilocal methods the performance of the MGGAC XC functional is quite encouraging and the same trend of results also follows for all I–III–VI2 semiconductors as the valence band maximum is influenced by the 4d states of I-group atoms. On the other hand, in the case of II–IV–V2 semiconductors, the bandgap character is not influenced by d states of II-group atoms, as those are highly localized and contribute to valence bands far from VBM [65].

In supporting information, we show the DOS and projected DOS for CuInSe2. In this case also, the opening of the bandgap can be explained similarly as discussed for CuInS2. The reduction in repulsion between Cu–3d and Se–4p states is responsible for the opening of bandgap. For MGGAC, this repulsion reduces at the VBM and the CBM is shifted toward the higher energy. This results in the opening of the bandgap more than that in case of SCAN.

5. Formation enthalpies

We now discuss the enthalpy formation energies of chalcopyrites and competing binary phases of Cu–Se, computed using different meta-GGA functionals. In the thermodynamical framework, the enthalpy formalism energy per atom for a chalcopyrite system is defined as:

$$\Delta H = \frac{\varepsilon_{\text{system}} - \sum_i n_i \varepsilon_i}{m},$$  \hspace{1cm} (4)

where $\varepsilon_{\text{system}}$ is the energy of the chalcopyrite system, $n_i$ and $\varepsilon_i$ are the number and energy of the $i$th constituent in the system, and $m$ is the total number of atoms in the system. All energies are calculated in their stable solid form. A negative (positive) enthalpy formation energy indicates that the system is stable (unstable).

The table 3 shows the formation enthalpies of CuInSe2 and AgInSe2 computed using different functionals. For these solids, the experimental formation enthalpies have been reported in reference [75]. The PBE and HSE06 results in table 3 are taken from reference [69]. As can be seen, the PBE underestimates the formation energies of both the
Figure 7. DOS for CuInS$_2$ calculated from different methods. Right panel shows the DOS in energy range $-0.5 \text{ eV} < (E - E_F) < 0.0 \text{ eV}$. The Fermi energy ($E_F$) is set to 0 eV and is same as $E_{\text{VBM}}$.

Table 3. Enthalpy formation energies (eV/f.u.) of CuInSe$_2$ and AgInSe$_2$ as obtained from different methods. PBE and HSE06 values are taken from ref. [69]. Numbers in the parentheses represent the percentage deviation.

| Solids    | PBE     | SCAN    | TM       | MGGAC | HSE06 | Expt. [75] |
|-----------|---------|---------|----------|-------|-------|------------|
| CuInSe$_2$| –1.78   | –2.02   | –1.39    | –2.35 | –2.40 | –2.77      |
|           | [–35.6] | [–27.1] | [–49.5]  | [–15.1]| [–13.4]|            |
| AgInSe$_2$| –1.71   | –1.90   | –1.26    | –2.25 | –2.22 | –2.51      |
|           | [–31.8] | [–24.3] | [–49.5]  | [–10.3]| [–11.4]|            |

The SCAN method improves the enthalpy estimates as compared to those obtained using PBE. The SCAN values are underestimated by less than 30%. Further, table 3 shows that the formation enthalpy estimates are improved significantly with the use of MGGAC functional, which performs as accurately as hybrid HSE06 functional and with computational cost much lesser than that of HSE06.

It may be noted that the PBE functional does not properly describe different bondings such as metallic, covalent, and/or ionic in different solids [76–78]. The bonding nature is much better described by meta-GGA [53] functionals, which is reflected in the performance of SCAN and MGGAC. This is because the meta-GGA functionals are generally better than GGA in describing the covalent, metallic, and non-covalent interactions [53, 54].

Incidentally, the TM functional fails drastically in providing reasonable estimates of formation energies as it exhibits error more than PBE. This failure of the TM may be attributed to its order-of-limit problems, which is important for estimating the formation of enthalpies [37]. In case of the HSE06, the good performance is due to reasonably correct description of the $d$-states of Cu and Ag atoms.

Further the formation enthalpy of CuInSe$_2$ computed using MGGAC and HSE06 is in close agreement with the experiments, which is expected due to improved estimates of energy eigenvalues, In–$4d$ states, band structure and DOS (see supporting material).

Next, we assess the functionals performance for the several competing candidate binary phases of Cu–Se. The formation enthalpies per atom for different Cu–Se phases are plotted in figure 8. As expected, PBE underbinds the formation enthalpies, with a positive $\Delta H$ for Cu$_2$Se compound. The HSE06 estimated formation energies are found to be in closest agreement with the experimental values. The SCAN and MGGAC perform closely, albeit SCAN performance slightly better than MGGAC in all cases. This may be partially attributed to the metallic character of the CuSe, CuSe$_2$, and Cu$_3$Se$_2$, which is better described by the SCAN functional as it takes into account the slowly varying second/fourth order terms in the gradient expansion of the exchange. Furthermore, the SCAN correlation is free from spurious one-electron self-interaction which tends to improve the formation enthalpy estimates. Nevertheless, both SCAN and MGGAC formation energies are negative (including semiconductor Cu$_2$Se) and therefore are much better estimated as compared to those by PBE–GGA. Figure 8 also shows that the performance of the TM functional is quite poor for all the binary phases of Cu–Se. As can be seen, the TM functional incorrectly predicts CuSe$_2$...
and Cu$_3$Se$_2$ as unstable. This significantly poor performance of the TM functional in providing formation enthalpy estimates may be attributed to its order-of-limit problem [37].

6. Relation between performance and mathematical features of functionals

Next, we discuss the plausible reasons behind improvement in performance of MGGAC functional over GGA or SCAN methods. To analyze the results, let us consider the behavior of the exchange enhancement factor ($F_\alpha$) of SCAN and MGGAC functionals. It also may be noted that the gKS potential of the meta-GGA functionals is related to the derivative discontinuity ($\Delta_x$), which is connected with the localized $d$- or $f$-states, often encountered in the chalcopyrite systems. In figure 9, we plot the $F_\alpha$ as a function of meta-GGA ingredient $\alpha$ for different values of reduced density gradient $s$. The MGGAC $F_\alpha$ does not depend on $s$ and is much smoother than that for SCAN. Also, its slope $\partial F_\alpha/\partial \alpha$ is more negative in the energetically relevant regions of solids ($0 < s \leq 1$) resulting in inclusion of more $\Delta_x(\propto \partial F_\alpha/\partial \alpha)$. In fact the negative slope $\partial F_\alpha/\partial \alpha < 0$ is also connected to the ultra-nonlocality effect which results in polarization effect in solids [56]. Furthermore, the $\alpha$ is also interpreted as the measure of the well-known electron localization factor via the exchange energy, similar to the exact exchange (EXX) [56]. Importantly, because of the more enhanced $\alpha$ dependent and $\partial F_\alpha/\partial \alpha < 0$, some amount of inherent on-site Coulomb interaction ($U$) is included in the orbital energies and eigenvalues corresponding to MGGAC functional. The on-site Coulomb interaction ($U$) is important to treat the highly delocalized band states of rare-earth elements and strongly localized late transition metal elements. It may be noted that the SCAN functional also includes some amount of inherent $U$ [79] which results in improved performances as compared to PBE $+ U$ and SCAN-no-$U$ [80–84]. However, because of the more realistic and enhanced $\partial F_\alpha/\partial \alpha < 0$, the MGGAC is a slightly better in treating the $d$- and $f$-orbitals. This actually results improved performance for chalcopyrite systems and results are often close to the HSE06, where the 25% HF exact exchange is used to treat the strongly localized $d$-bands. It may be noted that along with the localized $d$-states, the $s$- and $p$-states are also well described by the MGGAC. From the structure of the DOS plot shown earlier (also see figure 7 and figure S3 of supporting information) as obtained using the MGGAC functional, one can readily observe that it treats the non-bonded Cu–3$d$ and hybridized 3$d$–4$p$ (of Cu and Se) states in a bit better way than PBE and SCAN functionals. This results in the reduction of strong localization effect of 3$d$ states, which in turn opens a sizable bandgap between occupied and unoccupied sub-bands. Also, the success and overall improvement of MGGAC functional vis-a-vis LDA, GGA, and SCAN functionals are retained for other chalcopyrite systems discussed in this article.

7. Concluding remarks

The comparative assessment of the structural properties, electronic properties, and formation energies of Cu-based multinary semiconductors is performed using GGA, meta-GGA, and hybrid density functionals within the framework of DFT. In particular, we assess the performances of SCAN, TM, and MGGAC meta-GGA functionals, which are very recent and reasonably successful XC functionals in predicting various solid-state properties. To assess the structural properties, the tetragonal distortion ($\eta$) and/or anion displacement ($u$) are first computed from different functionals. The PBE–GGA functional is found to be inadequate to estimate accurately the electronic structures and associated properties of Cu-based chalcopyrite systems due to its inability to describe the intrinsic localization and/or strong correlation of the $d$ electrons.

Our results for PBE and HSE06 are in agreement with earlier reported studies, wherein it was shown that the HSE06 generally improves over PBE because of less delocalization error, which in turn improves the bandgap, and DOS estimates. The estimates of various quantities computed using MGGAC and SCAN are found to be significantly improved
as compared to those obtained using GGA. Further, the performances of MGGAC is found to be encouraging among meta-GGA functionals and quite close to that of the HSE06 in providing the estimates of \( \eta, u \), band structures, and enthalpy formation energies of Cu-based multinary semiconductors. The reasonably improved and better performance of MGGAC is attributed to its a better description of strongly localized d electrons in these systems.

In addition, the performance of the aforementioned functionals is also explored for several competing candidate binary phases of Cu–Se. For these phases also, the MGGAC is found to be quite accurate. However, the SCAN functional performs slightly better than MGGAC for binary phases. The performance of TM functional is found to be poor in comparison to other meta-GGA functionals possibly due to its order of limit problem. Overall, our results strongly suggest that MGGAC (meta-GGA) functional can be highly useful for studying Cu-based multinary semiconductors as well as other systems with d-electrons, due to its good performance and low computational cost. Recently, a revised form of the MGGAC functional is also proposed [47], which can be worthy for further study of the chalcopyrite properties.

8. Computational details

The density functional calculations are performed using the plane-wave formalism as implemented in Vienna ab initio simulation package code [85–88]. The core-valence electron interaction is approximated using the projected augmented wave method [89]. A kinetic energy cutoff of 600 eV is used to expand the KS single-particle orbitals on a plane-wave basis. The BZs are sampled using Monkhorst-Pack 9 \( \times \) 9 \( \times \) 9 \( k \)-points grid for atomic relaxations and 17 \( \times \) 17 \( \times \) 17 grid for the DOS calculations. The electronic energies are allowed to converge up to 10^{-6} eV (or less) to achieve self-consistency in the calculations. The atomic relaxations are performed till the Hellmann–Feynman forces on atoms are reduced to less than 0.01 eV \( \text{Å}^{-1} \).

Acknowledgments

AG would like to thank INSPIRE fellowship, DST, India for financial support. SJ would like to thank NISER, Bhubaneswar for partial financial support. Calculations are performed high performance computing (HPC) clusters of IITH, Hyderabad. Part of calculations are also performed in the KALINGA and NISER-DFT high performance computing (HPC) clusters of NISER, Bhubaneswar.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Appendix A. Brief overview of SCAN and MGGAC functionals

A.1. SCAN

The exchange enhancement factor of the SCAN functional is given by [33].

\[
F_x^{\text{SCAN}}(s, \alpha) = h_1(x, \alpha) + f_x(\alpha)[1.174 - h_1(x, \alpha)]g_x(s),
\]

(A.1)

where \( g_x(s) = 1 - e^{-a_1 s^{1/2}} \), \( f_x(\alpha) = e^{c_1 \alpha / (1-\alpha)} \theta(1 - \alpha) \), \( h_1(x, \alpha) = 1 + \frac{h_1}{k_{1+}} \)

\[
x = \frac{\mu g_e s^2}{\mu g_e} + b(1 - \alpha) e^{-b_2(1-\alpha)^2}.
\]

(A.2)

The constants \( a_1 = 4.9479, \mu g_e = 10/81, b_2 = \sqrt{5913/405000}, b_1 = (511/13500)/(2b_1), b_3 = 0.5, b_4 = \mu g_e/k_{1-} - 1606/18225 - b_1^2, c_{1x} = 0.667, c_{2x} = 0.8, d_{1x} = 1.24 \) and \( k_1 = 0.065 \), are determined by satisfying known constraints or norms. The correlation part of SCAN is as follows [33].

\[
E_c^{\text{SCAN}} = \int \text{d}^3 \rho \left[ \epsilon^{x_0}_c + f_c(\alpha) \left( \epsilon^{x_1}_c - \epsilon^{x_0}_c \right) \right].
\]

(A.3)

where the interpolation function \( f_c(\alpha) = e^{c_1 \alpha / (1-\alpha)} \theta(1 - \alpha) - d_2 e^{c_2(1-\alpha)} \theta(\alpha - 1) \) with \( c_{1x} = 0.64, c_{2x} = 0.7 \) and \( c_{2x} = 1.5 \). See reference [33] for the details of the \( \epsilon^{x_0}_c \) and \( \epsilon^{x_1}_c \).

A.2. MGGAC

The exchange enhancement factor of the MGGAC functional is given by [35].

\[
F_x^{\text{MGGAC}}(x|\alpha) = \frac{1}{6} \left( \frac{2\pi^2}{3} \right)^{1/3} x^{2/3} \left( -x^2 - 5x + 8e^x - 8 \right),
\]

(A.4)

where \( x \) satisfies the following non-linear equation

\[
\frac{(1 + x)^5}{x - 3} e^{-2\alpha/3} = \frac{\beta_1 + \beta_2 \alpha + \beta_3 \alpha^2}{1 + \beta_1 \alpha + \beta_2 \alpha^2}.
\]

(A.5)

The constants are as \( \beta_1 = 3.712, \beta_2 = 2.0, \beta_4 = 0.1, \beta_3 = 2.595 + 0.5197 / \beta_4 + 0.559 / \beta_2, \) and \( \beta_5 = -3 \beta_3 \). The MGGAC correlation takes the same form as PBE expression [18], with the second-order gradient expansion coefficient \( \beta = 0.030 \).

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