

ELECTRONIC STRUCTURE OF Cu_2MoS_4 : A HYBRID FUNCTIONAL APPROACH

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ABSTRACT

A sustainable "Green Development" requires hydrogen as energy rather than fossil fuels, geothermal and other energy resources. Innovative eco-friendly techniques are required for hydrogen production. Photo-electrochemical water splitting has emerged as an innovative, challenging and eco-friendly process to produce renewable molecular hydrogen and oxygen. Copper and Sulphur based compounds have been predicted to be chemically active for photo-electrochemical water splitting. Cu_2MoS_4 is one of the semiconductors with a band gap of 1.7 eV which is more than sufficient to absorb visible spectrum of sunlight for hydrogen production. It includes two species which are members of the d-electron systems i.e. Cu ($\text{Ar}3d^{10}4s^1$) and Mo ($\text{Kr}4d^55s^1$). Therefore, it is essential to use such approach which can handle d-electrons contribution in an appropriate manner. Keeping this in view, in the present work, a recently developed alternative which involves less in the way of arbitrary parameters has been used. In the method postulated in this paper, a component of exact exchange (α) is introduced for the relevant Kohn–Sham orbitals. One could tune the value of α for a particular system, and the most appropriate value of α can be determined, which gives the best results. After a detailed study, a value of $\alpha = 0.4$ here with the PBE functional has been selected for Cu_2MoS_4 . We have studied the ground state electronic structure properties and absorption spectra in UV-visible region, which is in good agreement with the experimental results.

Keywords: Carbon emission, Density functional theory, Hybrid functional, Photo-electrochemical water splitting.

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INTRODUCTION

Carbon emission is a major threat for all countries in the world. The issue hogged the limelight once again during the United Nation Climate Change Conference at Paris, France [1]. Hydrogen is considered to play very vital role for the future of our planet. It is of great importance for the industrial as well as the sustainable social life. A sustainable "Green Development" requires hydrogen as energy rather than fossil fuels, geothermal and other energy resources. Innovative eco-friendly techniques are required for hydrogen production. There are various pathways available for such task like solar-thermal route, photovoltaic-electrolysis and photo-electrochemical (PEC) water splitting process.

In last few years, PEC water splitting has emerged as an innovative, challenging and eco-friendly process to produce renewable molecular hydrogen and oxygen. For a semiconductor material to photo-electrochemically split water, it must satisfy several criteria. Some of those are as follow:

- (i) The band gap must be a minimum of 1.7 eV to provide the potential necessary for electrolysis and overcome other energy losses in the system;
- (ii) The minority band edge and the Fermi level of the material must straddle the hydrogen and oxygen redox potentials for current to flow through the circuit;
- (iii) The material must be stable in contact with the electrolyte;
- (iv) Have high efficiency in the conversion of photons to separated electron/hole pairs; and
- (v) Charge transfer at the interface must be fast enough to prevent accumulation of minority carriers at the semiconductor surface that can shift the band edges out of the overlap position.

No known semiconductor system achieves all of the above criteria, though some have come close. In this series, a lot of materials had been proposed. In the recent years, sulfides as a kind of promising photo-catalysts for splitting of water have been studied extensively [2-6]. Ternary sulfide NaInS_2 has been reported to split water for H_2 production, showing good activity [7].

Copper chalcopyrite thin films have shown much better absorbance of solar energy. Band gap tailoring from 1.0 eV in CuInSe_2 , 1.6 eV in CuGaSe_2 , and up to 2.43 eV in CuGaS_2 [8-10] has been found to be of great advantage for such a system. The CuGaSe_2 bandgap is good for PEC applications [11]. But stability, surface kinetics and surface energetics are still not good enough. As bulk materials, tungsten and molybdenum sulfides are excellent hydrogen catalysts, but their band gaps (below 1.2 eV) are too low for PEC water splitting. Band gap has been increased upto 2.5 eV by using nanostructures [12]. High-quality crystalline semiconductor compounds of gallium, indium, phosphorous and arsenic have been studied for decades [13].

In addition to that, high cost and life time are the major challenges which need to be taken care of. Recently Cu_2MoS_4 has been proposed which can play a role for PEC water splitting [14]. Cu_2MoS_4 is a semiconductor with a band gap of approximately 1.76 eV and

includes two species which are members of so called d-electron systems i.e. Cu ($\text{Ar}3d^{10}4s^1$) and Mo ($\text{Kr}4d^55s^1$). Usually d-electron system show strongly correlated behavior and theoretically utmost care is required to deal with such systems. In the present work, we have studied the ground state properties like lattice parameters and band-gap determination as well as absorption spectra within the UV-visible range.

CALCULATIONS

Density Functional Theory (DFT) with local density approximation (LDA) and generalized gradient approximation (GGA) has been widely used in Solid-state Physics to study the ground state properties. As far as band-gap determination is concerned, the shortcoming of LDA [15] as well as GGA [16] is related to the insufficient cancellation of the self-interaction correction. To overcome the shortcomings, modifications in the methodologies such as LDA+U [17, 18] (where U is the Hubbard parameter with a range of few eVs in d-electron systems) and many-body perturbation theory (GW) approximation has been applied. Both the modifications are capable to remove the incomplete self-interaction correction present in LDA. But LDA+U method is associated with two semi-empirical parameters and GW approximation demands high computational time.

We have applied a recently developed alternative which involves less in the way of arbitrary parameters. We can use an on-site hybrid [19] based upon an approach such as the PBE0 functional [20, 21]. A small component of exact exchange (which we will refer to as α) has to be added for the relevant Kohn–Sham orbitals (d-electrons only here), which can be calculated rather simply within the muffin tin of an APW method. This is similar to a LDA/GGA + U method, but with a U value that will vary with local environment avoiding the need to tune U for specific cases.

In principle, one could tune the value of α for a particular system, i.e. a compromise can be used. The value of $\alpha = 0.4$ with the PBE functional gives the better results as far as the band gap determination is concerned, but at the same time lattice parameters deviate from the experimental values with considerable extent. Therefore a value $\alpha = 0.4$, would have been used for Cu_2MoS_4 which gives better comparison for both band gap as well as lattice parameters. We will stress that this particular value for α is for Cu_2MoS_4 , and cannot be implicitly generalized to other systems. To calculate the lattice parameters of Cu_2MoS_4 , we have used full-potential linear augmented plane-wave (FLAPW) method as implemented in the WIEN2k code [22].

RESULTS AND DISCUSSIONS

Evans *et. al.* had synthesized and determined the structural characterization of body-centred polymorph of Cu_2MoS_4 using hydro- thermal methods. Cu_2MoS_4 crystallises in space group I-42m with experimental cell parameters $a=b=5.410 \text{ \AA}$, $c=10.35 \text{ \AA}$ and has new structure type containing layers of edge-sharing CuS_4 and MoS_4 tetrahedra. The structure was determined by powder X-Ray diffraction data [23].

The purpose of using present proposed technique is to get results of lattice parameters

and band gap with a balance between both computational and experimental values. For this purpose, we have done calculations with GGA and value of $\alpha = 0.4$ with the PBE functional and compared the results given by these two approximations. Using value of $\alpha = 0.4$ with the PBE functional gives lattice parameters with space group I-42m with cell parameters $a=b=5.510 \text{ \AA}$, $c=10.110 \text{ \AA}$ which does not deviate much from the experimental values.

A trend has been observed in which the band gap increases with increase in the value of α . The optimized volume and lattice parameters decrease with increase in the value of α . Therefore the value of α can be chosen such that the balance can be maintained between both the lattice parameters calculations and band gap determination.

Therefore a value $\alpha = 0.4$, would have been used for Cu_2MoS_4 which gives better comparison for both band gap and lattice parameters. The calculated structure has been shown in Figure 1. Calculated X-ray spectra have been shown in Figure 2, which is also in full agreement with the experimental observation. Figure 3 shows the partial density of states of Cu_2MoS_4 using GGA approximation which gives the band gap about 1.1 eV. From Figure 3(a) & 3(b), it is clear that Mo is contributing mainly in absorption. Whereas Figure 3(c) and 3(d) shows that S & Cu are contributing in emission spectra. In Figure 3(b), 3(c) & 3(d), left panel shows the contribution of "s", "p", "d" & "f" states, middle panel shows contribution of "s" & "p" states and right panel shows contribution of "d" states respectively.

Figure 4 shows the partial density of states with value of $\alpha = 0.4$ with the PBE functional. In Figure 4(b), 4(c) & 4(d), left panel shows the contribution of "s", "p", "d" & "f" states, middle panel shows contribution of "s" & "p" states and right panel shows contribution of "d" states respectively. It is clear that Cu 3d orbital could hybridize with S 3p orbital to form a valence band. It was also reported that Mo 4d orbital could hybridize with other metallic orbital to form a conduction band. Cu (I) 3d orbital could split into two orbital, one is full and the other is empty. Therefore, it is clear that the valence band of Cu_2MoS_4 is made up of the full orbital of Cu 3d and S 3p and the conduction band contains the empty Cu 3d orbital and Mo 4p orbit. It is clear that band gap increases compared to GGA functional and comes out to be 1.6 eV.

We also tried with increased value of $\alpha = 0.6$ with the PBE functional to improve the value of band gap towards experimental value. The value of band gap improves and comes equal to experimental values 1.76 eV, but $\alpha = 0.6$ with the PBE functional takes the lattice parameters far away from the experimental values. Therefore value of $\alpha = 0.4$ with the PBE functional is an appropriate value for Cu_2MoS_4 , which makes a balance between lattice parameters and band gap.

CONCLUSIONS

In the present work, we have carried out Density Functional Study of Cu_2MoS_4 using PBE functional with a small component of exact exchange (defined as α). In the present case $\alpha = 0.4$ has been found to be appropriate for the lattice structure calculation and band structure calculation. This technique has given the results which are in good agreement with

the experimental results. This technique requires very less computational resources compared to LDA/GGA + U or many-body perturbation theory (GW) approximation. For other materials “ α ” can be chosen in such way so that results for both the lattice parameters and band gap calculations can be determined without doing much compromise in comparison to the experimental values.

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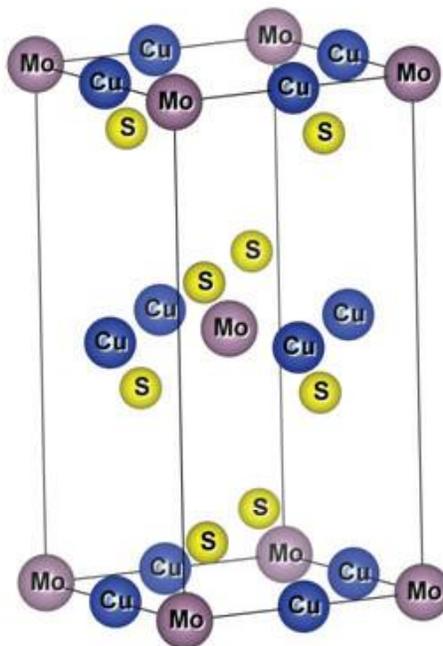


Figure 1: Structure of Cu_2MoS_4

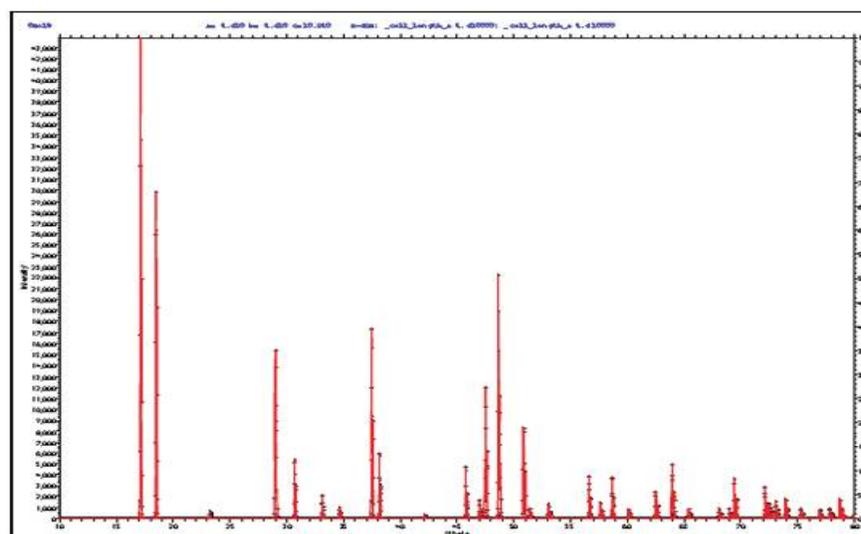


Figure 2: Calculated X-ray diffraction of Cu_2MoS_4

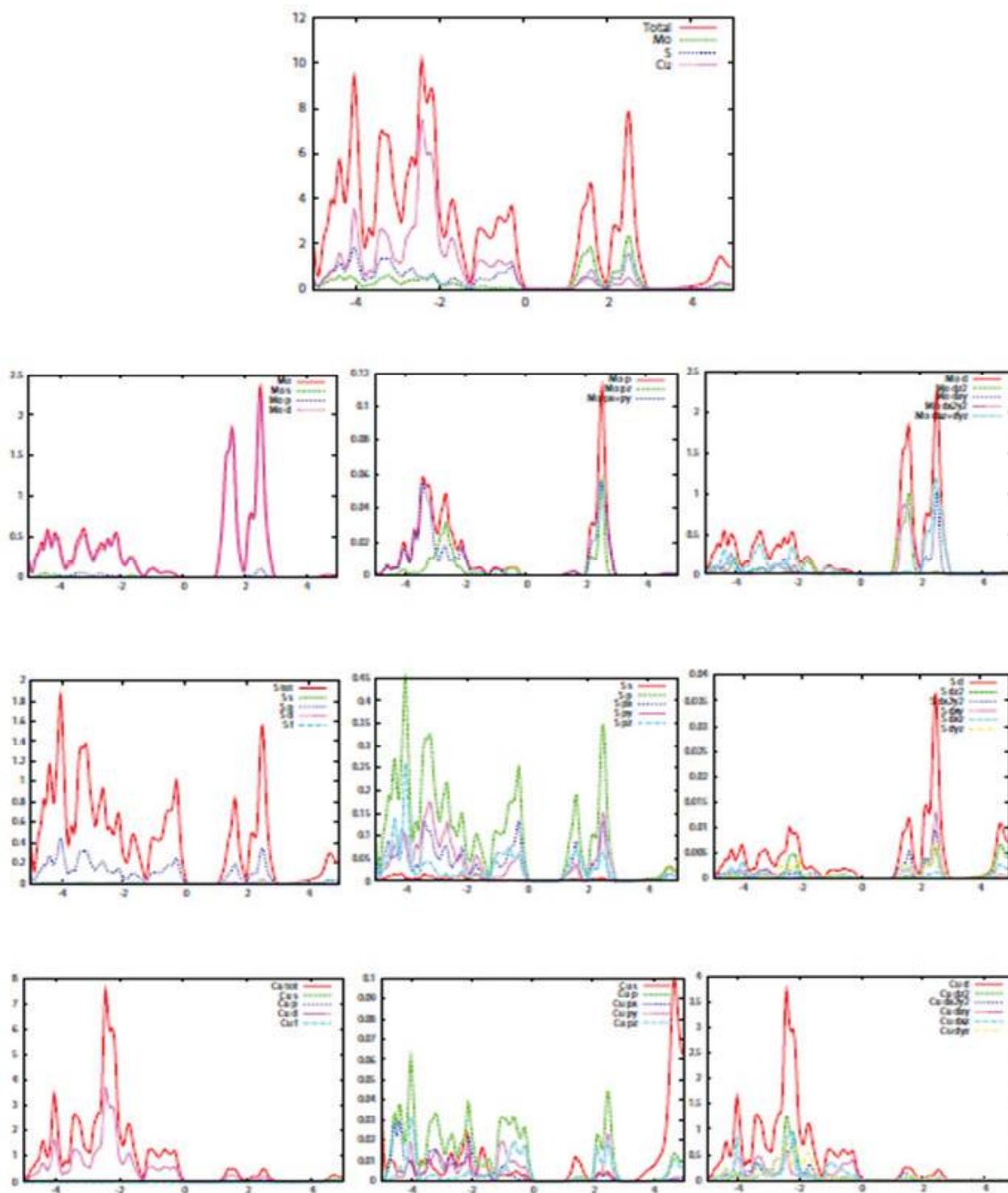


Figure 3: (a) Density of States of Cu_2MoS_4 using GGA (b) Partial Density of States of Mo in Cu_2MoS_4 using GGA (c) Partial Density of States of S in Cu_2MoS_4 using GGA (d) Partial Density of States of Cu in Cu_2MoS_4 using GGA (in (b), (c) & (d) left panel shows the "s", "p", "d" & "f" states, middle panel shows contribution of "s" & "p" states and right panel shows contribution of "d" states respectively.

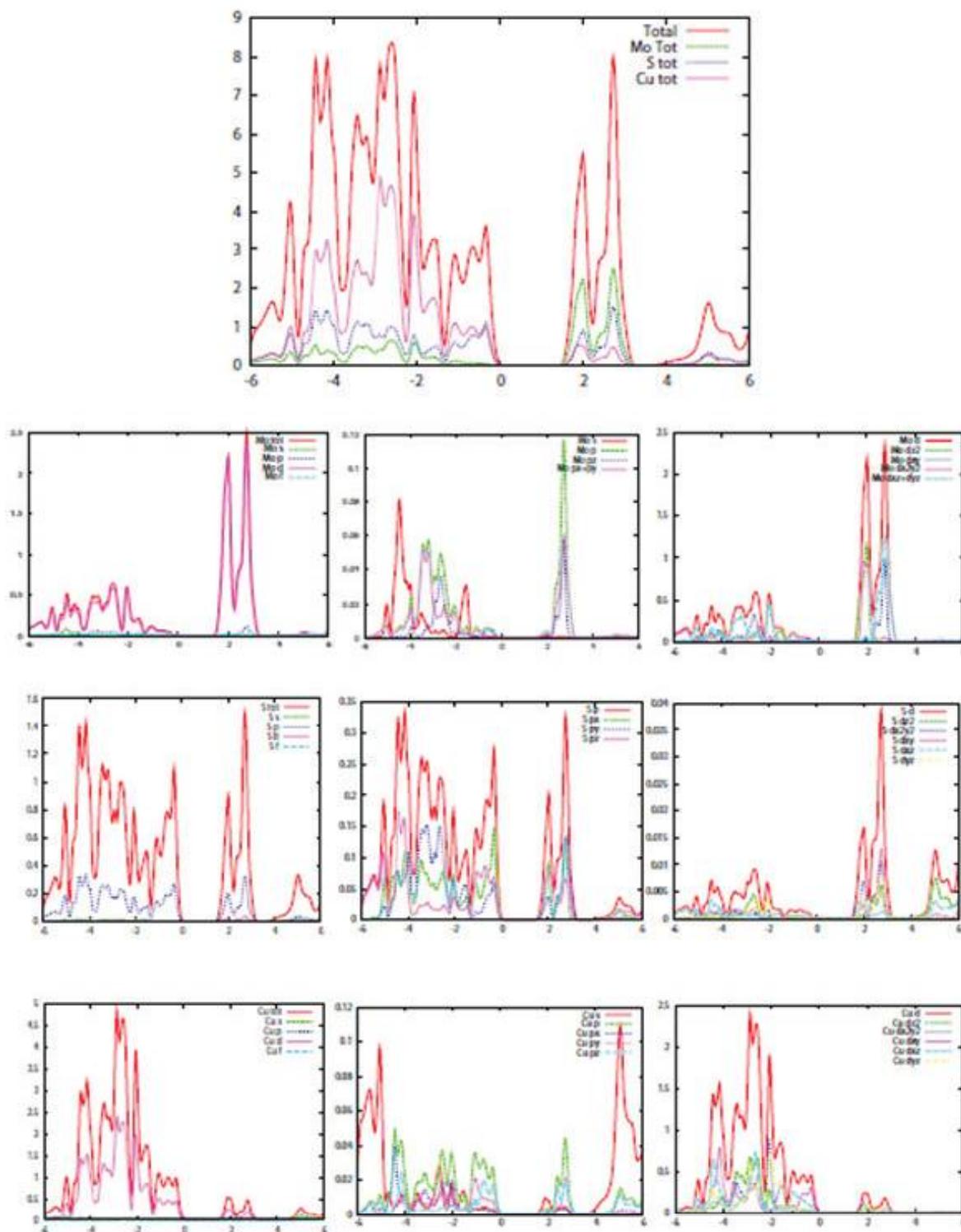


Figure 4: (a) Density of States of Cu_2MoS_4 using $\alpha = 0.4$ (b) Partial Density of States of Mo in Cu_2MoS_4 using $\alpha = 0.4$ (c) Partial Density of States of S in Cu_2MoS_4 using $\alpha = 0.4$ (d) Partial Density of States of Cu in Cu_2MoS_4 using $\alpha = 0.4$ (in (b), (c) & (d) left panel shows the "s", "p", "d" & "f" states, middle panel shows contribution of "s" & "p" states and right panel shows contribution of "d" states, respectively).

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