



### DFT Calculations on Electronic Density of States and Band Structures of Three Selected Systems

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Electronic density of states (DOS) and band structures are key factors in condensed matter physics and material science that help understand the electronic properties of different materials and systems. In the present study, these parameters were determined in three selected systems namely: bcc Iron (Fe), fcc Gold (Au), and fcc Diamond Silicon (Si) using First-principle calculations based on Density Functional Theory (DFT). The DOS profiles of these materials show that Fe is magnetic while Au and Si are non-magnetic. The results on band structures further reveal that Fe and Au are both metallic and conductors while Si is semiconductor. Moreover, the findings in this work are in agreement with that of previous calculations done on similar systems.

#### 1. Introduction

Electronic density of states (DOS) plays a tremendously important role in determining the electronic properties of different materials [1]. Researchers in the fields of solid-state and condensed matter physics carefully diagnose density distributions of free electrons in metals to understand scientific concepts that are hidden in such density distributions (e.g., the d-band center theory) [2] and to develop new materials [3, 4]. In solid state and condensed matter physics, DOS of the system describes the number of states that are to be occupied by the system at each level of energy. It is the number of electron states with energies in the interval  $E$  and  $E + dE$ . The DOS is directly related to the dispersion relations of the properties of the system. High DOS at a specific energy level means that many states are available for occupation [5].

In addition, the density of states appears in many areas of physics and helps to explain a number of quantum mechanical phenomena. Among its applications are in quantization and photonic crystals. Interesting systems are in general complex, for instance compounds, biomolecules, polymers, and many more. Because of the complexity of these systems, the analytical calculation of the DOS is in most cases impossible. However, computer simulations offer a set of algorithms to evaluate it with high accuracy [6].

There are several points that have to be considered in calculating the DOS. First, a large number of  $k$  points is necessary. Second, energies must be plotted not in terms of an absolute energy but instead relative to the Fermi energy,  $E_f$ , which is the energy of the highest occupied electronic state. Using the DOS, you can describe the material as being metallic, semiconductor, or insulator. Also, deeper analysis of the DOS can provide information on the hybridization of the orbitals and the nature of bonding between atoms.

A more nuanced view of a material's electronic structure is often possible by examining the material's band structure. The band structure represents the energy of the available electronic states along a series of lines in a reciprocal space that typically form a closed loop beginning and ending at the gamma point. Using band structure calculations, we can identify that bands that cross the Fermi level, calculate the direct and indirect band gap, among others.

Furthermore, the electronic band structure, describes range of energies that an electron within the solid can or cannot have. The range of energies that the electron can have is referred to as the energy bands or the allowed bands while the energies that the electron cannot have is referred to as the band gaps or the forbidden bands.

The band structure is given as a function of the of the wave vector  $k$  in the reciprocal space. The band structure can be used in identifying the bands that crosses the Fermi level to determine if the material is metallic or not. Moreover, the band structure is also a helpful tool in calculating the direct and indirect band gap in characterization of the electrical conductivity of the solid. Generally, substances with large bandgaps are insulators, those with smaller bandgaps are semiconductors and those that have either very small or no bandgaps are conductors [7, 8].

In this work, the electronic density of states and the band structures of three systems were determined using first-principle calculations based on DFT. Using Burai 1.3 (GUI of Quantum Espresso), systems were set-up as body-centered cubic iron (Fe), face-centered cubic gold (Au), and face-centered cubic diamond silicon (Si).

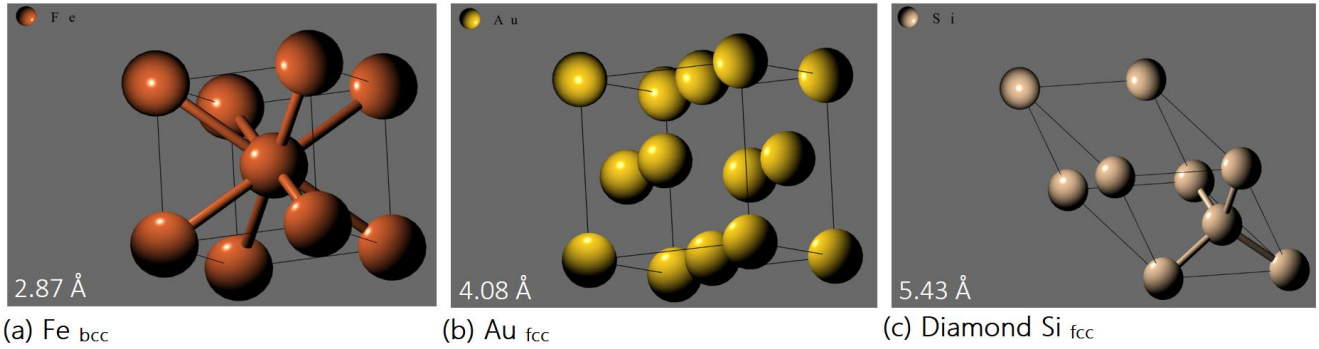


Figure 1. Visualization of (a) Body-centered cubic Fe, (b) Face-centered cubic Au, and (c) Face-centered cubic diamond Si.

## 2. Results and Discussion

Crystalline structure models of bcc Iron, fcc Gold, and fcc diamond Silicon were visualized using Burai 1.3 - GUI of Quantum Espresso (Figure 1). The lattice constants used in generating the set-ups were adapted from the literature, which are 2.87, 4.08, and 5.43 Å respectively. The total density of states, atom-projected density of states, orbital projected density of states, and electronic band structure were calculated for the three materials. Furthermore, the two parameters were plotted side-by-side to illustrate a comparison of the electronic properties of these materials by analyzing the DOS and band structures. The results are shown in Figures 2a, b, c.

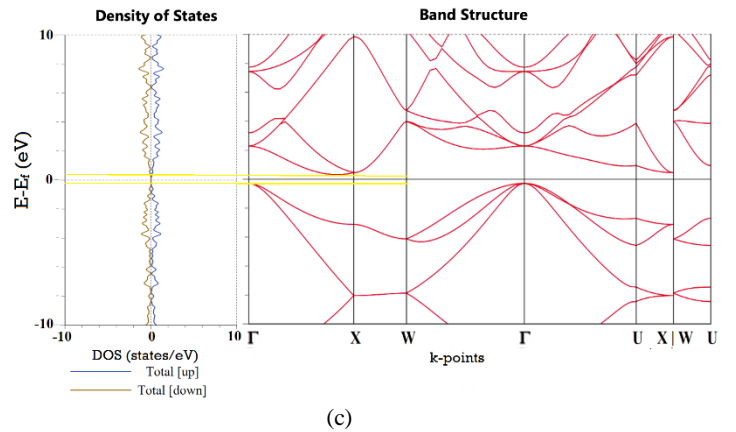
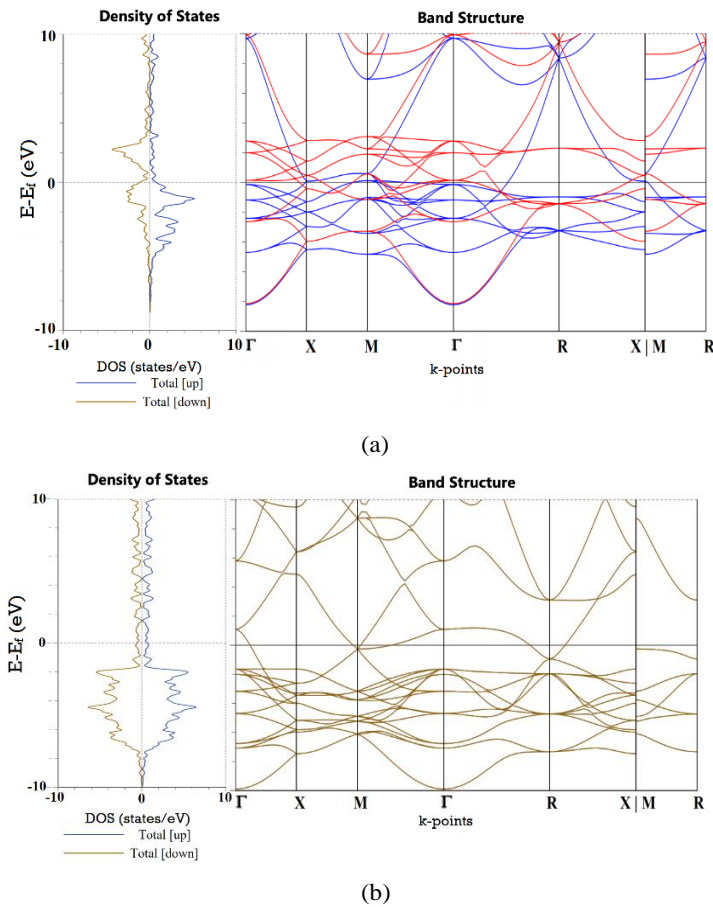


Figure 2. Electronic density of states and band structures of (a) bcc Fe, (b) fcc Au, and (c) fcc Diamond Silicon (Si) systems. (Note: The yellow lines in (c) shows the band gap.)

In the density of states (DOS) plots, high DOS at specific energy levels illustrates that more states are available to be occupied. The states with negative energy values are occupied states while those with positive energies are unoccupied or available states. Results show that bcc Fe and fcc Au have more occupied states than unoccupied. On the contrary, fcc diamond Si has more or less the same number of occupied and unoccupied states [5, 8, 9, 10].

The symmetry of the spin up and spin down DOS for these systems describes the magnetic state of the material. The DOS for bcc Fe is non-symmetrical (Figure 2a) suggesting that the material has a net magnetization and that it is magnetic. Spin polarization is the degree to which spin is aligned with a given direction. This property pertains to the spin, hence to the magnetic moment, of conduction electrons in ferromagnetic metals like Fe, giving rise to spin-polarized currents [10, 11]. Spin is connected for ferromagnetic materials because spontaneous magnetization breaks time-reversal symmetry, which allows the electronic states within the material to become spin-dependent.



For Fe, the DOS is different for the two spin states. Conventionally, majority spin is referred as “spin up” while minority spin is “spin down”. In this case, the DOS of Fe exhibits asymmetry which allows it to generate, manipulate, and detect spin [10, 12].

On the other hand, the DOS in fcc Au and fcc diamond Si exhibit symmetry showing that these two materials are non-magnetic (Figure 2b and 2c). In non-magnetic materials, time reversal symmetry forces the electronic states to come in pairs with the same energy but opposite spin, thus leading to a density of states that must be independent of spin [12, 13].

The graphs on band structures illustrates that several bands for the bcc Fe system and a few bands for the fcc Au system cross the Fermi level. These bands crossing the Fermi level indicate partially filled bands suggesting that both Iron and Gold are metallic. These overlapping bands result to electrons in the conducting band moving freely within the crystal lattice serving as charge carriers to conduct electric current. Thus, Fe and Au are classified as conductors [7, 13]. The electronic band structure is the energy schema describing the conductivity of these conductors, insulators, and semiconductors. The schema consists of two energy bands (valence and conduction) and the band gap. In conductors like iron and gold, the valence band is either not fully occupied with electrons, or the filled valence band overlaps with the empty conduction band. Generally, both states occur at the same time, the electrons can therefore move inside the partially filled valence band or inside the two overlapping bands. In the band structure plots for these metals, there are no band gaps between the valence band and conduction band (Figure 2a and 2b) [7, 10].

In contrast, the fcc diamond Si system does not exhibit these crossing bands, instead an energy gap or band gap at the Fermi level where electron states cannot exist. Figure 2c shows the electronic band structure of the system, where the bandgap (marked by yellow lines) is illustrated as the indirect gap between the valence band maximum and the conduction band minimum near the gamma ( $\Gamma$ ) symmetry. This band gap is the energy required to promote a valence electron to the conduction band. In this case, the band gap at approximately 0.5 eV suggests that silicon is a semiconductor. Semiconductors are materials with a relatively small band gap, typically 1 eV or less, between filled valence band and an empty conduction band. Furthermore, band minima and maxima for this system are at different points (Figure 2c), showing that Si is an indirect semiconductor [10, 12, 13].

However, the value of band gap in the current work is relatively small compared to that of values reported in related studies [7, 9, 10]. These differences in the values could be attributed to the so-called ‘band gap problem’, in which DFT in LDA/GGA fails to correctly predict the energy gaps between occupied and unoccupied states [13].

In general, materials with large band gaps are referred to as insulators, while those that have smaller band gaps are semiconductors, and those that have either very small or no bandgaps are conductors [7, 8]. With the results illustrated in the electronic density of states and band structures of these materials, it can be inferred that both Fe and Au are categorized as metals and conductors while Si is semiconductor. In addition, Fe is magnetic while Au and Si are non-magnetic. These results are in agreement or comparable with other previous related researches done on the same systems [14, 15, 16].

### 3. Conclusion

Electronic density of states (DOS) and band structures are significant parameters in understanding the electronic properties of different materials. The electronic density of states and band structures of bcc Fe, fcc Au, and fcc diamond Si systems were determined using First-principles calculations based on DFT. Results from these calculations were used to describe and understand the electronic and magnetic properties of these systems. The DOS profiles reveal that Fe is magnetic while Au and Si are non-magnetic. The calculations on band structures further show that Fe and Au are both metallic and conductors while Si is a semiconductor. DFT calculation is an effective tool to determine the DOS and band structure profiles of these systems to further understand their electronic properties. Finally, these findings are important to explore more on the applications of these systems in many fields like solid state and condensed matter physics as well as material science.

### Computational Model

DFT calculations were implemented using Quantum Espresso with exchange-correlation term described using the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) functional. The interaction between ions and electrons were described using the projector augmented wave (PAW) method. Plane wave basis sets were employed with an energy cut-off of 600 eV. The surface Brillouin zone integrations were performed on a grid of 8 x 8 x 8 Monkhorst-Pack k-points using Methfessel-Paxton smearing of  $\sigma=0.2$  eV.

**Notes and references**

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