First-Principles Study on Possible Half-Metallic Ferrimagnetism in Double Perovskites Pb$_2$XX'O$_6$ (X = Ti, Zr, Hf, V, Nb and Ta, X' = Tc, Ru, Os and Rh)

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Abstract: Pb-based double perovskite compounds with chemical formula Pb$_X$X'O$_6$ (X = Ti, Zr, Hf, V, Nb and Ta, X' = Tc, Ru, Os and Rh) have abundant physical properties in the spintronic field. Among all the features, the spin interaction of half-metallic (HM) is regarded as an important performance measure because of its high potential in spintronic devices. In this research study, we calculate density of state (DOS) to investigate possible half-metal candidates by executing structural optimization based on the method of generalized gradient approximation (GGA) and strong correlation effect (GGA + U). Furthermore, following the earlier methods by calculating and comparing energy difference of various compounds with the four initial magnetic states: ferromagnetic, ferrimagnetic, antiferromagnetic and nonmagnetic, we can determine which magnetic state is more stable. Results indicate that there are 13 possible ferrimagnetic HM candidates in these combinations, including Pb$_2$NbTcO$_6$, Pb$_2$TaTcO$_6$, Pb$_2$TiRuO$_6$, Pb$_2$ZrRuO$_6$, Pb$_2$HfRuO$_6$, Pb$_2$VRuO$_6$, Pb$_2$NbRuO$_6$, Pb$_2$TadRuO$_6$, Pb$_2$ZrOsO$_6$, Pb$_2$HiOsO$_6$, Pb$_2$VoOsO$_6$, Pb$_2$ZrRhO$_6$ and Pb$_2$HfRhO$_6$ under GGA and GGA + U schemes. The stability of analysis by analyzing the energy gap illustrates that all 13 possible candidates are half metals and ferrimagnetic states, so our studies could provide guidelines for scientists to fabricate new double perovskites in future.

Keywords: double perovskites; first-principle calculation; half metal; ferrimagnetic state

1. Introduction

Half metals (HMs) are potential and popular materials in the field of spintronics device research [1–8] owing to their function of inducing 100% spin polarization. With an aim to discover more HMs, the group of double perovskites is an ideal selection because they account for an enormous majority of known HMs, including Sr$_2$FeMoO$_6$ [5,9–11], Sr$_2$FeReO$_6$ [9,12], La$_2$VtCoO$_6$ [12], La$_2$VCuO$_6$ [12], La$_2$MoTcO$_6$ [13], La$_2$WReO$_6$ [14], BiPbVRuO$_6$ [15], Bi$_2$CrCoO$_6$ [16] and Bi$_2$FeNiO$_6$ [16], mixed valance perovskite structures manganese oxide Ln$_{0.5}$Ca$_{0.5}$MnO$_3$ [17] and Ln$_{0.7}$Sr$_{0.3}$MnO$_3$ [18,19], spinel Fe$_3$S$_2$S$_4$ [20,21] and Mn-doping GaAs [22,23]. On the other hand, the topic of magnetism has also received significant attention in the discussion of double perovskites family, the magnetic state ranging from antiferromagnetic [24–29] to ferrimagnetic [30–32] and ferromagnetic [33–35]. Among them, ferrimagnetic materials are widely used in non-volatile memory devices such as hard drives, which utilize their ability to easily switch the spins of electrons and be magnetized.

Due to the structural and compositional flexibility of the double perovskites structure, many researchers are continually disclosing new HM materials from the group of double perovskites $A_2XX'$O$_6$, where $A$ is a relatively large cation [36–38], and X and $X'$ are metal ions. It is anticipated that study of the replacement of the large lead(II) cation in A site...
element [39] could provide opportunities to find stable HM candidates in related research, because Pb\(^{2+}\) has a suitable size to be combined with smaller X and X\(^{\prime}\) site cations to satisfy the tolerance criterion (t) noted by Goldschmidt [40], with t having a value close to unity for stable perovskite structures. In this regard, some compounds of Pb\(_2\)XX\(^{\prime}\)O\(_6\) in previous studies were experimentally synthesized [41–43], in which there are indeed some HM materials, i.e., Pb\(_2\)TcReO\(_6\) [44], Pb\(_2\)MoOsO\(_6\) [44], Pb\(_2\)FeRuO\(_6\) [45], Pb\(_2\)FeMoO\(_6\) [45], Pb\(_2\)CrRuO\(_6\) [46] and Pb\(_2\)CrOsO\(_6\) [46]. It is evident that the choice to select X and X\(^{\prime}\) allows one to decide the physical properties of double perovskites because of their cation size and valance distribution of d (or f) orbitals [47–49].

However, in the strictest sense, perfect half-metallicity is limited to ideal crystals at zero Kelvin temperature; real HMs mainly exhibit dramatic decreases in the spin polarization due to thermal effects and intrinsic crystal and surface imperfection [50], which are ignored by the calculation of density functional theory (DFT) [51]. Nevertheless, for conquering the implicated synthesis processes of double perovskite compounds, some researchers indeed found good agreement of experimental synthesized results about HMs with the theory predictions such as Sr\(_2\)FeReO\(_6\) [52,53]. For the magnetic property of Pb\(_2\)MnWO\(_6\) [54], Ivanov et al. used DFT-based calculations to predict the presence of a low-temperature magnetic ordering, which matches their experimental results. Consequently, the DFT calculation also makes it possible to predict the properties of some compounds in the condition of zero Kelvin temperature, and provides limited but useful information at finite temperature.

Following the solid work that shows that some cyclical behaviors could be determined by the XX\(^{\prime}\) pairs [55,56], we will focus here on the transition metal combination of IVB/VB group and VIIB/VIIIB group and attempt to thoroughly investigate potential HM candidates in the group of Pb\(_2\)XX\(^{\prime}\)O\(_6\). The method with which we calculate these double perovskites is based on DFT and the procedure is shown as follows: First, we optimize our structure by the method of generalized gradient approximation (GGA) [57]. After that, through the process of optimization, we determine whether or not the material is an HM candidate by two rules: one is the integer spin magnetic moment from compounds, and the other one is the energy gap existing in the single-side channel provided by density of states (DOS). In other words, the band gap of either spin-up or spin-down is indeed observed and exists in the single channel. Next, the consideration of strong correlation effect (GGA + U) [58–60] is also checked to make sure that there is stability of the energy gap, which is then computationally convenient for accurate calculations of electronic structures. Last, the same method is executed repeatedly with four initial states, i.e., ferromagnetic (FM), ferrimagnetic (FiM), antiferromagnetic (AF) and nonmagnetic (NM). Finally, magnetic states of these double perovskites are then verified by the energetic comparison of these results.

2. Materials and Methods

The Pb-based double perovskites consist of Pb, IVB/VB transition metals (Ti, Zr, Hf, V, Nb and Ta) paired with VIIB/VIIIB transition metals (Tc, Ru, Os and Rh) and oxygen, as shown in Figure 1. In total, there are 24 kinds of compounds counted upon which structural optimization is executed in order to check which one is the more stable HM material candidate. Furthermore, this study begins with the four types of initial magnetic states, i.e., ferromagnetic (FM), ferrimagnetic (FiM), antiferromagnetic (AF) and nonmagnetic (NM) for each compound, as shown in Figure 2. Accordingly, based on results, comparison between each state can provide information about the stable situation for all compounds. Lastly, density of states (DOS) is analyzed for d-orbital electrons to confirm not only magnetic but also half-metallic properties. By doing so, HM candidates could be picked up through protracted and complex processes. Last, all candidates are examined in consideration of the strong correlation effect (GGA + U).
Figure 1. An ideal ordered double perovskite structure of Pb₂X₂O₆.

Figure 2. The schematic diagram of four magnetic states: FM, FiM, AF and NM.

Next, we determine whether the structures are stable or not after full structural optimization, implying two structures being discussed. One is the tetragonal structure (space group of I4/mmm, No. 139), and it is made of two non-equivalent types of oxygen atoms, in which the locations of O₁ atoms are on the z-axis and there are four O₂ atoms existing on the xy-plane, as shown in Figure 1. Accordingly, they are the cases of F(i)M existing on the xy-plane, as shown in Figure 1. Accordingly, they are the cases of F(i)M found in the AF state.

The schematic diagram of four magnetic states: FM, FiM, AF and NM.

In the FM and FiM states, each X and X' ion has similar spin states (that is, (X, X, X', X') = (m, m, m', m') = FM or (m, m, −m', −m') = FiM), which can cause the assumption of the half-metallicity of the double perovskite. By the self-consistent process, most of the initial FM and FiM states all converge into one of the states. In the AF states, the spin state of (X, X', X') can be noted as (m, −m, m', −m'). The induced equivalence in the charge is Q'[X(X')] = Q'[X(X')], which can be observed from the symmetry of the spin-up and spin-down in the total figure of density of state (DOS). No spin polarization is observed in the NM state. Calculation results for all four magnetic phases are performed to find the most stable magnetic phase. (However, when we put spin polarization into consideration, the calculation results show that the compounds become more stable.) The self-consistent process with high convergence requirement is also performed to guarantee the accuracy of the result.

In this research, we present electronic structure calculations with generalized gradient approximation (GGA) plus on-site coulomb interaction (GGA + U). Structural optimization calculations are carried out through the full-potential projector-augmented wave [61] (PAW) method by using the code of the Vienna Ab Initio Simulation Package (VASP) [62–64] to determine the theoretical lattice constraints and atomic positions. The calculation for the Brillouin zone is conducted using 8 × 8 × 6 Monkhorst–Pack k-grid sampling. The cut-off energy of the plane wave basis is set to 450 eV. The energy convergence criteria for the full structure optimization and self-consistent calculations are set to 1 × 10⁻⁵ and 1 × 10⁻⁷ eV,
respectively. The Wigner–Seitz radius of the Pb atom is set as 3.3 atomic units (a.u.), 1.6 a.u. for O atom and 2.7 a.u. for X(X′) ion. For the final and equilibrium structures, the forces and stresses acting on all the atoms are less than 0.3 eV/Å and 0.9 kBar, respectively.

3. Results and Discussion

After calculation under the GGA scheme, we find that 13 out of the 24 compounds in the Pb$_2$XX′O$_6$ are categorized as HMs, including Pb$_2$NbTcO$_6$, Pb$_2$TaTcO$_6$, Pb$_2$TiRuO$_6$, Pb$_2$ZrRuO$_6$, Pb$_2$HfRuO$_6$, Pb$_2$VRuO$_6$, Pb$_2$NbRuO$_6$, Pb$_2$TaRuO$_6$, Pb$_2$ZrOsO$_6$, Pb$_2$HfOsO$_6$, Pb$_2$VOsO$_6$, Pb$_2$ZrRhO$_6$ and Pb$_2$HfRhO$_6$. Based on these results, Tc, Ru, Os and Rh are suitable for substitute X′ site element, and we follow this order to systemically discuss all possible HM candidates. For clearer description with the GGA scheme, Figure 3a–d describe the DOS of Pb$_2$NbTcO$_6$, Pb$_2$TaTcO$_6$ and PDOS of d-orbital in Pb$_2$NbTcO$_6$ and Pb$_2$TaTcO$_6$, respectively. In comparison with these figures, Figure 4a–d illustrate the same compounds just under the GGA + U scheme. Following the figure arrangement of GGA and GGA + U, Figures 5a–l and 6a–l, Figures 7a–f and 8a–f and Figures 9a–d and 10a–d illustrate the DOS and PDOS of Pb$_2$XRuO$_6$ (X = Ti, Zr, Hf, V, Nb and Ta), Pb$_2$XOsO$_6$ (X = Zr, Hf and V) and Pb$_2$XRhO$_6$ (X = Zr and Hf), respectively.

![Figure 3](https://example.com/fig3)

**Figure 3.** Based on the GGA calculation, the calculated total and partial DOS values of (a) Pb$_2$NbTcO$_6$ and (b) Pb$_2$TaTcO$_6$ and the partial DOS of e$_g$ and t$_{2g}$ spin orbitals for (c) Nb and Tc and (d) Ta and Tc.
Figure 4. Under GGA + U (U of Nb, Ta and Tc set up as 2) schemes, the calculated total and partial DOS values of (a) Pb$_2$NbTcO$_6$, (b) Pb$_2$TaTcO$_6$ and the partial DOS of $e_g$ and $t_{2g}$ spin orbitals for (c) Nb and Tc and (d) Ta and Tc.

Figure 5. Cont.
Figure 5. Cont.
Figure 5. Based on the GGA calculation, the calculated total and partial DOS values of (a) Pb$_2$TiRuO$_6$, (b) Pb$_2$ZrRuO$_6$, (c) Pb$_2$HfRuO$_6$, (d) Pb$_2$TiRuO$_6$, (e) Pb$_2$ZrRuO$_6$ and (f) Pb$_2$HfRuO$_6$ and partial DOS of eg and t$_{2g}$ spin orbitals for (g) Ti and Ru, (h) Zr and Ru, (i) Hf and Ru, (j) V and Ru, (k) Nb and Ru, (l) Ta and Ru.

Figure 6. Cont.
Figure 6. Cont.
Figure 6. Under GGA + U (U of Ti, Zr, Hf, V, Nb, Ta and Ru set up as 2) schemes, the calculated total and partial DOS values of (a) Pb$_2$TiRuO$_6$, (b) Pb$_2$ZrRuO$_6$, (c) Pb$_2$HfRuO$_6$, (d) Pb$_2$VRuO$_6$, (e) Pb$_2$NbRuO$_6$ and (f) Pb$_2$TaRuO$_6$ and the partial DOS of eg and t$_{2g}$ spin orbitals for (g) Ti and Ru, (h) Zr and Ru, (i) Hf and Ru, (j) V and Ru, (k) Nb and Ru, (l) Ta and Ru.

Figure 7. Cont.
Figure 7. Based on the GGA calculation, the calculated total and partial DOS values of (a) Pb$_2$ZrOsO$_6$, (b) Pb$_2$HfOsO$_6$ and (c) Pb$_2$VOsO$_6$ and the partial DOS of e$_g$ and t$_{2g}$ spin orbitals for (d) Zr and Os, (e) Hf and Os and (f) V and Os.

Figure 8. Cont.
Figure 8. Under GGA + U (U of Zr, Hf, V and Os set up as 2) schemes, the calculated total and partial DOS values of (a) Pb$_2$ZrOsO$_6$, (b) Pb$_2$HfOsO$_6$ and (c) Pb$_2$VOsO$_6$ and the partial DOS of $e_g$ and $t_{2g}$ spin orbitals for (d) Zr and Os and (e) Hf and Os and (f) V and Os.

Figure 9. Based on the GGA calculation, the calculated total and partial DOS values of (a) Pb$_2$ZrRhO$_6$ and (b) Pb$_2$HfRhO$_6$ and partial DOS of $e_g$ and $t_{2g}$ spin orbitals for (c) Zr and Rh and (d) Hf and Rh.
Figure 10. Under GGA + U (U of Zr, Hf and Rh set up as 2) schemes, the calculated total and partial DOS values of (a) Pb_2ZrRhO_6, (b) Pb_2HfRhO_6 and the partial DOS of e_g and t_2g spin orbitals for (c) Zr and Rh and (d) Hf and Rh.

3.1. FiM-HM Compounds: Pb_2XTcO_6 (X = Nb and Ta)

In Table 1, it shows the energy difference between AF and FiM states; note that ΔE = FiM—AF and their values are −21 and −96 meV/f.u. for Pb_2NbTcO_6 and Pb_2TaTcO_6, respectively. Furthermore, with the GGA + U scheme, the values of ΔE decrease to −26 and −178 meV/f.u., indicating a more stable state of FiM for these compounds, thus illustrating direct evidence that these materials are ferrimagnetic. Table 2 lists all the energy of AF and FiM states in detail.

As shown in Figure 3a,b, the band gaps of Pb_2NbTcO_6 and Pb_2TaTcO_6 occur in the spin-up channel, while some electrons occupy the Fermi level of the spin-down channel, which provides obvious evidence for HM materials. As to the second indicator for half-metal compound, it is the integer value of m_tot. Here, the values of m_tot are 2.000 μB/f.u. in the case of Pb_2NbTcO_6 and Pb_2TaTcO_6, which illustrates HM property for these compounds. In addition, Pb_2TaTcO_6 still maintains the possibility of being HM material under the GGA + U scheme with a little fluctuation of magnetism because the m_tot value of Pb_2TaTcO_6 changes from 2.000 to 2.011 μB/f.u.

However, these variations (+U, the coulomb interaction potential) do not change the magnetic states of compounds; instead, the tendency of being FiM material under the GGA + U scheme is more stable than that under the GGA scheme. In addition, under these
two schemes, the distributions of electrons whose energy is higher than Fermi energy are almost the same.

Next, we discuss the electronic configuration of the two compounds. For \( \text{Pb}_2\text{NbTeO}_6 \), the ideal electronic distributions of Nb and Tc we expected are \( \text{Nb}^{5+} (3d^{10}4s^24p^6; t^6_{2g}e^0_{2g}) \) at \( S = 0 \) and \( \text{Tc}^{5+} (4d^{4}s^54p^4; t^9_{2g}e^0_{2g}) \) at \( S = 1 \). From the result of calculations with the GGA method, the electron distributions are \( \text{Nb}^{2+} (4d^2) \) and \( \text{Tc}^{2+} (4d^4) \), and those with the GGA + U scheme are \( \text{Nb}^{3+} (4d^1) \) and \( \text{Tc}^{2+} (4d^4) \).

Table 1. Physical properties of the selected FiM-HM family of \( \text{Pb}_2\text{XX'O}_6 \) (\( X = \text{IVB, VB X}' = \text{Rh, Hf, Os and Tc} \)) in double perovskite structure by GGA and GGA + U calculations. The parenthesis behind \( U \) presents the on-site coulomb parameters: 3 eV for \( U_{\text{V}} \), and 2 eV for \( U_{\text{V}} \), \( U_{\text{Nb}} \), \( U_{\text{Tc}} \), \( U_{\text{Rh}} \), \( U_{\text{Hf}} \), \( U_{\text{Os}} \), and \( U_{\text{Tc}} \) (0,0) denotes the absence of GGA + U calculations. \( \Delta E \) refers to the energy difference between FiM and AF states. The spin magnetic moments for \( X, X' \) and the total moment are listed in the table as \( m_X \), \( m_{X'} \), and \( m_{\text{tot}} \), respectively. The number of electrons in the spin-up and spin-down orbitals is recorded for \( X(X') \) element.

| Materials \( \text{Pb}_2\text{XX'O}_6 \) | \((U_X,U_{X'})\) | Spin Magnetic Moment (\( \mu_B/\text{f.u.} \)) | \( d \) Orbital Electrons ↑/↓ | Band Gap (eV) | \( \Delta E \) (meV/\text{f.u.}) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( \text{NbTc} \) | \((0,0)\) | \(-1.527\) | \(1.846\) | \(2.000\) | \(1.016/1.112\) | \(3.200/1.375\) | 0.47/0.00 | -21 |
| \( \text{TaTc} \) | \((0,0)\) | \(-1.886\) | \(1.980\) | \(2.000\) | \(0.913/1.034\) | \(3.251/1.292\) | 0.95/0.00 | -26 |
| \( \text{TiRu} \) | \((0,0)\) | \(-0.072\) | \(1.588\) | \(2.000\) | \(1.054/1.119\) | \(3.099/1.527\) | 0.30/0.00 | -96 |
| \( \text{ZrRu} \) | \((0,0)\) | \(-0.116\) | \(1.691\) | \(2.011\) | \(1.004/1.115\) | \(3.141/1.467\) | 0.80/0.00 | -178 |
| \( \text{HfRu} \) | \((0,0)\) | \(-0.036\) | \(1.406\) | \(2.000\) | \(0.720/0.750\) | \(3.708/2.317\) | 1.52/0.00 | -106 |
| \( \text{ZrOs} \) | \((0,0)\) | \(-0.028\) | \(1.386\) | \(2.000\) | \(0.737/0.780\) | \(3.729/2.323\) | 1.18/0.00 | -55 |
| \( \text{HfOs} \) | \((0,0)\) | \(-0.054\) | \(0.990\) | \(1.000\) | \(1.614/1.964\) | \(3.492/2.998\) | 0.62/0.00 | -18 |
| \( \text{VOs} \) | \((0,0)\) | \(-0.875\) | \(1.174\) | \(1.000\) | \(1.341/2.193\) | \(3.613/2.452\) | 1.23/0.00 | -139 |
| \( \text{NbRu} \) | \((0,0)\) | \(-1.886\) | \(1.980\) | \(2.000\) | \(0.913/1.034\) | \(3.251/1.292\) | 0.95/0.00 | -26 |
| \( \text{TaRu} \) | \((0,0)\) | \(-0.072\) | \(1.588\) | \(2.000\) | \(1.054/1.119\) | \(3.099/1.527\) | 0.30/0.00 | -96 |
| \( \text{ZrOs} \) | \((0,0)\) | \(-0.116\) | \(1.691\) | \(2.011\) | \(1.004/1.115\) | \(3.141/1.467\) | 0.80/0.00 | -178 |
| \( \text{HfOs} \) | \((0,0)\) | \(-0.036\) | \(1.406\) | \(2.000\) | \(0.720/0.750\) | \(3.708/2.317\) | 1.52/0.00 | -106 |
| \( \text{VOs} \) | \((0,0)\) | \(-0.875\) | \(1.174\) | \(1.000\) | \(1.341/2.193\) | \(3.613/2.452\) | 1.23/0.00 | -139 |
| \( \text{ZrRh} \) | \((0,0)\) | \(-0.028\) | \(1.386\) | \(2.000\) | \(0.737/0.780\) | \(3.729/2.323\) | 1.18/0.00 | -55 |
| \( \text{HfRh} \) | \((0,0)\) | \(-0.054\) | \(0.990\) | \(1.000\) | \(1.614/1.964\) | \(3.492/2.998\) | 0.62/0.00 | -18 |

**Materials:** Pb₂XXO₆ (X = IVB/VB X′ = Rh, Hf, Os and Tc) in double perovskite structure by GGA and GGA + U calculations. The parenthesis behind U presents the on-site coulomb parameters: 3 eV for U_V, and 2 eV for U_VB, U_Nb, U_Tc, U_Rh, U_Hf, U_Os, and U_Tc (0,0) denotes the absence of GGA + U calculations. ΔE refers to the energy difference between FiM and AF states. The spin magnetic moments for X, X′ and the total moment are listed in the table as m_X, m_X′, and m_tot, respectively. The number of electrons in the spin-up and spin-down orbitals is recorded for X(X′) element.
In the case of Pb$_2$TaTcO$_6$, the valance states are Ta$^{3+}$ (4d$^{14}$5d$^{0}$6s$^{0}$t$^{2}$2g$^{0}$ e$^{0}$) at S = 0 and Tc$^{3+}$ (4d$^{4}$5s$^{0}$t$^{2}$2g$^{0}$ e$^{0}$) at S = 1. After the GGA calculation, we find that the actual valance states of Ta and Tc are 2.1 and 4.6, as shown in Table 1. We notice Ta$^{2.8+}$ (5d$^{2.2}$) and Tc$^{2.4+}$ (4d$^{4.8}$). With the GGA + U scheme, the $d$ orbital electrons of Ta and Tc are 2.2 and 4.5, which imply the electronic configurations are Ta$^{2.8+}$ (5d$^{2.2}$) and Tc$^{2.4+}$ (4d$^{4.8}$).

The significant feature of this group is Pb$_2$TaTcO$_6$, also illustrating half-metallic property under the GGA scheme and GGA + U scheme, while it is considered to be a little fluctuation of magnetism under the GGA + U scheme. This phenomenon may be confirmed through experiments in the future; our calculations just provide an accurate answer about whether this compound is a possible HM candidate.

3.2. FiM-HM Compounds: Pb$_2$XX'O$_6$ (X = Ti, Zr, Hf, V, Nb and Ta)

In the case of Pb$_2$XX'O$_6$, all combinations can be categorized into the half-metal family, namely Pb$_2$TiRuO$_6$, Pb$_2$ZrRuO$_6$, Pb$_2$HfRuO$_6$, Pb$_2$VRuO$_6$, Pb$_2$NbRuO$_6$ and Pb$_2$TaRuO$_6$. All of them are FiM materials, indicated by $\Delta E$ values, which are $-43$, $-55$, $-50$, $-18$, $-49$ and $-22$ meV/f.u. for these compounds, respectively. With examination of the cases under the GGA + U scheme, they also remain in the same magnetic state; $\Delta E$ values of them are $-24$, $-106$, $-92$, $-139$, $-115$ and $-60$ meV/f.u., respectively. As a result, all compounds in this group are FiM materials under these schemes.

As seen in Table 1, $m_{tot}$ for Pb$_2$TiRuO$_6$, Pb$_2$ZrRuO$_6$ and Pb$_2$HfRuO$_6$ are 2.000 $\mu_B$/f.u., but those of the others are maintained at 1.000 $\mu_B$/f.u. Even though their values are not the
same, all of them are FiM-HM materials because their $m_{tot}$ are integers except zero. The other evidence for half-metal property is provided by Figure 5a–l. The band gaps of these compounds only occur in the spin-up channel, while the spin-down channel is conductive.

When we monitor electrons near Fermi energy, the distribution of $Pb_{2}TiRuO_{6}$ is like the cases of $Pb_{2}ZrRuO_{6}$ and $Pb_{2}HfRuO_{6}$, and DOS of $Pb_{2}VRuO_{6}$ is analogous to those of $Pb_{2}NbRuO_{6}$ and $Pb_{2}TaRuO_{6}$. The difference between them is the DOS of X site element in the spin-up channel. PDOS of Ti, Ru and Hf are almost concentrated, ranging from about 2 to 5 eV, and in the case of V, Nb and Ta, PDOS of them ranges from about 1 to 5 eV. When compared with Table 1, this phenomenon leads to the band gap values of $Pb_{2} commodities presenting half-metallic property. In the aspect of magnetic state, these six compounds belong to the FiM phase category, and $\Delta E$ of them are significant enough to determine it.
3.3. FiM-HM Compounds: \( \text{Pb}_2 \text{XOsO}_6 \) (\( \text{X} = \text{Zr, Hf and V} \))

After full structural optimization, the magnetic states for \( \text{Pb}_2 \text{ZrOsO}_6, \text{Pb}_2 \text{HfOsO}_6 \) and \( \text{Pb}_2 \text{VOsO}_6 \) converge to FiM state. Under the GGA scheme, \( \Delta E \) for these compounds are \(-27, -28 \) and \(-30 \text{ meV/f.u.} \), and with the GGA + U scheme, they decrease to \(-112, -97 \) and \(-309 \text{ meV/f.u.} \), respectively. All the evidence illustrates a greater tendency for the FiM state.

As seen in Table 1, \( m_{\text{tot}} \) for \( \text{Pb}_2 \text{ZrOsO}_6 \) and \( \text{Pb}_2 \text{HfOsO}_6 \) is \( 2.000 \mu \text{B/f.u.} \), and \( m_{\text{tot}} \) for \( \text{Pb}_2 \text{VOsO}_6 \) is \( 1.000 \mu \text{B/f.u.} \). Table 1 also shows the energy gaps for these compounds, which are \( 0.38, 0.47 \) and \( 0.65 \text{ eV} \). When we refer to Figure 7a,b, a few electrons occupy the energy range of \( 0.5 \) to \( 1 \text{ eV} \), so this phenomenon makes the band gaps of the group compounds narrower than others. These results also provide direct evidence indicating that these compounds belong to the FiM-HM family.

Next, we investigate ideal electron configuration with covalent electron theory. For \( \text{Pb}_2 \text{ZrOsO}_6 \), it has electron configuration \( \text{Zr}^{4+}(4d^0,6s^2e^0g^2) \) at \( S = 0 \) and \( \text{Os}^{4+}(4f^{14}5d^{15}s^0, t_2^0 e^0g^2) \) at \( S = 1 \). Table 1 shows the electron configurations of \( \text{Pb}_2 \text{ZrOsO}_6 \), describing \( \text{Zr}^{2.5+}(4d^{1.5}) \) and \( \text{Os}^{2.5+}(5d^{5.4}) \) under the GGA scheme, which indicates that \( \text{Zr} \) and \( \text{Os} \) contribute almost the same electron numbers for the bond. With the GGA + U scheme, the results are similar to previous results; with the GGA scheme, the electron configurations are also \( \text{Zr}^{2.5+}(4d^{1.5}) \) and \( \text{Os}^{2.6+}(5d^{5.4}) \). In the case of \( \text{Pb}_2 \text{HfOsO}_6 \), we assume the electronic configurations are \( \text{Hf}^{4+}(5d^0,6s^2e^0g^2) \) at \( S = 0 \) and \( \text{Os}^{4+}(4f^{14}5d^{15}s^0, t_2^0 e^0g^2) \) at \( S = 1 \). Then, calculation results provide that the valance states are \( \text{Hf}^{2.4+}(4d^{1.6}) \) and \( \text{Os}^{2.6+}(5d^{5.4}) \). With the GGA scheme, the valance states are also \( \text{Hf}^{2.4+}(4d^{1.6}) \) and \( \text{Os}^{2.6+}(5d^{5.4}) \), which are similar to the case under the GGA scheme. The valance states of \( \text{Pb}_2 \text{VOsO}_6 \) could be represented by \( \text{V}^{5+}(3d^0, t_2^0 e^0g^2), S = 0 \) and \( \text{Os}^{3+}(4f^{14}5d^{15}s^0, t_2^0 e^0g^2) \) at \( S = 1/2 \). According to our calculation results, they imply the true valance states are \( \text{V}^{1.5+}(3d^{3.5}) \) and \( \text{Os}^{2.6+}(5d^{5.4}) \) based on the GGA method. With the GGA + U scheme, electrons of \( d \) orbital are 3.5 and 5.4 for \( \text{V}^{1.5+}(3d^{3.5}) \) and \( \text{Os}^{2.6+}(5d^{5.4}) \), suggesting that the distribution is identical to results with the GGA scheme.

In the cases of \( \text{Pb}_2 \text{ZrOsO}_6 \), \( \text{Pb}_2 \text{HfOsO}_6 \) and \( \text{Pb}_2 \text{VOsO}_6 \), they not only have half-metallic property, but also boast narrower band gap when compared with other HMs in this paper. Under the GGA + U scheme, the gaps of compounds become wider; however, they are still remarkably smaller than those of others under the same scheme.

3.4. FiM-HM Compounds: \( \text{Pb}_2 \text{XRhO}_6 \) (\( \text{X} = \text{Zr and Hf} \))

In this group of compounds, there are two HM candidates, namely, \( \text{Pb}_2 \text{ZrRhO}_6 \) and \( \text{Pb}_2 \text{HfRhO}_6 \). With the GGA and GGA + U scheme, their final stable states belong to FiM rather than AF, as shown by the \( \Delta E \) listed in Table 1. However, \( \Delta E \) values of them are very small, at \(-8 \) and \(-10 \text{ meV/f.u.} \) under the GGA scheme. The values of \( \Delta E \) are too small to distinguish the preferred state of \( \text{Pb}_2 \text{ZrRhO}_6 \) and \( \text{Pb}_2 \text{HfRhO}_6 \), although they are negative. Nevertheless, the situation disappears while the calculation is in consideration of the GGA + U scheme. The results mean \( \text{Pb}_2 \text{ZrRhO}_6 \) and \( \text{Pb}_2 \text{HfRhO}_6 \) are considered as possible FiM-HM candidates.

Last, for \( \text{Pb}_2 \text{ZrRhO}_6 \), the electron configurations are \( \text{Zr}^{4+}(4d^0,6s^2e^0g^2) \) at \( S = 0 \) and \( \text{Rh}^{4+}(4d^5s^0, t_2^0 e^0g^2) \) at \( S = 1/2 \). After calculation, the results showing the real valance states are \( \text{Zr}^{2.5+}(4d^{1.5}) \) and \( \text{Rh}^{2.5+}(4d^{4.5}) \) with the GGA scheme. With the GGA + U scheme, the distributions of electron number are \( \text{Zr}^{2.5+}(4d^{1.5}) \) and \( \text{Rh}^{1.9+}(4d^{2.1}) \). In the case of \( \text{Pb}_2 \text{HfRhO}_6 \), the electron configurations we expected are \( \text{Hf}^{4+}(5d^0,6s^2e^0g^2) \) at \( S = 0 \) and \( \text{Rh}^{4+}(4d^5s^0, t_2^0 e^0g^2) \) at \( S = 1/2 \). Calculation results point out that the valance states of \( \text{Pb}_2 \text{HfRhO}_6 \) are \( \text{Hf}^{2.4+}(5d^{1.6}) \) and \( \text{Rh}^{2.3+}(4d^{6.7}) \), while with the GGA + U scheme, the valance states are \( \text{Hf}^{2.6+}(5d^{1.4}) \) and \( \text{Rh}^{2.1+}(4d^{6.9}) \).

In the last group, the properties of \( \text{Pb}_2 \text{ZrRhO}_6 \) and \( \text{Pb}_2 \text{HfRhO}_6 \) studied here imply that they are the possible HM candidates. When the magnetic state is discussed, \( \Delta E \) of \( \text{Pb}_2 \text{ZrRhO}_6 \) and \( \text{Pb}_2 \text{HfRhO}_6 \) are so small that we cannot determine whether they are in the
FiM state or not under the GGA scheme. In consideration of the scheme with GGA + U, the $\Delta E$ decreases to $-36$ and $-34$ meV/f.u., and therefore we still categorize this group of compounds into FiM materials.

4. Conclusions

By the calculations with the GGA and GGA + U schemes, our work provides 13 possible FiM-HM candidates, namely Pb$_2$NbTcO$_6$, Pb$_2$TaTcO$_6$, Pb$_2$TiRuO$_6$, Pb$_2$ZrRuO$_6$, Pb$_2$HfRuO$_6$, Pb$_2$VRuO$_6$, Pb$_2$NbRuO$_6$, Pb$_2$TaRuO$_6$, Pb$_2$ZrOsO$_6$, Pb$_2$HfOsO$_6$, Pb$_2$VoOsO$_6$, Pb$_2$ZrRhO$_6$, and Pb$_2$HfRhO$_6$. Then, we categorize these compounds in four groups according to $X'$ site element. We first analyze the case of the group of Pb$_2$TcO$_6$. Omitting the small fluctuation of magnetic moment, Pb$_2$TaTcO$_6$ still remains with a possibility of being HM material when the strong correlation effect (GGA + U) is considered in the calculation, so it is still categorized in HM families. Fortunately, Pb$_2$NbTcO$_6$ retains its half-metallic property under the GGA + U scheme. Then, we also discuss the significant features for other groups. In the case of Pb$_2$XRuO$_6$, this group contains an abundance of HM candidates, which account for half of HM materials. Groups Pb$_2$XOsO$_6$, Pb$_2$ZrOsO$_6$, Pb$_2$HfOsO$_6$, and Pb$_2$VoOsO$_6$ have a narrower band gap in comparison with other compounds. Compounds in the category of Pb$_2$XRhO$_6$ converge to an uncertain magnetic state (AF or FiM) and the $\Delta E$ decreases to $-36$ and $-34$ meV/f.u. under the scheme with GGA + U. Therefore, we still categorize this group of compounds into FiM materials. In short, the calculation within DFT provides 13 possible FiM-HM candidates, and we hope this result for the prediction of Pb-based double perovskites could provide systematic guidelines for future research on high-potential spintronics devices.

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