**Three-step method for band offsets and its application to inorganic ABX3 halide perovskites**

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Band alignment between valance band maximum (VBM) and conduction band minimum (CBM) of different semiconductor compounds is a very important parameter that determines the transport properties of electronics near the interface of different compounds in the device. The computation of the natural band offset is usually a tough problem. In this paper, we proposed a new method to accurately predict the natural band offset. Comparing with previous method, the present method is more direct, and can easily applied to the systems with larger lattice mismatch and also to the systems with lower symmetry. Using the newly proposed three-step method, we successfully calculate the natural band offset between the inorganic halide perovskites ABX3 (A = Cs; B = Sn, Pb; X = Cl, B, I) in the cubic and orthorhombic phase. We show that the band gap decreases as X site ion ranges from Cl to Br to I, while the band gap increases as B site ion varies from Sn to Pb or as the compound transforms from the cubic phase to the orthorhombic phase. The band gap difference between all these compounds can be attributed primarily to the valance band offset, with a much smaller contribution from the conduction band offset.

I-IV-VII3 materials with halide perovskite structures (noted as ABX3, such as CsSnI3, CH3NH3PbI3 *et al.*) have shown a great potential to be good solar-cell materials and have drawn great interest.1-22 Based on CH3NH3PbI3, Jeon *et al.* have achieved a power conversion efficiency of 16.7%, which is comparable to those of today’s best thin-film photovoltaic devices.8 To improve the performance of these compounds, their stability, resistivity, absorption spectra and mobility have experimentally studied.8-10 In addition to the nature of the material itself, the interface properties is one of the determining factors for the device performance. And the natural band offset between different compounds is an important parameter in the interface design as it determines the transport properties of electronics in the interface of different compounds in the device. If we can predict the band alignments between ABX3 type halide perovskite photovoltaic materials, it will be great favorable for the performance optimization of device composed of these compounds.

The computation of natural band offset is a nontrivial problem due to the uncertainty of energy zero in the infinite system. Wei and Zunger23 followed the procedure in photoemission core level spectroscopy24 and constructed a superlattice to calculate the valence band offset between two hypothetical compounds *L* and *R*, where the valence band offset is defined as

(1)

Here,

(2)

is the core level to valance band maximum energy separations for pure *L* (and similar for *R*), and

(3)

is the difference in core level energy between *L* and *R* on each side of the interface, which can be obtained from the calculation of an *L*n/*R*n (001) heterojunction supercell. Here, core levels of *L* and *R* in the bulk are assumed to be the same as that in the supercell, ignoring the influence from the volume deformation to the core level, so this method is suitable only for systems with small lattice mismatch.25-27 To predict the “natural” valence-band offset more accurately, Li *et al* developed an absolute deformation potential (ADP) correction method.28-30 They first calculate the band offsets when the two compounds are in their averaged lattice, that is

(4)

, and are the same as illustrate above, just need to pay attention to the lattice constants. Then calculate the VBM absolute volume-deformation potential of *L* and *R* as the procedure proposed by Li *et al*.28,29 After and are obtained, shift the VBM states from the averaged lattice constant to equilibrium lattice constant for both *L* and *R* to get the final natural band offset. But this method only applicable for systems with high symmetry, the calculation of VBM absolute volume-deformation potential is also very complex. Here we need to calculate the band offset between ABX3 type compounds with different structures such as cubic and orthorhombic, ADP correction method is doesn’t work. To solve this problem, we develop a three-step approach to predict the “natural” valence-band offset. In this paper, we first discuss the three-step approach in detail, then we present our calculated results and discuss the general chemical trends of the calculated results.

To calculate the valance band offset, we develop a three-step approach based on the method developed by Wei and Zunger.23 For two hypothetical compounds *L* and *R* with a lattice constant of (a1, a2, a3) and (b1, b2, b3), respectively, , the valence band offset is defined as

(5)

Here,

(6)

is the core level to valance band maximum energy separations for pure *L* (and similar for *R*). The procedure to calculate the core level difference between these two compounds can be decomposed to three steps as illustrated in Fig. 1. The first step, we expand *L* along (100) by (if the value is negative, *L* will be compressed), the expanded compounds can be noted as *L’* with a lattice constant of (b1, a2, a3). The core level difference between *L* and *L’* can be obtained from the calculation for the *L*n/*L’*n superlattices with (100) orientation. The second step is similar to the first step, we expand *L’* along (010) by and get *L’’* with a lattice constant of (b1, b2, a3). The core level difference between *L’* and *L’’* can be obtained from the calculation for the *L’*n/*L’’*n superlattices with (010) orientation. At last, the core level difference between *L’’* and *R* can be obtained from the calculation for the *L’’*n/*R*n superlattices with (001) orientation. Then in formula (5) can be written as

(7)

The final formula to calculate the valence band offset between two compounds *L* and *R* can be written as

(8)

Actually, *L’* and *L’’* act as two bridge compounds here. We can also choose *R’* with a lattice constant of (a1, b2, b3) and *R’’* with a lattice constant of (a1, a2, b3) as the bridge compounds and calculate the core level difference with the same procedure. We can even choose four bridge compounds, expanded *L* with a lattice constant of (, a2, a3) and (, , a3), and compressed *R* with a lattice constant of (, , b3) and (, b2, b3), and calculate the core level difference with five steps similar to the three-step approach. According to our tests, all these approaches predict similar results. To obtain the conduction band offsets , we use the relationship

(9)

where is the measured band gap difference between *L* and *R*. We apply the three-step approach to calculate the band offsets of Si/Ge and GaAs/InAs, the valance band offset of these two systems are 0.68 eV and 0.41 eV, respectively, which is very close to the results predicted by the ADP correction approach of 0.72 eV and 0.37 eV, respectively. Experimentally, the valance band offset of Si/Ge is predicted to be range from ~0.35 eV to ~0.95 eV31,32 and the valance band offset of GaAs/InAs is predicted to be 0.46 eV,33 our calculation results agree well with the experimental results.

Our calculations are performed using the density functional theory (DFT) as implemented in the plane wave Vienna ab initio simulation package (VASP)34 code. For the exchange-correlation functional, the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)35 is used. The projector augmented-wave (PAW) pseudopotentials36 are used with an energy cutoff of 500 eV for the plane-wave basis functions. Because PBE underestimates band gaps, we also use the GW0 method37 to recalculate the band structures. Large number of *k*-points sampling for the Brillouin Zone integration are used to ensure the convergence of the calculated results. The lattice vectors and atomic positions of each primitive cell are optimized according to the guidance of atomic forces, with a criterion that requires the calculated force on each atom smaller than 0.01 eV/Å. The spin-orbit coupling (SOC) effect is demonstrated to be very strong in these compounds,15-17 so it’s included in all the calculations.

Now we will calculate the band alignment between ABX3 type compounds with different phases using the three-step approach. ABX3 type compounds shows various phases under different temperatures,13,14 but cubic structure (α-phase, Fig. 2a) is a typical high temperature phase and orthorhombic structure (γ-phase, Fig. 2b) is a typical low temperature phase, so we focus on these two phases in this paper. Firstly, we calculate the valance band offset between CsSnCl3, CsSnBr3, CsSnI3, CsPbCl3, CsPbBr3 and CsPbI3 in the cubic phase using Eq. (8). Then we calculate the valance band offset between the cubic and orthorhombic phase for each compound. Once the position of VBM is obtained, the position of CBM can also be predicted using Eq. (9). Since PBE even HSE underestimates the band gaps of this system,15,16 we perform the GW0 calculation to correct the band edges of each compounds and can obtain the accurate band alignments.

Band alignment results of the cubic compounds calculated using the PBE functional and GW0 approach are plotted in Fig. 3a. It’s clear that GW0 correction induces a large down-shift of the VBM and relatively smaller up-shift of the CBM. Fig. 3b shows the corrected band edges of both cubic and orthorhombic compounds. The band gaps of α-CsPbCl3, α-CsPbBr3 and γ-CsSnI3 calculated using GW0 approach are 3.03 eV, 2.30 eV and 1.34 eV, respectively, in good agreement with the experimental results of 3.0 eV, 2.3 eV and 1.3 eV, respectively.2,38 We want to note that we also calculate the band alignment between cubic ABX3 compounds using the ADP correction approach and the results are similar to the three-step approach. In the following, we will analyze the chemical trends of the band edges in detail based on the GW0 corrected results.

As B site ion varies from Sn to Pb, both VBM and CBM down-shift, but the down-shift of VBM is much larger than that of CBM, so the band gap becomes larger. According to our recent calculation,15 the VBM of ABX3 is mainly the anti-bonding component of the hybridization between B *s* states and X *p* states, while the CBM is almost a non-bonding state dominated by the X *p* orbitals. Table I lists the atomic orbital energy level of Sn, Pb, Cl, Br and I. It can be seen that Sn 5*s* orbital energy is higher than that of Pb 6*s*, and closer to the X *p* energy levels, so the *s*-*p* hybridization is stronger between Sn *s*-X *p* than that of Pb *s*-X *p*. The stronger coupling between Sn *s* and X *p* up-shifts the VBM, which induces the VBM becomes lower with B site ion changes from Sn to Pb. While the Sn 5*p* states is 0.2 eV higher than that of Pb 6*p*, CBM down-shifts with a magnitude of about 0.2 eV with B site ion changes from Sn to Pb due to the non-bonding nature of the CBM.

As X site ion changes from Cl to Br to I, both VBM and CBM up-shift, but the up-shift of VBM is much larger than that of CBM, so the band gap decreases. VBM contains some *p* states of the X ion, the energy level of X *p* states increases from Cl to Br to I (Table I), thus the VBM becomes higher with X changes from Cl to Br to I; e. g., the X *p* states orbital level increase is 0.89 eV and 1.20 eV with X changes from Cl to Br and from Br to I, but the difference is reduced by *s*-*p* hybridization, because the bond length is B-Cl < B-Br < B-I, hybridization becomes weaker and the anti-bonding VBM level shifts down with X ranges from Cl to Br to I. As a result, the valance band offsets between α-CsPbCl3 and α-CsPbBr3 is reduced to 0.78 eV, and the valance band offsets between α-CsPbBr3 and α-CsPbI3 is reduced to 0.91 eV (and similar for Sn based compounds and compounds in the γ-phase). The lattice constant becomes larger with X changes from Cl to Br to I, as a result, the Madelung energy becomes larger, which induces the non-bonding CBM state down-shifts.

As shown in Fig. 2, each B ion has six neighboring X ions, when ABX3 transfers from the high temperature cubic phase to the low temperature orthorhombic phase, the B-X bond length will no longer be the same as that in the cubic phase and become three different larger values as shown in Table II. Since the B-X bond length becomes longer with the phase transition, the hybridization becomes weaker and the anti-bonding VBM state shifts down with the phase transition. While the CBM will up-shift a little bit due to the larger Madelung energy in the orthorhombic phase.

According to the calculated band alignment in Fig. 3, the band gap difference between ABX3 type compounds can be attributed primarily to the valance band offset, with a much smaller contribution from the conduction band offset. According to the doping limit rule, a material is difficult to be doped n-type if the CBM energy is high and is difficult to be doped *p*-type if the VBM energy is low.39 Previous experiments have demonstrated that γ-CsSnI3 shows *p*-type conduction behavior.2 The small conduction band offset and large valance band offset shown in Fig. 3 indicates the *n*-type conductivity should be excepted with I substituted by Cl or Br.

In summary, we have developed a three-step approach to accurately predict the “natural” band offset between compounds with different structures, the calculated results are similar with the available ADP correction results. Using this approach, the band offset between cubic and orthorhombic ABX3 type compounds are predicted. Spin-orbit coupling effect is included in all the calculations and we also use the GW0 method to correct the band gaps. The band gaps we calculated agree well with the available experimental results. The band gap difference between compounds with different B site ions, different X site ions or different structures attributed primarily to the valance band offset, with a much smaller contribution from the conduction band offset, this can be explained by the nature of the band edges. Based on these results, we predict that the band gap of ABX3 can be tuned by atom substitution or phase transformation, which mainly changes the position of the VBM and can tune the conductivity of ABX3 in the halide perovskite photovoltaic devices.

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FIG. 1. (color online) The model for calculating the valance band offset using the three-step approach.



FIG. 2. (color online) A perspective of the (a) cubic and (b) orthorhombic phase of ABX3 halide perovskite.



FIG. 3. (color online) Calculated natural band alignment for the VBM and CBM of CsSnCl3, CsSnBr3, CsSnI3, CsPbCl3, CsPbBr3, and CsPbI3 (a) in the cubic phase using the PBE functional (black lines) and GW0 approach (red lines) and (b) in the cubic (red lines) and orthorhombic (blue lines) phase using the GW0 approach. The VBM of cubic CsSnI3 calculated using the PBE functional is set to zero as the reference. Note that the effects of spin-orbit coupling are included in both situations.



TABLE I. Calculated atomic orbital energy level for Sn, Pb, Cl, Br and I using the GW0 approach.



TABLE II. Calculated B-X bond length (in Å) of ABX3 compounds (with A = Cs; B = Sn, Pb; X = Cl, Br, I) in the cubic and orthorhombic phase.