Density Functional Theory Study on the Surface Properties and Floatability of Hemimorphite and Smithsonite

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Abstract: Hemimorphite and smithsonite are all-important zinc oxide minerals. The beneficiation and separation of them using flotation method is usually considered difficultly. Minerals surface wettability and its regulation are the core issues in the flotation process, which closely correlate with the surface properties of the minerals. Therefore, an in-depth understanding of the surface properties of the two minerals is of great significance for the study of the flotation technology of them. In this study, the surface properties of the hemimorphite (110) surface and the smithsonite (101) surface, and their relationships to the mineral floatability have been investigated by first-principle calculation method based on density functional theory. The calculation results demonstrated that the hemimorphite (110) surface exhibited more obviously surface reconstruction. For the orbital energy level of the surface atoms of two minerals, the O 2p orbital is closer to the Fermi level than the Zn 3d. Chemical bond Mulliken population value indicated that the ionicity of the unsaturated linkage on the smithsonite (101) surface was stronger than that on the hemimorphite (110) surface. The absolute values of the ratios of negative charges to positive charges on the surfaces of hemimorphite and smithsonite were 1.529 and 1.256 respectively. These results implied that the O atoms on hemimorphite (110) surface are more impede collector molecule, such as hydroximic acid, bond with Zn atom, hemimorphite (110) surface is more readily wetted by water. This study provides comprehension at an atomic level to the relationship between surface properties and the floatability of hemimorphite and smithsonite.

Keywords: hemimorphite; smithsonite; density functional theory; surface properties; floatability

1. Introduction

As an important base metal, zinc is widely used as a raw material in various industries such as electroplating, batteries, automobile manufacturing, etc. [1,2]. The zinc-containing ores are mainly classified into two types: zinc sulfide ores and zinc oxide ores. With progressive exhaustion of natural zinc sulfide ores, zinc oxide ores are becoming increasingly attractive as the alternative materials for the recovery of zinc. However, compared with zinc sulfide ores, the beneficiation of zinc oxide ores are much more difficult due to their complex structures, varied surface characteristics and components of the minerals [3]. Zinc oxide ores generally occur as silicate or carbonate forms in different places around the world. Among them, hemimorphite [Zn₄Si₂O₇(OH)₂·H₂O] and smithsonite [ZnCO₃] are the typical zinc oxide minerals [2,4–6].
The traditional technique for treating low-grade zinc oxide ores is hydrometallurgy [3]. However, this technology has some drawbacks such as a large acid consumption and environmental hazards. In practice, flotation is the commonly used method for recovery of these zinc oxide minerals due to its various advantages such as lower cost, good controllability and simple operation [7,8]. Flotation is a separation process that exploits natural and induced differences in surface properties of the minerals. However, the flotation of hemimorphite and smithsonite is relatively difficult due to their poor floatability [9]. Most of the existing studies mainly focus on the sulfidization-amine flotation process, i.e., sulfidization using sodium sulfide as the sulfurizing agent and using amine as the collector [10,11]. However, the separation efficiency of the sulfidization-amine flotation process is relatively low, and there are still some problems such as low selectivity of collector, low concentrate grade and the harmful impact of slime and dissolved ions on the flotation process. The new high-efficiency collectors, especially the chelating collectors, are considered to be effective methods for solving the current unsatisfactory separation effect due to their high separation efficiency [12,13]. The collector aim to make sufficiently hydrophobic state of the surface of target minerals, thus, the design of new collector molecule and its adsorption mechanism on the mineral surface are inseparable from the profound understanding of the surface properties of the minerals. Therefore, it is indispensable to study the properties of the surface that collector or floatation reagents adsorbing on and the relationship between the surface properties and the floatability of minerals.

Cleavage is the tendency of a mineral to break along smooth planes parallel to zones of relative weak bonding. These planes of relative weakness are a result of the regular locations of atoms and ions in the crystal [14]. Therefore, the cleavage plane has the lowest surface Gibbs free energy in all the new formed faces after minerals crystal was broken and are the most common observed crystal faces after mineral crystal was broken. For the reason of the wettability of the mineral surface and its regulation are the core issues of the flotation process. Thus, in-depth understanding of the nature of the cleavage surface of the hemimorphite and smithsonite is of great significance for the investigation of the flotation behavior of them. The cleavage planes of the hemimorphite and smithsonite are (110) face [15] and (101) face [16], respectively.

In this work, the crystal simulation parameters and convergence tests were performed to obtain optimum crystal bulk models of hemimorphite and smithsonite. After that, the hemimorphite (110) slab surface model and smithsonite (101) slab surface model with different layer depth and vacuum layer thickness were cleaved from the pre-optimized bulk models of the two minerals, and which were tested, to calculate electronic structure, for analyzing bonding ability, charge distribution and bond covalency of surface atoms. Subsequently, the native floatability and the floatability in different collector system were comparatively investigated at an atomic level. The study provides an essential and comprehensive understanding of the cleavage plane properties and the relationship between surface properties and the floatability of hemimorphite and smithsonite.

2. Computational Details

Density functional theory (DFT) is a computational quantum mechanical modeling method used in physics, chemistry and especially material science to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules and condensed phases. Using this theory, the properties of a many-electron system can be determined using functionals, i.e., functions of another function, which in this case is the spatially dependent electron density. DFT is among the most popular and versatile method available in condensed-matter physics, computational physics, and computational chemistry. DFT calculation can be conducted by many quantum chemistry software packages, such as Cambridge sequential total energy package (CASTEP), DMol3 and Gaussian. In this work, CASTEP program, which was a product of BIORVIA Company (San Diego, CA, USA), was employed to perform DFT calculation. Ultra-soft pseudopotential was used for performing the plane-wave expansion of density functional theory based on the first-principles.
The convergence criteria of the structure optimization and properties calculation were set as (a) energy tolerance $2 \times 10^{-5}$ eV/atom, (b) force tolerance 0.05 eV/Å, (c) displacement tolerance 0.002 Å, and (d) stress 0.1 GPa. For self-consistent electronic minimization, the Density Mixing method was employed with a convergence tolerance of $2.0 \times 10^{-6}$ eV/atom.

2.1. Optimization of Hemimorphite and Smithsonite Crystal

Up to present, generalized gradient approximation (GGA) and local density approximation (LDA) are the most widely used method applied in DFT study of solid material property. LDA depends solely upon the value of the electronic density at each point in space, while GGA also takes into account the gradient of the density at the same coordinate [17]. For getting accurate calculation result of surface property, several functions associated with GGA framework inside the CASTEP program, such as Perdew–Burke–Ernzerhof (PBE), revised Perdew–Burke–Ernzerhof (RPBE), Perdew–Wang’s 1991 (PW91), Wu–Cohen (WC), Perdew–Burke–Ernzerhof solide (PBESOL), and Ceperley–Alder–Perdew–Zunger (CA–PZ), were tested for optimizing hemimorphite and smithsonite crystals. To obtain the high quality hemimorphite and smithsonite crystal models, the essential parameter setting of exchange-correlation potential, of kinetic cutoff energy and Brillouin zone k-point were tested.

All of the calculated lattice parameters were compared with the experimental values to verify the validity and rationality of the parameters setting.

2.2. Optimization of Hemimorphite (110) and Smithsonite (101) surfaces

Surface energy ($E_{\text{surface}}$) is the index for measuring the thermodynamic stability of surface structure. A lower value implies a more stable surface. The $E_{\text{surface}}$ in slab model was calculated by Equation (1) [18].

$$E_{\text{surface}} = E_{\text{slab}} - \left( \frac{N_{\text{slab}}}{N_{\text{bulk}}} \right) \times E_{\text{bulk}}$$  \hspace{1cm} (1)

Where, $N_{\text{slab}}$ and $N_{\text{bulk}}$ are the number of atoms contained in the slab and the bulk models, respectively; $E_{\text{slab}}$ and $E_{\text{bulk}}$ are the total energy of the surface slab and the bulk models, respectively; $A$ is the area of the surface slab model; and 2 indicates two new surfaces formed when constructed surface slab model from bulk model.

A three-dimensional periodic lattice model consisting of a bottom surface slab and a vacuum layer at the top, were used for simulating the two-dimensional cleavage plane structures of the minerals, which can ensure the new cleaved surfaces were identical reflections of one another [19]. All surface slab models were cleaved from the optimized bulk hemimorphite unit cell and bulk smithsonite unit cell. For obtaining the accurate three-dimensional periodic lattice to simulate hemimorphite (110) and smithsonite (101) slab surface structures. Four three-dimensional periodic lattices consisting of the slab depth from 6.598 Å to 26.392 Å (containing 1–4 layers of H$_4$O$_{16}$Si$_2$Zn$_4$ units, respectively) and the vacuum thickness from 10 Å to 16 Å (step is 2 Å) were built for simulating hemimorphite (110) slab structure. Five three-dimensional periodic lattices consisting of the slab depth from 3.892 Å to 19.459 Å (containing 1–5 layers of C$_2$O$_6$Zn$_2$ units, respectively) and vacuum thickness from 10 Å to 16 Å (step is 2 Å) were built for simulating the smithsonite (101) slab structure. The surface energy calculation were performed under the condition of cutoff energy fixed at 340 eV and Monkhorst-Pack mesh set as $3 \times 2 \times 4$ for hemimorphite and $4 \times 4 \times 2$ for smithsonite, respectively.

2.3. X-Ray Diffraction (XRD) Analysis

The experimental XRD pattern of the single mineral of hemimorphite and smithsonite samples were determined by using an XRD system (PANalytical X’Pert Pro) with Cu Kα1 radiation ($\lambda = 1.5406$ Å) in the 2θ range of 5–90°. Reflex module of Materials Studio program was employed to simulate XRD pattern of the minerals basing on the optimized crystal models. The parameter setting of the XRD pattern calculation were consistent with experimental.
3. Results and Discussion

3.1. Preparation of Hemimorphite and Smithsonite Bulk Crystals

The initial lattices of the bulk hemimorphite and bulk smithsonite were built according to the crystal structure parameters measured by Hill, R. [20] and Effenberger, H. [21]. The lattice constant of hemimorphite was $a = 8.367 \text{Å}$, $b = 10.730 \text{Å}$, $c = 5.115 \text{Å}$, $\alpha = \beta = \gamma = 90^\circ$ and of smithsonite was $a = b = 4.653 \text{Å}$, $c = 15.026 \text{Å}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. Five DFT methods correlating to GGA had been tested with kinetic cutoff energy was set as 300 eV and Brillouin zone k-point was set as $1 \times 1 \times 1$. The curves of total energy and lattice parameter as a function of Brillouin zone k-points mesh and parameter setting were obtained, which is 4.491% with a total energy of $19066.613 \text{eV}$. Five DFT methods correlating to GGA had been tested with kinetic cutoff energy was set as 300 eV and Brillouin zone k-point was set as $1 \times 1 \times 2$ for hemimorphite and $3 \times 3 \times 2$ for smithsonite. The results were listed in Table 1.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hemimorphite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td>8.367</td>
<td>10.730</td>
<td>5.115</td>
<td>7.438</td>
</tr>
<tr>
<td>GGA-PBE</td>
<td>8.684</td>
<td>10.878</td>
<td>5.231</td>
<td>4.264</td>
</tr>
<tr>
<td>GGA-RPBE</td>
<td>8.765</td>
<td>10.945</td>
<td>5.312</td>
<td>5.602</td>
</tr>
<tr>
<td>GGA-PW91</td>
<td>8.693</td>
<td>10.834</td>
<td>5.235</td>
<td>7.225</td>
</tr>
<tr>
<td>GGA-WC</td>
<td>8.580</td>
<td>10.803</td>
<td>5.153</td>
<td>3.975</td>
</tr>
<tr>
<td>GGA-PBESOL</td>
<td>8.591</td>
<td>10.781</td>
<td>5.166</td>
<td>4.142</td>
</tr>
<tr>
<td><strong>Smithsonite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td>4.653</td>
<td>4.653</td>
<td>15.026</td>
<td>9.916</td>
</tr>
<tr>
<td>GGA-PBE</td>
<td>4.772</td>
<td>4.772</td>
<td>15.745</td>
<td>5.956</td>
</tr>
<tr>
<td>GGA-PW91</td>
<td>4.761</td>
<td>4.761</td>
<td>15.645</td>
<td>8.782</td>
</tr>
<tr>
<td>GGA-WC</td>
<td>4.708</td>
<td>4.708</td>
<td>15.341</td>
<td>4.491</td>
</tr>
<tr>
<td>GGA-PBESOL</td>
<td>4.708</td>
<td>4.708</td>
<td>15.350</td>
<td>4.534</td>
</tr>
</tbody>
</table>

For hemimorphite, as shown in Table 1, when exchange-correlation potential is set as GGA-WC, the minimum lattice parameter difference is obtained, which is 3.975% with a total energy of $-22963.476 \text{eV}$. As for smithsonite, when exchange-correlation potential is set as GGA-WC, the minimum lattice parameter difference is obtained, which is 4.491% with a total energy of $-19066.613 \text{eV}$.

The curves of total energy and lattice parameter as a function of Brillouin zone k-points mesh and kinetic cutoff energy were displayed in Figures 1 and 2, respectively.

![Figure 1](image-url)

**Figure 1.** Total energy and lattice parameter difference as a function of the k-points set mesh with the kinetic cutoff energy of 300 eV for hemimorphite (a) and smithsonite (b).
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As shown in Figures 1 and 2, when the exchange-correlation potential and the kinetic cutoff energy are set as GGA-WC and 300 eV, either hemimorphite or smithsonite, the curve of total energy as a function of the k-points set mesh shows the variation tendency of gradual decreasing until stable. When the k-point set mesh is set as $3 \times 2 \times 4$ for hemimorphite and $4 \times 4 \times 2$ for smithsonite, the minimum value of lattice parameter differences of the hemimorphite and hemimorphite is 3.038% and 4.039%, respectively, and the convergence of the total energy is accredited. On the other hand, when the k-point set mesh is set as $3 \times 2 \times 4$ for hemimorphite and $4 \times 4 \times 2$ for smithsonite respectively, the curves of the total energy and lattice parameter difference as a function of kinetic cutoff energy of both minerals show the same variation tendency. For any of the two minerals, when the cutoff energy is higher than 340 eV, the changes of the total energy and lattice parameter difference are little, indicating that the 340 eV cutoff energy is sufficient to meet the accuracy requirements of the calculation.

It can be seen that, when exchange-correlation potential was set as GGA–WC and kinetic cutoff energy was set as 340 eV as well as Brillouin-zone k-point set mesh for hemimorphite was set as $3 \times 4 \times 2$ and for smithsonite was set as $4 \times 4 \times 2$, the lattice parameters of the hemimorphite lattice and the smithsonite lattice used for the simulation could be ascertained, which were listed in Table 2.

### Table 2. Simulation and experimental lattice parameters of hemimorphite and smithsonite crystal.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Parameter</th>
<th>Experiment</th>
<th>Simulation</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a/Å</td>
<td>8.367</td>
<td>8.500</td>
<td>1.548</td>
</tr>
<tr>
<td>Hemimorphite</td>
<td>b/Å</td>
<td>10.730</td>
<td>10.780</td>
<td>0.462</td>
</tr>
<tr>
<td></td>
<td>c/Å</td>
<td>5.115</td>
<td>5.086</td>
<td>0.562</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>a/Å</td>
<td>4.653</td>
<td>4.684</td>
<td>0.665</td>
</tr>
<tr>
<td></td>
<td>b/Å</td>
<td>4.653</td>
<td>4.684</td>
<td>0.665</td>
</tr>
<tr>
<td></td>
<td>c/Å</td>
<td>15.026</td>
<td>14.991</td>
<td>0.232</td>
</tr>
</tbody>
</table>

As shown in Table 2, the simulated lattice parameters of hemimorphite lattice and smithsonite lattice coincide well with the experimental values. When exchange–correlation potential is set as GGA–WC and Brillouin zone k-points mesh is set as $3 \times 4 \times 2$ as well as kinetic cutoff energy is set as 340 eV, the difference values of $a$, $b$, and $c$, of hemimorphite lattice between experiment and simulation, are 1.548%, 0.462%, and 0.562%, respectively. Whilst, when exchange–correlation potential is set as GGA–WC and Brillouin zone k-points mesh is set as $4 \times 4 \times 2$ as well as kinetic cutoff energy is set as 340 eV, the difference values of $a$, $b$, and $c$, of smithsonite lattice between experiment and simulation, are 0.665%, 0.665%, and 0.232%, respectively. Figure 3 presents the simulated and experimental XRD

![Figure 2](image_url). Total energy and lattice parameter difference as a function of kinetic cutoff energy with the k-point mesh of $3 \times 2 \times 4$ for hemimorphite (a) and $4 \times 4 \times 2$ for smithsonite (b).

![Figure 3](image_url). Simulation and experimental lattice parameters of hemimorphite and smithsonite crystal.
pattern of the two minerals. As shown in Figure 3, simulated XRD pattern and experimental XRD pattern are almost identical, which also proves that the parameter setting of the simulation calculation is appropriate on the other hand.

![Figure 3. XRD pattern of hemimorphite (a) and smithsonite (b) by simulated and experimental methods.](image)

3.2. Surface Slab Model Optimization

The slab depth and vacuum thickness exhibit a conclusive effect on the relaxation of the surface atoms [13]. As the mineral crystal is broken in a direction along a crystal plane, the equilibrium of the forces prior acting on the surface atoms will be destroyed. As a result, the relaxation of the surface atoms will be occurred, which is driven by the attraction force from the crystal interior, to reconstruct the surface structure to achieve the state with the lowest surface Gibbs free energy. Moreover, because the DFT calculation is carried out under the condition of three-dimensional periodicity, the interaction between the two identical reflections surfaces must be avoid to promise the accuracy of the calculation results, thus a large enough vacuum thickness is essential.

The surface energy of the minerals slab surface structures with different slab depth and vacuum thickness is illustrated in Table 3.

<table>
<thead>
<tr>
<th>Slab depth (Å)</th>
<th>Surface energy (J·m⁻²)</th>
<th>Vacuum thickness (Å)</th>
<th>Surface energy (J·m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.896</td>
<td>1.532</td>
<td>1.783</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>1.780</td>
<td>1.783</td>
<td>1.788</td>
</tr>
<tr>
<td><strong>Smithsonite</strong></td>
<td>3.892</td>
<td>7.784</td>
<td>11.675</td>
</tr>
<tr>
<td></td>
<td>0.688</td>
<td>1.079</td>
<td>1.364</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>1.470</td>
<td>1.478</td>
<td>1.481</td>
</tr>
</tbody>
</table>

According to Table 3, when the surface slab model of the hemimorphite (110) surface contains three or more layers and the surface slab model of the smithsonite (101) surface contains four or more layers, the surface energy trend to invariant, which approximate converge within 0.02 J·m⁻² and 0.05 J·m⁻², respectively. In the case of vacuum thickness, 10 Å vacuum thickness can provide enough shielding for preventing the electrostatic interactions between two sides of a slab either for hemimorphite (110) surface or for smithsonite (101) surface. The surface slab model of hemimorphite (110) surface with slab depth of 19.794 Å (3 layers) and vacuum thickness of 10 Å, the surface slab model of smithsonite (101) surface with slab depth of 15.567 Å (4 layers) and vacuum thickness of 10 Å, are used for simulating the hemimorphite (110) surface structure and smithsonite (101) surface.
structure, respectively. The geometry structures of the hemimorphite (110) surface slab model and the smithsonite (101) surface slab model before and after optimization are shown in Figure 4.

As presented in Figure 4, for hemimorphite (110) surface slab model, atom relaxation results in the O atoms move toward outside the bulk and Zn atoms move toward inside of the bulk, which leads to increased density and negative charge of surface O atoms, and obvious surface structure reconstruction. Whilst, for smithsonite (101) surface slab model, atom relaxation only makes O atoms slightly move toward outside the bulk and there is barely perceptible surface structure reconstruction.

3.3. Relationship between Surface Property and Floatability

3.3.1. Electronic Structures and Properties of Mineral Surface

The hydrophilic groups of the collector molecules (ions) interact with the active sites on the mineral surface result in the collector molecules (ions) adsorb on the mineral surface, thereby, making the mineral surface hydrophobic. For the collectors that interacts with the mineral surface through chemisorption, the sign (minus or positive) of the adsorption energy can be used for estimate whether the adsorption occur or not. This is determined by the nature of the collector’s hydrophilic groups on the one hand and determined by the valence electron properties of the atoms on the mineral surface on the other hand [22].

The activity of the electron near the Fermi level is the strongest [23]. Therefore, by observing the density of states of electrons near the Fermi energy, the reactivity of surface atoms in chemical reaction can be judged. The density of states of electrons in the surface atoms (1 layer depth) for two minerals are calculated, and the results are presented in Figures 5 and 6, respectively.
Figure 5. Calculated total and partial density of states of the atoms for the hemimorphite (110) surface.

Figure 6. Calculated total and partial density of states of the atoms for the smithsonite (101) surface.
For hemimorphite, as shown in Figure 5, the Zn 4s and 3p orbitals make a major contribution to the conduction band. The Si 2s and 2p orbitals as well as the O 2p orbital also make a small contribution to the conduction band. The Zn 3d orbital and the O 2p orbital (O belongs to the silicon–oxygen tetrahedron) make a major contribution and the Si 2p and 2s orbitals make a small contribution to the upper valence band ($-8.0 \sim 0$ eV). The Si 2s orbital and the O 2p orbital make a major contribution to the deep valence band ($-10.0 \sim -8.0$ eV). The bottom of the valence band ($-21 \sim -16$ eV) is mainly composed of the O 2s orbital (O belongs to the silicon–oxygen tetrahedron), and the Si 2s and 2p orbitals and the H 1s orbital make a small contribution. Meanwhile, the density of states of the Zn 3d orbital electrons presents a sharp state, which indicates the electrons in the Zn 3d orbital have a large effective mass and a large degree of locality, and the scalability of atomic orbital is very weak. In addition, the energy level of the Zn 3d orbital is lower than that of the O 2p orbital and Si 2p orbital (belongs to the silicon–oxygen tetrahedron). This indicates that the bonding atoms in the polar group of collector molecule need to break through the barriers from the O and Si when bonding to the surface Zn atom.

For smithsonite, as seen from Figure 6, the Zn 4s and 3p orbitals, the C 2s and 2p orbitals and the O 2p orbital make a major contribution to the conduction band. The Zn 3d orbital, the O 2p orbital and the C 2p orbital make a major contribution and the O 2s orbital and the C 2s orbital make a small contribution to the upper valence band ($-12.5 \sim 0$ eV). The O 2s orbital and the C 2p orbital make a major contribution to the deep valence band ($-22.5 \sim 21.0$ eV). The bottom of the valence band ($-26 \sim -24$ eV) is mainly composed of O 2s orbital and C 2s orbital. Meanwhile, the density of state of Zn 3d orbital electrons presents a sharp state, which indicates that the electrons in the Zn 3d orbital have a large effective mass and a large degree of locality, and the scalability of atomic orbital is very weak. In addition, the energy level of the Zn 3d orbital is lower than that of the O 2p orbital. This also indicates that the bonding atoms in the polar group of collector molecule need to break through the barriers from the O when bonding to the surface Zn atom.

As shown from the above analysis, the degree of locality of the valence electron of the surface Zn atoms of hemimorphite and smithsonite is large. Due to the relatively lower energy level of Zn 3d orbital compared with the O 2p orbital, the O atoms will affect its bonding. This will lead to that the collector with weak electronegativity of solid-affinity groups cannot chemisorb on the surfaces of the two minerals. Only the collectors with strong electronegativity of solid-affinity groups, such as hydroximic acid can bond with Zn atoms and chemisorb on the surfaces of the two minerals [24,25]. Additionally, the 2p orbital energy level of O atoms in the surface layer of hemimorphite is closer to the Fermi level (0 eV) compared with it of smithsonite. This indicates that the reactivity of the O atoms in the surface layer of hemimorphite is higher than that of the O atoms in the surface layer of smithsonite, and the inhibitory effect on the Zn atom bonding is stronger.

3.3.2. Unsatisfied Bond Properties of Minerals Surface

Flotation is the most common and effective method for recovering hemimorphite and smithsonite [26,27]. The wettability of mineral surface and its adjustment are the core issues in the flotation process. The floatability of the minerals is mainly determined by the wettability degree of mineral surface by water [14]. Wettability is the hydration of the adsorption of water molecules on solid particle surface. When mineral crystal is broken, comparing with the atoms locate inside the crystal, the atoms locate in the new formed surface will in an asymmetric force field, which results in the surface have excess free energy. Since a system always tends to reduce its free energy, thus the surface atoms will attract the water molecules to reduce the asymmetry of force field, thereby reducing the free energy of the surface. Therefore, ability of surface atoms to attract water molecules will decide the natural floatability of minerals.

The chemical bonds in mineral surface can be divided into two types, strong ionic bonds and weak molecular bonds. The mineral surface with ionic bonds has strong polarity or chemical activity, which exhibits great attraction to polar water molecules. The stronger the ionicity of the chemical bonds is, the easier the mineral surface is wetted by water, and correspondingly the worse the mineral
floatability is. Mulliken population analysis is a commonly used method to analyze the property of the chemical bonds [28]. The smaller the Mulliken population value (greater than 0), indicating the stronger ion type of chemical bonds. Correspondingly, the greater it is, indicating that the ionicity of the chemical bond is stronger. When the hemimorphite crystal and smithsonite crystal is ruptured along the (110) face and (101) face, respectively, the breakages of the Zn–O bonds and Si–O bonds occur. The Mulliken population values of Zn–O bonds and Si–O bonds in the interiors of mineral crystal and in the mineral surface layers were shown in Table 4.

Table 4. Mulliken bond population of internal and surface chemical bonds of hemimorphite and smithsonite.

<table>
<thead>
<tr>
<th></th>
<th>Hemimorphite (Σ (Zn–O, Si–O Bond))</th>
<th>Smithsonite (Σ Zn–O Bond)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interior value</td>
<td>3.7</td>
<td>1.23</td>
</tr>
<tr>
<td>Surface value</td>
<td>3.34</td>
<td>0.81</td>
</tr>
</tbody>
</table>

The results demonstrate that the Mulliken population values of chemical bonds in the interiors of the two minerals crystals are larger than that of chemical bonds in the surface layers. This indicate when the hemimorphite and smithsonite crystals are ruptured along the (110) face and (101) face, respectively, the ionicity of the chemical bonds in the surface layers of the two minerals crystals increase. The sum value (1.23) of Mulliken bonding character population of the chemical bonds in hemimorphite (110) surface is larger than that (0.81) of the chemical bonds in smithsonite (101) surface. This indicate the covalency of the unsaturated chemical bonds in hemimorphite (110) surface is stronger, that is, the ionicity of the unsaturated chemical bonds in smithsonite (101) surface is stronger than that of the chemical bonds in hemimorphite (110) surface. Thus, comparing with the hemimorphite (110) surface, the smithsonite (101) surface is more easily wetted by water, that is, the contact angle of hemimorphite will be larger than that of smithsonite [4]. Therefore, the native floatability of hemimorphite is higher than that of smithsonite.

3.3.3. Surface Charge of Mineral Surface

Hemimorphite and smithsonite usually be enriched and recovered using sulfidization-amine flotation method. Since amine cation collectors adsorb on the mineral surface mainly through the electrostatic interaction between the mineral surface and the cation of collector, the zeta potential of the mineral surface has a conclusive impact on the interaction between collector and minerals. According to the Stern double layer theory, when the mineral surface is charged, the ions with opposite charges in the aqueous solution will be attracted and adsorb on the mineral surface. As the result, a double layer (DL) structure appears on the surface of the mineral surface when it is expose to water. The DL refers to two parallel layers of charge surrounding the mineral surface. The first layer, the surface charge (either positive or negative), consists of ions that usually be called potential determining ions adsorbed onto the mineral surface. The second layer is composed of ions attracted to the surface charge via the Coulomb force, electrically screening the first layer. This second layer is loosely associated with the object. It is made of free ions that move in the water under the influence of electric attraction and thermal motion rather than being firmly anchored. It is thus called the "diffuse layer". The potential difference between the first and the second layer mentioned above is zeta potential [29].

The pH when the charge of mineral surface is zero is iso-electric point (IEP). In the case of there is no specific adsorption in the solution system, if the surface potential of mineral surface is zero, thus the zeta potential also is zero, at this time, the IEP equal to the point of zero charge (PZC) [29]. Because the PZC is related to the electrical properties of the mineral surface, the conjecture can be made that there may be some kind of connection between the original charge of mineral surface and PZC. The calculation results of the atomic charges of the hemimorphite (110) surface layer atoms and the smithsonite (101) surface layer atoms are shown in Table 4, where R is the absolute value of the ratio of negative charges to positive charges.
As shown in Table 5, the values of R of hemimorphite (110) surface and smithsonite (101) surface are 1.529 and 1.256, respectively. A larger value of R means a larger ability on attracting cation than attracting anion. Due to the H\(^+\) and OH\(^-\) ions are the potential determining ions for hemimorphite and smithsonite [30], thus it can be conjectured that the PZC of hemimorphite is lower than smithsonite, which conforms to the experimental results [31], but the evidence is where future work is needed.

| Table 5. Charges on the hemimorphite (110) surface and smithsonite (101) surface. |
|-----------------------------------------|-----------------|-----------------|-----------------|
|                                        | ∑ Negative Charge | ∑ Positive Charge | R               |
|                                        | (x 10\(^{-19}\) C) | (x 10\(^{-19}\) C) | (Negative/Positive) |
| Hemimorphite                           | -1.248 ([SiO\(_4\)]\(^{4-}\)) | 0.816           | 1.529           |
| Smithsonite                            | -0.752 ([CO\(_3\)]\(^{2-}\)) | 0.624           | 1.256           |

4. Conclusions

Under the conditions of essential parameters of exchange-correlation potential approximated by GGA–WC, kinetic cutoff energy 340 eV, and Brillouin-zone k-point mesh of hemimorphite 3 × 4 × 2 and of smithsonite 4 × 4 × 2, the bulk unit cell errors of hemimorphite and smithsonite were optimized within 2.0% and 1.0%, respectively. The lattice models with slab depth of 19.794 Å (contain 3 layers H\(_4\)O\(_{10}\)Si\(_2\)Zn\(_4\) unit) and vacuum thickness of 10 Å used for simulating hemimorphite (110) surface, and the model with slab depth of 15.567 Å (contains 4 layers C\(_2\)O\(_6\)Zn\(_2\) unit) and vacuum thickness of 10 Å for simulating smithsonite (101) surface, were identified for surface property calculation.

When the two minerals crystals were cleaved along the (110) face and the (101) face respectively, the surface atom relaxation occurred on both the hemimorphite (110) surface and the smithsonite (101) surface, which resulted in an obvious surface reconstruction. Whether the hemimorphite (110) surface atoms or the smithsonite (101) surface atoms, the upper valence band was mainly composed of the Zn 3d orbital and the O 2p orbital. The O atoms on the hemimorphite (110) surface exhibited stronger ability on impeding the collector bond with the Zn atoms than that on the smithsonite (101) surface did. The smithsonite (101) surface exhibited stronger attraction to water molecules compared with the hemimorphite (110) surface, which resulted in the contact angle of smithsonite in water was smaller than that of hemimorphite, and thereby leading to a lower native floatability.

This study provides an essential and comprehensive understanding of the surface atoms relaxation behavior, chemical bond property, electronic structure of cleavage plane atoms and surface charging property, and of the relationship between these properties and minerals floatability. The results of this work can provide guidance for the adjustment of the surface properties of hemimorphite (110) surface and smithsonite (101) surface as well as the development of new high efficiency collectors.

Author Contributions: C.H. carried out the lattice models construction, DFT calculation and the draft preparation of this paper. T.L. conducted writing-original draft preparation. W.Z. and H.Z. carried out the software and the minerals sample preparation. S.Z. and Y.A. performed XRD analysis and calculation data analysis. D.W. and Y.S. proposed conceptualization, and made writing-review and editing.

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